UNIVERSITY OF LATVIA

Karina Stankeviča

CHARACTER OF SAPROPEL PROPERTIES BASED ON ITS FORMATION CONDITIONS AND POSSIBILITIES OF ITS USE

Promocijas darba
kopsavilkums

SAPROPEĻA ĪPAŠĪBU RAKSTURS ATKARĪBĀ NO VEIDOŠANĀS APSTĀKĻIEM UN TĀ IZMANTOŠANAS IESPĒJAS

UNIVERSITY
OF LATVIA

FACULTY OF GEOGRAPHY AND EARTH SCIENCES

Karina Stankeviča

CHARACTER OF SAPROPEL PROPERTIES BASED ON ITS FORMATION CONDITIONS AND POSSIBILITIES OF ITS USE

Doctoral Thesis

Submitted for the PhD Degree in Earth Sciences,
Physical Geography and Environmental Sciences
Subfield – Environmental Sciences

Scientific advisors:
Prof. *Dr. habil. chem.* **Māris Kļaviņš**
Dr. geogr. **Laimdota Kalniņa**

RIGA, 2020

Supervisors:
  Prof. *Dr. habil. chem.* **Māris Kļaviņš**
  Dr. geogr. **Laimdota Kalniņa**

Reviewers:
  1) Doc. *Dr.* **Vaidotas Valskys** (Vilnius University, Lithuania)
  2) Prof. *Dr.sc.ing.* **Ainis Lagzdiņš** (Latvia University o f Life Sciences and Technologies)
  3) Asoc. prof. *Dr.biol.* **Gunta Spriņģe** (University of Latvia)

Doctoral committee:
  1) Prof. *Dr.biol.* **Viesturs Melecis**, chairman of Council
  2) Prof. *Dr. geogr.* **Oļģerts Nikodemus**
  3) Prof. *Dr. habil.chem.* **Māris Kļaviņš**
  4) Prof. *Dr. habil. paed.* **Raimonds Ernšteins**
  5) Assoc. prof. *Dr. geogr.* **Iveta Šteinberga**
  6) Assoc. prof. *Dr.biol.* **Gunta Spriņģe**
  7) Doc. *Dr.geogr.* **Juris Burlakovs**
  8) Doc. *Dr.geogr.* **Oskars Purmalis**, secretary of Council

The Thesis will be defended at the public session of
the Doctoral Committee of Environmental Science, the University of Latvia, at the
Faculty of Geography and Earth Sciences of the University of Latvia
(Jelgavas Street 1, Riga, Latvia) on October 30, room 702 at 10:00.
The Thesis is available at the Library of the University of Latvia,
Kalpaka Blvd. 4, Riga, Latvia

References should be addressed to:
Dr.georg. **Oskars Purmalis**
University of Latvia, Faculty of Geography and Earth Sciences
Raina Blvd. 19, Riga LV-1586, Latvia
e-mail: *Oskars.Purmalis@lu.lv*

ABSTRACT

Within the doctoral thesis, changes in the properties and uses of sapropel depending on the conditions of its formation were investigated by analysing the data on sapropel deposits in Latvia and after a detailed analysis of sapropel profiles in three lakes (Padelis, Pilcine and Pilvelis).

A GIS database of freshwater lake sapropel was created, and classification of sapropel types was adapted aiming to systematize and compile the data on sapropel research in Latvia, to determine the total amount of the resource and to conduct the research on the characteristic features of the formation of sapropel resources, as well as evaluate possible ways of sapropel application.

For characterisation of the regularities in sapropel accumulation under the influence of climate and environment, the research of three lake profiles was carried out using a multidisciplinary method approach which included the analyses of the palaeobotanical and chemical composition of the sediment profile. Additionally, the age of sediments was determined with the possibility to reconstruct the environmental and climate conditions.

The results reveal that the reserves of sapropel identified in the lakes of Latvia (the total number of which is more than 2,200) are currently estimated ~975 million m^3 or 530 thsd. t (with a humidity of 60%).

The accumulation of sapropel is characteristic to the lakes formed in Upper Pleistocene sediments, and the type of sapropel depends on the nature of these sediments. Sapropel deposits are typical to the lakes of glacigenic origin with flow-through and runoff water regime.

The most considerable amount of sapropel deposits can be found in eutrophic and hypereutrophic lakes. The type and composition of sapropel vary within each deposit and depends on the chemical composition, depth and temperature of the water. In recent sediments, a higher concentration of metals was observed in comparison to the background that is associated with the anthropogenic impact.

Keywords: *freshwater sapropel, gyttja, sediment formation conditions, Holocene, accumulation of metallic elements, pollen, macro- and microfossils, malacofauna, lakes of Latvia*

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ABBREVIATIONS AND GLOSSARY

sapropel	*freshwater sapropel* quaternary freshwater organic sediments (containing more than 15% of organic matter) that accumulate due to the deposition of remains of aquatic plants and animals, mixed with mineral components
cal BP	*calibrated (calendar) years before present* corrected raw radiocarbon dates expressed in time scale used to specify sapropel formation character in the past in studied research sites January 1, 1950, is used as 'present' time ('0' year)
MiZ	*microfossil zone* biozone characterized by the association of three or more taxa of microfossils
MaZ	*macrofossil zone* biozone characterized by the association of three or more taxa of macrofossils
MalZ	*malacofauna zone* biozone characterized by the association of three or more taxa of mollusc remains
LPAZ	*local pollen assemblage zones* biozone characterized by the association of arboreal (tree) and nonarboreal (herb) pollen and spores
FWSDB	freshwater sapropel database the author has created and, in this Thesis, described GIS database of freshwater sapropel deposits in Latvia
HS	humic substances
PReg	*planning region of Latvia* the planning regions of Latvia are not administrative-territorial divisions; the boundaries of five planning regions (Kurzeme, Latgale, Riga, Vidzeme, Zemgale) aligns to the borders of the municipalities of Latvia following the municipality reform of July 1, 2009
major elements	*major elements* elements that compose 95% of the earth's crust
heavy metals	*heavy metals* metallic elements that have a relatively high density and are toxic at low concentrations
thsd.	thousands
m ASL	meters above sea level
LOI	loss-on-ignition
DM	dry matter

INTRODUCTION

Sapropel is one of the national natural resources of Latvia. The volume of sapropel is approximately 170 to 190 million tons. These organogenic lake sediments are formed during postglacial or the Holocene (last 11,000 years) and accumulated in the aquatic environment of the lake. Sapropel is an essential resource with economic value, as well as in terms of nature protection. In this respect, it is necessary to improve the understanding of the processes occurring in water bodies, especially on the factors influencing sedimentation conditions and sediment composition.

Investigation of lake sediments is considered as a topic of scientific research with the main reasons as follows:

1. Lake sediments are like nature archive of the past, which reflect historical climatic conditions, vegetation, land use pattern, and thus sediment analysis can be used as a tool for the reconstruction of environmental history.

2. The composition of sediments accumulated during the lake development is strongly related to their formation environment, paleogeographical and paleoecological conditions, including lake water level fluctuations. It may reveal natural events, for example, volcanic eruptions, forest fires and human impact.

3. Multidisciplinary studies of lake sediments are of importance to understand reasons and character of climate and local environmental changes through the time, which affect sedimentation processes and sediment properties.

4. In lake sediments, a large volume of organic carbon, nitrogen and phosphorus compounds can be found. Thus, lake sediments can be considered as a significant natural resource with broad application potential. Practical use of lake sediments is substantial due to extensive application possibilities, including agriculture, horticulture and forestry. Organic-rich sediments can be applied as a fertilizer and soil conditioner or as an additive for farm animal feed. Furthermore, certain sediments are suitable as a raw material for the chemical and construction industry as well as can be applicable in medicine or cosmetology as a therapeutic mud. They can be used as a raw material for chemical or pharmaceutical production.

5. Results of sediment studies allow a better understanding of what measures should be taken into account for lake ecosystem protection, especially for lakes which disappear due to intensive overgrowing processes and organic sediment accumulation.

Sapropel refers to lake sediments containing a large amount of flora and fauna remains, usually rich in organic matter. It is valuable and partially renewable earth resource formed during the Quaternary period. Different terms are used to distinguish these sediments in scientific literature and regarding practical activities: sapropel (Bambalov, 2013; Kurzo *et al.*, 2004; von Post, 1862), gyttja (Punning *et al.*, 2003; Stivrins, 2015; Terasmaa *et al.*, 2013), or dy (Hansen, 1959). Using a specific term depends on the research schools working on this material, as well as understanding sapropel as a mineral resource. In this work, the term 'sapropel' will be used to describe deposits of inland freshwater bodies rich in organic matter (organic matter content exceeds 15%) which are formed from the remains of aquatic animals and vegetation mixed with mineral components (Stankeviča *et al.*, 2017a).

Sapropel can be considered as a highly complex material as many external factors influence its composition. Until now, mostly monodisciplinary approaches have

been applied to study either sapropel formation conditions or metal accumulation processes of sapropel (Kozlovska *et al.*, 2015; Lepane *et al.*, 2007; Yao and Gao, 2007), or impact of climate change on sapropel composition (Stivrins, 2015; Stivrins *et al.*, 019). However, it is crucial to develop a new understanding of sapropel properties and conditions of its formation to find new application fields for sustainable use of this natural resource. Latvia is not rich in ore and other significant strategical raw deposits; therefore, development of the state industry is based on such local natural resources like wood and local non-ore deposits including sand, gravel, peat and sapropel.

Sapropel has a broad range application, and, therefore, it is a significant natural resource which may be used in agriculture, gardening, forestry, livestock farming, chemistry and construction industry, balneology and cosmetology. Besides, sapropel can be applied as a valuable resource of nutrients, trace elements and macroelements (Stankeviča *et al.*, 2016) and its use can contribute and support the development of bioeconomy, biological agriculture and other fields of a sustainable economy.

Metallic elements, their concentration and accumulation rate in sediment layers of various times of lake development and sedimentary phases is a significant issue within the research of mechanisms of biogeochemical cycles and contribution of human-induced versus natural processes. Studies of element content in sediments can help to discover peculiarities of metal accumulation process in limnic systems and biogeochemical element cycling. The information gathered also is essential for the development and improvement of remediation management of water bodies and practical utilisation of sedimentary material after its extraction from a lake (Maltsev *et al.*, 2014).

Up to now, sapropel exploration has been performed for 1,600 lakes of Latvia, where sapropel deposits have been estimated at approximately 930 million m^3 (Stankeviča *et al.*, 2017b). It allows identifying sapropel as an essential natural resource of Latvia. Vast application possibilities of sapropel (Stankeviča and Kļaviņš, 2013) makes it as a strategical natural resource not only in Latvia but also in Lithuania (Kozlovska *et al.*, 2015), Estonia (IBP, 2015), Belarus (Kurzo *et al.*, 2012), Russia and other countries (Shtin, 2005). To make more efficient use of sapropel and, at the same time, to preserve and protect the lake ecosystem, extensive comprehensive multidisciplinary studies have been carried out on the formation and properties of sapropel.

The aim of the study

To study the conditions of freshwater sapropel accumulation in overgrowing water basins, the nature of the accumulation of metallic elements and the effect of sapropel formation on its properties and opportunities for use.

The tasks of the Thesis

1. To adapt the classification system of freshwater sapropel in Latvia and to study its usage possibilities on the example of certain lakes in Latvia;
2. To evaluate the potential of sapropel and explore the possibilities of its use.
3. To create a database of freshwater sapropel resources in lakes of Latvia and to evaluate the economic potential of its use;

4. To perform an investigation of sapropel composition using paleolimnological, biological and chemical investigation methods;
5. To analyse and characterize sapropel sediment composition accumulated during the Holocene, taking into account geological structure, relief of lake basin area and genesis of lake depression in the studied lakes.

The focus of the Thesis

Sapropel properties and evaluated possibilities of its use based on formation conditions, that author elaborated on four studied aspects: (1) Origin and formation conditions of sapropel, (2) Sapropel properties, (3) Systematisation and classification of freshwater lake sapropel resource in Latvia and (4) Sapropel application possibilities. These four aspects are divided into seven research topics and discussed in eighteen scientific papers (Table 1).

Table 1

The list of scientific articles reflecting the studied aspects of the Thesis

Step	Studied aspect	Research topic	No.(*)	Title of publication
1	Origin and formation conditions of sapropel	Formation regularity of sapropel	1(5)	Sapropel deposits exploration using radiolocation approach
			2(12)	Reconstruction of the Holocene paleoenvironmental conditions accordingly to the multi-proxy sedimentary records from Lake Pilvelis, Latvia
			3(19)	Paleovegetation changes in the Lake Pilvelis
			4(21)	Ontological mapping of lake sediment formation/exploitation within an environmental management framework
			5(24)	Character of paleovegetation change in lakes Pilcines, Pilveļu, Padēlis
2	Composition and properties of sapropel	Inorganic matter	6(1)	Accumulation of metals and changes in composition of freshwater lake organic sediments during the Holocene
			7(4)	Impact of micro- and macroelement content on potential use of freshwater sediments (gyttja) derived from lakes of eastern Latvia.
			8(11)	Records of the anthropogenic influence on different origin small lake sediments of Latvia
			9(23)	Accumulation of metals in sapropel
		Organic matter	10(2)	Role of humic substances in agriculture and variability of their content in freshwater lake sapropel

Table 1 (continued)

The list of scientific articles reflecting the studied aspects of the Thesis

Step	Studied aspect	Research topic	No.(*)	Title of publication
3	Systematization of sapropel resources and its classification in Latvia	Resources	11(6)	Systematization of sapropel resources and division of regional potential for exploitation in Latvia
		Classification	12(7)	Sapropel's definition and classification options
4	Application possibilities of sapropel	Application	13(3)	Granulation of fly ash and biochar with organic lake sediments – A way to sustainable utilisation of waste from bioenergy production
			14(8)	Freshwater sapropel (gyttja): Its description, properties and opportunities of use in contemporary agriculture
			15(10)	Testing sapropel (gyttja) as soil amendment: assessment of plant germination and early seedling development.
			16(14)	Influence of sapropel (gyttja) on *Trifolium pratense* seeds germination in presence of copper
			17(15)	Environmental and economic aspects of small freshwater lake sustainable use: Lake Pilvelis example
			18(16)	Effects of sapropel on the growth of radish (*Raphanus sativus L.*)
			19(17)	Organic-rich freshwater sediments (sapropel) as potential soil amendment for recultivation of areas contaminated with heavy metals
			20(18)	Sapropel and its application possibilities
			21(20)	Insulation boards of sapropel/peat, sapropel/wood chips and their properties
			22(22)	Lake sapropel: A valuable resource and indicator of lake development

(*) Correspond with No. of the Author's Scientific Publications list

The novelty of the research

- Multi-proxy approach application for analysis of sapropel composition;
- Determined:
  - The accumulation pattern of major elements and heavy metals in sapropel;
  - The impact of environmental factors on sapropel formation and properties;
  - Identification of relations between sapropel composition and sapropel formation;
- Developed Sapropel Classification System relevant for sapropel sediments in Latvia.

Hypothesis

Application potential of sapropel as evaluated natural resource depends on its formation conditions, primarily environmental factors, processes influencing sapropel elemental composition, accumulation of major elements and heavy metals during the sapropel formation. Sapropel sediments can be considered as a valuable resource with diverse application possibilities simultaneously supporting the restoration of water bodies.

Practical importance

- Formation of a database for sapropel as a resource considering its application possibilities;
- Evaluation of sapropel application possibilities considering sapropel properties;
- Support for new innovative application possibilities of sapropel;
- Development of sapropel characterisation methods supporting its application.

Approbation of the results

The results of the doctoral Thesis are published in 24 scientific articles (including 12 articles in SCOPUS and Web of Science) and discussed in 24 international and 16 local scientific conferences. The obtained results have been used for one patent preparation.

Scientific publications

1. **Stankevica, K.**, Vincevica-Gaile, Z., Klavins, M., Kalnina, L., Stivrins, N., Grudzinska, I., Kaup, E. (2020). Accumulation of metals and changes in composition of freshwater lake organic sediments during the Holocene. *Chemical Geology, 539*, 119502, https://doi.org/10.1016/j.chemgeo.2020.119502 (SCOPUS; Web of Science)

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3. Vincevica-Gaile, Z., **Stankevica, K.**, Irtiseva, K., Shishkin, A., Obuka, V., Celma, S., Ozolins, J., Klavins, M. (2019). Granulation of fly ash and biochar with organic lake sediments – A way to sustainable utilisation of waste from bioenergy production. *Biomass and Bioenergy, 125*, 23-33, doi:https://doi.org/10.1016/j.biombioe.2019.04.004 (SCOPUS)

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1. Kalniņa, L., **Stankeviča, K.**, Kļaviņš, M., (2019, August 20-23). *Diversity of pollen composition in small lake sediments from Latgale Upland during their history.* 12th International meeting of Pollen Monitoring Programme (PMP 2019), Riga, Latvia.

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8. Vincevica-Gaile, Z., Stapkevica, M., **Stankevica, K.**, Burlakovs, J. (2015, May 13-15). *Testing sapropel (gyttja) as soil amendment: assessment of plant germination and early seedling development.* Annual 21st International Scientific Conference "Research for Rural Development", Jelgava, Latvia.

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12. **Stankevica, K.**, Burlakovs, J., Klavins, M., Vincevica-Gaile, Z. (2014, June 19-25). *Environmental and economic aspects of small freshwater lake sustainable use: Lake Pilvelis example.* 14th SGEM Geoconference on Ecology, Economics, Education and Legislation, Albena, Bulgaria.

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9. **Stankeviča, K.**, Vincēviča-Gaile, Z., Muter, O. (2015, February 4). *Mikroorganismu daudzveidības analīze dažāda tipa sapropeļa nogulumos [Microbial diversity analysis in sapropel of various types].* 73rd Scientific Conference of the University of Latvia, Riga.

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14. Rūtiņa, L., **Stankeviča, K.**, Kļaviņš, M. (2013, January 31). *Humusvielu satura mainība Latvijas ezeru sapropelī [Variability in the content of humic substances in lake sapropel of Latvia].* 71st Scientific Conference of the University of Latvia, Riga.

15. **Stankeviča, K.**, Rūtiņa, L., Kļaviņš, M. (2012, February 17). *Metālu saturs Latvijas ezeru sapropelī [Content of metallic elements in lake sapropel of Latvia].* 70th Scientific Conference of the University of Latvia, Riga.

16. **Stankeviča, K.**, Rūtiņa, L., Kļaviņš, M. (2012, February 17). *Sapropeļa praktiskās izmantošanas iespējas [Practical possibilities of sapropel use].* 70th Scientific Conference of the University of Latvia, Riga.

Patent

Stankeviča, K. (2015) Bioloģiski aktīvu humusvielu iegūšanas paņēmiens [Method for producing biologically active humic substances]. *Patent of Latvia No. LV 15014 A.*

Author's contribution

The author has obtained and studied 206 organic-rich freshwater sediment samples of 3 freshwater sediment profiles in Latvia. During the research, sapropel samples were collected from Lake Padelis, Lake Pilcine and Lake Pilvelis. Sediment profiles were described according to an adapted protocol (Givelet *et al.*, 2004).

The type of sapropel was determined using an adapted classification system of Latvian freshwater sapropel (Stankevica *et al.*, 2017a). Preparation and analysis of sapropel samples were done at the Faculty of Geography and Earth Sciences (University of Latvia).

The author has contributed to direct work with sediment research performing following activities: collection and preparation of sapropel samples from three lakes (Lake Padelis, Lake Pilcine and Lake Pilvelis), analysis of moisture, organic matter, ash, carbonate and mineral matter, analysis of metal content, biogenic phosphorus, detection of content of total humic substances, microfossil identification, as well as summarization, evaluation, and analysis of all research results, assessment of the relationship between different parameters and properties. The author has also performed seed germination and plant growth tests using sapropel as a growing media.

The author has had principal responsibility for the creation of freshwater sapropel database (FWSDB) using the data from previous studies and explorations of freshwater sapropel in Latvia (GEO-Konsultants, 1995, 1996, 1997, 1998a, 1998b, 1999; Latvgeologija, 1991a, 1991b, 1992; Latvijas ģeoloģija, 1994). The author's contribution within the creation of the database included collection, processing, input and systematisation of information in GIS software, statistical data analysis, as well as data interpretation in the field of sapropel potential application in the regions of Latvia. Within this work, the definition of freshwater sapropel was developed by the author and adapted classification system of freshwater sapropel for the environment of Latvia was offered.

Structure of the Thesis

The structure of the Thesis includes an introduction, three main chapters and a section of literature review.

In the first part of the Thesis, various theories and standpoints on the definition of modern freshwater organogenic sediments are reviewed and critically analyzed; information about the sapropel research history in the world and especially in Latvia is aggregated, as well as the scientific literature on the composition of sapropel is generalized. Modern mainstream development for sapropel application possibilities is considered in detail.

The second part presents information about the study area, sampling sites and methodology of the research and experimental equipment for sapropel analytical research used during this study. Structure and creation steps of freshwater sapropel database are described, and statistical methods for data interpretation are outlined.

The third part compiles the results of the studied topics: (1) Typology, amount, distribution and formation regularities of freshwater sapropel in the territory of Latvia; (2) Environmental and lake conditions during the sapropel formation in studied lakes Padelis, Pilcine and Pilvelis; (3) Distribution, chemical associations and factors influencing the accumulation of metals and other elements in sapropel.

The Thesis consists of 144 pages and is supplemented with illustrations – 32 pictures and 28 tables.

1 LITERATURE REVIEW

1.1 Definitions, classification of sapropel and history of its research in Latvia

Lake sediments, their composition, development and properties were one of the first objects studied in aquatic systems. Considering considerable differences in water bodies, climatic factors, geological processes, sediment composition, significantly differing results were obtained. Another factor aggravating the studies included a variety of diverse perspectives on the study object – lake sediments – as they have been studied from the perspective of geology, biology, chemistry, medicine and other sciences, sometimes yielding controversial opinions on the same object and various classification approaches.

Sapropel also called as 'gyttja' or 'dy', is a renewable natural resource, which can be found as the quaternary freshwater organic sediments that accumulate due to the deposition of remains of aquatic plants and animals, mixed with mineral components. Sapropel is a unique geological formation occurring at the bottom of a water body throughout its existence (Lopatin, 1983; Lopotko, 1974). Formation of sapropel is highly dependent on the processes in the lake, and formation of sapropel sediments can take place only due to the disruption of the substances and energy circulation, which is a process widely observed in eutrophic lakes (Kurzo, 1988). In a narrower sense, 'sapropel' (from Greek, 'sapros' rotten + 'pelos' mud) denotes contemporary or subfossil, colloidal sediments of continental water bodies. They are characteristic with a fine structure that contains significant quantities of organic matter and remains of microscopic water organisms with a small amount of inorganic biogenic component content and admixture of mineral ingredients, which may include sand, clay, calcium carbonate and other minerals (Lācis, 2003).

Among the pioneers studying the lake sediments following scientists can be mentioned: S. Pauli, E. Chladni, C. von Esenbeck, J. Berzelius, F. von Grotthuß, J. Kniphof, C. Ehrenberg, H. Göppert, F. Cohn and F. Kolenati (Aharon, 2010; Berzelius, 1822). Very various opinions were expressed on the genesis and properties of lake sediments; however, as the cornerstone for contemporary understanding, the studies performed by H.-A. von Post (1862) can be considered. H.-A. von Post published his developed classification of modern coprogenic material/ soil classes – gyttja, dy, peat and compost. He defined gyttja as grey or reddish-grey elastic sediments which settle on the bottom of the clear and clean waters with well-developed mats of filamentous algae *(Conferva, Zygnema, Lyngbya)*. Gyttja mainly consists of decomposed plant, diatom frustules, exoskeleton fragments of insects and crustaceans, as well as quartz and mica grains, spongilla spicules; moreover, a large number of diatoms are still alive, but desmids – green. Gyttja was subdivided into five types: meadow gyttja (Ängsgyttja), spring gyttja (Källgyttja), dam gyttja (Dammgyttja), river gyttja (Flodgyttja) and lake gyttja (Sjögyttja). H.-A. von Post in 1862 noted: '*in lakes with brown water forms dy instead of gyttja. Dy consists of plant parts and foliage cell walls, a number of diatoms and high concentration of lower aquatic animals (larvae, crustaceans, shells, infusoria, etc.) absorbed in humic substances and mixed with detritus*'.

C. Wesenbeeg-Lund (1901) after investigation for two years of different deposits in the beds of Danish lakes concluded that the main condition for the formation of lake gyttja is a production of organic matter in greater quantity than the bottom fauna and bacteria of the lake ecosystem can transform.

Even this brief analysis illustrates the highly diverse approaches used for the development of definitions describing lake sediments. During the last centuries, many definitions and terms of organic-rich freshwater sediments have been put forward. A structured account for the terms and definitions is given in Table 2.

Table 2

Historical development of the terms and definitions for organic-rich sediments found in lakes

Term	Definition	Reference
Lake gyttja	Grey or reddish-grey elastic sediments, which settle on the bottom of clear and clean waters with well-developed mats of filamentous algae (*Conferva, Zygnema, Lyngbya*). Gyttja mainly consists of fragments of decomposed plants, diatom frustules, insects' and crustaceans' exoskeletons, as well as quartz and mica grains, spongilla spicules; moreover, a large number of diatoms are still alive, but desmids – green	von Post, 1862
Dy	Brown to black-brown sediments, which settle on the bottom of brown water lakes. Dy consists of plant parts and foliage cell walls, remains of diatoms and high concentration of lower aquatic animals (larvae, crustaceans, shells, infusoria, *etc.*) absorbed in humic substances and mixed with detritus	von Post, 1862
Lake gyttja	The surface layer of sediments with coprogenic nature, which occur at the bottom of pure, limpid waters and which commonly contain a considerable amount of clay and lime (20-30%), and only a slight amount of undigested material. Organic matter origin traced partly to plankton, partly to flora and fauna of the region, and partly to the littoral zone of a lake	Wesenbeeg-Lund, 1901
Sapropel	Gyttja as defined by H.-A. von Post (1862) adding a note: mixed with acidic humus colloids	Potonié, 1910
Gyttja	Limnic sediments with a predominance of the material of autochthonous origin	Nauman, 1922
Dy	Limnic sediments with a predominance of the material of allochthonous origin	Nauman, 1922
Gyttja	A mixture of remains of all dead organisms in lake chemical precipitation and minerogenic matter	Hansen, 1959
Dy	Gyttja mixed with a dopplerit	Hansen, 1959
Sapropel	Organic sediments with a content of H_2S and CH_4 deposited during strongly anaerobic conditions	Hansen, 1959

Scientific interest about sapropel in Latvia arose at the beginning of the last century as part of peatland and peat resources exploration. In 1939, the Research Institute of Earth Treasure was built, where from 1939 until 1942 the research on sapropel deposits embedded in peat bogs were carried out under the supervision of engineering technologist P. Nomals. The studies resulted in a detailed exploration of 35 sapropel deposits and identification of more than 400 sapropel deposits

under the peat layer in bogs. Later these studies were continued by the Laboratory of Peat Research at the Institute of Hydraulic Engineering and Land Reclamation Science of Latvia (Kalniņa *et al.*, 2017; Nomals, 1943). Chemical and technological investigation of sapropel began in 1950, and from 1957 to 1967 it was carried out at the Institute of Wood Chemistry of the Latvian Academy of Sciences. The first in-depth purposeful research on lake sapropel began under the leadership of chemist N. Braksh. The studies performed at the Institute of Forestry Problems, the Institute of Wood Chemistry and the Latvian Academy of Agriculture have revealed the binding ability of sapropel useful for the production of boards (plywood) from wood fibre and agricultural waste as well as various composite materials (Grosvalds and Alksnis, 2007). During this period (1920-1960), 250 lakes of Latvia were surveyed obtained sapropel samples were exposed to various chemical analyses to investigate its application possibilities mainly to be used as a soil fertilizer. However, in the 1970s, with the development of chemically-based fertilizer industry, sapropel research was discontinued, citing the higher efficiency of artificial fertilizers. Only in the late 1980s, realising the importance of natural organic soil fertilizers, the company 'Latvijas agrokimija' (later called 'Raziba') resumed the studies and practical use of sapropel in agriculture. The research was also resumed by the Latvian Academy of Agriculture and the Institute of Agricultural Research. From 1990 to 2000, the search for sapropel deposits in the lakes of Latvia was carried out. The reports on the search for sapropel summarize both, the results of previous surveys of sapropel deposits and new findings taking into account subdivision of the territory of Latvia into administrative districts (GEO- Konsultants, 1995, 1996, 1997, 1998a, 1998b, 1999; Latvgeologija, 1991a, 1991b, 1992; Latvijas ģeoloģija, 1994).

Formation of uniform terminology and classification of lake sediments is burdensome because each interested science field has developed its own classification and list of terms, which corresponds to the direction, objectives and specific aims of individual research (Kireicheva and Khokhlova, 1998; Lundquist, 1927; Titov, 1950). German scientist R. Lauterborn extended the existing classification of modern coprogenic material by adding the term 'sapropel' describing sediments characteristic with hydrogen sulphide odour (Hansen, 1959; Kurzo, 1988). H. Potonié has introduced a contemporary understanding of the term 'sapropel'. Classifying lake sediments, H. Potonié singled out two groups: 1) 'sapropel' – viscous, finely dispersed residue, containing 25-90% of organic matter, and 2) mineralized sediments – 'sapropelite', which further can be split according to their mineral components: diatomite, lime, iron and sand (Kurzo *et al.*, 2012; Potonié, 1910, 1915). Contemporary use of the terms and definitions also depend on the regional location of scientists, i.e., in Eastern and Western Europe more popular term is sapropel, however, in publications in English, the use of terms much depends also on the context of a study.

A.P. Pidoplichko and R.I. Grishchuk (1962) provided more detailed and most often used classification of sapropel. According to their suggestion, lake sediments can be subdivided into seven types:
– Clayey sapropel is highly mineral; usually, it is deposited in lakes naturally. It is pasty, heavy, in grey or grey-blue colour;

– Calcareous sapropel is characteristic with ash content higher than 35% (including 50-65% CaO); deposits are formed in locations of calcium-rich groundwater outflows. It is grey-green, but after drying out it forms unbound, whitish-grey mass;

– Silicate sapropel has a high ash content – greater than 30% (including SiO_2 >30% and CaO <10%). It is grey-green or green with sand grains and dark-coloured dense dykes;

– Mixed sapropel has very high ash content (about 70-80%); it can contain a large amount of calcium and silicates, silicates and clay or clayey particles and calcium; such mixed lake sediments are mainly formed from plankton organisms. Mineral supply source for this type of sapropel can be ground or surface waters. It can be greyish, dark green, blue-green or greyish-brown;

– Organic (fine detritus) sapropel has a low ash content, not exceeding 30%. It is green, and with an admixture of humus – greenish-brown. Organic sapropel is formed in water bodies that do not have massive mineral matter inflow;

– Coarse detritus sapropel has a low ash content. It accumulates in the lakes, where in addition to planktonic organisms there are many vascular aquatic plants, which residues remain in sapropel in large quantities. This sapropel usually is dark green, and the higher aquatic plant trace inclusions can be observed therein. It is usually deposited over the other sapropel types and does not form thick layers;

– Peaty sapropel is formed when the peat deposits come into contact with a lake, or results from overgrowing of eutrophic water bodies littoral. It is the intermediate form between sapropel and peat; brown and containing a variety of thelmatic plants – residues of reeds, sedges, horsetails and other plants. When pulverized, peat sapropel does not smear, nor stain. It is characterized by very low ash content (8-10%) and high decomposition level (around 25-30%). This type of sapropel is deposited in layers between peat and sapropel deposits due to fluctuations in water level at the lake.

During the 1970s, Belarussian scientists developed sapropel classification (Table 3), taking into account the requirements of industry and the principles of sapropel genesis (BSSC Institute, 2010; Yevdokimova *et al.*, 1980). This classification is based on quantitative analysis of seven indicators describing the chemical structure of sediments.

Each isolated type of sapropel is defined as a raw material for a specific direction of use. Therefore, this is the most complex sapropel classification.

According to the ratio between the organic and mineral part, the authors classify sapropel as a low ashy (ash content less than 30%) and a high ashy (ash content of 31-85%) sapropel. Low ashy sapropel is divided into four types, according to the ratio of humic substances and easily hydrolysable substances associated with the genesis of proteins in sediments. The first type of sediments contains a larger amount of allochthones humic material. The other three types of organic sapropel contain humic substances formed of autochthonous material. The sapropel group with a high ash content is further categorized into three subtypes based on the chemical analysis of the mineral part: silicate sapropel, carbonate sapropel and mixed sapropel.

Table 3

Industrially-genetic classification of sapropel (BSSC Institute, 2010)

Type	Form	Label	A_c, %	Biological composition and oxides, %		Utilisation	Diagnostic indicators
Organic	Peaty	Opr_1	<30	Thelmatic plants	>70	Growth promoters, HS products, fertilizers, production of construction materials	A_c^*
	Organic, with a high HS content	Opr_2	<30	Thelmatic and vascular aquatic plants	50-70	Therapeutic mud, biologically active substances, fertilizers	
	Organic, with a medium HS content	Opr_3	<30	Diatoms and cyanobacteria	-	Fillers, drilling solutions, therapeutic mud, fertilizers	
	Organic, with a low HS content	Opr_4	<30	Green algae	-	Binder substances, drilling fluids, therapeutic mud, fertilizers	
Silicate	Silicate (low ash content)	Kp_1	30-50	Diatoms	>90	Fertilizers, drilling fluids, production of construction materials, therapeutic mud	A_c SiO_2/CaO Fe_2O_3
				SiO_2/CaO	>2		
				Fe_2O_3	<10		
	Silicate (high ash content)	Kp_2	50-85	Diatoms	>90	Soil colmation, tamponage solutions, fertilizers	
				SiO_2/CaO	>10		
				Fe_2O_3	<10		
	Autogenous silicate	Kp_3	30-50	Diatoms	>90	Growth promoters, therapeutic mud	
				SiO_2/CaO	>2		
				Fe_2O_3	<10		
	Silicate ferruginous	Kp_4	>30	Diatoms	>90	Therapeutic mud	
				SiO_2/CaO	>2		
				Fe_2O_3	>10		
Carbonate	Carbonate	$Kap6_1$	>30	SiO_2/CaO	<0.4	Animal feed additives rich in minerals and vitamins, therapeutic mud, soil liming	A_c SiO_2/CaO Fe_2O_3 Minerals = $A_c + CO_2$
				Fe_2O_3	<5		
	Carbonate ferruginous	$Kap6_2$	>30	SiO_2/CaO	0.4-0.7	Soil liming, tamponage solutions, therapeutic mud	
				Fe_2O_3	>5		

*A_c – ash content, %

Table 3 (continued)

Industrially-genetic classification of sapropel (BSSC Institute, 2010)

Type	Form	Label	A_c, %	Diagnostic properties		Utilisation	Diagnostic indicators
				Biological composition and oxides, %			
	Mixed organic silicate carbonate	CM_1	>30	SiO_2/CaO	0.7-2.0	Fertilizers, construction material production, therapeutic mud	
				SiO_2/Fe_2O_3	>4		
				CaO/Fe_2O_3	>3		
				SO_3	>10		
	Mixed silicate carbonate ferruginous	CM_2	>30	SiO_2/CaO	0.7-2.0	Drilling solutions, construction material production, therapeutic mud	
				SiO_2/Fe_2O_3	1.0-4.0		A_c
				CaO/Fe_2O_3	0.4-3.0		SiO_2/CaO
				SO_3	<10		SiO_2/Fe_2O_3
	Mixed organic silicate ferruginous	CM_3	>30	SiO_2/CaO	0.7-2.0	Therapeutic mud	CaO/Fe_2O_3
				SiO_2/Fe_2O_3	<1		SO_3
				CaO/Fe_2O_3	<0.4		
				SO_3	<10		
Mixed	Mixed organic carbonate sulphate	CM_4	>30	SiO_2/CaO	0.7-2.0	Therapeutic mud	
				SiO_2/Fe_2O_3	>1		
				SO_3	>10		

Taking into account the composition and properties of sapropel, given classification determines the most rational use of sapropel as a mineral resource (Braksh, 1971). Also in Latvia nowadays the term 'sapropel' is dominant like in Eastern and Western Europe.

1.2 Formation of freshwater sapropel

Various freshwater sediments, including sapropel, are widely distributed in many water bodies of the world. The most intensive formation and accumulation of organic-rich lacustrine sediments are characteristic to the temperate zones: northern regions of Europe, the European part of Russia, in the north of Asia and Siberia (Leonova and Bobrov, 2012; Maltsev *et al.*, 2014), as well as in North America (Malloy and Price, 2017; Yu and McAndrews, 1994).

Organic-rich sediment deposits in water bodies, including sapropel, appeared after the glacier retreat. In the Baltic countries, it happened 12-15 thousand years ago (Zelčs and Markots, 2004). Massive sapropel formation in this region took place in the Holocene (12,300 cal BP – present) (Heikkilä and Seppä, 2010; Klavins *et al.*, 2011; Ozola *et al.*, 2010; Stančikaitė *et al.*, 2009, 2015; Stankevica *et al.*, 2015; Stivrins, 2015; Stivrins *et al.*, 2014, 2015, 2019; Terasmaa *et al.*, 2013).

H. Potonié theorized the first scientific opinion regarding the formation of sapropel. He thought that sapropel formation is a mechanical accumulation

of plankton decomposition remains – waxes and fats – in the water basins (Potonié, 1915), ignoring the role played by a synthesis of hydrocarbons, higher plant proteins and new compounds (Dmitriyeva, 2003; Vimba, 1956).

Y. Kazakov (1950) later criticized the theory proposed by H. Potonié, arguing that the other sapropel formation elements must be taken into account. These include higher aquatic plants, benthic forms of flora and fauna – the processes of their disintegration and synthesis such as the emergence of compounds belonging to the type of humic substances formed from carbohydrates and protein split products (Figure 1).

Simplified theory of sapropel formation define that sapropel is formed as a result of fast reproduction of simple plants and animals, and their accumulation in large quantities in the bottom of the lake. After expiring, they settle at the bottom of a lake in the form of sediments. For example, in the summer, a variety of phytoplankton species, cyanobacteria, green algae, diatoms, *etc*. develop within the watercourses. As they die, the remains of these organisms, rich in fats, proteins, phosphorus, potassium, calcium and cellulose, become sapropel components. Humic substances, calcium and iron salts in water accelerate coagulation and sedimentation processes (Largin, 1983; Lopotko and Kislov, 1990; Potonié, 1915).

However, the formation of sapropel is a more complicated and long-lasting process, and its accumulation begins in the lake depressions.

The theory of the lake sediment formation explains the formation of basic sediment layer's fine-layered structure, and it can serve as a historical chronicle of the water body and its surroundings. The theory is based on the idea that sediment layers are annual layers, and from their number, the life span of the watercourse can be estimated (Zolitschka and Enters, 2009).
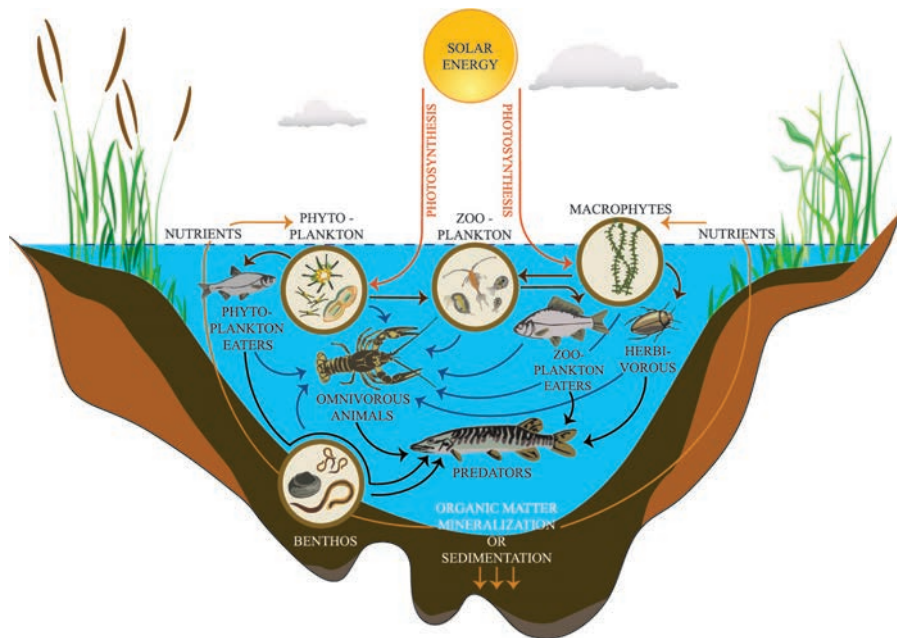

Figure 1. **Nutrient cycling in a water body** (author's work out)

In comparatively shallow (2-20 m deep) and small water bodies (without flow-through), which are protected from storms, favourable conditions are established for the accumulation of organic-rich sediments. Waters of such lakes contain a sufficient amount of nutrients, which, as a result of the chemical and biochemical processes ongoing in the sediments, transform, changing the demersal water layer composition. Sediments emit gases: CH_4 75-95%, H_2 5-15%, CO_2 up to 3%, part of which dissolves in water and does not reach the surface. These gases are emitted by the sediment surface layers, which are 1 m thick. Besides, gas discharge is characteristic to shallow, well-heated lakes (eutrophic and dystrophic) with a large amount of sediments that are rich in organic matter.

In the process of sapropel formation, two stages can be determined: sedimentogenesis and diagenesis (Bambalov, 2013; Kholodov, 2010).

During the stage of sedimentogenesis, in the bottom of a lake, a mixture of sapropel-forming raw materials is formed that consists of organic, mineral and organo-mineral substances of various genesis (Figure 2; Table 4).
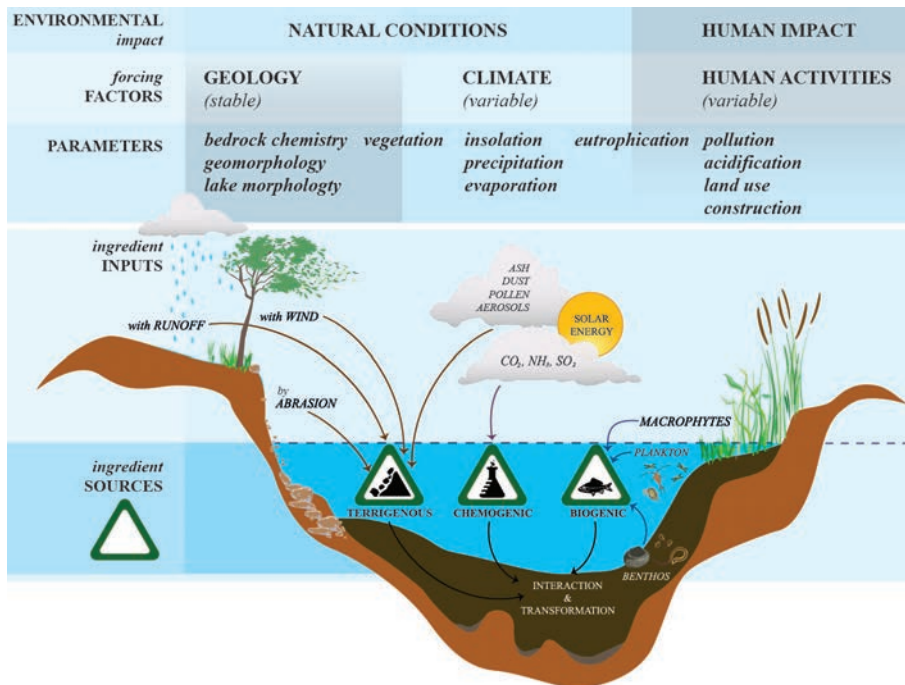
Figure 2. **Simplified scheme of forcing factors, parameters, ingredient inputs and sources that lead to the formation of sapropel** (author's work out according to Bambalov, 2013; Zolitschka and Enters, 2009)

This stage begins when insoluble organic mineral constituents and their complexes appear in the water. Deposition of these particles can take from a few seconds (for sand particles) to several months (for colloids). At this stage, the initial transformation of the substances also takes place. Deposition of particles is governed by sedimentation laws (De, 2017), which, together with water mass movements,

determine the distribution of particles in the lake depression. Typically, larger particles settle closer to the lake shores, while small particles disperse throughout the middle part of the lake. Hydrolysis, oxidation and enzymatic processes, ion exchange, coagulation, sorption and particle attachment during the stage of sediment-genesis of sapropel result in significant chemical and physical changes in the composition of the sapropel parent material. The water layer is also heterogeneous; aerobic and anaerobic layers can be distinguished in it that undergo both, oxygen and non-oxygen, decomposition and processes of synthesis, (de)nitrification, nitrogen fixation, sulphur and phosphorus conversion. Sedimentation stage ends when the particles of sapropel-forming raw material (detritus) are fixed on the bottom of the lake and water movement do not rise them up. At the concluding stage of the lake's development, as the lake overgrows, a source of organic detritus is provided by plants (macrophytes), which form a coarse detritus and gives sapropel a dark colour. Detritus, which is formed from the lower plant and animal residues and their excrements, forms a colloidal, soft, fatty mass, which can be of different colours (Lopotko, 1974).

As a result of the processes of sedimentation stage, sediments are gradually formed at the bottom of the lake, which in the vertical section are divided into two layers: (1) Pelogenic – oxygen-containing and biologically active surface layer. It is inhabited by benthic organisms and varies in thickness from 0.20 to 0.60 m (Dmitriyeva, 2003); (2) Conservation area – anaerobic, biologically inert layer where secondary transformations of substances appear (Bambalov, 2013).

Diagenesis – the second stage of sapropel formation begins in pelogen. This layer contains sufficient amount of dissolved oxygen in the water for the action of benthic and aerobic microorganisms, and as a result of biological, biochemical, physical, chemical, geochemical and geological processes, intensive conversion of raw material into sapropel occurs. Pelogen is characterized by fermentation, biogenic mineralisation, humidification of organic matter, as well as hydrolysis, oxidation and reduction, substitution reactions, ion exchange, condensation, depolymerisation, (de)hydration, (de)sorption and other processes. Leading and determining processes in the pelogen are the conversion of raw materials into sapropel in the presence of aerobic living organisms.

B. Perfilyev (1972) contends that the mechanism of sapropel formation in the water-sediment layer is based on the properties of two opposite diffuse flows. The flows are formed as dissolved oxygen resulting from photosynthesis, and the environment of layers embedded below, formed by anaerobic processes, come into contact with each other. Diffusion of these flows is reduced in the upper layers, as gases with low water solubility appear and cause bubbles when rising to the surface. The entry of oxygen into the sediments in the direction from top to bottom promotes the vertical passages of worms and larvas. Sapropel becomes a biologically inert substance in the anaerobic environment, passing from the biological sphere into geological one, where within low-temperature thermolysis, most of the organic substances gradually become insoluble.

Three main ingredient sources for freshwater sapropel formation take place. The main source is dead organisms of a lake and its water basin – plankton, benthos and macrophytes. The second source is mineral, organic and organo-mineral components of allochthonous origin brought to the lake with winds, rains, water runoff or

groundwaters. The third source is precipitated substances formed in the lakes in the result of chemical and physical-chemical processes (Bambalov, 2013).

According to the estimates provided by J. Chauncey (1942), the total plant mass in the lakes is 6-20 times higher than that of the animals living therein. The amount of dissolved organic matter is always greater than the total weight of organic material – live animals, plants and detritus because all living organisms emit and expel secretions and excrements, they all die, and their residues decompose, thereby supplementing the organic matter dissolved in water (Chauncey, 1942). This group of substances includes compounds containing nitrogen (proteins, peptides, amino acids), hydrocarbons, lipids, organic acids, vitamins, hormones.

The complex chemical structure characteristic to different types of sapropel is determined by the biodiversity and relationships of lake flora and fauna, as well as their components. The diversity of all hydrobionts (Koperski, 2011), sapropel-makers in aquatic ecosystems are divided into two major groups according to their significance and formation (Dodds and Whiles, 2020):

–   Producers (plants and a part of microorganisms) forming new organic substances and accumulating mobile mineral substances. Producers in water systems can be divided into microphytes (microscopic algae, plankton and benthos) and macrophytes (vascular plants, mosses, liverworts, encrusting lichens, and a few large algal forms such as the Charales) (Wilzbach and Cummins, 2008). In sapropel, four main classes of microscopic algae are determined: diatoms, green algae, chrysophytes and cyanobacteria (Korde, 1960). Vascular aquatic plants are also considered to be significant sapropel-formers, they are divided into the following groups: mosses (Bryophyta), horsetail (Equisetales), pondweed (Potamogeton), frog's-bits (Hydrocharitaceae), grasses (Poaceae), sedges (Cyperaceae), *etc.* The predominance of the lake macrophyte and peat-forming plants is characteristic to sapropel of dystrophic water bodies and swamps. These sediments are also characterized by a high concentration of spores and pollen (up to 19%). Higher plant residue ranges from 1 to 80% of the total biomass.

–   Consumers (bacteria, fungi, animals): form organic matter from organic substances generated by the primary producers or their disintegration products, and which biomass is 2-3 times smaller than the biomass of the producers (Yevdokimova *et al.*, 1980).

Sapropel formed mineral materials (Table 4) may be of autochthonous origin such as silica and lime sediments have formed in lakes as a result of chemical processes. For example, carbonates, of autochthonous origin (Largin, 1991), are formed in waters supersaturated with bicarbonate (HCO_3^-). During the intensive development time of zooplankton, phytoplankton and benthos, the water saturation with CO_3^{2-} occurs, and it forms the basis of carbonate crystal formation (Lippmann, 1973; Stankevica *et al.*, 2013). Mineral material of allochthonous origin comes into the lake from the catchment area and the lake's tributaries. In high concentrations, it is found in river deltas and near steep slopes facing lakes (Horne and Goldman, 1994). Generally, mineral material in large concentration is observed during the early development stage of the lake, but as the lake overgrows and becomes shallower and the shores flatten, the influx of these substances decreases. The tributary waters entering the lake from the surrounding areas can contain many minerals, thus significantly affecting the mineral composition of lake sediments, which are deposited in the parts of the

Table 4

Precursors of sapropel formation and marks for their identification

(according to Korde, 1960; Miko et al., 2013; Smol et al., 2001a; Smol et al., 2001b)

Inputs	Origin	Genetic	Group	Types	Subtype	Identification marks	Identification method
watershed, atmospheric	alloch-thonous	terri-genous	minerals	(alumo-)silicate	amphibole, mica, epidote, garnet, feldspar, olivine, pyroxene	minerals' particles	x-ray diffraction, electron diffraction, polarized light microscopy, light microscopy;
				sulphate	celestine, gypsum		
				sulphur	sulphur		
				sulphide	pyrite,		
				carbonate	dolomite, calcite		
				oxide, hydroxide	goethite, hematite, quartz, magnetite, chalcedony,		
			clay mineral	(alumo-)silicate	kaolinite, illite, smectite, glauconite	minerals' particles	
		biogenic	fossils	amber	succinite	fossils	organoleptic, gas chroma-tography
			live organisms (producers)	terrestrial vascular plants	tree, shrubs, grasses, sedge	pollen, spores, plant fossils, conifer stomata, phytolith	light microscopy, stereo microscopy, electron microscopy, biogenic silica, sedimentary pigments
				thelmatic vascular plants	eleocharis, buttercups, tormentils	pollen, spores, plant fossils, conifer stomata, phytolith	
				mosses	mosses	sphagnum	
lake	autoch-thonous			aquatic vascular plants (macro-phytes)	horsetails, pondweeds, frog's-bits, water lilies	pollen, spores, plant fossils, conifer stomata, phytolith	
				algae (micro-phytes)	chrysophytes, diatoms, green algae, cyanobacteria	scale, statospores , frustules, outermost cells , akinete	

Table 4 (continued)

Precursors of sapropel formation and marks for their identification

(according to Korde, 1960; Miko et al., 2013; Smol et al., 2001a; Smol et al., 2001b)

Inputs	Origin	Genetic	Group	Types	Subtype	Identification marks	Identification method
lake	autoch-thonous	biogenic	live organisms (consumers)	bacteria		bacteria colony	light microscopy, stereo microscopy, electron microscopy, biogenic silica, sedimentary pigments
				fungi		ascospore, chlamydo-spore conidia, hyphopodia	
				animals	protozoans	shell, siliceous plate	
					sponges	spicule	
					brachiopods	shell, head shield and pore, claw, postabdomen, carapace, ephippia	
					molluscs	shell	
					insects	head capsule, mentum, frontoclypeus, pronotum, ligula, antennas, hypostoma, mandible, pharyngeal, elytron, pronotum, chitin, egg	
					arthropods	prodorsum, setae, leg, sensillus	
					crustaceans	antennas, head, spine, carapax shell, leg	
groundwater, watershed, atmospheric, lake		chemo-genic	sedimentary rock	carbonate	dolomite, calcite	particles	x-ray diffraction
				sulphate	gypsum, etc.	particles	x-ray diffraction

lake with stagnant water. The smaller is the lake, the more it is affected by inflow waters and the influx of mineral particles from the shores.

Organic substances of autochthonous origin are influential in the shaping of the lake sediments as they form the basis of many food chains and determine the productivity of a lake – the sum of solar energy converted by plants and autotrophic phytoplankton through photosynthesis into organic substances. Producers are the only manufacturers of organic matter, creating the stocks of nutrients for the rest of the food chain representatives. Decomposition and destruction of these organic substances take place in the other stages of the feed cycle using oxygen and energy scattering (Golterman, 1975).

At the final phase of each feed cycle, a material complementing the lake sediment layer is formed, but it is limited by the mineralisation of organic matter which is caused by aerobic microorganisms. Interaction between production and destruction of organic substances is one of the main factors that determine the properties and type of lake sediments (Shtin, 2005).

The hydrological regime of a lake, characteristics and size of the drainage basin are important factors for the lake sediments formation. Sapropel can be of autochthonous origin if its accumulation takes place due to the lake biomass deposits (remains of algae and zooplankton, exoskeleton fragments of insects and crustaceans, spongilla spicules). Furthermore, sapropel can be of allochthonous origin where sediments accumulate a large number of substances which enter the lake from surrounding areas and marshes (leaves, pollen and plant spores, silica grains) (Cranwell, 1975; Golterman, 2004; Largin, 1991).

Currently, the average annual sediment accumulation layer ranges from 0.1 mm in small lakes without runoff up to 4.3 mm in large flow-through lakes. It can be used as a multiannual average indicator: small lakes without a runoff – 1.05 mm, small flow-through lakes – 3.56 mm and large lakes with flow-through – 6.64 mm (Shtin, 2005).

Sediment thickness, properties and composition are mainly dependent on the geographic conditions of the region and human activities.

If the climate impact on the lake conditions mainly alters its water level, i.e., in dry periods the water level falls, in wet periods – rises, continuous sediment accumulation in a lakebed is the most critical factor in the development of a lake. F.A. Forel (1895) divided lakes into age periods according to the lakebed development stages: youth, maturity, old age, decline and decease. Each age corresponds to the specific lake type, but ultimately any lake will become dystrophic due to eutrophication, and in the process of overgrowing or entering the decease period turns into a swamp. Therefore, 1/3 of sapropel deposits in Latvia are located in the current bogs under the peat layer (Kalnina et al., 2019; Stankevica et al., 2019).

1.3 Composition of sapropel

Sapropel has a complicated chemical structure that is determined by the biological and biochemical variety of organisms and the compounds forming it from three main components – organic matter, minerals and water.

It should be noted that the total content of organic matter in various sapropel types is different: in organic sapropel more than 70%, in silicate and carbonate

sapropel – 15-70%, in mixed sapropel – 15-70% (Kireicheva and Khokhlova, 1998; Lopotko, 1974; Pidoplichko, 1975; Yevdokimova *et al.*, 1980). Sediments of saline lakes contain a smaller amount of organic substances (approximately ≥10%); flora and fauna are poorer in these lakes, and mineralization processes are faster (Whitton and Potts, 2012).

Organic substances of sapropel exist as dissolved molecules, colloids, and particles (Perdue and Ritchie, 2003); they can be defined as:

– A sum of biological and organic components consists of fine particulate remains of plants and animals, and dissolved, colloidal substances (Göltenboth and Lehmusluoto, 2006);

– A complex of low-molecular-weight organic compounds and biopolymers, and adsorption complexes with minerals (Lopotko *et al.*, 1991).

According to the elemental composition, freshwater sapropel is similar to soil organic matter. Average elemental composition of sapropel organic substances is as follows: C=55; H=6.7; N=2.5; O=35.0, C/H ratio ≈7.0-8.9 (expressed as normalized %) (Braksh, 1971). Changes of nitrogen content in vertical sections of sediments as well as other chemical indicators can be used for sapropel layer splitting in certain stratigraphic horizons. Content of nitrogen in various types of sapropel ranges from 2.7 to 6% of organic substances and from 0.5 to 4.0% of dry weight. Organic substances of sapropel, which include animal residues, contain more nitrogen (4.4-4.8%) than algae (3.0-4.2%) or peat-forming plant residues (2.6- 3.5%) (Ponomareva, 2002). Content of sulphur in organic matter of sapropel ranges from 0.1 to 1.8%, not exceeding 3% of dry mass, but while industrially preparing and storing of sapropel, sulphur compounds are oxidized, thus acidity increases (Kazakov and Pronina, 1941; Lopotko *et al.*, 1991; Yevdokimova *et al.*, 1980). The highest sulphur concentration in organic substances is present in carbonate sapropel (Kireicheva and Khokhlova, 1998).

Any carbon-containing fossil sediments consist of various groups of chemical compounds. Identification of different compound groups extracted from the organic mass of sapropel is based on fractionation methods; therefore, according to these methods several variations of composition with individual components can be outlined (Baksheev, 1998; Kireicheva and Khokhlova, 1998; Poznyak and Rakovskiy, 1962):

– Bitumen and lipids (extracted with non-polar solvents such as benzene, diethyl ether, *etc.*);

– Water-soluble substances (hydrocarbons) (extracted with hot water);

– Easily hydrolysable substances (extracted after hydrolysis using 2% HCl);

– Humic and fulvic acids (extracted with alkaline solutions);

– Hardly hydrolysable substances – cellulose (extracted after hydrolysis using 80% H_2SO_4);

– Non-hydrolysable substances (remaining after the sequential extraction of all fractions).

After comparing the group of chemical compounds in various sapropel samples, it was established that the groups of substances (*e.g.*, humic acids, non-hydrolysable substances), according to their chemical nature from different sites, are not identical. In great extent, they are dependent on the properties of sapropel forming organisms (*e.g.*, plankton, vascular plants, humic substances) and conditions of their transformation (Braksh, 1971).

In a study done by L.V. Kireicheva and O.B. Khokhlova (1998), it is mentioned that bitumen extracted from sapropel has a more considerable molecular weight of fatty acids than peat bitumen; furthermore, sapropel storage on the field for two months increased concentration of bitumen in sapropel by 1.5 times (Karpukhin, 1998). Bitumen is an organic substance (lipid) that can be extracted from sapropel with a variety of organic solvents. Composition of bitumen is characterized by a content of fatty acids, steroids, carotenoids, paraffin, waxes and glycerol (Holý and Remišová, 2019). Sapropel bitumen components attract particular attention because they have high bactericidal, bacteriostatic and antioxidant activity. Several studies have focused on easy and efficient methods to obtain these substances from sapropel (Kireicheva and Khokhlova, 1998; Šīre, 2010). Organic substances that have been only slightly altered are composed of peloid bitumen (therapeutic mud) which contains a large number of double bonds and functional groups – carotene, phospholipids, unsaturated fatty acids and alcohols (Goossens *et al.*, 1989).

Extracting bitumen with gasoline and alcohol-benzene mixture results in obtaining it at low content from 2 to 9.9% (Lopotko and Yevdokimova, 1986; Poznyak and Rakovskiy, 1962). In sediments of low ash and medium ash, the quantity of bitumen usually does not exceed 5%; rarely, it can reach 6.0-8.1% of the organic mass (Ponomareva, 2002). Content of bitumen in sapropel is lower than in peat; sapropel's bitumen predominantly consists of saturated compounds. Sapropel's bitumen differs from peat bitumen with a lower acidity level and lower saponification that indicates a content of neutral character compounds – hydrocarbons (Kazakov and Pronina, 1941).

A low amount of carbohydrates characterizes sapropel because during the sapropel formation an active decomposition of the carbohydrates to carbon dioxide and humification (formation of the humic substances in the reactions of amino acid condensation) appear. The average quantity of hemicellulose in the organic matter of sapropel is 6-25%, but cellulose – 1-8% (Barnes and Barnes, 1978). Components of sapropel contain 1-2% of cellulose. Carbohydrate complex of sapropel consists of ≥80% of hemicellulose; therefore, it can be used in the production of animal feed additives and fertilizers applicable in agriculture and horticulture (Lopotko *et al.*, 1992).

Composition and properties of sapropel humic substances are determined by their most important features such as biological activity, biochemical stability, binding ability (Makarov *et al.*, 2017). Depending on the content and the specific relationship of humic substances, sapropel that is brought into the soil may variously affect biochemical processes, the formation of soil structure resulting in the quality of agricultural products. Sapropel humic substances differ from soil humic substances with a higher carbon/hydrogen ratio and absence of saturated aromatic rings (Kurzo, 2005; Orlov *et al.*, 1996). Humic substances of sapropel are more reduced and possess higher activity than soil humic substances. Humic acids are the largest group of organic substances. They are usually extracted from the sediments with alkaline solvents and precipitated into the acid environment (pH 1-2) (Eglīte, 2007; Kitapova and Ziganshin, 2015; Šīre, 2010). The dark brown colour is characteristic of humic acids. In humic acids of fen and raised peat the amount of carbon ranges from 57.7 to 64.2%, while hydrogen from 4.3 to 5.4% (Purmalis, 2015). Humic acids of sapropel differ from peat in the sense of elemental composition as follows: hydrogen content is higher than in peat humic acids, which indicates the presence of fatty acids.

Y. Kazakov (1950) stated that higher content of nitrogen in sapropel humic acids testifies to humin like compounds – melanoids, generated by the condensation of protein decomposition substances (amino acids and substances formed as a result of carbohydrates destruction). The types of sapropel humic substances vary in elemental composition, the content of functional groups and fragments, which are determined by sapropel forming substances, and the humification conditions of a particular reservoir (Stepanova, 1996).

Valuable findings indicate the presence of water-soluble vitamins in sapropel: ascorbic acid (C) and B group vitamins – thiamine (B_1), riboflavin (B_2), pantothenic acid (B_5), pyridoxine (B_6), folic acid (B_9) and cyanocobalamin (B_{12}). Large quantities of fat-soluble vitamins – tocopherol (E), vitamins D and P were also found (Klavina *et al.*, 2019; Shtin, 2005). Sapropel containing cyanocobalamin (vitamin B_{12}), which is concentrated in the upper layer (up to 1 m) of sediments, has a high value to be applied as a livestock feed additive. Experimental studies reveal that many microorganisms synthesize vitamin B_{12} in mud sediments. It plays an important role in protein exchange and other processes, but as many vitamins are not stable substances, refrigeration or long-term storage of sapropel reduces the content of cyanocobalamin (Dmitriyeva, 2003; Karelina, 1999).

Mineral components of sapropel are essential for the characteristics of sediment type and the application potential in agriculture. The formation process of mineral components in the bottom sediments is associated with the sedimentation of terrigenous runoff minerals as well as organic and chemical deposition of mineral ions dissolved in a lake water body. Usually, terrigenous runoff minerals are quartz (SiO_2), dolomite ($CaMg(CO_3)_2$), silicates and aluminosilicates (*e.g.*, feldspar, hydromica, chlorites, kaolinite). Biochemical processes held in a watercourse lead to the accumulation of calcite and aragonite (carbonates of Mg, Ca, Sr, Ba, Fe, Mn), pyrite (FeS_2), gypsum ($CaSO_4 \cdot 2H_2O$), hematite (Fe_2O_3), marcasite (FeS_2) and vivianite into sapropel (Korde, 1960; Lopotko and Yevdokimova, 1986; Treshnikov *et al.*, 1986; Wetzel, 2001).

Among the iron minerals, brown oxides are prevalent – iron (III) oxyhydroxides, hydrogoethite (FeOOH), more rarely – iron pyrite and phosphates, rarely – siderite ($FeCO_3$). Iron heptahydrate minerals are typical for the lower part of the sapropel layer, where siderite and part of iron phosphates are formed. It happens due to the decomposition of organic matter and any reduction conditions resulting thereof. Iron phosphates, as well as brown iron oxides, are common in all genetic types of sapropel, and the content of iron phosphate increases with the decrease of carbonates. Content of these phosphates in carbonate sapropel is about 0.4%, in mixed sapropel – 0.8%, but in sapropel containing silica – 1.4%. Calcium phosphates in sapropel occur in the form of apatite, iron phosphates – in the form of vivianite (Treshnikov *et al.*, 1986). The total amount of iron in sapropel constitutes 2-18%, rarely as much as >25%. Iron generally enters the sediments in the form of colloidal organo-mineral compounds together with the clay particles. Fe_2O_3 in organic sapropel typically constitutes 4.9%, in sapropel containing silicon dioxide – 5.6%, in carbonate – 4.7%, in mixed sapropel – 8.4%, but sometimes the amount may reach 30-50% of the ash volume (Shtin, 2005). Large quantities of iron, especially in mobile forms, have suppressing influence on plants (Yevdokimova *et al.*, 1980). Intensive mineral depletion takes place in the aquatic environment, thereby, the quantity of iron mobile forms increases, and may represent up to 80% of the total iron mass (Lopotko *et al.*, 1991). Reduction and

mobility of iron compounds decrease in the process of drying and ventilating in the air; and a part of hydrated forms transit into crystals. Mobile iron compounds do not exceed 1% in air-dried samples (Lopotko and Yevdokimova, 1986; Yevdokimova *et al.*, 1980).

At the integrated level, the mineral composition of sapropel is evaluated according to the composition/content of ash. The most significant part of the ash is made up of iron and calcium phosphates. Within the ash composition, not less than 1% of certain compounds (SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO, Na_2O, K_2O, P_2O_5) are found in the form of stable oxides (Nikolayev, 2003; Yevdokimova *et al.*, 1980).

Correlations of silicon component accumulation in various types of sapropel showed that silicon enters sapropel in the form of suspension from the remains of diatoms and accumulates in bacteria. A significant component of the ash characteristic to organic sapropel is SiO_2, while other silicon compounds are present in tiny quantities. Significant differences in silicon compounds in the ash of organic sapropel were not determined (Kireicheva and Khokhlova, 1998; Lopotko and Yevdokimova, 1986). Mixed sapropel contains a slightly more substantial quantity of ash, but its content is identical to that of organic sapropel (SiO_2 dominates in the ash). If mixed sapropel contains carbonates, then CaO+MgO content is 7.9-16.6%, but the ash content of such sapropel can reach 60%. Silicate sapropel contains silicon oxide in free form (quartz) and quartz in the form of various silicates and aluminosilicates, and the content ranges from 30.3% to 70.0% (Kurzo, 1988). Diatoms sapropel contains amorphous silicic acids, which are more available to plants (Lopotko, 1974), but the abundance of silicon does not have a toxic effect on plants (Nikolayev, 2003).

The main mineral component of carbonate sapropel is calcium carbonate. The mineral form of calcium is dolomite, clayey-ferruginous carbonate aggregates and biogenic calcite. Carbonates (about 20-50% of the total content) are present as amorphous and colloidal compounds, which have an organic origin and high degree of mobility (Yevdokimova *et al.*, 1980). The content of CaO in carbonate sapropel may reach 90%, but in organic sapropel – 0.4-5.25% of ash. Mixed sapropel contains 0.9-12.5% of CaO, but silicate sapropel – 1.2-12.3% of dry matter, on average in different sapropel types CaO content ranges from 0.7 to 37% of dry matter.

Calcite precipitation in eutrophic water bodies is promoted by the photosynthesis of plants, which bind CO_2, and organisms (molluscs, small barnacles) that during their lifetime accumulate calcium in the cells. As the amount of sulphates in water increases, the reduction of sulphates may occur, resulting in calcareous sediments. The presence of calcium in the watercourse accelerates the decomposition of organic matter and increases the content of calcium in sediments (Stable, 1986). Due to increased acidity, which is caused by more substantial content of CO_2 in the organic matter degradation process, carbonates may also fail to deposit (Nikolayev, 2003).

The content of aluminium in sapropel changes within the range from 0.3 to 11.0%, usually it is within the range of 2-4%, and its higher concentration can be found in silicate sapropel, as it contains clay minerals. The studies of sapropel in Belarus did not reveal the presence of amorphous forms of aluminium which are highly toxic to plants (Kurzo, 1988; Wetzel, 2001).

Biological components of freshwater ecosystems consist of many hydrobionts, which life cycle is a part of the life cycle of a whole water body, and that leads to the accumulation of organic matter as sediments in the ecosystem.

Prokaryotes are among the most important contributors to the transformation of complex organic compounds and minerals in freshwater sediments. Besides, they can be assessed as essential components of the benthic food chain as well as of nutrient cycling (Tamaki *et al.*, 2005). Microorganisms richly populate freshwater sapropel – depending on the type of sapropel colony forming units (CFU) varied from $5.20 \cdot 10^3$ to $6.88 \cdot 10^6$ CFU per g of dry matter (Stankevica *et al.*, 2014). It is characteristic that the number of microorganisms decreases with the depth of sediments (Kuznetsov, 1970). There is evidence that microorganisms able to produce antibiotics can be found in sapropel. Such microorganisms are antagonistic to the series of pathogen saprophytic microorganisms. This finding is valuable for the safe use of sapropel in medicine, cosmetology, balneology (Platonov *et al.*, 2014). Antibiotics and sulphonamides are synthesized in sapropel by fungi and actinomycetes, while vitamins – by bacteria and algae. Azobacteria promote nitrogen transfer to the form available to plants. Various bacteria and groups of water fungi are specific decomposers of organic substances (decomposes dead hydrobionts, splitting them into individual fragments) and are involved in the biochemical processes – secondary organic matter synthesis (humification) of sapropel (Nikolayev, 2003).

Regarding living organisms in sapropel, range of substances' transformation are carried out, not only the formation of sapropel sediments but also regeneration and preservation of sediment properties over time. Microorganisms are involved in the mineralization and synthesis of organic substances in sapropel; it determines the presence of various gases (*e.g.*, hydrogen sulphide, ammonia, methane) and their quantity in sediments. Biochemical substances formed by microorganisms in biological processes also determine some physical-chemical properties of sapropel. Sediments like sapropel are tended to accumulate biologically active and antibacterial substances, which are of great importance in balneology, as well as in agriculture and soil recultivation perspective.

1.4 Application possibilities of sapropel

Sapropel has a broad range of possible application ways in various fields of national economics, among which agriculture currently takes the most significant part (Figure 3). Sapropel can be applied widely, from raw material to production of processed products, but until now its wide variety and fragmented research data rarely have lead the extraction and utilization of sapropel to development of a cost-effective, sustainable and well-grounded market niche.

The crisis in sapropel research and exploitation in Latvia began in 1993 when extraction of sapropel deposits continued in small amounts only in Spigu Bog. Obtained sapropel was processed by the company 'Dobele' for the production of animal feed, complex fertilizer, compost and adhesives (Segliņš and Brangulis, 1996). Industrial extraction and exploration of sapropel were restarted in 2008. However, extracted volumes nowadays are still negligible if compared to the total amount of sapropel deposits in Latvia. The reasons for low exploitation level of sapropel are lack of information about the application ways, insufficient data on research, low demand of sapropel as a natural resource in the world and local markets. It has been proven that sapropel can be valuably used in agriculture, horticulture and forestry as a fertilizing and soil-improving agent, but in cattle breeding, it serves as an additive

for animal feed. Besides, sapropel is also a suitable raw material for the chemical and construction industries, as well as can be applied in medicine and veterinary medicine, *e.g.*, as therapeutic mud in balneotherapy (Galkina, 2000; Lopotko *et al.*, 1992). Nevertheless, until now, sapropel in Latvia has been used mainly for soil fertilization.
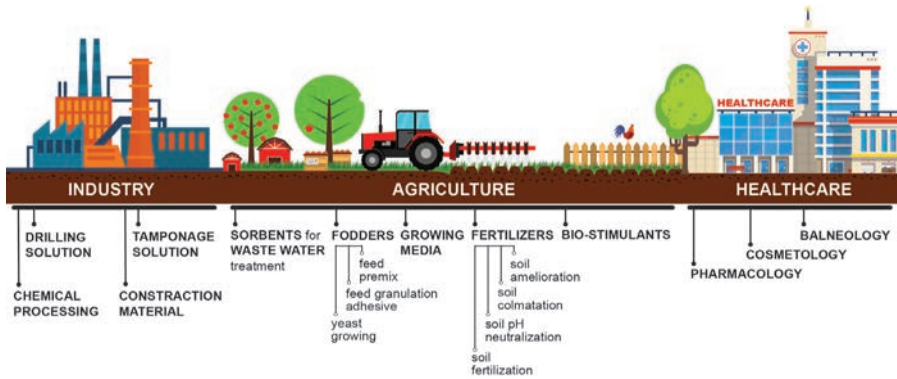

Figure 3. **Options for application of sapropel in the fields of national economics** (author's work out)

Identified uses of sapropel include the following areas:
– Agriculture and cattle breeding – for liming, fertilizing, production of vitamin-mineral feed, as a green mass;
– Construction and building industry:
  ▪ Binder for building composite materials such as chipboard;
  ▪ Binder for thermal insulation composite materials such as insulation boards;
  ▪ Sapropel concrete;
  ▪ Pores-forming material for construction articles such as drainage pipes and bricks.
– Chemical industry – in production of plastics, phenols, solvents, ammonia, lubricating oils, varnishes, paraffin, methyl alcohol;
– Mining and quarrying:
  ▪ Flotation reagent for ore enrichment;
  ▪ Viscosity reducer in drilling operations;
– Heat or thermal energy industry – in production of solid fuels, liquid fuels, coke, gas;
– Medicine and veterinary medicine – as therapetic mud and applications, in production of curative waters and preparations, pharmaceutical materials.

Among all types of sapropel, organic sapropel is the most valuable for practical use. Sapropel of autochthonous origin with maximum organic matter content is considered to be more valuable, since the initial biomass, its biochemical degradation and transformation into organic substances does not create polycyclic aromatic hydrocarbons such as benzopyrene, which is characteristic to humic substances of soil, peat and particularly coal (Dmitriyeva, 2003).

Organic sapropel can be further subdivided taking into account concentration of humic substances, as the amount of humic acids in various types of sapropel

can vary widely – from a few per cent to over 70% (in organic matter). The ratio between humic acids and readily hydrolysable substances also reflects the diversity of the composition of sapropel. Elevated content of humic acids and their structural properties indicate such properties of sapropel as biological activity, biochemical stability, adhesion and binding abilities, possible balneological effects. In turn, the presence of readily hydrolysable substances in sapropel is significant for energy-providing components (*e.g.*, amino acids, carbohydrates), and it indicates the potential for biosynthesis and transformation of primary structures. Besides, within the framework of its genetic abilities, organic sapropel is a rich source of vitamins such as C, B, E, D, P (Klavina *et al.*, 2019) and contains high levels of trace elements if compared to peat. Therefore, regardless of the relationship between humic acids and easily hydrolysable substances, due to the high content of vitamins and trace elements, organic sapropel can be useful in cattle breeding. It can serve as a vitamin and mineral supplement for feed production to increase livestock weight and milk yield, for example by adding 1-1.5% organic sapropel to daily feed, livestock weight and milk yield may increase by 8 to >20% (Shtin, 2005).

Currently, the most rational use of sapropel is attributed to industry and agriculture. However, the economic value of this natural resource can be increased by applying more valuable types of sapropel in medicine and cosmetics as well as the chemical industry. In contrast, those sapropel types with a higher rate of mineralization still remain applicable in the subfields of agriculture.

Agriculture and recultivation

Sapropel can be applied for the production of humic preparations, plant growth stimulators, fertilizers. Sapropel is a high-quality natural organic fertilizer by its own or a component for fertilizers that can outperform even high-quality manure in terms of the efficiency. Chemical composition of organic sapropel allows all forms of sapropel, which may have a slightly higher ash content (50% in dry matter), to be used in the production of organic fertilizers. The effectiveness of organic fertilizers and sapropel has been proven in numerous studies (Blečić *et al.*, 2014; Bunere *et al.*, 2014; Lopotko *et al.*, 1992; Makarov *et al.*, 2017; Vincevica-Gaile *et al.*, 2015), and only some studies disclaim positive effects of sapropel used as fertilizer (Naumova *et al.*, 2017). Differences of sapropel efficiency depend on high variability of sapropel types and properties as well as different soils and climatic conditions. To avoid poor water return, organic sapropel can be composted with manure, which promotes the mutual conversion of organic matter from manure and sapropel into substances that are more readily available to plants as nutrients, as well as binds volatile nitrogen compounds that reduce nitrogen losses during the storage of fertilizers. Furthermore, the advantage of making sapropel-manure compost is that sapropel as a sorbent binds ammonia, which is usually partially evaporated from manure (Kurzo, 2005; Shtin, 2005; Sokolov *et al.*, 2008). Organic sapropel can be widely used as a component for obtaining a balanced organic-mineral fertilizer for immediate application in soil, as a substrate (growth media) for greenhouses or as a substrate for seedling cultivation. Even if the concentration of humic acids in sapropel is not high, acid-alkali hydrolysates make organic sapropel more valuable than peat and peaty sapropel by biological activity, which has been proven by seed germination and plant growth tests. Plant growth promoters produced from peaty sapropel

with a characteristic ratio of humic acids to easily hydrolysable substances >3 have exceptionally high biological activity (Bunere *et al.*, 2013; Kurzo, 2005).

Notable results in the functional performance of soil fertilization using sapropel were achieved in 1954-1955 in Latvia at the Bulduri Horticultural Technical College (Vimba, 1956). Experiments revealed that if sapropel was used in humic soil pots, and humic soil was replaced with sapropel, early cabbage seedlings in sapropel pots developed much better and were stronger than the seedlings in usual humus pots. Besides organic sapropel, also sapropel with high mineral matter content (containing about 75% of mineral matter) derived from the Lielupe River (Latvia) was tested. Compared with control, application of sapropel with high mineral matter content increased the carrot yield by 40%, potatoes yield by 41% and cucumber yield by 60% (Vimba, 1956). Another, ten years long study done by Lithuanian scientist using carbonate sapropel revealed that sapropel addition to soil might change not only soil acidity but also can increase the moisture level of soil as well as total porosity, independently from meteorological conditions. After all fertilizer treatments, changes in soil density were not detected. The use of carbonate sapropel as soil fertilizer can improve soil physical properties better than limestone applications. Data analysis of crop productivity changing season by season increased in higher-level after applications of carbonate sapropel in comparison with limestone due to sapropel's mineral content and plant nutrition potential (Daugvilienė *et al.*, 2014).

Due to highly valuable natural properties, sapropel derived from the lakes of Latvia can be effectively applied for essential conditioning and fertilization of barren soils. Studies have revealed that the long-term average yield increases were higher for crops and vegetables (15-30%), cereals (10-15%) using 3-6 c/ha of sapropel, but for potato cultivation, if applying 25-43 c/ha of sapropel (Anspoks, 1989; Baksiene, 2009; Blečić *et al.*, 2014). Use of sapropel as fertilizer also improves the taste of vegetables, increases the content of dry matter and mineral matter in crops. In general, sapropel can be assessed as a versatile organic fertilizer suitable for a variety of crops, as well as for use in agricultural fields, greenhouses, glasshouses, orangeries and indoor plant cultivation. The value of sapropel as a fertilizer is determined by its essential chemical and physical properties, its rich microflora and absence of weed seed contamination (Grantina-Ievina *et al.*, 2014).

Also, after biological activation (drying, aeration, composting), sapropel can be used for fertilization. Using fresh, unventilated sapropel as a fertilizer may not result in the desired effect after the first year because nitrogen and external nutrients in sapropel slowly mineralize for several years and, thus, obtain a higher degree of bioavailability. During the aeration and composting, the reduced compounds oxidize and the action of microorganisms activates, the process of mineralization accelerates that allow plants to utilize nitrogen and nutrients from sapropel faster and more efficiently (Sokolov *et al.*, 2008). Sapropel cannot be stored for long-term without freezing it through – freezing is required to gain a loose and lighter consistency of sapropel. If sapropel is not frozen, it dries, and a waterproof, hard, dolomite-like layer is formed. Fresh as well as frozen sapropel is applicable for composting, for example, together with manure, slurry, bird droppings, peat, sawdust and other components (ratio 1:0.5-1.5). After mixing with organic manure, the mass has to be mechanically homogenized 2-3 times and stacked in 2-4 m wide and 1.5-2.0 m high risers, covered with a soil or peat layer, composted for 3-6 months. The moisture content of the composted mass must not be lower than 55%. It is recommended to add 10-15 kg/t of

phosphorus and potassium fertilizing components to activate and improve the quality of sapropel-containing compost (Agafonova *et al.*, 2015; Anspoks, 1989; Kireicheva and Khokhlova, 1998).

Sapropel-based fertilizers can be used effectively for the deep repair of sandy, eroded and other barren areas. Due to relatively slow decomposition of sapropel in soil, it radically improves the physical and chemical properties of soil. Thus, sapropel-based fertilizers are usefully applicable for recultivation of degraded, eroded and barren soils (Blečić *et al.*, 2014).

Indicative application rates of sapropel containing more than 50% of organic matter (with a standard humidity of 60%) are similar to the rates of manure, i.e., 40-80 t/ha, but for degraded soils up to 120 t/ha (average sapropel rate – 100 t/ha). Application rates for sapropel with less than 50% of organic matter are twice as high as those of sapropel. However, in each case, application rates of sapropel for fertilization of crop fields should be adjusted depending on the results of agrochemical analysis of applicable sapropel, taking into account total nitrogen content and the fact that in the first year plants will only be able to use up to 50-60% of the total nitrogen that contains sapropel (Sokolov *et al.*, 2008).

Organic sapropel is a nutrient-rich environment enriched with carbon, nitrogen, mineral salts, soluble substances that are beneficial for the cultivation of tuber bacteria. For such purpose, sapropel with ash content up to 30% and containing 52-56% carbohydrates, as well as 3.5-6.0% nitrogen in organic matter can be applied. Chalk may be added to sapropel to stabilize pH, but carbonate sapropel is more effective liming material than dolomite flour and chalk. Cultivation of tuber bacteria is valuable for inoculation of legumes; productivity of legumes can be improved by 12-55% (Kurzo, 2005).

Another highly important application way of sapropel in agriculture is its use for the preparation of soil substrates or growth media. Significant criteria in this respect are the content of organic matter and balance of pH in sediments (Semakina *et al.*, 2001). Sapropel as a soil substrate can be used in the form of mixtures with peat, sludge and any kinds of composted biowaste (Kurzo, 2005). Some authors suggest also supply of mineral fertilizers to improve the application potential of sapropel (Skromanis *et al.*, 1989). Most widely, the possibilities of sapropel application in soil substrates or soil amendments have been tested in Belarus, where the actual application of sapropel in agriculture reached 1.5 million tons per year (Kurzo, 2005).

In order to increase nutrient stability and to reduce leaching of mineral components, it is optimal to granulate fertilizing additives together with sapropel. The process of granulation helps to prevent the fertilizing product from collapsing during storage, improves the chemical-physical properties of the product, increases the concentration of trace elements and organic substances. Sapropel has better adhesion properties if its humidity is 10-25% (Kurzo, 2005; Obuka *et al.*, 2017; Vincevica-Gaile *et al.*, 2019). According to the data provided by N.A. Kurmysheva (1988), keeping sapropel on the field for two months the quantity of bitumen increases twice, but storing the sapropel in settling tanks for one year the amount reduces by 1.5-2 times. However, in the case of sapropel storing in settling tanks, the analyses of samples from the upper layer are useful. The tests revealed increase in bitumen quantity by 6.0-7.6%. Observed changes are analogous to those if sapropel is stored on the field and where, with time, appropriate microflora was developed as well. After storing sapropel in settling tanks for five years, the amount of bitumen increased

but did not reach the original scores. Multiple freezing and refreezing of sapropel did not significantly influence the quantity of bitumen fractions (Kireicheva and Khokhlova, 1998).

Recently developed field of sapropel application is a production of liquid sapropel-based fertilizers and sapropel extracts containing a complex of biologically active substances, predominantly taking into account content and specifics of humic substances (Didkovskaya *et al.*, 2010; Ferdman *et al.*, 2012). Extracts of sapropel and mixtures containing humic substances can be obtained using extraction with alkaline solutions and dispersion technologies. Recent studies have demonstrated high efficiency of such formulations for various crop cultures and extension of application options (Bunere *et al.*, 2014; Ferdman *et al.*, 2012; Pastukh and Popov, 2007). The efficiency of raw sapropel application can be influenced by several factors such as chemical state of humic substances as they might present in other forms than salts, as well as a deficiency of K^+ ions that stimulate seed germination and plant development (Ponomareva, 2002). Two years long field experiment of crops cultivation fertilizing them only three times during a vegetation period using a liquid containing 0.01% potassium sapropel humates was performed. The results indicated an increase in crop yield for tomato cultivars (30-35%), potato (20-25%), cucumber (45-50%), sweet pepper (25-35%), sugar beet (25-45%), wheat (30-35%). Besides the crop yield increase, application of potassium sapropel humates elevated crop resistance against several plant diseases such as peronosporosis, *Botrytis cinerea*, bacteriosis and verticillium wilt (Ponomareva, 2002).

In general, all types of sapropel are applicable as soil fertilizing agents, and regarding this application, sapropel conditionally can be divided into three groups (Shtin, 2005):

Group 1: sapropel with organic matter content above 50% is used to produce organic mineral fertilizers. Composting this type of sapropel does not require the addition of different organic materials (such as peat or other);

Group 2: sapropel with organic matter content 10-50% is used for the production of complex mineral fertilizers, which are rich in lime, phosphoric acid, total nitrogen and organic matter;

Group 3: mineralized sediments with organic matter content up to 10% are mainly used to improve soil texture and mechanical content. If such sediments have a high concentration of CaO, field application of them reduces soil acidity.

Cattle breeding

Among the possible applications of sapropel, animal feed production already is an existing field. Alkali extracts of sapropel, similarly to lignite and peat extracts, contain 40% humic substances. Improvement of animal feed mixtures' efficiency using sapropel has been extensively studied in Russia, Lithuania and Belarus during the second half of the 20th century.

Sapropel feed additives improve functions of animal liver and stomach, blood formation and circulation, reduces the occurrence of diseases and increases the resistance of animal health to adverse environmental conditions (Lishtvan and Lopotko, 1976; Shtin, 2005; Soldatenkov, 1976; Yevdokimova *et al.*, 1980).

The most valuable type of sapropel for use in feed additives is deemed to be organic sapropel with microfossils mainly consisting of algae. It contains 23-70% water-soluble and easily hydrolysable fraction, as well as 7-40% humic

acids, which determine the antibacterial properties of sapropel. Organic sapropel is not toxic, harmless; content of heavy metals, radioactive compounds, nitrates and nitrites do not exceed permissible concentrations; thus, it is appropriate for animal feed. It contains proteins, vitamins, enzymes and other biologically active substances and ash that also contain macroelements (calcium, phosphorus, magnesium, *etc.*) and microelements (iron, copper, zinc, manganese, cobalt, iodine) (Bulatov, 2006; Krymskij, 2006; Malceva, 2000). The studies conducted in Lithuania have shown that almost all types of sapropel can be used in the production of feed additives (Soldatenkov, 1976). The most significant parameters to be determined are as follows: the content of organic matter, nitrogen, calcium, iron and the main trace elements, and vitamin B_{12}. As a feed additive sapropel with a small content of minerals, sand, clay can be used – not more than 20-30% (excluding calcium carbonate). Whereas, sapropel with mineralization level of >40% should be evaluated as a mineral fertilizer or it can be used in human and veterinary medicine as therapeutic mud. High levels of nitrogen (up to 6%) are desirable for sapropel used as an animal feed additive since 35-55% of nitrogen in sapropel is a component of amino acids. Carbonate sapropel (with the content of calcium carbonate ≥30%) and mixed type sapropel (with the content of calcium carbonate not less than 12% in dry matter), if SiO_2 content is not exceeding 15% and Fe_2O_5 5% also are suitable as feed additives.

Sapropel is generally considered to be a mineral-vitamin supplement to the daily base feed of livestock. It can be assumed that a part of easily hydrolysable components can be taken up and assimilated in the animal body. Sapropel, as an additive to animal feed, can be used in fresh condition or dried in granules or powder (Bulatov, 2006; Krymskij, 2006; Malceva, 2000; Sherbakova, 2000).

Introduction of 10% organic sapropel into the diet of chickens helped to increase their growth rate by 2.5%. Besides, the amount of feed mixtures was reduced by 12.5%, as well as the cost of diet was reduced by 7.24-17.74%. During the productivity audit at the breeding of 1000 broilers fed with full-feed mixtures with free access to sapropel with a humidity of 60%, profit was obtained by more 23.2% than from broilers fed with only full-feed mixtures, with 26.09% profitability of broiler meat production (Malceva, 2000).

Use of 4.5-6% sapropel of its weight in compound-feed contributed to increasing in the retention of geese by 2%. Besides, egg production rose by 7.3%, the yield of hatching eggs by 1.9%, and feed costs for ten eggs decreased by 10.1%. Improvement in digestibility of protein by 3.8%, fat by 0.9% and fibre by 1.4% in comparison to the control group was observed (Bulatov, 2006).

The dose of sapropel at 6% of the main diet for ducklings was stated as optimal and allowed to increase live weight by 6.7-9.9%, average daily growth by 6.78-7.80%, retention of ducklings by 0.5-2.0%, as well as reduce feed costs by 3.4-4.64% per 1 kg of increase in live weight and the cost of production by 6.25-8.34%. Introduction of sapropel into feed mixture of ducklings improved the chemical composition of meat. Furthermore, the amount of crude protein increased (from 18.1 to 20.2%). At the same time, decrease by 8.2% in crude fat was observed, which is a positive sign for duck breeding (Krymskij, 2006).

Sapropel is suitable for use as a filler for premixes after preliminary preparation such as drying to a moisture content of 8-39% and subsequent grinding. Such fillers made from sapropel have better physicochemical properties in comparison with fillers derived from organic remains (*e.g.*, bran): their acidic level is close to slightly acidic

(pH 5.8); bulk density in the range of 534-669 kg/m and, therefore, need for a sealant is useless, ensuring the homogeneity of the mixture and preserving from separation (stratification). The angle of repose for sapropel fillers is estimated 31.6-37.5 degrees, as well as better bulk flowability is ensured (bulk flow coefficient 0.243-0.312). With increasing humidity of sapropel fillers, the physical and technical properties of premixes based on them were improved. Use of sapropel with a moisture content of 8% as a filler had a positive effect on the preservation of vitamins in the premix: loss of vitamin A was reduced by 3.1-5.6%, vitamin E by 2.9-5.1%, vitamins B_3 and B_5 by 13.5-15.0% if compared with bran premixes (Korsheva, 2009).

Sapropel is an effective agent for growing green feed for piglets and sows during winter months. Studies revealed that growing oats or peas in a sapropel-based substrate yields to higher productivity than growing these crops in hydroponics or clay soils. Enriching the grass meal with sapropel can help to preserve carotene (a precursor of vitamin A). It was found that a sapropel additive of 12% with a moisture content of 94% ensures higher retention of carotene in grass meal by 35% even after six months of storage. Feeding calves and ducks with daily feed enriched with such grass meal resulted in higher daily live weight increase (Shtin, 2005).

Not only increased daily live weight gain but also increased bactericidal activity in blood plasma was observed in pigs and piglets feeding them with the addition of granulated sapropel minerals and vitamins. Furthermore, following benefits were noted: increase in humoral and cellular defence factors, increased resistance to diseases, prevention of rickets, improved supply of minerals in the organism, stimulation of physiological and biochemical processes, growth intensification, as well as reduced feed consumption, which contributes to the overall economic viability of livestock farming. For fattening pigs, the addition of sapropel to the feed may increase the average daily weight gain by 18-20%, reduces the number of feed units and protein consumption for 1 kg live weight gain by 12-15%. Dosage of sapropel as a feed additive for pigs is following: for piglets up to 2 months of age – as much as they eat, 2-4 months of age – 200-300 g per day, for unsworn pigs and boars up to 1 kg per day, for pregnant and lactating pigs – up to 1.5 kg daily. Sapropel can also be used as a feed additive in poultry and fish farming (Kozlovceva, 2005). Sapropel intended for use in pig and poultry feed should have a high content of vitamin B_{12} (above 20 μg/kg). Vitamin B_{12} is more abundant in the upper layers of sapropel deposits than in others, which also contain higher levels of cobalt, a component of vitamin B_{12}. Content of ferments and enzymes in sapropel also is relevant; it contributes to complete use of organic matter and reduces the losses resulting from degradation processes. Biological activity of sapropel and its effectiveness can be enhanced by applying ammonification (Lenchevskij, 2011).

Currently increasing topicality is attributed to the production of feed additives from alkaline solutions of sapropel like sodium humate. These humic formulations balance the diet of animals and result in an increase in weight, improvement of individual haematological parameters, strengthening of the immune system. Besides, may enhance oxidation processes in the animal body, i.e., helps to increase and accumulate proteins in blood and body mass, supports the formation of erythrocytes in the red bone marrow, improves the synthesis of vitamin A and other vitamins, normalizes metabolism and is useful in the treatment of toxicities (Kurzo, 2005; Shtin, 2005). These effects lead to increased resistance of animals when infected with an anaerobic toxigenic culture of *Clostridium perfringens*. Humic,

hematomelanic and fulvic acids exhibit antibiotic activity against E. coli, St. aureus, C. albicans, C. diphtherie, moreover, the specificity of the biological action correlates with their chemical composition (Dmitriyeva, 2003).

Construction and building industry

In the production of building materials, low-ash content sapropel with organic content of >85% and nitrogen content of >3.3% on a dry basis is suitable for preparation of adhesives and binders that can replace albumin-based adhesives used in the manufacture of wood-fibre boards. Sapropel can be used as a binder for heat insulation materials made from wood, linen, paper and cardboard waste. Efficacy of sapropel applied as a binder depends on parameters such as adhesion ability, total nitrogen content and physical-mechanical properties at 0.2 MPa. For material production, sapropel suspension containing 5% dry residues has to be added. Slabs of saw, linen fibre and other materials should be dried at 105 °C. The binder properties of sapropel are provided by the presence of nitrogenous compounds, including amino acids. An important role also plays the molecular structure of the humic acids of organic sapropel; thus it is optimal to use sapropel with ash content of up to 20%, high nitrogen content (3.5%) and a ratio of humic acids to easily hydrolysable substances of 0.8-0.9 (Obuka *et al.*, 2015, 2016). Such type of sapropel can also be used for the production of household heating materials – briquettes or pellets from wood waste or by-products.

A promising field is the use of sapropel with low ash content as a pores-forming additive in the production of drainage pipes and porous ceramic materials, as well as for production of expanded clay. Advantage of using dried sapropel particles is that they do not get wet and do not collapse as a result of the mechanical treatment of the clay mass, but, after burning, they form pores of appropriate size in the ceramic material and entirely or partially reduce the use of other technological raw materials (Birjuleva, 2000; Shtin, 2005).

Chemical industry

Organic sapropel is a useful raw material for the production of carbonaceous materials, for example, to produce activated carbon with low mineral content and high sorption capacity. Carbonate and silicate sapropel is useful for the synthesis of carbon-mineral porous materials.

Production of a carbon adsorbent involves the carbonation process of organic sapropel at 250-260 °C, followed by grinding and mixing with an activator K_2CO_3 or $CaCO_3$ and heating up to 950-1050 °C. Carbonate sapropel with the content of $CaCO_3$ at >60% in a dry matter can also be used as a calcium source. After activation, the mass is rinsed with acidified water to remove soluble minerals entirely; it is needed for more effective formation of specific surface and sorption capacity of the resulting sapropel carbon, as well as to approximate the properties of the resulting carbon to the charcoal. The properties of the resulting sapropel carbon can be adjusted depending on raw materials selected and the activation conditions. Treatment of sapropel with acid before the activation with K_2CO_3 or $CaCO_3$ allows not only the production of ash-free activated carbon but also the use acidic filtrate containing dissolved metal oxides (Al, Fe, Mg, Ca) and dispensing co-precipitated porous substances of hydroxides (Shtin, 2005). Such porous substances can be applied as adsorbents to purify liquid media from polar impurities, such as used oils

in refining processes. Production of carbon and hydroxide adsorbents promotes the expanded application of sapropel (Birgėlaitė *et al.*, 2016).

Depending on the degree of mineralization as well as other parameters and chemical properties, sapropel can be used either for chemical-technological processing (mostly mineralized deposits) or agricultural purposes. Sapropel reserves can be used for accelerated thermolysis (production of thermo-waxes and other chemical products), extraction to obtain solid bitumens, pyridine bases, phenols, *etc.*, for production of fertilizers (organic-mineral granules) and production of adhesives. By hydrolysing sapropel without reducing agents, the hydrolysate can yield valuable nitrogen-containing compounds such as amino acids and others (Nikolayev, 2003; Ohochinskaja, 2000; Ponomareva, 2002; Vimba, 1956).

Mining and quarrying

Due to its chemical composition, availability, safety and relatively low cost, sapropel can be widely used in drilling applications for the production of environmentally safe drilling solutions. Organic sapropel is the most applicable for this purpose. Low ash containing sapropel can be used for the preparation of drilling solutions because it contains the necessary components such as high molecular weight compounds and natural biopolymers, humic substances and their compounds, carbohydrates, hemicellulose and cellulose, lignin, bitumen and others. An essential component of sapropel, which plays a significant role in the preparation of drilling fluids, is humic acids produced by alkaline extracts. Besides, the action of alkali on sapropel significantly increases the activity of sapropel's particles, which results in an improvement of the structural-rheological properties of the dispersion. Micro-disperse minerals and oxides (amorphous silica oxide, particles of carbonates and clay, iron and aluminium oxides) in sapropel have a high reactivity potential, if binding with organic substances, and form stable organic-mineral complexes. They are capable of providing drilling solutions with high rheological properties. The highest value in the preparation of drilling solutions has organogenic sapropel, which is based on aquatic plants and has a ratio of <1 to humic acids and easily hydrolysable substances (Polosina *et al.*, 2010).

Organic sapropel with a humic acids content of 35-70% can be used to prepare sapropel-alkali reagents. Direct and inverse emulsions for the production of drilling solutions can also be obtained from sapropel using as emulsifiers synthetic products or waste, or by-products from chemical production (Shtin, 2005).

Healthcare and veterinary

Sapropel can be used in healthcare and veterinary as a peloid or therapeutic mud for external applications and baths, for the production of healing waters, pharmaceutical preparations and materials. Peloids are multicomponent systems containing mineral waters, clay minerals, organic matter and organic-mineral complexes, and are used in therapeutic procedures (Badalov and Krikorova, 2012).

Chemical composition, presence of trace elements and organic substances such as hormones, amino acids, as well as the biological composition of sapropel influence its biological activity. A factor affecting sapropel application possibilities in medicine also includes its thermal capacity. Among the substances of importance for medical applications can be mentioned the presence of humic and fulvic acids, water-soluble vitamins (ascorbic acid (C), thiamine (B_1), riboflavin (B_2), pantothenic acid (B_5),

pyridoxine (B_6), folic acid (B_9), and cyanocobalamin) and fat-soluble vitamins – tocopherol (E), vitamins D and P (Kireicheva and Khokhlova, 2000; Szajdak and Maryganova, 2007).

Traditional is the use of sapropel (usually named as a lake mud) in balneotherapy and cosmetology (Badalov and Krikorova, 2012). There is enough evidence that sapropel has biostimulating effects, stimulates metabolism and immune system (Anderson, 1996; Basili *et al.*, 2001). The ability of sapropel to scavenge free radicals (Fedko *et al.*, 2005) also is of importance for application in medicine as supposed due to the presence of humic substances as well as other polyphenolics.

Sapropel application in balneology include the following effects (Badalov and Krikorova, 2012; Suraganova *et al.*, 2014):
– Improvement of blood and lymph flow, strengthening of blood vessels, improvement of oxygen exchange;
– Antibacterial activity against pathogen microorganisms;
– Supply to human skin with calcium, magnesium, bromine, iodine, potassium and amino acids;
– Antioxidative and immunostimulatory activity;
– Improvement of skin structure, reduction of wrinkles, swellings;
– Improvement of nail and hair growth and prevention of hair loss;
– Reduction of symptoms of some skin diseases (*e.g.*, psoriasis, seborrhoea, acne).

Indications for peloid therapy are following: bone and muscle disorders and post-traumatic conditions such as joint and spine diseases, bone fractures, periostitis, myositis, osteomyelitis, trophic ulcers; peripheral and central nervous system disorders and post-traumatic conditions such as radiculitis, neuralgia, consequences of poliomyelitis (Bellometti *et al.*, 2000); inflammatory processes of internal organs in the exacerbation and remission phases, skin diseases (chronic eczema, limited neurodermatitis, scleroderma) (Carabelli *et al.*, 1998). Contraindications for peloid therapy are acute and chronic inflammatory processes in the exacerbation phase, benign and malignant formations, tuberculosis, cachexia, systemic blood diseases, severe endocrine organ dysfunction, decompensation phase of cardiovascular diseases, bleeding, infectious diseases in acute or infectious stage (Kurzo, 2005).

Sapropel has antimicrobial properties, thus supporting its use in medicine and veterinary medicine (Suraganova *et al.*, 2014). It was revealed that sapropel has activity against *Staphylococcus aureus* (Tretjakova *et al.*, 2015) as well as against *Escherichia coli*, *Clostridium perfringens* and *Pseudomonas aeruginosa* (Galkina, 2000; Platonov *et al.*, 2014). Sapropel contains a large number of microorganisms that have antimicrobial activity against pathogens (Tretjakova *et al.*, 2015). Some studies reveal that sapropel lipids (the products of vital activity of blue-green algae) have bacteriostatic and bactericidal activity as well as anti-inflammatory effect (Muradov, 2014).

The direct etiological factor is the occurrence of endometritis in the presence of microflora in uterus containing such microorganisms as *E. coli*, *Staphylococcus aureus*, *S. epidermidis*, *S. pyogenes*, *Streptococcus agalactiae*, *Proteus vulgaris*, saprophytic microorganisms and others. In the treatment of acute endometritis for cows using sapropel, an increase in fertility by 14.1% and reduction of days of infertility by 18±1.6 days was observed if compared to the control. In the treatment of latent endometritis using sapropel, fertility was higher by 39.9%, the period of infertility was reduced by on average of 48.3 days. Morphological studies confirmed that under

the influence of sapropel, the structure of endometrium and its integumentary epithelium was almost completely restored, the inflammatory reaction in various membranes of the uterine wall disappeared, granulation tissues formed, the secretory function of the glandular epithelium was restored, and the contractile function of muscle cells was enhanced (Vasilkova, 2003).

All forms of organic sapropel, except some types of peaty sapropel, have high thermal (heat-insulating) abilities and viscoplastic properties, homogeneous structure and a wide range of micronutrients and macronutrients, as well as a significant amount of free amino acids, vitamins and enzymes (Tserenpil *et al.*, 2010). Thus, sapropel is useful in medicine and veterinary medicine as therapeutic mud for body applications, baths, wrappings and fomentations. Content of organic matter in such sapropel should be at least 50%, but the optimum concentration of cations in aqueous solutions of sapropel should be as follows: NH^{4+} 2-50 mg/L, K^+ 15-50 mg/L, Na^+ 2-120 mg/L, Ca^{2+} 2-200 mg/L, Fe^{2+} and Fe^{3+} up to 25 mg/L, HCO^{3-} 5-400 mg/L, Cl^- 10-125 mg/L, SO_4^{2+} 60-800 mg/L (Suárez Muñoz *et al.*, 2015). Sapropel applications and fomentations do not induce rapid haemodynamic changes in the human body but have a beneficial effect on the exchange reactions, *e.g.*, at musculoskeletal system diseases (Muradov, 2014). The application parameters of sapropel fomentations and balneological procedures are summarized in Table 5.

Healing effects of sapropel are greatly influenced by the presence of humic acids. At the same time, more effective transfer of humic acids transcutaneously (through the skin) is provided by peloids with pH 7-8, which can be ensured by adding $NaHCO_3$ to a peloid (usually 1 g $NaHCO_3$ per 100 g of peloid is used). However, if a soda/acid solution is added to sapropel, it reacts with humic acids, resulting in the formation of sodium humates, which are highly soluble in water. Holding for 30-35 min at 20 °C is sufficient time for $NaHCO_3$ to be dissolved entirely and for transfer of significant amounts of organic matter from the solid phase of peloid to the aqueous solution.

Table 5

Recommended parameters for sapropel application as a peloid in fomentation therapy
(Yasoveev *et al.*, 2005)

Age of patient, years	Length of procedure, min	Temperature of a balneological preparation, °C	Number of procedures within one therapy course, times	Interval between the procedures within one therapy course
2-3	7-10	38-40	8-10	
3-7	12-15	39-40	10-12	Every second day
7-14		40-42	12	
14-18	15-20		12-14	
>18		40-55	12-15	

Mixing peloids with $NaHCO_3$ and heating the mixture for 1 hour at 65 °C provides a change of pH that maximizes the effect of a peloid and also increases the concentration of humic acids by about 2.4 times in the aqueous solution of peloid if compared to the mixture derived without heating. In such manner processed sapropel peloids, as well as peat peloids, are applicable in neurology and physiotherapy. Studies showed that organogenic sapropel, which organic matter is based on aquatic plants, can be used in mud therapy for stomach diseases, but peaty sapropel for peripheral nervous system diseases (Kostjanova, 1985).

Still a broad potential for the use of sapropel in medicine and cosmetology exists. Sapropel and its extracts are successfully used in cosmetic products due to its ability to prevent and reduce the ageing effects, improve regeneration of skin and regulate skin moisture levels as well as improve the natural ability of the skin to protect the body against ultraviolet light. Sapropel also has antibacterial properties, and many cosmetic products using sapropel have been invented and patented like soaps, tonics, cleansing masks, massage oils, shampoos and other products (Correia *et al.*, 2016; Gomes *et al.*, 2013).

2 MATERIALS AND METHODS

2.1 Study area and research sites

Data derived from the surveys of complex geological exploration expeditions (GEO-Konsultants, 1995, 1996, 1997, 1998a, 1998b, 1999; Latvgeologija, 1991a, 1991b, 1992; Latvijas ģeoloģija, 1994) carried out in Latvia over the decades were used to design a freshwater sapropel database (FWSDB) (Table 9), as well as other relevant information sources (Braksh *et al.*,1967; Leinerte, 1988). FWSDB was employed to detect and characterize the amount of sapropel as a national strategic resource of Latvia as well as to identify determining parameters regarding the formation of sapropel deposits. According to FWSDB, there are 2,200 lakes in Latvia. Until now, searching of sapropel has been carried out in 1,286 lakes (Figure 4) – up to 55% of all lakes in Latvia.
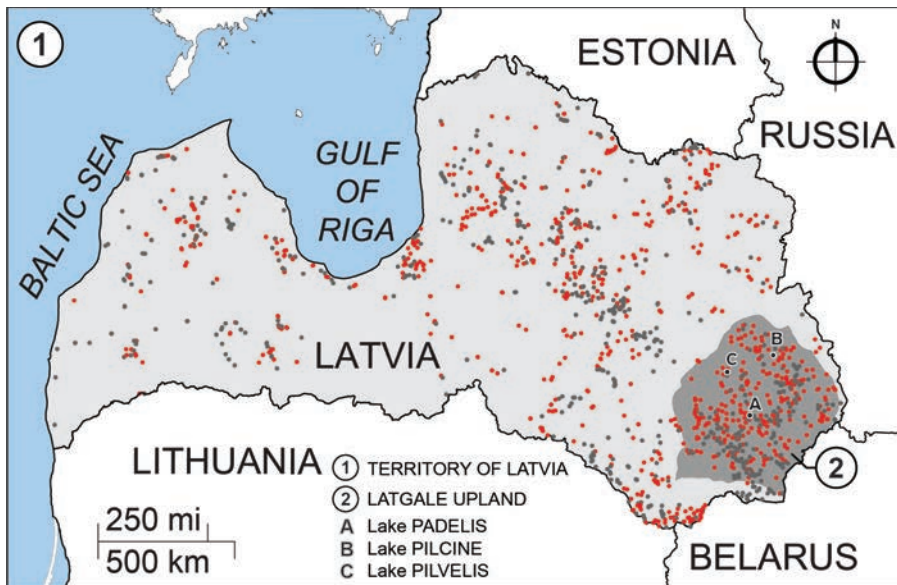
Figure 4. **(A) Location of the studied sites in the territory of Latvia: red points – industrially significant sapropel deposit, grey points – sapropel deposit not significant for industry; (B) the Latgale Upland nature areas with the location of detailed study sites**

To characterize the detailed impact of environmental conditions on the properties and possibilities of application of different types of sapropel – organogenic, carbonate and clastic – and interaction of them with climatic changes and lake development stages, three lakes located in the Latgale Upland (Latvia) were chosen (Figure 4) – Lake Padelis, Lake Pilcine, Lake Pilvelis. Preliminary data of primary deposit types of sapropel and their characteristic were obtained analyzing the Lake Sapropel Deposit Passports (GEO-Konsultants, 1998b).

Lakes located in the Latgale Upland were chosen as the study sites due to several reasons. The Latgale Upland is the largest upland in Latvia; it covers 6,376 km² (Markots, 2011) situated in the south-eastern part of Latvia. Most of the lakes have been filled by ice melting waters and formed as glaciolimnic lakes at the end of the Late Glacial. The surface of the lake depressions and catchment areas are represented mainly by Late Pleistocene deposits which were affected by an admixture of fragments of bedrock deposits (dolomites, marlstones and limestones) to the glacial deposits during deglaciation process as well as glaciolacustrine sediments (Dauškans, 2013). Deglaciation and at the same time morphologically well-expressed zones of ice-marginal formations with linear depressions nowadays occupied by lakes and rivers (Zelčs *et al.*, 2011) in the Latgale Upland had started in the Dagda phase – earlier than in the remaining territory of Latvia (Dauškans, 2013; Markots, 2011). Therefore, freshwater sapropel sediments in this region had formed since the begging of the Holocene when the climate began to become warmer, and vegetation in lakes and catchment areas were well developed (Ozola, 2013; Stivrins, 2015). Sapropel formation in uplands was not affected by the stages of Baltic Ice Lake and Littorina Sea (Zelčs *et al.*, 2011).

2.1.1 Lake Padelis

Lake Padelis (Figure 5A) is a round-shaped tiny lake (3.5 ha) of a glacial origin, located at the elevation 156 m ASL in the southern part of Malta Lowland area, at the middle of the Latgale Upland. In this area, extensive lowering surrounded by small morainic hills which were

formed by a glacier and its meltwater activities. After the runoff of ice meltwaters, two lakes appeared in the deepest parts of the depressions. The largest and deeper part of this lowering was occupied by Lake Stiebrajs, but the smallest by Lake Padelis. The location of both lakes at the same depression with the same elevation 156 m ASL, and that only 100 m wide belt with fen divide Lake Padelis west coast from Lake Stiebrajs, indicate that they were connected during the end part of the late glacial. Glaciofluvial sediments (coarse sand, gravel) are distributed in the depression and point on the water flows during the late glacial. In both lake depressions, coarse sand has been covered by sand and clay.

Lake Padelis nowadays is shallow with the average water depth 1.5 m, and maximum – 1.7 m, while at the beginning of the Holocene a depth of the lake was approximately 8 m. Since that time, sapropel has been accumulated reaching an average thickness of 5.3 m, maximum 6.1 m and fills more than 80% of the lake's depression. It is a eutrophic lake, surrounded with 5-10 m wide reed belt and has a slight runoff to Lake Stiebrajs. The area is uninhabited, and the surrounding area mostly is covered with boggy forests. The total amount of sapropel sediments in Lake Padelis is estimated 132,000 m³ (Rozenbergs, 1998a).

2.1.2 Lake Pilcine

Lake Pilcine (Figure 5B) is a small eutrophic overgrowing lake of glacial origin with water area 7.0 ha. The lake is situated in the western part of Burzavas Hilly Area, the north of the Latgale Upland at the elevation 146 m ASL. The lake was formed in the depression surrounded by three plateau-like hills with highest elevations
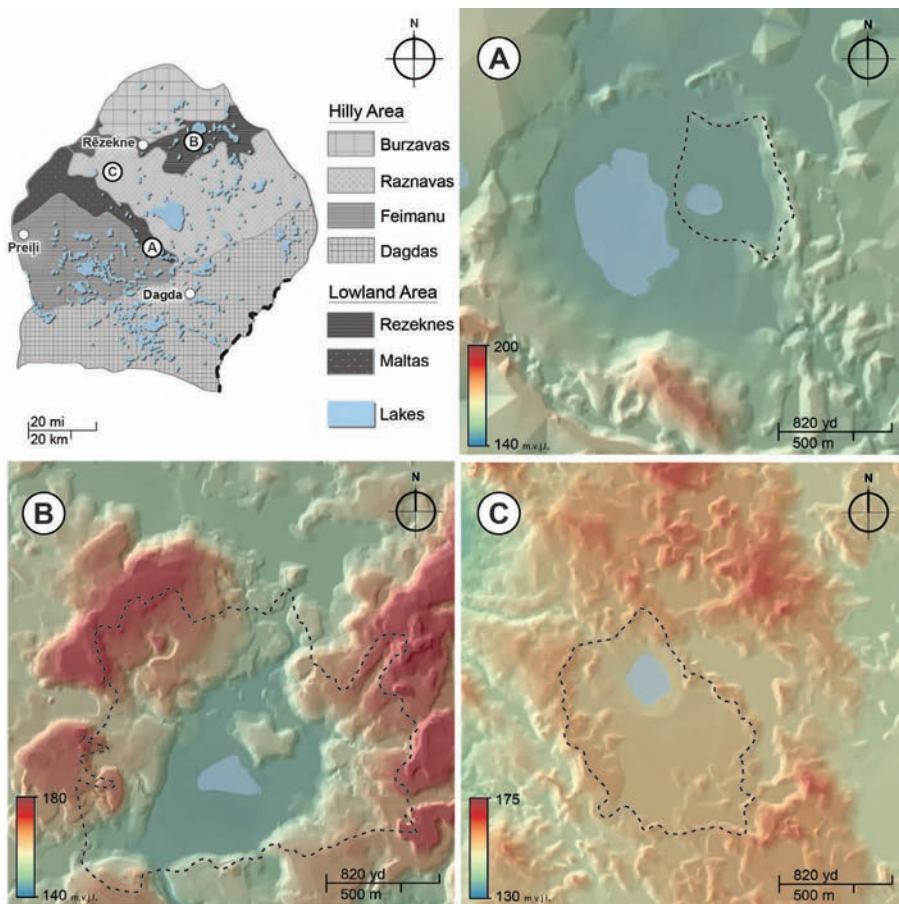
Figure 5. **Nature areas of the Latgale Upland with the location of particular study sites. Relief of catchment areas (black line) of (A) Lake Padelis, (B) Lake Pilcine, (C) Lake Pilvelis**

171, 181 and 189 m ASL, which establish its catchment basin. Lake Pilcine is an inter-hilly water body of glacial origin. Sedimentation of Lake Pilcine was affected by the admixture of dolomites, marlstone and carbonates bedrock fragments to the glacial deposits during the deglaciation process (Markots, 2011). Average water depth of the lake is 40 cm, maximum – 90 cm. There are no inflow-out-flow streams in the lake. Sapropel fills more than 90% of the lake's depression, with an average thickness of 410 cm, maximum 610 cm. The total amount of sapropel deposits in Lake Pilcine is estimated 287,000 m³ (Rozenbergs, 1998b).

2.1.3 Lake Pilvelis

Lake Pilvelis (Figure 5C) is a small (8.7 ha), shallow diseutrophic overgrowing lake of glacial origin at the elevation 156 m ASL, situated in the western part of Raznavas Hilly Area, in the north-west part of the Latgale Upland. Initially, the lake was filled by a discharge of water from the ice-dammed lake. It is located inside a

relatively broad glacial depression created by the Razna glacier tongue during the earliest deglaciation phases of the Latgale Upland (Zelčs and Markots, 2004; Zelčs *et al.*, 2011). After the melting of the local glacier during the Late Glacial period, several lakes were formed in the middle of hummocky, morphologically higher-situated hilly depressions. The area around Lake Pilvelis is classified as a small-sized morainic-hilly relief, where hummocky hills exceed 10 m relative height. Their elevation above the sea level exceeds 160-170 m. This area is one of the highest parts of the Latgale Upland formed on the Devonian bedrock uplift, where approximately 40 m thick glacigenic till represented by glaciofluvial sand and gravel interlayers cover the dolostones of the Upper Devonian Daugava Formation (Mūrnieks *et al.*, 2004). These Pleistocene deposits are overlaid by the Holocene lake sediments, including sapropel (GEO-Konsultants, 1998a). Westwards from the lake, between till and glaciofluvial sediments, a glacier contact slope has been formed (Meirons, 1975; Zelčs and Markots, 2004).

The average water depth of the lake is 0.9-1.0 m, and there are no inflow-outflow streams in the lake. Sapropel fills more than 90% of the lake's depression, with an average thickness of 4.5 cm, maximum – 5.9 m. Along Lake Pilvelis, the shore is formed as an approximately 30 m wide reed *(Phragmites)* marsh belt. The lake catchment basin area occupies 138.5 ha of slightly undulated mainly represented by clayey poorly permeable till covered by clay, which is the reason of bog formation in the area. The total amount of sapropel deposits in Lake Pilvelis is estimated 360,000 m³ (Rozenbergs, 1993c).

2.2 Field studies

Fieldwork is a significant part of lake sediment studies because the correct selection of study sites and coring points and accurate sediment sampling for further research in laboratories is essential. In the frame of this study, fieldwork sites were carried out to obtain more information on the formation of sapropel and changes in its properties during the development of different lakes choosing Lake Padelis, Lake Pilcine and Lake Pilvelis.

The obtained data of sediment thickness, properties and distribution of sapropel layers provides significant information for the research. Therefore, sediment sampling points in studied lakes were selected according to the data of lake depression characteristics (including the topography of lake catchment area, lake depression bathymetry, thickness and composition of lake sediments). Preliminary investigation data of sapropel layers in the chosen location were analyzed to find out the most representative point in the lake for sediment sampling following the study aim. Coring was done in winter through the ice at:

– South-eastern part of Lake Padelis (56°28'33,23" N, 27°7'45,64" E);
– North-eastern part of Lake Pilcine (56°39'45,21" N, 27°17'31,40" E);
– A central part of Lake Pilvelis (56°39'45.21" N, 27°17'31.40" E).

Sediment coring was carried out using a Russian-type peat sampler consisting of a 100 cm long camper with a diameter of 10 cm, which allows obtaining sufficient sediment volume for the planned analyzes. However, parallel overlapping sediment cores at approximately 50 cm were carried out. To obtain the best quality lake sediment samples, the coring was done during wintertime from ice.

Before the coring of sediments, a corer chamber was opened and then pressed into a depth of 100 cm or 200 cm or more in-depth. The corer was turned 180⁰ clockwise to close the chamber. When the corer with sediment was driven out, it was placed into a horizontal position, and its chamber was opened. Obtained sediment sample monolith was documented (photographed and described in a field notebook) and replaced from the corer chamber to a plastic cartridge (plastic semi-tubes) of the same length and slightly larger diameter. Ten parallel overlapping sediment cores for each research site were documented according to the protocol for collecting and handling of peat (Givelet *et al.*, 2004). The name of coring site and depth interval was written on the cartridge, as well the beginning and end of the interval were marked with an arrow indicating the coring direction. The sediment monolith with cartridge was packed in a polyethene film to prevent contamination and drying of the sample. Characteristics of the monolith were also written on the polyethene film after packing and preparation for transportation to the laboratory.

Sapropel monoliths were subsampled with interval 5 cm. The number of subsamples for each site is listed in Table 8, and data were analyzed using each of the selected methods to obtain multi-proxy data.

2.3 Chronology

The chronologies of the investigated sediment cores from Lake Padelis, Lake Pilcine and Lake Pilvelis (Figure 12) were based on ^{14}C radiocarbon dates from three 10-cm-thick bulk samples (Table 6) and ^{210}Pb sediment dating from ten 1-cm-thick bulk samples and were done for each site (Table 7).

Table 6

^{14}C dating and absolute age of sediments from Lake Padelis, Lake Pilcine and Lake Pilvelis

No	Depth, cm	Laboratory reference	^{14}C yr BP	δ13C, ‰	Model age (cal yr BP)	Calibrated age (cal BP) 95%
			Lake Padelis			
1	176-186	Tln3401	6,671±70	-26.3	7,600	7,436-7,624
2	279-289	Tln3402	7,885±80	-27.4	8,870	8,547-8,989
3	390-400	Tln3403	10,090±80	-26.0	11,660	11,330-11,997
			Lake Pilcine			
4	150-160	Tln3398	4,139+-55	-31.2	4,770	4,526-4,829
5	200-210	Tln3399	4,925+-55	-30.3	5,750	5,584-5,752
6	290-300	Tln3400	6,253+-65	-30.0	7,200	6,995-7,310
			Lake Pilvelis			
7	180-190	Tln3394	4,947±60	-30.6	5,730	5,588-5,761
8	240-250	Tln3395	5,292±55	-30.4	6,210	5,932-6,207
9	390-400	Tln3396	8,983±85	-20.2	10,100	9,881-10,273

Samples of sapropel were dated using a conventional liquid scintillation method; the analyses were done at the Institute of Geology, Tallinn University of Technology, Estonia. Radiocarbon dates were converted to calendar years (Table 6) using

the IntCal13 calibration dataset (Reimer *et al.*, 2016) and Clam 2.2 programme deposition model (Blaauw, 2010) with a 95.4% confidence level. R environment was used for age-depth modelling purposes (R Core Team, 2018).

210Pb dating of sediments from Lake Padelis, Lake Pilcine and Lake Pilvelis

No	Depth, cm	Laboratory reference	210Pb specific activity (Bq/kg)	±26 (Bq/kg)	Years (cal AD)	Model age (cal BP)
Lake Padelis						
1	0-1	1626	90	25	2012	-62
2	3-4	1627	172	30	2001	-51
3	6-7	1628	90	32	1992	-42
4	9-10	1629	70	21	1983	-33
5	12-13	1630	50	18	1974	-24
6	15-16	1631	39	15	1965	-15
7	18-19	1632	7	6	1955	-5
8	21-22	1633	8	5	1946	3
9	24-25	1634	14	9	1937	12
10	29-30	1635	12	9	1922	27
Lake Pilcine						
11	0-1	1636	150	28	2012	-62
12	3-4	1637	120	30	2005	-55
13	6-7	1638	125	25	1999	-49
14	9-10	1639	115	20	1993	-43
15	12-13	1640	110	25	1988	-38
16	15-16	1641	90	28	1982	-32
17	18-19	1642	79	20	1976	-26
18	21-22	1643	40	18	1970	-20
19	24-25	1644	57	20	1964	-14
20	29-30	1645	42	18	1955	-5
Lake Pilvelis						
21	0-1	1616	115	20	2012	-62
22	3-4	1617	136	30	2011	-51
23	6-7	1618	145	35	2010	-42
24	9-10	1619	110	20	2009	-33
25	12-13	1620	90	25	2008	-24
26	15-16	1621	94	28	2007	-15
27	18-19	1622	100	30	2006	-5
28	21-22	1623	74	28	2005	3
29	24-25	1624	45	20	2004	12
30	29-30	1625	50	25	2002	27

In addition to ^{14}C dating, ^{210}Pb dating technique was exploited. ^{210}Pb is widely used in the dating of recent lake sediments, especially in studies of human impact on lake catchments and ecosystems (Appleby, 1998; Appleby and Oldfield, 1992). Samples from the upper layer of sediments (30 cm) at each research site were dated using the ^{210}Pb determination (Table 7) method (radiochemical liquid scintillation counting based on ^{210}Pb – ^{210}Bi equilibrium) (Ebaid and Khater, 2006; Schönhofer and Wallner, 2001) at the Laboratory of Nuclear Geophysics and Radioecology of the Nature Research Centre, Lithuania. The age of sediments was calculated by the model with no sediment compaction and mean linear sedimentation rate of 0.33 cm per year.

The age of sediments given in the text refers to calibrated years before present (cal BP). For the chronological subdivision of the Holocene, recommendations of the Working Group of INTIMATE were used (Walker *et al.*, 2012).

2.4 Analytical methods of sediment analysis

The multi-proxy approach was applied to characterize changes in sapropel core composition in each lake and to link data with lake development and environmental factors. Contents with performed analysis of obtained data are listed in Table 8.

Table 8

Number of the sapropel subsamples used by applied analytical methods

No.	Analytical method	Number of the samples			Method description subchapter
		Lake Padelis	Lake Pilcine	Lake Pilvelis	
Biological methods					
1	Pollen analysis	30	30	40	2.5.1
2	Plant macrofossils analysis	30	30	40	2.5.2
3	Microfossils analysis	30	40	40	2.5.3
4	Malacofauna analysis	30	-	-	2.5.4
Physical-chemical methods					
5	Bulk density	30	40	40	2.5.5
6	Loss-on-ignition (LOI)	30	40	40	2.5.5
7	Elemental composition	15	17	20	2.5.6
8	Content of humic substances	30	30	40	2.5.7
9	Content of metallic element	15	17	25	2.5.8
10	Biogenic phosphorus content	30	30	40	2.5.9
11	Granulometry	-	-	40	2.5.10

2.4.1 Pollen analysis

For determination of vegetation response to past regional climate change during the sapropel formation in Table 8 is listed the number of sediment samples derived from investigated lakes which were prepared for pollen analysis according to known methodology (Bennett and Willis, 2001).

In each sample, at least 400 pollen grains were counted using light microscope Motic DM-B1 at 400-1,000× magnification. Pollen atlases were used for pollen identification (Beug, 2004; Faegri and Iversen, 1989; Moore and Webb, 1978; Nilsson *et al.*, 1977). Counted pollen grains and spores were arranged in the groups of trees, shrubs, cultivated plants, ruderal plants, aquatic plants, herbs and spore plants, arranging the pollen group allocation and variety dependent on pollen amount and diversity (Ozola, 2013).

The basic sum calculation for pollen percentage was based on the sum of all pollen, except the aquatic plant pollen (Berglund and Ralska-Jasiewiczowa, 1986). For the processing of pollen data, Tilia v.2.1.1 software was used (Goring, 2016) to complete pollen diagrams.

2.4.2 Plant macrofossils analysis

Plant macrofossils analysis of lake sediments gives evidence of past vegetation, ecosystems and climate reconstruction specifics (Birks, 2001; Salonen *et al.*, 2012).

The samples (Table 8) in a volume of approximately 50 cm^3 for macrofossils analysis were washed through 0.25 mm sieves with a gentle spray of water, packed into plastic bags and kept wet and cold until identification procedure. Macrofossils were suspended in a Petri dish and systematically examined under stereomicroscope Stemi 2000C at 10-40× magnification until the whole sample was looked through. Remains of interest were picked out, sorted, identified by comparison with atlases (Cappers *et al.*, 2012; Katz *et al.*, 1965, 1977; Sloka, 1978; Velichkevich and Zastawniak, 2006, 2008) and herbarium collection reference materials (Laboratory of Quaternary Environment of the Faculty of Geography and Earth Sciences at the University of Latvia; the Latvian Museum of Natural History). Macrofossils for each lake were set in the groups of trees and shrubs, telmatic plants, cultivated plants, ruderal plants, aquatic plants, aquatic animals.

Macrofossils were counted, and the sum of each macrofossils type was tabulated (Birks, 2001) using MO Excel 2013 software. Macrofossils diagrams were compiled using Tilia v.2.1.1 software (Goring, 2016).

2.4.3 Microfossils analysis

Microfossils of various origin such as algae, aquatic animals, vascular plants are essential indicators not only for habitat and climate change reconstruction (Smol *et al.*, 2001a) but also in a practical approach for sapropel type identification and application (Kurzo *et al.*, 2012; Shtin, 2005).

In this study, microfossils analyses were carried out for the number of samples listed in Table 8. Samples for microfossils were prepared as follows: 1 cm^3 of a sample was diluted with 10 ml of water and vortexed for 15 min to destroy sample colloidal structure. One drop of well shook obtained dilution was analyzed in 400-1,000× magnification under Digital Microscope Motic DM-B1 until at least 1,000 remains were counted. For the identification of organic remains, atlases of algae, freshwater and mire plants (Bellinger and Sigee, 2015; Berg *et al.*, 2004; Katz *et al.*, 1977) were used. Biological remains were identified and arranged in the groups of vascular plants, green algae, diatoms, cyanobacteria, aquatic animals, fungi and moss.

The basic sum calculation for microfossils percentage was based on the sum of all identified remains and visualized in a diagram using Tilia v.2.1.1 software (Goring, 2016).

2.4.4 Malacofauna analysis

Studies of Quaternary freshwater molluscs provide information about ancient lakes and water level changes of rivers, the basis for biostratigraphic zonation of sediments and reconstruction of local habitat and climatic conditions (Miller and Tevesz, 2001). Malacofauna analyses were done for calcareous sediments of Lake Padelis (Table 8). Mollusc shells in other samples of studied lakes were not discovered because they may remain only in sediments deposited in alkaline waters (Sanko *et al.*, 2010).

The samples for malacofauna analysis ($\approx$50 cm^3) were washed through 0.25 mm sieves using a slight water spurt. Whole mollusc shells and shell remains were picked out, dried and kept in plastic containers until identification. Each whole mollusc shell in the sample was identified under stereomicroscope Stemi 2000C at 10-40× magnifications using atlases (Okland, 1990; Rudzīte *et al.*, 2010) and consultations with a member of the Malacological Society of Latvia *Dr.biol.* Elga Parele. All shell remains in each sample were counted.

Obtained data were counted, and the sum of each identified mollusc species was tabulated to complete malacofauna diagram using Tilia v.2.1.1 software (Goring, 2016).

2.4.5 Bulk density and loss-on-ignition (LOI)

The main sediment parameter of sapropel identification, as well sapropel type determination is the percentage of data obtained with loss-on-ignition analysis (BSSC Institute, 2010; Shtin, 2005). In paleoenvironmental studies, water-sediment LOI data is used to characterize lake development stages (Punning *et al.*, 2005), changes in sedimentation condition (Fuhrmann, 2003; Ozola, 2013), anthropogenic impact (De Vleeschouwer *et al.*, 2009; Pujāte, 2015) on the ecosystem and communities of living organisms (Kurzo, 1988; Kurzo *et al.*, 2012).

This method was applied in order to estimate bulk density, percentage of moisture and dry matter, organic matter and ash, carbonates and mineral matter content in the studied sediments (Dean, 1974; Heiri *et al.*, 2001). At first, bulk density of the sediments was determined weighting fixed fresh sediment volume expressed as g/cm^3. In the second step, moisture was determined for the same sample after drying sample at 105 °C. The content of organic and carbonate matter was estimated by incinerating the samples sequentially for 4 h at 550 °C and 2 h at 950 °C.

The basic sum calculation for moisture, organic and mineral matter and carbonates percentage was tabulated and calculated in MS Excel 2013 software using known formulas (Heiri *et al.*, 2001).

2.4.6 Elemental composition

The concentration of carbon (C_{org}), hydrogen, nitrogen (N_{org}), oxygen and sulphur (S_{org}) in the samples of sapropel listed in Table 8 were detected by a combustion-gas

chromatography technique using Elemental Analyzer Model EA-1108 (Carlo Erba Instruments) (detection limit 10 ppm, accuracy 0.3-0.5%, repeatability 0.2%). The instrument was calibrated using cystine (Sigma-Aldrich Inc.) as a standard. All sapropel samples were analyzed in duplicate.

2.4.7 Content of humic substances

Content of humic substances was determined as follows: 0.5 g of air-dried and finely ground sample of sapropel was treated in N_2 with 25 ml of 2% NaOH for 24 h applying stirring. The obtained suspension was filtered, diluted 100 times, and absorption at 410 nm was measured. Calculation of the content of humic substances was performed using a calibration method as recommended by the International Humic Substances Society (Tan, 2005).

2.4.8 Quantitative analysis of metallic elements

Concentrations of metallic elements in samples listed in Table 8 were determined after the acid extraction of samples (Csuros and Csuros, 2002). Finely-ground samples of dried sapropel (1 g) were treated with 25 ml of 50% HNO_3 and 5 ml of 30% H_2O_2 and left for 24 h. Sample solutions were heated at 150 °C until half of the liquid has evaporated, then another 25 ml of 50% HNO3 were added, and heating was continued at 100 °C. Afterwards, sample solutions were filtered and diluted to 50 ml.

Measurements of element concentration were done by atomic absorption spectrometry using AAnalyst 503 (PerkinElmer) techniques. Concentrations of Na, Mg, K, Mn, Ni, Fe, Cu and Zn were measured in acetylene-air flame; Ca – in acetylene/N2O flame. For concentration measurements of Cd, Co, Cr and Pb, graphite furnace atomic absorption was used. The concentration of Si was measured using X-ray fluorescence. Precision and accuracy of the analytical results were derived by preparation and analysis of samples in triplicate and by using blank, and reference samples ISE 1998.3-921 (Wageningen Evaluating Programmes for Analytical Laboratories) and BSCC Coastal Marine Sediments (Analytical Chemistry Standards NRC, Canada). The precision of the results was detected within 10% for trace elements (Ca, Fe, K, Mg, Na) and 1-3% for heavy metals (Cd, Co, Cu, Cr, Mn, Ni, Pb, Zn). Recovery on average varied from 83% for Zn to 98% for Cr (mean recovery 94%).

2.4.9 Content of biogenic phosphorus

Analysis of biogenic phosphorus (P_{bio}) was performed by a standard method (Johengen, 1996). 0.1 g of sediments were treated with 30 ml 0.1 N NaOH for 17 h by stirring. Then samples were neutralized with 3 ml 1 N HCl and, after precipitation for an hour, filtered and diluted to 50 ml. The concentration of P was detected by the ascorbic acid method.

2.4.10 Granulometry

The grain size distribution of sapropel mineral matter from Lake Pilvelis (Table 8) was determined by Horiba laser scattering particle size analyser at the

Institute of Geology of Tallinn University of Technology. Organic matter was removed by burning a 10 ml sapropel sample at 550 °C, then mixing it with distilled water. The grain-size classification followed the Udden-Wentworth scale (Last, 2001). Before performing the granulometric analysis, it was necessary to get rid of organic substances in sapropel samples because the content of organic matter in such sediments is very high (average 80% of dry mass). Several methods, including acid digestion, were tested, but this was assessed as the most efficient to eliminate organic remains (*e.g.*, exoskeletons of Caldocera, Pediastrum, pollen, spores) from samples.

2.5 Statistical analysis of the data

In this study, for identification of the contribution of different impact factors on lake sediments, the multi-proxy approach was applied including research of lake development processes combined with physical and chemical characterisation of sediments after the statistical analysis.

FWSDB data on different types of sapropel deposits (n=1,793) were used to perform statistical data processing by PC-ORD7. Statistical analysis included following parameters: type of sapropel (organogenic, diatom, organogenic-silicate, silicate, carbonate and ferruginous), an average thickness of sapropel layer in a deposit, detected average layer thickness of a particular type of sapropel in a deposit, moisture content, ash content, the concentration of Ca and Fe, Upper Pleistocene and Holocene sediments in the territory, type of lakebed, lake water regime, trophic nature of a lake and filling factor of the lakebed. The data were compiled in the scatterplot and scatterplot matrix.

Correlation analysis with a data set for Lake Padelis (n=15), Lake Pilcine (n=17), Lake Pilvelis (n=25) of metallic elements, loss-on-ignition data (organic and mineral matter, carbonates) and total content of phosphorus and humic substances was performed using MS Excel Correlation analysis tool. Statistically significant correlation was applied regarding critical values for Pearson's correlation coefficient (Fisher, 1970).

Multivariate statistical analysis (principal component analysis, PCA) was chosen for simplification of the research dataset with many variables. This analysis is extensively applied to assess the levels of metallic elements and other parameters in different types of sediments, including soil (Zhiyuan *et al.*, 2011), peat (Klavins *et al.*, 2008) and street dust (Yongming *et al.*, 2006).

PCA (rotation method VARIMAX with Kaiser normalisation; rotation converged in 8 iterations) was conducted using PC-ORD 7 for Windows. Data were partitioned into two matrices: the first, main matrix includes data of sapropel element components, like data of loss-on-ignition, elemental composition, metallic elements (Na, Mg, K, Ca, Fe, Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb), humic substances and total phosphorus content; the second matrix includes potential sapropel formation materials, like cyanobacteria, green algae, diatoms, vascular plant and aquatic animal remains and detritus.

The data were processed using MS Excel 2016, TILIA, CLAM, ArcGIS 10, PC-ORD 7 and Adobe Illustrator CC. Data processing was followed by analysis, comparison and interpretation.

2.6 Freshwater sapropel database

FWSDB is based on GIS in ESRI Shapefile format using LKS-92 TM system of coordinates with a certainty of scale 1:5,000 and UTF-8 encoding of characters; it consists of two layers. The layer of the lake polygons was established based on the water body layer of GIS Latvia 10.2 open-access database (Envirotech, 2013). This layer contains information about the parameters of the object of the database – the lake (Table 9), which were derived from the data of complex geological exploration expeditions as well as using available information at the database *www.ezeri.lv*. The lakes which were not included in the water body layer of GIS Latvia were added using another new-created layer by combining the data from orthophoto and large scale topographical maps (ORTOFOTO 3 NIR, 2009; TOPO 10K PSRS, 1963).

Table 9

Description and attributes of a sapropel deposit layer

Title	Deposits of sapropel
Title of database (DB)	Sapropela_atradnes_poligons
Description	Lake sapropel deposits that were included in the surveys of complex geological exploration expeditions
Type	Polygon
Coordinate system	LKS-92 TM
History	Established based on the layer udenstilpes_poly of GIS Latvia 10.2 open-access database, as well as applying the data derived from complex geological exploration expeditions
Certainty of scale	1:5,000

No.	Title	Title of DB	Type	Description/Notes
1.	ID	ID	Real[10,0]	Individual number of sapropel deposit corresponds to ESI_NR. In cases, if some objects had the same ESI_NR number, the new individual number was chosen
2.	Number of lake sapropel deposit	ESI_NR	Integer[10,0]	Code of deposit (lake/bog/river) that was assigned in the surveys of complex geological exploration expeditions
3.	Type of deposit	TIPS	String[10]	Type of deposit – lake (with a possibility to choose another type (bog, river) if the DB is extended)
4.	Title of deposit	NOSAUKUMS	String[100]	Name, the title of deposit (lake/bog/river)
5.	Field of polygon	LAUKUMS	Real[20,1]	Marked field of deposit's polygon (lake/bog/river), m^2

Table 9 (continued)

Description and attributes of a sapropel deposit layer

No.	Title	Title of DB	Type	Description/Notes
6.	Area of deposit	OBJ_ LAUKUMS	Real[10,1]	Lake water area (ha) in accordance with the information source
7.	Average water depth in deposit	UD_VID	Real[10,1]	Average lake water depth (m) in accordance with the information source
8.	Maximum water depth in deposit	UD_MAX	Real[10,1]	Maximum lake water depth (m) in accordance with the information source
9.	The legal form of industrially significant sapropel deposit	RUP_IEGULA	String[10] Ir – object is considered as industrially significant sapropel deposit; Nav – object is not considered as industrially significant sapropel deposit	
10.	The reason why the deposit is not considered as industrially significant	IEMESLS	Integer[10] Deposits located in protected areas and in which economic activity is restricted by law; Deposits where sapropel is not found or average depth of sapropel is ≤ 1 m; Deposits composed of silicate (sandy, silty and clayey) and ferruginous (limonite type of sapropel) sapropel; Deposits where sediments contain a low content of organic matter (≤15%), silicate or ferruginous sapropel layer thick over ≥0.5 m covers deposits; Deposits above which water layer is ≥5 m; Deposits with increased anthropogenic load; Worked out deposits	The reason why the deposit is not considered as industrially significant in accordance with the surveys of complex geological exploration expeditions If the deposit has several reasons why it is not considered as industrially significant, the number of reasons are counted in numerical order (1-7) without commas and spaces
11.	Water regime of deposit	UD_REZIMS	String[100] confluent flows running-through flows runoff flows no flows	Water regime of a lake in accordance with the information source

Table 9 (continued)

Description and attributes of a sapropel deposit layer

No.	Title	Title of DB	Type	Description/Notes
12.	Lake trophic states	TROF	String[100] oligotrophic; mesotrophic; eutrophic; hypereutrophic; dyseutrophic; dystrophic	Lake trophic state in accordance with the information source
13.	Lake filling coefficient	AIZPILD	Real[5,1]	Indicator that shows how much of lake volume is filled with sapropel sediments Value from 0 to 1
14.	Level of exploration of the deposit	IZPETE	String[5] M – searches; I – assessed; D - detailed	
15.	Investigator of deposit	IZP_V	String[100]	Name and surname of the investigator, year in which the study was carried out
16.	Information source	AVOTS	Integer[10,0] Latvgeologija, 1991a,b: Liepāja, Ventspils Regions Latvgelogija, 1992: Rīga, Limbaži Regions Latvijas ģeoloģija, 1994: Daugavpils Region GEO-Konsultants, 1995: Madona Region GEO-Konsultants 1996: Dobele, Kuldīga, Saldus, Talsi, Tukums Regions GEO-Konsultants 1997: Valka, Valmiera, Cēsis, Ogre, Bauska, Aizkraukle Regions GEO-Konsultants 1998b: Rēzekne, Preiļi, Jēkabpils Regions GEO-Konsultants 1999: Alūksne, Balvi, Gulbene, Ludza Regions GEO-Konsultants 1998a: Krāslava Region	Surveys of complex geological exploration expeditions by regions

The information on lake sapropel deposits was entered into the database, creating a second layer which is the sapropel deposit (dot) layer, where each object represents the parameters of a particular type and form of sapropel deposit (Table 10).

Table 10

Description and attributes of a deposit layer of lake sapropel

Title	Deposits of sapropel
Title of DB	Sapropela_iegulas_points
Description	Lake sapropel deposits that were included in the surveys of complex geological exploration expeditions
Type	Point
Coordinate system	LKS-92 TM
Certainty of scale	1:5,000

No.	Title	Title of DB	Type	Description/Notes
1.	ID	ID	Integer[10,0]	Individual number of sapropel deposit corresponds to ESI_NR. In cases, if some objects had the same ESI_NR number, the new individual number was chosen
2.	Number of lake sapropel deposit	ESI_NR	Integer[10,0]	Code of deposit (lake/bog/river) that was assigned in the surveys of complex geological exploration exp.
3.	Title of deposit	NOSAUKUMS	String[100]	Name, the title of deposit (lake/bog/river)
4	The reason why the deposit is not considered as industrially significant	IEMESLS	Integer[10] Deposits located in protected areas and in which economic activity is restricted by law; Deposits where sapropel is not found or average depth of sapropel is ≤1 m; Deposits composed of silicate (sandy, silty and clayey) and ferruginous (limonite type of sapropel) sapropel; Deposits where sediments contain a low content of organic matter (≤15%), silicate or ferruginous sapropel layer thick over ≥0.5 m covers deposits; Deposits above which water layer is ≥5 m; Deposits with increased anthropogenic load; Worked out deposits	The reason why the deposit is not considered as industrially significant in accordance with the surveys of complex geological exploration expeditions

If the deposit has several reasons why it is not considered as industrially significant, the number of reasons are counted in numerical order (1-7) without commas and spaces |
| 5 | The legal form of industrially significant sapropel deposit | RUP_IEGULA | String[10] Ir – object is considered as industrially significant sapropel deposit (ISSD); Nav – object is not considered as ISSD | |

Table 10 (continued)

Description and attributes of a deposit layer of lake sapropel

No.	Title	Title of DB	Type	Description/Notes
6.	Order of sapropel deposit	KLASE	String[10] O – organogēns; KR – kramaļģu; OS – organogēnais-silikātu; S – silikātu; K – karbonāWWtu; DZ – dzelzi saturošs	Order of sapropel deposit in accordance with the classification of sapropel types used in the Surveys of complex geological exploration expeditions by regions In English: O – organogenic; KR – diatom; OS – organogenic silicate; S – silicate; K – carbonate; DZ – ferruginous
7.	Type of sapropel deposit	VEIDS	String[20] za – zaļaļģu; zi – zilaļģu; da – dažādaļģu; ku – kūdrainais; zo – zoogēns-aļģu; kr – kramaļģu; s – smilšains; a – aleirītisks; m – mālains; os – organogēni-smilšains; oa – organogēni-aleirītisks; om – organogēni-mālains; krs – kramaļģu-smilšains; kra – kramaļģu-aleirītisks; krm – kramaļģu-mālains; ks – kaļķaini-smilšains; ka – kaļķaini-aleirītisks; km – kaļķaini-mālains; ok- organogēni-kaļķains; sk – smilšaini-kaļķains; ak – aleirītiski-kaļķains; mk – mālaini-kaļķains; k – kaļķains; ol – organogēni-limonītisks kl – kaļķaini-limonītisks; l – limonītisks; sf – sulfīdu	Type of sapropel deposit in accordance with the classification of sapropel types used in the Surveys of complex geological exploration expeditions by regions In English: za – green algae; zi – cyanobacteria; da – different algae; ku – peaty; zo – zoogenic-algae; kr – diatom; s – sandy; a – silty; m – clayey; os – organogenic sandy; oa – organogenic silty; om – organogenic clayey; krs – diatomic sandy; kra – diatomic silty; krm – diatomic clayey; ks – carbonate sandy; ka – carbonate silty; km – carbonate clayey; ok – organogenic carbonate; sk – sandy carbonate; ak – silty carbonate; mk – clayey carbonate; k – carbonate; ol – organogenic limonite kl – carbonate limonite; l – limonite; sf – sulphide

Table 10 (continued)

Description and attributes of a deposit layer of lake sapropel

No.	Title	Title of DB	Type	Description/Notes
8.	Average thickness of sapropel	BIEZ_VID	Real[10,1]	Average thickness of sapropel layer, m
9.	Maximum thickness of sapropel in deposit	BIEZ_MAX	Real[10,1]	Maximum thickness of all the sapropel layer in a lake, m
10.	Area of industrial deposit	PLATIBA	Real[20,1]	Area of sapropel industrial deposit, ha
11.	Volume of sapropel	APJOMS	Real[20,1]	Volume of sapropel involving natural moisture, thousands m³
12.	Sapropel resources	RESURSI	Real[20,1]	Sapropel resources with moisture 60%, thousands t – calculated using the formula: $P_{60\%}=V \times V60\%$, V – volume (thousands m³), V60% - volumetric mass (t/m³) of sapropel with moisture 60% which was calculated using the formula: $V60\%=-0.29 \times W+2.8666$, which were derived from average parameters in calibration graph of sapropel natural moisture (W) and volumetric mass
13.	Natural moisture of sapropel	MITRUMS	Real[10,1]	Average natural moisture of sapropel, %
14.	Ash content of sapropel	PELNI	Real[10,1]	Average ash content of sapropel, %
15.	Content of calcium oxide	CaO	Real[10,2]	Average content of calcium oxide in deposit, %
16.	Content of iron oxide	FeO	Real[10,2]	Average content of iron oxide in deposit, %
17.	Bottom of lake	PAMATNE	String[100]	Mineral bottom of the lake under the sapropel deposit

3 RESULTS AND DISCUSSION

3.1 Typology, amounts, distribution and formation regularities of freshwater sapropel in the territory of Latvia

3.1.1 Classification of freshwater sapropel

In Latvia, as in other countries such as Russia, Ukraine, Belarus, classification of sapropel was developed due to its use as a valuable natural resource applicable in agriculture, industry, balneology and other fields. Classification of sapropel was based on various criteria selected by scientists, thus, leading to several classification systems.

In order to create and easily add new data to the elaborated sapropel database to evaluate the economic potential of sapropel use, the author of the Thesis proposes sapropel definition and adaptation of the classification system of freshwater sapropel in Latvia and to study its usage possibilities on the example of certain lakes in Latvia. The elaborated Sapropel Classification System was developed as an adapted classification system of freshwater sapropel used in the surveys of complex geological exploration expeditions (GEO-Konsultants, 1995, 1996, 1997, 1998a, 1998b, 1999; Latvgeologija, 1991a, 1991b, 1992; Latvijas ģeoloģija, 1994).

Currently, sediments such as sapropel in Latvia are defined by law as 'an organogenic sediments with the content of organic matter 60-95%, containing at least 5% impurity of mineral particles <0.25 mm, that is formed by the decomposition of plant and microorganism residues in stagnant or slow-flowing water basins' (MK 570, 2012).

A similar description of sapropel can be found in the provisional recommendations for the use of sapropel for agricultural purposes in Latvia (Skromanis *et al.*, 1987; Vucāns, 1989). At the time of these studies (the end of 1980s), sapropel competed with organic fertilizers, essential properties of which were the amount of organic matter and macronutrients. For this purpose, sapropel was classified according to its content of organic matter: true sapropel (50-85%), sapropel with reduced content of organic matter (10-50%) and sapropel with poor content of organic matter (below 10%); however, it is not enough to evaluate the widespread use of sapropel only with a percentage of organic and mineral matter.

The author proposes the following terms to be used in the Sapropel Classification System (Table 11):

Freshwater sapropel – subfossil colloidal sediments of continental water bodies with a fine-grained or gelatinous structure, containing a significant amount of organic matter (15% or more by dry weight), consisting of residues of plants and aquatic organisms and predominantly with low content of inorganic constituents.

Class of sapropel – the highest taxonomic unit of the Sapropel Classification System which combines sediments with the introduction of similar substances.

Order of sapropel – a taxonomic unit of the Sapropel Classification System which combines sediments with a similar ratio of organic and mineral matter and conditions of accumulation.

Type of sapropel – a lower taxonomic unit of the Sapropel Classification System that combines sediments with a defined ratio of organic and mineral matter and composition determined by certain conditions of sedimentation and the state of the key elements.

Sapropel microfossils – a percentage of various groups of algae, aquatic animals and plants that form up the organic matter of sapropel.

HS products – products composed partly of humic substances (HS), which are used as soil amendments, fertilizer additives, agents for soil and water remediation, dietary supplements and livestock feed additives.

Growth stimulators – natural and synthetic compounds that enhance plant growth capacity.

Fertilizers – substances that provide plants with nutrients and are intended to enhance soil fertility.

Therapeutic mud – sediments that have therapeutic effects on the human/animal body in accordance with the technical provisions of the regulatory enactments. Chemical and sanitary-bacteriological parameters of these sediments correspond to the standards for use in therapeutic-preventive and recovery purposes.

Binder – sapropel applied as a binder for manufacturing of environmentally friendly composite (construction) materials – plaster/finishing materials and thermal insulation materials.

Drilling fluids – drilling mud used to aid the drilling of boreholes in the ground.

Raw sapropel for chemical processing – raw material applied for chemical processing to produce substances which may be used in the manufacture of high added-value products.

Soil improvers – materials which improve soil structure and its mechanical properties.

Feed additives – natural and/or artificial substances that are added to animal feed at the manufacturing stage in order to ensure specific nutritional properties and/or preserve their quality.

Soil lime – soil additive which improves water penetration and increases pH of acidic soil, improves the uptake of major nutrients for plants in acidic soils and provides soils with the source of Ca and Mg.

In the Sapropel Classification System, freshwater organic sediments are classified into *Class*, *Order* and *Type* according to the percentage of ash (A, %) in sediments, the total content of calcium and iron in dry matter (Ca, Fe, g/kg), the percentage of microfossils and mineralogical composition. The classification offers stratigraphic designations for various types of sapropel and provides possible fields of application (Table 11).

In the proposed classification, the quantities of Ca and Fe are expressed as total amounts, not in the form of oxides as in other classifications (BSSC Institute, 2010; Shtin, 2005), expressed as g/kg of dry matter rather than as a percentage. This approach is consistent with modern methodology for detecting these elements using acid digestion extraction and spectroscopic methods for detecting the content of elements.

Table 11

Sapropel Classification System adapted for Latvia

Class	Order	Type	Symbol	Diagnostic marks				Possibilities of use
				Ash, %	g/kg DM		Microfossil and granulometric composition, %	
					Ca	Fe		
Biogenic	Organogenic (O)	Peaty	(symbol)				vascular plants >35	HS products, growth stimulators, binder, fertilizers
		Zoogenic	(symbol)				animals >15	Therapeutic mud, fertilizers, source of biologically active substances, raw for chemical processing
		Algae	(symbol)	<30	<60	<140	total algae >45	
		Cyanobacteria	(symbol)				cyanobacteria >35	Binder, drilling fluids, therapeutic mud, fertilizers
		Green algae	(symbol)				green algae >35	
	Diatomic (D)	Diatomic	(symbol)	<65	<60	<140	diatoms >35	Growth stimulators, therapeutic mud, fertilizers
Silicate	Organogenic silicate (OS)	Organogenic sandy	(symbol)				organic remains 40 / sand >30	
		Organogenic silty	(symbol)				organic remains 40 / silt >30	Fertilizers, therapeutic mud, drilling fluids, raw for chemical processing
		Organogenic clayey	(symbol)	30–65	<60	<140	organic remains 40 / clay >30	
		Diatomic sandy	(symbol)				diatoms <20 / sand >30	
		Diatomic silty	(symbol)				diatoms <20 / silt >30	Therapeutic mud, raw for chemical processing
		Diatomic clayey	(symbol)				diatoms <20 / clay >30	

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Table 11 (continued)

Sapropel Classification System adapted for Latvia

Class	Order	Type	Symbol	Ash, %	g/kg DM Ca	g/kg DM Fe	Microfossil and granulometric composition, %		Possibilities of use
Silicate	Silicate (Si)	Sandy					sand	30-50	
		Silty		65-85	<60	<285	silt	30-50	Soil improvers
		Clayey					clay	30-50	
		Organogenic carbonate		<30	60-140	<140	organic remains calcite	40 <20	Fertilizers, feed additives, raw for chemical processing
		Sandy carbonate		30-65	60-140	<140	calcite sand	<20 30-50	
		Silty carbonate					calcite silt	<20 30-50	Fertilizers, soil lime
		Clayey carbonate					calcite clay	<20 30-50	
	Carbonate (C)	Carbonate sandy		65-85	60-140	<140	calcite sand	<20 >50	
		Carbonate silty					calcite silt	<20 >50	Soil improvers
		Carbonate clayey					calcite clay	<20 >50	
Carbonate		Carbonate		<85	>140	<140	calcite	>20	Soil lime, therapeutic mud, feed additives

Table 11 (continued)

Sapropel Classification System adapted for Latvia

Class	Order	Type	Symbol	Diagnostic marks					Possibilities of use
				Ash, %	g/kg DM		Microfossil	and granulometric composition, %	
					Ca	Fe			
	Ferruginous (F)	Organogenic limonite		<65	<60	140-285	limonite	5-10	Fertilizers
		Carbonate limonite		<65	60-140	140-285	limonite	5-10	Soil lime, therapeutic mud
		Limonitic carbonate		<85	>140	140-285	limonite	5-10	Soil lime
		Limonite		<85	<140	>285	limonite	>10	Not applicable
	Sulphur (Su)	Sulphide		<85	<140	<140	sulphide	>10	
Mixed	Mixed (M)	Organogenic silicate carbonate		<30	60-140	<140	silicate calcite sulphide	<10	Fertilizers, binder, therapeutic mud
		Silicate carbonate limonite		<30	60-140	140-285	sulphide	<10	Drilling fluids, binder, therapeutic mud
		Organogenic silicate limonite		<30	<140	140-285	sulphide	<10	Therapeutic mud
		Organogenic carbonate sulphide		<30	60-140	<140	sulphide	>10	Therapeutic mud

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In terms of sapropel as a resource, it is classified into a solid fuel group which includes peat, wood, lignin (Podgorodetskii *et al.*, 2015); therefore, worldwide recognized and proven methods should be used to determine the type of sapropel:

1. Ash content on a dry basis (%) (LVS/STK/38, 2011) means the ratio by mass of the dry mass of inorganic residue remaining after the combustion under certain conditions. This method is described in Section 2.5.5 of this work; the applied method is supplemented;

2. Content of calcium and iron in dry matter (expressed as g/kg) is detected by extraction of air-dried samples applying acid digestion and determined by atomic absorption spectrometry or inductively coupled plasma mass spectrometry. It is a commonly used methodology for the analysis of various environmental samples (Krūmiņš, 2016; Silamiķele, 2010; Vincēviča-Gaile, 2014);

3. Microfossils are determined in provided classification (Table 11) for organogenic order of sapropel by the method described in Section 2.4.3;

4. Granulometry is determined in provided classification (Table 11) applying for organogenic silicate, silicate, carbonate and mixed sapropel orders by the method described in Section 2.4.10.

Commission Implementing Regulation (EU) No. 354/2014 of 8 April 2014 amending and correcting Regulation (EC) No. 889/2008 laying down detailed rules for the implementation of Council Regulation (EC) No. 834/2007 'On organic production and labelling of organic products with regard to organic production, labelling and control' regarding organic-rich sediment from freshwater bodies formed under exclusion of oxygen (*e.g.*, sapropel) states: '*Only organic sediments that are by-products of freshwater body management or extracted from former freshwater areas. When applicable, extraction should be done in a way to cause minimal impact on the aquatic system. Only sediments derived from sources free from contaminations of pesticides, persistent organic pollutants and petrol like substances*'. This Regulation sets down the maximum permissible element levels for sediments with a high content of organic substances, including sapropel (expressed on dry matter): cadmium 0.7 mg/kg; copper 70 mg/kg; nickel 25 mg/kg; lead 45 mg/kg; zinc 200 mg/kg; mercury 0.4 mg/kg; chromium (total) 70 mg/kg; chromium (VI): not detectable.

3.1.2 Estimated amount of lake sapropel deposits in Latvia

FWSDB was designed to systematize and summarize available information on the results of lake sapropel searching works. Up to now, searching of sapropel has been carried out at more than a half of Latvia's lakes (the total number of lakes in Latvia exceed 2,200), in which estimated sapropel amount is approximately, 975 billion m^3, indicating the lake sapropel as a significant natural resource of Latvia. Therefore, the designed freshwater sapropel database is an important step in identifying and systematizing natural resources in Latvia, both in terms of location and availability, which is important not only at the national level but also useful for promoting regional business. The database provides more efficient estimation and economic calculations of utilization potential for the sapropel resources. It allows to obtain information on sapropel deposits in lakes of Latvia, to evaluate the quantity and quality of sapropel resources, which encourage the selection for the use of the most promising type of sapropel as well as helps for practical planning of sapropel extraction. FWSDB can also be used to select the lakes for further investigation.

The database was designed using GIS software where the data were digitized; thus, FWSDB is linked to the lake and parish layers of GIS according to the administratively territorial division of Latvia which is valid from January 3, 2011, i.e., 110 regional communities and 9 republic cities.

The total amount of identified lake sapropel in Latvia is 974,982.2 thsd. m³ (or 527,938.5 thsd. tons with a moisture content of 60%); from which as industrially significant sapropel deposits can be admitted 712,213.3 thsd. m³ or 287,746.3 thsd. tons. Assuming the planning region (PReg) territory, the highest density of lakes is in Latgale PReg (3.27%), followed by Kurzeme PReg (1.54%), Riga PReg (1.21%) and Vidzeme Preg (1.03%). Searching works for sapropel resources the most completely have been performed in Latgale PReg, where 590 (61.58%) of total 958 lakes have been studied. In Kurzeme PReg sapropel searching works have been performed in 121 (of total 395) lakes, in Vidzeme PReg in 356 (of total 583) lakes, in Riga PReg in 132 (of total 244) lakes, Zemgale PReg in 84 (of total 185) lakes (Table 12, Figure 6).

Table 12

Information on sapropel deposits and the total amount of sapropel in Latvia

	Latgale	Kurzeme	Vidzeme	Riga	Zemgale	Total
PReg area, km²	14,564.9	13,598.5	15,251.2	10,440.1	10,734.2	64,588.9
Total No. of lakes	958	393	583	244	185	2363
Lakes area, km²	475.8	209.9	156.4	126.1	50.4	1018.6
No. of investigated lakes	590	121	356	132	84	1283
Deposit area, km²	457.1	164.1	144.9	107.9	37.9	911.3
Sapropel research degree in the region, %	61.58	30.63	61.06	54.09	45.40	54.30
Sapropel amount, thsd. m³	414,403.3	73,117.7	240,741.2	154,415.0	92,305.0	974,982.2
Sapropel resources, thsd. t	184,902.9	53,582.2	141,035.1	109,199.2	39,219.1	527,938.5
Industrially significant deposits amount, thsd. m³	338,818.3	28,723.1	188,643.7	76,456.0	60,714.0	693,355.1
Industrially significant deposits resources, thsd. t	114,769.0	16,268.9	96,946.9	37,189.8	13,848.4	279,023.0

The most substantial available total amount of sapropel refers to Latgale PReg: 414,403.3 thsd. m³ or 184,902.9 thsd. tons, of which 338,818.3 thsd. m³ (or 114,769.0 thsd. tons) are assessed as industrially significant sapropel resource – that accounts for 48.86% of all identified industrially significant sapropel stocks in Latvia. Latgale PReg is followed by Vidzeme PReg, which intentionally significant stocks of sapropel account for 27.21%. The lowest sapropel stocks refer to Kurzeme PReg – 73,117.7 thsd. m³ (or 53,582.2 thsd. tons), of which only 28,723.1 thsd. m³ are industrially significant (16,268.9 thsd. tons), which is only 4.14% of all industrially relevant sapropel amount in Latvia (Figure 6, Table 12).
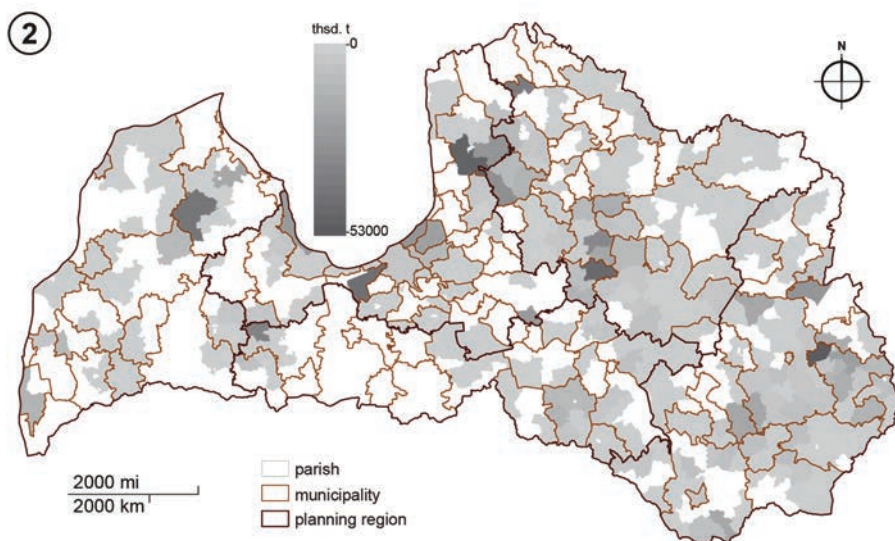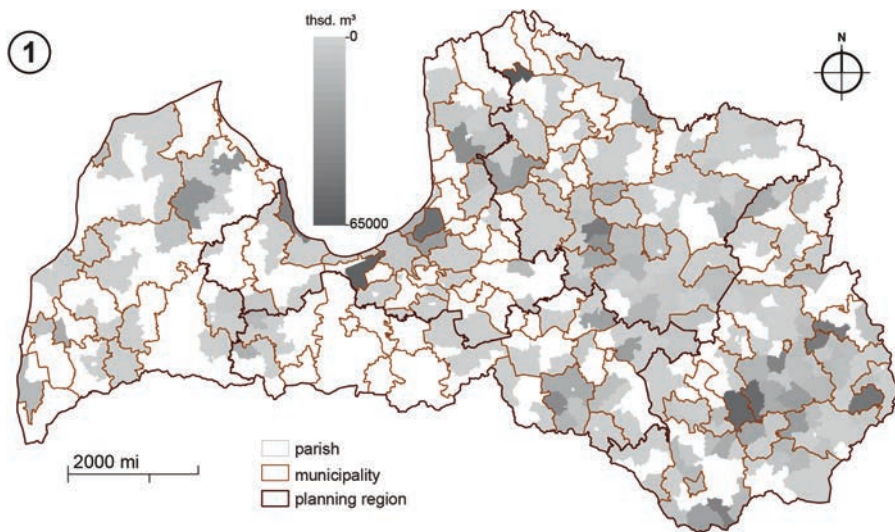
Figure 6. **Location of total investigated sapropel:**
(1) amount, thsd. m3; (2) resources, thsd. t

Organogenic sapropel order is the most valuable with more extensive possibilities of use which accounts for 18.68% of the total sapropel amount. The largest deposits of this sapropel order also can be found in Latgale PReg (44.43%) and Vidzeme PReg (23.10%) (Figure 7, Table 12).
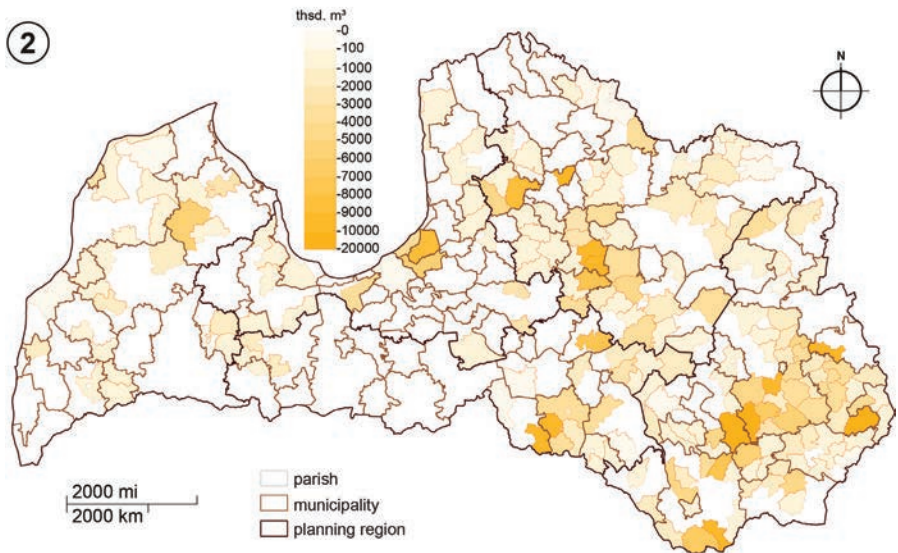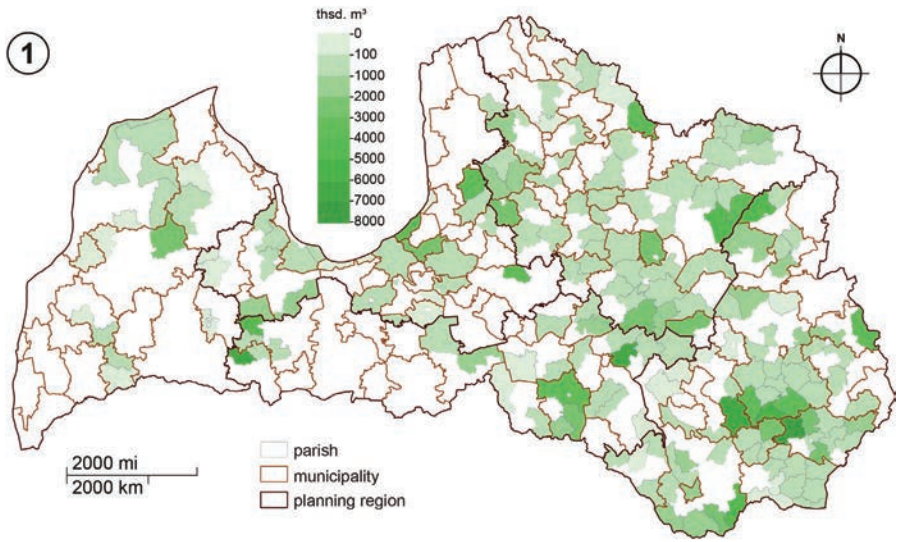
Figure 7. **Distribution of investigated sapropel deposits in Latvia by forms:**
(1) organogenic, (2) organogenic silicate

In total, 49.78% of all identified sapropel resources in Latvia are organogenic silicate sapropel order, of which >54% are located in Latgale PReg, 22.62% in Vidzeme PReg, 10.57% in Zemgale PReg (Figure 8, Table 13).
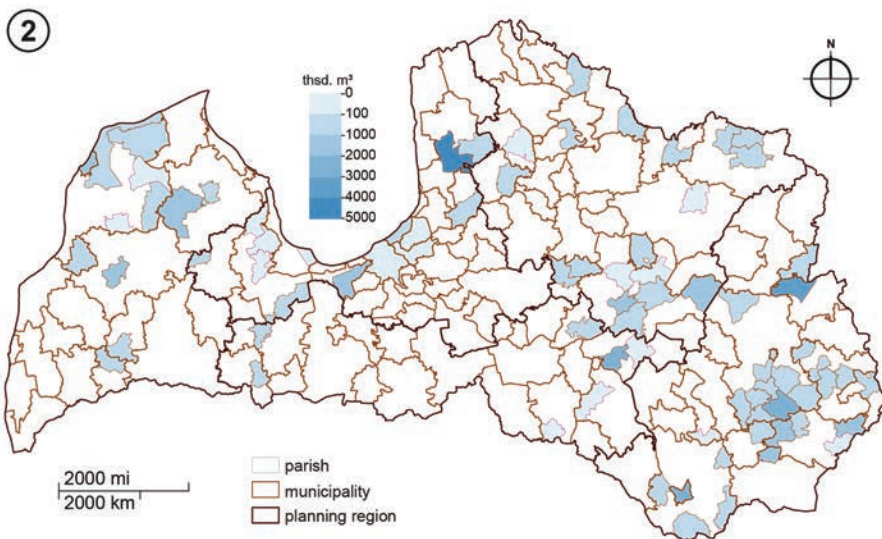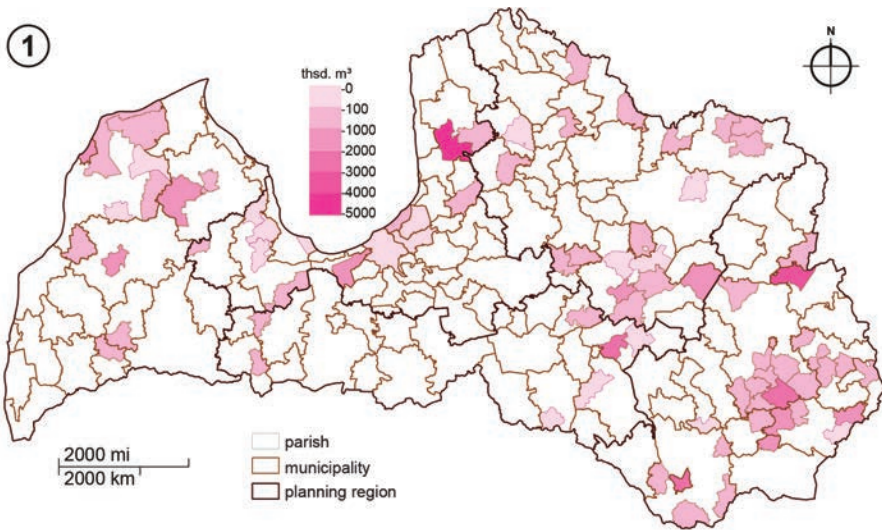
Figure 8. **Distribution of investigated sapropel deposits in Latvia by forms:
(1) carbonate, (2) ferruginous**

Although the area of lakes in Kurzeme PReg is 1.54% of the region area, sapropel deposits are the smallest – the total amount is about 73,117.7 thsd. m³ (Table 12), moreover, 47.86% of these resources consist of silicate sapropel with low potential for practical use.

Table 13

Distribution of total sapropel resources by volume in planning regions of Latvia

|	O	D	OS	Si	C	F
Latgale	80,924.6	-	265,253.3	43,628.6	19,794.8	4,797.0
Kurzem	4,819.1	320.0	23,686.9	34,997.2	7,271.9	2,022.6
Vidzemes	42,080.0	3,187.0	109,753.8	11,241.3	8,265.3	66,213.8
Riga	19,984.0	-	35,327.0	63,172.0	17,335.0	18,597.0
Zemgale	34,330.0	794.0	51,276.0	1,917.0	3,720.0	268.0
Total in Latvia	182,137.0	4,301.0	485,296.9	154,956.1	56,386.9	91,898.4

Also in Riga PReg, where the total amount of sapropel is estimated at about 154,415.0 thsd. m^3, 41% of the deposits is a silicate and 12% ferruginous sapropel, which also has a low potential for use.

The data reveal that the sapropel filling ratio of lake depression is the highest in Latgale PReg (on average, 0.61), but the lowest in Kurzeme PReg (0.54). In other regions, lake depression filling is not significantly different, respectively 0.56-0.60.

3.1.3 Formation regularities of sapropel deposits

Sapropel is organogenic sediments formed in lakes from residues of aquatic plants and animal organisms with the presence of mineral particles in the result of geological processes. Usually, it consists of a mixture of plankton particles, mollusc shells, chitin remains from the exoskeletons of insects, pollen and spores of higher plants, and mineral particles, formed in eutrophic water bodies. Its formation is determined by the nature of the cycle of matter and energy in water bodies in various geological and paleoecological conditions. The lakebeds were formed as a result of complex, usually combined geological processes. Most of Latvia's lakes are of glacial origin, formed by a glacier and its melting waters. The first bodies of water were formed 14-15 thsd. years ago.

Analysis of the Quaternary sediment map prepared by the Geological Survey of Latvia and data survey of the origin and locations of the studied lakes, allow concluding that sapropel mainly accumulates in the lakebeds formed in the Upper Pleistocene glaciogenic, glaciofluvial and glaciolacustrine sediments accumulated as a result of geological processes caused by glaciers and its melting waters. Approximately 1.3% of lake deposits were formed on alluvial deposits.

It should be noted that before the Holocene, mainly mineral sediments accumulated in glacigenic lakebeds, because there are necessary several prerequisites for organogenic sediment, including sapropel formation and accumulation. Scientific studies had shown that sapropel in lakes of Latvia began to form and accumulate in the Early Holocene approximately before 11,000 years when the climate became favourable for the development of lake fauna and flora, which remains are essential in the composition of the organic part of sapropel.

Sapropel exploration works by the Geological Survey of Latvia were carried out with the aim to find out how extensive are the industrial resources of sapropel and of what kind are these deposits. Information from FWSDB reflects that sapropel exploration and deposit evaluation were carried out in lakes, where according to the

location of lake in the relief, the geological structure and physical parameters of the lakebed, a sapropel deposit of significant thickness was expected. It was found that sapropel deposits mostly are in lakes which lakebeds have formed and are located in the Late Pleistocene (Q_3) (Figure 9) and less in the Holocene (Q_4) (Figure 10) deposits, while sapropel is formed only in the Holocene. The accumulation of deposit components of local origin is known as an autogenic process. The formation of bottom deposits, including sapropel, is greatly influenced by catchment conditions, particularly essential parameters are surface features, the geological structure of the catchment, hydrological and hydrographic relations, and vegetation development.

Visualization of database information (Figure 9) reflects the location of deposits of different sapropel types depending on the sediments forming the catchment area and bottom of the lakebed. Organogenic sapropel was formed in the lakes located in areas of both glaciofluvial and glaciogenic deposits. This type of sapropel is characteristic for lakes located on the border of distribution of glacigenic and glaciofluvial deposits. These lakes or parts of them are usually shallower and more favourable to the accumulation of organic sediments. It is possible that in these places, the water currents in the lakes were not so fast to wash away everything organic and deep enough that peat would not start to form in them immediately.

Analysis of the cartographic materials and reports of geological exploration works of sapropel allows concluding that silicate sapropel usually forms the lower layer mainly in lakes which lakebeds have formed in the areas covered by glaciolacustrine deposits of the Late Pleistocene. It could be explained by the fact that these sediments are rich in SiO_2, Al_2O_3 and usually contain a large amount of silicate minerals mainly quartz, feldspar, mica and others.

In lakes with glaciofluvial deposits of the Late Pleistocene, in lakebeds bottom, different types of sapropel are accumulated such as carbonate and ferruginous
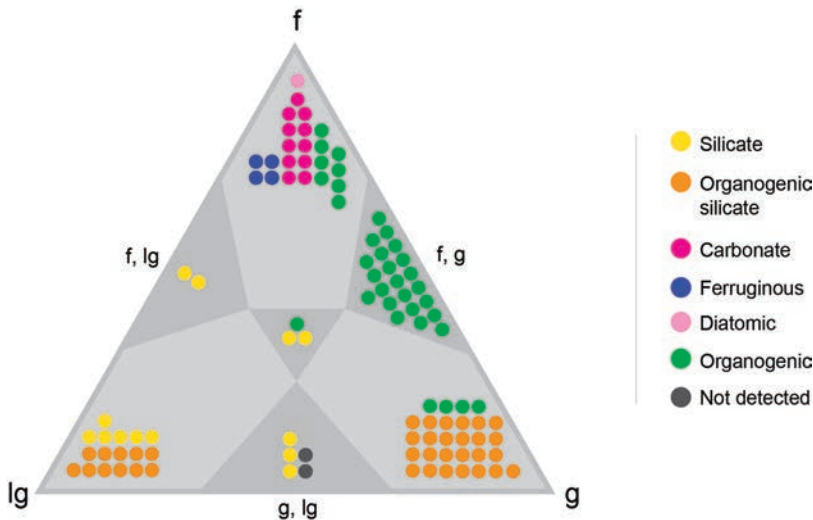

Figure 9. **The percentage (each point is 1%) of distribution of different sapropel deposits in lakes located in the area of the Late Pleistocene deposits:**
(g) glacigenic deposits (till); (f) glaciofluvial deposits (sand, gravel, pebble);
(lg) glaciolacustrine deposits (fine sand, silt, clay)
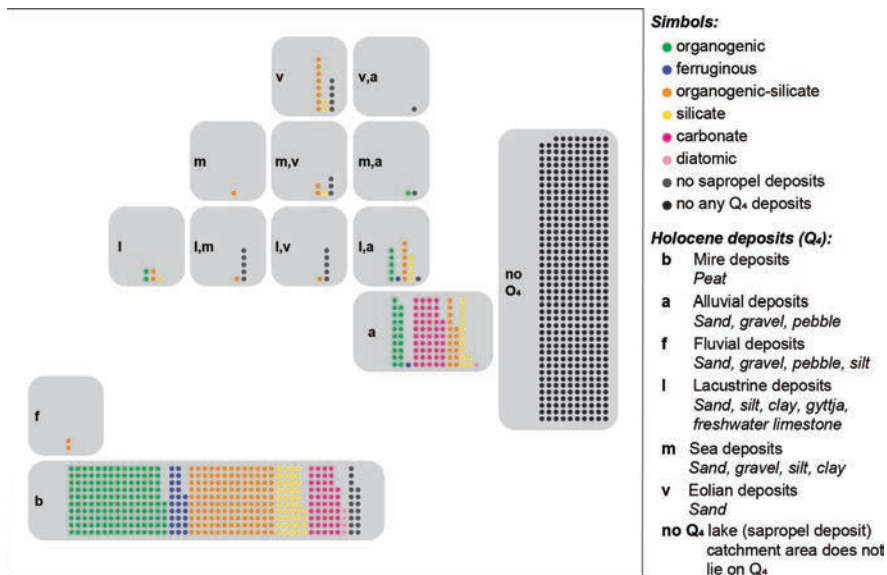
Figure 10. **The percentage (each point is 0.1%) of distribution of different sapropel type deposit in lakes located on the Holocene deposits**

sapropel. It happened because such lakes usually had large catchment areas, where runoff from the surrounding areas – predominantly morainic areas – washed away carbonates and iron-containing minerals in the water body. In some of these lakes, organogenic sapropel has accumulated, usually forming a deposit layer when the lake or its bays has already become eutrophic and shallow.

The newest lakebeds have formed in the Holocene sediments. These are mainly relics of basins, lagoons or bog lakes of the former Baltic Sea stage. The thickness of sapropel layers in these lakes usually is small and accounts for only 2.8% of all deposits studied. It can be explained by the fact that the lakes of the former lagoons are shallow, rapidly overgrow and fen peat is formed on a relatively thin layer of sapropel. Such sapropel deposits are not valuable for industrial extraction.

In the lakes located in the bogs, sapropel has accumulated only in the relict lakes of glacial origin, which are gradually overgrown and became surrounded by a bog. In such lakes, the largest amount of sapropel deposits of different types is found, like organogenic, organogenic-silicate and diatomic (Figure 10). Sapropel is practically not formed in lakes that have formed in raised bogs due to breaking of peat layers under the influence of gravity resulted by the formation of a bog cupola. Small lakes have formed in old rivers and former meanders, however, value sapropel deposits there is insignificant.

During the Holocene, organogenic, organogenic-silicate and carbonate sapropels have formed on the mineral lake sediments (sand, silt and clay) predominantly (Figure 9). On alluvial sediments most often are formed carbonate sapropels. The formation of organogenic sapropel is associated with the overgrowth of shallow lake bays, meanders or old rivers. The formation of carbonate sapropel, in turn, is associated with the leaching of carbonates by groundwater, both from limestone and dolomite-rich till deposits, as well as from shallow dolostone layers beneath them.

The correlation between sapropel types and lake properties, namely lake depression origin, water regime, lake trophic state and fulness of a lakebed, shows that in lakes of glacial origin usually all types of sapropel can be formed (Figure 11). These lakes are the oldest in the territory of Latvia, as they were formed during the last glacial glacier retreat and melting of ice. Lakes located in lowlands mainly are relics of ice-dammed lakes. Lakes of glacial origin were deep enough to avoid early overgrowth and bogging but were favourable for the development of live aquatic organisms for a longer period of time.

Organogenic-silicate and silicate sapropels in small amounts were also formed in old rivers and eolian sediments. Both old rivers and former river tributaries are peculiar, small and shallow, elongated or arched lakes in river floodplains. They are gradually smeared with alluvium and detritus, partly overgrown; organic and silicate rich sapropels have accumulated there. In the areas of the eolian sediments, small elongated lakes have developed between the dunes, where silicate sapropels have accumulated. Their composition has been significantly influenced by aeolian sand on the shores of lakes. In both of these types of lakes, the amount of sapropel is small, not valuable and economically viable for industrial extraction.

Although sapropel is formed in lakes with all types of runoff, it accumulates in more significant amounts in runoff lakes, slightly less in drain-off lakes. Sapropel is less common in closed lakes, as stagnant water is often poorly saturated with oxygen,
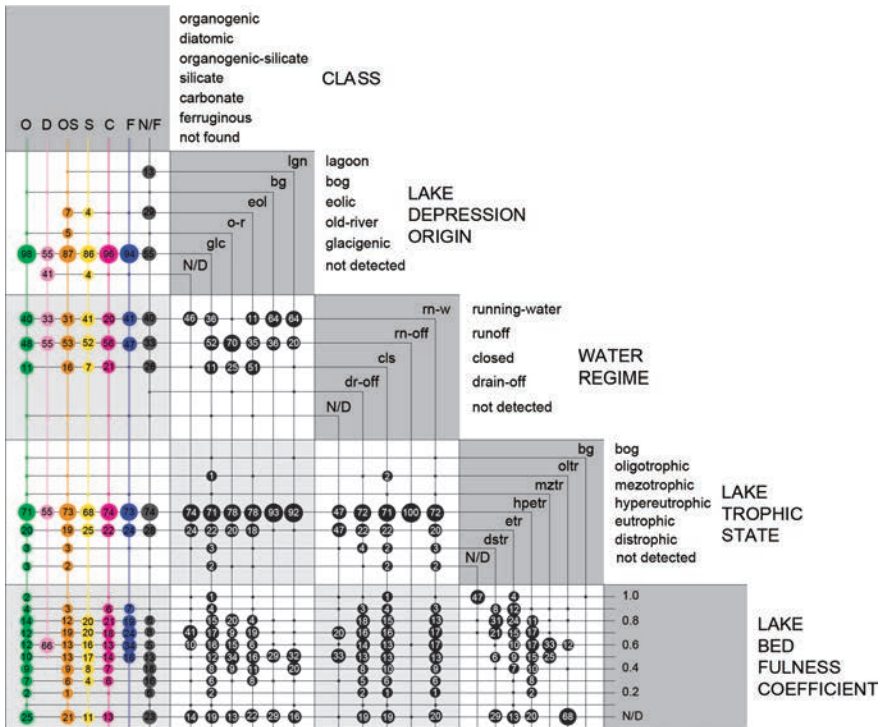

Figure 11. **The percentage of sapropel deposits of different order depending on the lake characteristics**

has reduced water transparency, water layers are not mixed. Particles suspended in water and introduced humic substances from surrounding areas cannot be transported by water flows. Such conditions in very shallow lakes cause very rapid eutrophication processes, in which peat-forming organisms and plant groups replace the lake biota.

A study of the trophic nature of the investigated lakes revealed that sapropel volumes suitable for industrial extraction have accumulated in lakes that are eutrophic and hypereutrophic nowadays. In dystrophic lakes, the accumulation of sapropel was stopped by bogging processes, which stopped the development of algae and aquatic plants. In oligotrophic and mesotrophic lakes, sapropel accumulation is low. It is also shown by the lakebed filling coefficient, where up to 0.5 volume of sapropel resources is small.

The analysis of FWSDB also revealed that the formation of sapropel is characterized by the accumulation of more mineral sapropel types – silicate and carbonate – at the beginning of the Holocene, but organogenic sapropel has accumulated during the lake overgrowth.

Reconstruction of environmental conditions and lake development during the formation of sapropel reveals that the type of sapropel is strongly related to the mineral component entering the lake, the size and overgrowth of the water catchment area, chemical composition and depth of water, as well as cold and drought events. When the lake ecosystem is still able to perform self-control, the events of cold and drought events are not reflected in the changes in the type of sapropel but appear in the composition of organic matter-forming organisms – macrofossils and microfossils. When the catchment area of the lake shrinks, swamping no longer provides the leaching of mineral components in a great extent, the water regime becomes too slow to flush out the organic material formed in the lake, and organic sapropel begins to form in the lake. The littoral sapropel formation is replaced by peat formation caused by the rapid development of peat-forming plants.

3.2 Reconstruction of environmental and lake conditions during the sapropel formation in studied sites

3.2.1 Water composition of studied areas nowadays

Composition of surface waters is an important parameter of the environment quality, as it determines the ecosystem and possibilities of the use of water body. Table 14 defines the main characteristics of water in studied lakes.

Following the European Community B system, which is determined by the Cabinet of Ministers Regulations No. 858 (MK 858, 2004), studied lakes correspond to the following types: Lake Padelis is a very shallow brown-water lake with high water hardness, but Lake Pilcine and Lake Pilvelis are very shallow brown-water lakes with low water hardness.

Table 14

Water characteristics of studied lakes nowadays (data derived in July 2013)

Parameter	Lake Padelis	Lake Pilcine	Lake Pilvelis
Analyses conducted on the field			
Water depth, cm	85	90	90
Temperature, °C	24.4	21.3	20.7
Transparency, cm	85	80	30
Electrical conductivity, µS/cm	171	127	65
pH	7.96	7.62	6.25
Total dissolved solids (TDS), mg/L	80.8	59.9	30.6
Oxygen saturation, %	113.4	116.0	52.9
Dissolved oxygen, mg/L	9.31	10.08	4.64
Laboratory analyses			
Water color, °Pt/Co	119	102	522
PO_4^{3-}, mg/L	0.04	0.02	0.01
Total C, mg/L		33.37	60.36
Total inorganic C, mg/L		12.90	2.25
Total organic C, mg/L		20.47	58.11
$N-NO_3$, mg/L	2.5	2.4	6.5
$N-NO_2$, mg/L	0.006	0.010	0.028
$N-NH_4$, mg/L	0.38	0.32	1.21
SO_4, mg/L	3	3	10
Si, mg/L	9.46	1.59	0.61
Fe, mg/L	0.76	0.39	0.64
Cl^-, mg/L	4.58	6.55	6.54

Investigated lakes are private properties. In such lakes, which area is not larger than 10 ha and the average water depth is less than 2 m, the processes of eutrophication are very rapid. The lakes are transforming to marshes; subsequently, the territories are lost for economic activities such as agriculture, aquaculture or tourism. At the same time, the lake owners are obligated to pay the taxes (LR Saeima, 1997). The owners of these three lakes expressed a wish to get rid of sapropel and to deepen and clean the lakes for further exploitation in rural tourism, development of aquaculture or as a freshwater reservoir for irrigation of agricultural land.

3.2.2 Chronology and lithostratigraphy of studied sites – lakes Padelis, Pilcine and Pilvelis

For evaluation and comparison of a diverse sequence of sapropel formation, three lakes were studied (lakes Padelis, Pilcine, Pilvelis). Preliminary data showed a distribution of carbonate sapropel in Lake Padelis, silicate rich sapropel in Lake Pilcine and organogenic sapropel in Lake Pilvelis.

Chronologies of the investigated sediment cores from the studied lakes (Figure 12) provide information on the time of sediment accumulation and allow to find out the intensity of accumulation, compare the climate and environment in which sediments have accumulated with other lakes in Latvia and worldwide. Studied sediment sequences from investigated lakes contain both mineral and organogenic sediments. Organic sediments are subdivided into lithostratigraphic units according to the investigation data (Figure 13). The type of sapropel was determined according to the author's adapted Sapropel Classification System (see Section 3.1.1).
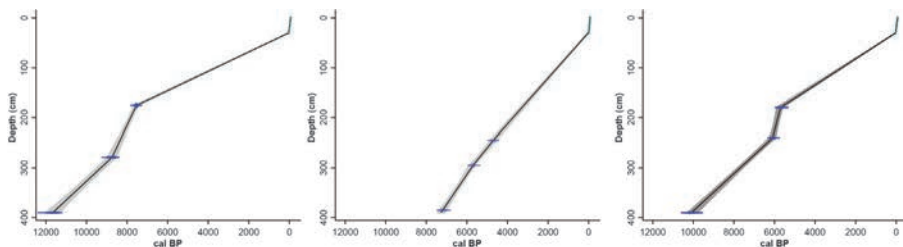
Figure 12. **The age-depth model of sediments in**
(A) Lake Padelis, (B) Lake Pilcine, (C) Lake Pilvelis

In Lake Padelis, the sediment profile consists of mineral sediments with ash content higher than 87%, different types of carbonate sapropel and reed peat (the upper meter of the profile, which was not analyzed in this work) (Figure 13A). Carbonate sapropel was subdivided into organogenic carbonate, carbonate and clayey carbonate sapropel types.

Carbonate sapropel began to form in Lake Padelis at 11,400 cal BP and formed up to 7,400 cal BP. This layer consists of 220 cm of mineral sediment interlayers that were formed at different times up to 8,300 cal BP. Ash content in this carbonate sapropel varies 65.92-82.30%, Ca – 233-342 g/kg, Fe – 2-7 g/kg. The layer of carbonate sapropel is separated from organic carbonate sapropel with a 10 cm transition layer – clay carbonate sapropel, which has decreased ash content (44.61%), Ca (123 g/kg) and Fe (5 g/kg) concentration compared to the lower layers.

From 6,700 cal BP to 3,600 cal BP, organogenic carbonate sapropel was formed in the lake. Ash content in this sapropel is only 6.93%, Ca – 134 g/kg, Fe – 4 g/kg. After 3,600 cal BP, reed peat accumulated in Lake Padelis, indicating that the borehole site became shallow enough for the emerged plants to grow.

In Lake Pilcine, sapropel began to form since 4,700 cal BP. Mineral sediments (sand) accumulated under the sapropel layer (Figure 13B). From 4,700 to 1,500 cal BP, organogenic silicate sapropel was accumulating with two 10 cm thick interlayers formed in 6,700-6,900 cal BP and 5,600-5,700 cal BP. Ash content of organogenic silicate sapropel is 41.15-54.81%, the concentration of Ca increases towards the upper layers from 8 to 14 g/kg, Fe is at a low concentration from 8 to 11 g/kg. Between 1,300 and 1,500 cal BP, diatomic sapropel was formed with ash content of 36.11%, Ca – 20 g/kg, Fe – 10 g/kg. Since 1,300 cal BP, reed peat was accumulating at the well. The studied sediment sequence from Lake Pilvelis contains organogenic and clastic orders of sapropel. The core was subdivided into eight

Sediment type	Ash	Ca	Fe	Microfossils, granulometry
Reed peat	-	-	-	-
Organogenic carbonate sapropel	6.93	134	4	organic remains - 40.63 silt - 78.73
Clayey carbonatic sapropel	44.61	123	5	clay > 50
Carbonatic sapropel	78.70	233	7	
Mineral sediments	87.40	268	6	ash > 85
Carbonatic sapropel	65.92	304	3	
Mineral sediments	87.75	326	3	ash > 85
Carbonatic sapropel	82.30	301	2	
Mineral sediments	87.86	325	3	ash > 85
Carbonatic sapropel	81.82	342	3	
Mineral sediments	88.21	306	5	ash > 85

Sediment type	Ash	Ca	Fe	Microfossils, granulometry
Reed peat	-	-	-	-
Diatomic sapropel	36.11	20	10	diatoms - 30.60; sand > 30
Organic sandy sapropel	41.15	12	10	sand > 30
Sandy sapropel	68.20	9	8	sand > 30
Organic sandy sapropel	54.81	11	11	sand > 30
Sandy sapropel	72.45	8	9	sand > 30
Mineral sediments	96.77	4	2	ash > 85

Sediment type	Ash	Ca	Fe	Microfossils, granulometry
Peaty sapropel	9.45	9	1	vascular plants - 50.33
Zoogenic sapropel	6.70	8	1	aquatic animals - 20.13
Peaty sapropel	8.95	8	1	vascular plants - 65.04
Hypnum peat	11.54	8	1	hypnum moss - 20.01
Peaty sapropel	10.35	8	1	vascular plants - 35.04
Various algae sap.	22.74	9	1	total algae - 45.15
Organic silty sap.	35.41	11	2	organic remains - 40.63 silt - 78.73
Cyanobacteria sapropel	17.33	9	3	cyanobacteria - 52.37
Mineral sediments	86.71	5	12	ash > 85

LOI Symbols
- Mineral Matter
- Carbonates
- Ash
- Organic Matter

Lithology Symbols

Peat
- Reed peat

Organogenic sapropel
- Peaty sapropel
- Cyanobacteria sapropel
- Various algae sapropel
- Zoogenic sapropel

Diatomic sapropel
- Diatomic sapropel

Carbonatic sapropel
- Organic carbonate sapropel
- Carbonatic sapropel
- Clayey carbonatic sapropel

Organogenic-silicate sapropel
- Organic silt sapropel
- Organic sandy sapropel

Silicate sapropel
- Sandy sapropel

Inorganic sediments
- Mineral sediments

Figure 13. **The sediment core characteristics of (A) Lake Padelis (B) Lake Pilcine (C) Lake Pilvelis: sediment age, depth, core picture, LOI data, lithostratigraphy and sediment type definition parameters according to the author's adapted Sapropel Classification System (see Section 3.1.1)**

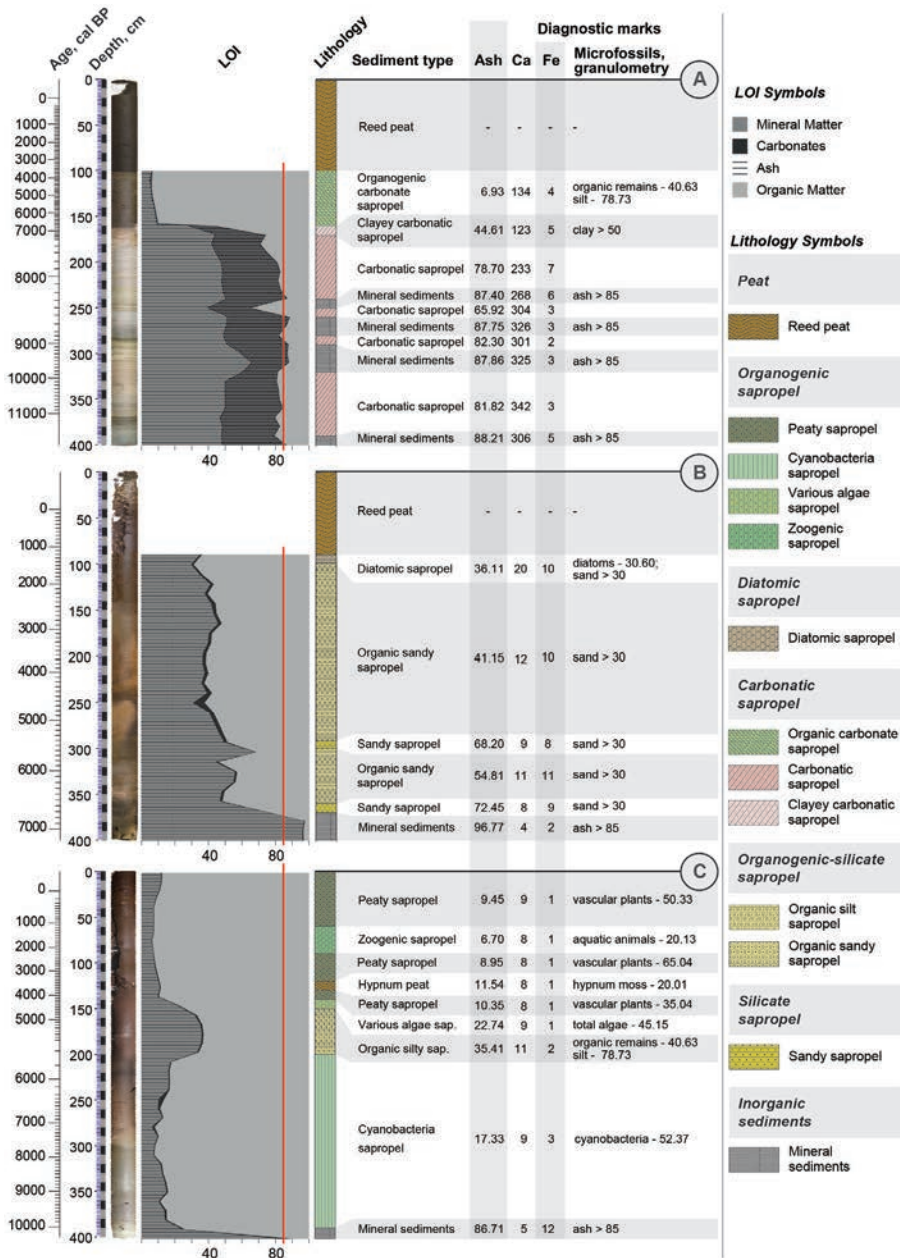lithostratigraphic units according to the investigation data (Figure 13C). The basal part of the Lake Padelis sediment section (390-400 cm) mineral sediments consists of bluish-grey clay with a high amount of ash content (86.71%) and is covered by organic-rich sediments – sapropel and peat.

Organogenic sapropel is subdivided into cyanobacteria, various algae, peaty and zoogenic sapropel types. Ash content in organogenic sapropel vary 6.70-22.74%, the concentration of Ca 8-9 g/kg, and Fe <3 g/kg. Sapropel in Lake Pilvelis sediment core with ash content in average 35.41%, Ca – 11 g/kg, and Fe – 2 g/kg was determined as organic-silt sapropel due to the particle size of 78.73% silicates that in this sapropel are defined as silt.

In Lake Pilvelis the accumulation of organogenic sediments, among which the organic matter was mainly formed by cyanobacteria, began at ~10,000 cal BP and continued until ~5,800 cal BP, with the maximum intensity at ~8,500 cal BP. Since ~5,800 cal BP up to 4,500 cal BP, organogenic-silt sapropel, which is characterized by higher ash content, was formed in the lake. However, after 4,500 cal BP until the present, sediments with organic content of less than 30% were formed in the lake covered by fen type peat.

3.2.3 Lake Padelis

Malacofauna

Determination of malacofossils is not suitable for all waterbody development reconstructions. One of the main factors limiting the development of molluscs is the amount of dissolved calcium carbonate in the water. Water bodies with $CaCO_3$ content less than 5 mg/L do not produce large mollusc biomass, and mollusc shells remain only in sediments with a basic, neutral environment, but in an acidic environment, it dissolves over time.

Table 15

Description of malacofauna zones at Lake Padelis

Depth (cm), Age (cal BP)	MalZ	Description and vegetation type	Sedimentary environment
160-180 *6,700-7,600*	Pd VI	*Shell fragments* During 7,600 cal BP, the diversity of species decreases, and the number of shell debris increases, but after 6,700 cal BP, the remains of molluscs are no longer found in the sediments of Lake Padelis. The content of minerals and carbonates in sediments rapidly decline. *Valvata macrostoma*, *Valvata cristata* and *Bithynia tentaculata* points to rich macro-vegetation and high content of organic matter in the water indicating an increase in eutrophication in the lake	Significant changes in water geochemical composition, the volume of carbonates decrease, and the amount of organic matter increase indicating intensification of eutrophication processes Water pH ≥7.4 Water hardness ≥3.5 °dH

Table 15 (continued)

Description of malacofauna zones at Lake Padelis

Depth (cm), Age (cal BP)	MalZ	Description and vegetation type	Sedimentary environment
180-230 7,600-8,200	Pd III	*Pisidium - Valvata – Planorbis* After 8,200 cal BP, the beginning of the Holocene climate optimum (Heikkilä and Seppä, 2010) is marked as the maximum in mollusc development – 12 species are identified. Warm water-loving species appear as *Planorbis planorbis*. The number of *Planorbarius corneus* decreases, possibly due to the rising water level of the lake. *Physa fontinalis* indicates that the lake water was clean and unpolluted. From 7,900 to 7,600 cal PB, snail diversity decreases to 6 species: *Valvata macrastoma, V. cristata, V. piscinalis, Planorbis planorbis* and *Bithynia tentaculata*. The number of snail individuals also declines. Analysis of microfossils indicates that, during this time, the diversity of cyanobacteria increases (Figure 15). The concentration of Ca, Mn begin to decrease (Figure 27A), indicating a decrease in water hardness	Water is getting warmer, fluctuations in water level are possible, some environmental changes appear that are not in favour of the development of molluscs Water pH ≥7.4 Water hardness ≥5.0ºdH
230-270 8,200-8,600	Pd II	*Valvata - Pisidium – Planorbarium* From 8,600 cal PB, snail diversity increases to 10 species: *Valvata macrostoma, V. cristata, V. piscinalis, Gyraulus albus, G. acronicus, Planorbarius corneus, P. planorbis, Bithynia tentaculata, Physa fontinalis, Pisidium nitidum*. The growth of mollusc species and their individuals indicates that both climatic (warm and humid) and lake parameters (sufficient food, favourable water parameters) were favourable for the development of these species at that time. Sediments with corresponding to 8,200 cal Agra Holocene shrubs reduce the number of mollusc individuals and the diversity of species, leaving only *Valvata macrostoma, Valvata cristata, Pisidium nitidum* and *Planorbarius corneus*; the number of individuals increases	The climate is getting warmer and moist, a sufficient amount of feed and favourable water parameters for the development of snails with a short-term unfavourable period zone in 8,200 cal BP Water pH ≥7.4 Water hardness ≥5.0ºdH
270-310 8,600-9,600	Pd I	*Pisidium – Valvata – Bithynia* Macro remains (Figure 16) show that in 9,600 cal BP, carbonate-loving aquatic plants *Characeae* replace *Najas marina* and the amount of minerals in the sediments increases indicating an increase in the water level. During this time, shells of *Pisidium nitidum* appear in the lake. These snails have adapted to live in colder waters up to 20 m deep; thus, they are often found in post-glacial sediments. *P. nitidum* likes clean, unpolluted waterbeds with good oxygen exchange. They have good adaptability and are limited only by the summer drying of the water body. In the upper part of the zone, the diversity of species increases; species appearing in water bodies with well-developed macro-vegetation: *Valvata macrostoma, Valvata cristata* and *Bithynia tentaculata*	High content of carbonates in the water, high water level, cool and clean water, waterbed with good oxygen exchange Water pH ≥7.4 Water hardness ≥3.5ºdH

Of the lakes studied, only mollusc fossils were found in Lake Padelis. Four zones of malacofossils (MalZ-Pd) were established in Lake Padelis (TAble 15; Figure 14). Shells of molluscs appear in the lake profile from 9,600 cal BP to 6,700 cal BP, (160-310 cm). Fossils of molluscs in Lake Padelis are represented mainly by gastropods such as *Valvata*, *Gyraulus*, *etc.*, except one bivalve mollusc specie *Pisidium nitidum*.

Microfossils

Five zones of microfossils (MicZ-Pd) were established in Lake Padelis (Table 16; Figure 15).

Description of microfossil zones at Lake Padelis

Depth (cm), Age (cal BP)	MicZ	Description and vegetation type	Sedimentary environment
100-170 *3,600-7,200*	Pd V	*Vascular plants – Cladocera – Bryales – Scenedesmus* The amount of vascular plant residues increases rapidly, on average, 45%. *Bryales* moss appears in the area. *Cladocera* residues increase from the bottom up. In general, *Lyngbya* still dominates, but the number of cyanobacteria and diversity of its species decline. *Cladophorales*, *Zygnematales* and *Cosmarium* disappear from green algae, but populations of *Botryoccocus* and *Scenedesmus* are present in the whole area. *Fungi* disappear	Rapid overgrowth of the lake, water transparency decreases, organic matter in water increases
170-230 *7,200-8,200*	Pd VI	*Cyanobacteria – Tetraedron – Botryococcus* Cyanobacteria dominate in the lake in the optimum Holocene climate, from which 5 species are identified: *Lyngbya*, *Microcystis*, *Anabaena*, *Chlorogloea* and *Gloeocapsa*. Green algae are also characterized by a large number (7) of species: *Scenedesmus*, *Botryococcus*, *Tetraedron*, *Pediastrum*, *Phacotus*, *Zygnematales* and *Cosmarium*. Few remains of aquatic animals represented by *Cladocera*. Residues of *Insecta* and *Fungi* are present	Increased water temperature, sufficient acronutrients for algal development
230-290 *8,200-9,000*	Pd III	*Lyngbya – Microcystis – Botryococcus* Mineral sediments are characteristic to the area. Residues of vascular plants do not exceed 25%. The lake is dominated by blue-green algae *Lyngbya* and *Microcystis*, from green algae *Botryoccocus*. *Insecta* and *Fungi* practically disappear. The number of *Cladocera* decreases on average compared to the previous zone. In general, the diversity of species in microfossils is low throughout the range, whereas malacofossils (Figure 11) indicate favourable conditions for the development of cold-resistant mollusc species. Macrofossils (Figure 13) indicate a decrease in littoral *Najas marina*, pointing out to cool weather and high water level	Clear water, fluctuating water level

Table 16 (continued)

Description of microfossil zones at Lake Padelis

Depth (cm), Age (cal BP)	MicZ	Description and vegetation type	Sedimentary environment
290-380 *9,000-11,400*	Pd II	*Lyngbya – Cladocera – Microcystis* Starting with this interval, diatoms disappear from the profile, indicating hydrochemical changes of the lake (Hall and Smol, 1999). Further, up to 3,600 cal BP, microfossils dominate by cyanobacteria. *Lyngbya*, *Microcystis*, *Insecta* and *Fungi* appear in the area	Chemical composition of water changes, organic silica in water disappears
380-400 *11,400-11,700*	Pd I	*Diatoms – Cladocera* A great diversity of diatom species appears (*Navicula*, *Fragilaria*, *Tabellaria*, etc.). Residues of water animals *Cladocera* and green algae *Pandorina* are found. Remains of vascular plants do not exceed 15%.	Cool, clear water, overgrowth of the lake is small Mesoeutrophic – mesotrophic

Macrofossils

Generally, based on the main assemblages of macrofossils, sediment core of Lake Padelis can be divided into six zones (MacZ-Pd) (Table 17; Figure 16).

Table 17

Description of plant macrofossil zones at Lake Padelis

Depth (cm), Age (cal BP)	MacZ	Description and vegetation type	Sedimentary environment
0-30 *before present-30*	Pd VI	*Characeae – Najas – Nymphaea* A large number of *Characeae* oogonia occurs. Submerged plants *N. marina, N. flexilis, Potamogeton pusillus* and floating-leaved plant *N. alba* seeds are found. In the layer from 30 cm to 20 cm, reed peat accumulates, but from 20 cm to the bottom smaller number of plant vegetative remains and a significant amount of aquatic plants epidermis detritus. They indicate that water level rised to 100 cm	Lake water level increases Water depth 100-150 cm
30-110 *30-4,100*	Pd V	*Pinus – Betula – Menyanthes* Some seeds of aquatic plants and marsh plants *Thelypteris palustris* still are prevalent in the bottom part of the zone, but in upper layers appear only seeds of *Betula* and fragments of *Pinus* needles. Sedge roots, plenty remains of *Hypnum* moss and reeds are found in detritus. In the bottom layer of the zone, remains of reeds are predominant, but in the upper layer – remains of *Hypnum* moss. It may be caused by continuing water level decrease because of overgrowth	Continuing water level decrease caused by the lake overgrowth Water depth ≤100 cm

Table 17 (continued)

Description of plant macrofossil zones at Lake Padelis

Depth (cm), Age (cal BP)	MacZ	Description and vegetation type	Sedimentary environment
110-160 *4,100-6,700*	Pd IV	*Characeae – Najas – Nymphaea – Betula* Amount of *Najas flexilis, N. alba* and *M. trifoliata* seeds and remains of mire's and coastal plants rapidly increases. Presence of *M. trifoliata* indicates that water level in the coring point was ≤100 cm. *C. mariscus* is a caulophitic rhizomatous perennial and grows on nutrient-poor, shallow water bodies; therefore, it means that water reaction was alkaline and the lake was shallow in this period. Border of the layer with underlying was sharp, indicating rapid changes in sedimentation conditions. Probably this layer represented time, when Lake Padelis was split from current Lake Stiebrajs because of overgrowth	Water reaction is alkaline, and the lake is shallow Water depth ≤100 cm
160-230 *6,700-8,200*	Pd III	*Picea – Najas – Characeae* Remains of aquatic plants *N. marina, Characeae,* trees – *Pinus* prevail. The amount of coastal plant remains is smaller, that indicates probable rising of water level. Fragments of plant epidermis still are the most common in detritus. *Hypnum* stems with leaves occurred from depth 200 cm.	Water depth 100-200 cm
230-320 *8,200-9,800*	Pd II	*Characeae – Najas – Picea – Bryozoa* *Characeae* are a dominant species in this zone. Remains of *Najas marina* occur in smaller amounts than in the deeper part of the core. Between 250 cm and 260 cm oogonia surface was covered with a thin layer of calcium carbonate. It may indicate that water level slightly decreased, and water temperature increased	Water level fluctuations and an increase in water temperature Water depth 100-200 cm
320-400 *9,800-11,700*	Pd I	*Najas – Betula – Bryozoa* *Characeae* oogonia occurred regularly in small amounts. *N. marina* is a submerged aquatic plant, which is present in mesotrophic lakes with alkaline water reaction. Optimum depth for the growing of *N. marina* is 50-200 cm. No remains of coastal plants are found in the zone. Detritus consists of zooplankton and aquatic plant fragments. It indicates that the lake was shallow and littoral belt was relatively near	Shallow mesotrophic lake with alkaline water reaction Water depth 100-200 cm

Composition and changes in macrofossil composition reflect plant diversity and dynamic, as well as water level fluctuations during the lake development since the beginning of the Holocene up to present. These data indicate water level fluctuation within 100-200 cm, while macrofossil composition in the upper part from depth 160 cm to 30 cm point out on continuing water level decrease caused by gradual lake overgrowth. Changes of macrofossil composition in the top layer 0-30 cm, where occurred a large number of *Characeae* oogonia and submerged plants *N. marina,*

N. flexilis, Potamogeton pusillus and floating-leaved plant *N. alba* indicate an increase in water level, which was caused by overflowing of fen peat formatted by sedge, *Hypnum* moss and reeds.

Pollen

Pollen analysis was carried out for 4 m long sediments sequence of Lake Padelis. Samples were taken in the shore area to obtain more extensive information on changes in sediment accumulation conditions and vegetation dynamics. Changes in pollen composition allow for subdividing seven local pollen assemblage zones (LPAZ-Pd) (Table 18; Figure 17).

The results of pollen analysis reflect the development of regional vegetation since the beginning of the Early Holocene, before 11,700 cal BP, and continues until today. During the beginning of carbonate sapropel formation and accumulation in the surroundings of the lake, sparse birch forest with some alder and pine stands were distributed. Presence of ruderal plants like *Artemisia* and *Chenopodiaceae* pointed on favourable conditions for the soil erosion. The reconstructed vegetation development based on pollen analyses indicate unstable, probably local environmental conditions during 8,300-9,300 cal BP, when fluctuations from mixt coniferous-deciduous forests to the broadleaved forest with spruce took place. Similar changes were also observed during 6,200-7,800 cal BP, when the tendency of mixed forest distribution with a significant presence of broadleaved trees was determined.

Table 18

Description of local pollen assemblage zones in the section of Lake Padelis

Depth (cm), Age (cal BP)	LPAZ	LPAZ description	Vegetation type in the area
100-150 *3,600-6,200*	Pd VII	*Betula – Alnus – Corylus – Poaceae* *Betula* (from 29 to 42.2%), *Pinus* (26.3%) and *Picea* increase in the zone, the number of broadleaved trees decrease. The prevalence of *Poaceae* increase, reaching 2.6%, *Cyperaceae* decreases. The zone ends with an increase in herbaceous – *Asteraceae, Solanaceae* and *Apiaceae*. Values of cultivated plants as *Secale cereale* in the zone reach about 1.5%	Mixed forest with a significant admixture of deciduous trees with grassland and agricultural land
150-200 *6,200-7,800*	Pd VI	*Corylus – Ulmus – Tilia – Quercus* Presence of *Betula* is low – 14.1%, *Alnus* about 19.4%, *Corylus, Ulmus* and *Tilia* in the range 3-5%, while the maximum values reach *Quercus* (8.9%) and *Fraxinus* (6.1%). At the end of the zone, *Corylus* decreases, but *Carpinus* increases. Decrease of *Pinus* and *Picea*, *Cyperaceae* and *Polygonaceae* is observed, as well as another herb pollen increase	Broadleaved forest with grasslands
200-230 *7,800-8,200*	Pd V	*Tilia – Corylus – Alnus – Picea* Some decrease is characteristic for coniferous and birch, while pollen of broadleaved trees, alder and *Corylus* tends to increase	Broadleaved forest with spruce

Table 18 (continued)

Description of local pollen assemblage zones in the section of Lake Padelis

| Depth (cm), Age (cal BP)	LPAZ	LPAZ description	Vegetation type in the area
230-260 *8,200-8,800*	Pd IV	*Betula – Pinus – Picea* *Betula* increases reaching 37%, *Corylus* (18.5%), *Tilia* (5.2%). *Quercus* gradually increases in a range from 1.2% to 6.2%. *Alnus* and *Ulmus* are above 5.8%. *Picea* pollen remains in a range of 2.4-5.3%, while *Pinus* values are reduced by 9%. Continues dominance of broadleaved *Corylus*, the average incidence in the whole zone is 17.8%. *Alnus* and *Fraxinus* increase at the end of the zone but the amount of *Betula* – decrease. Constant values retain *Tilia* and *Quercus* in the range of 4-7.3%. *Ulmus* varies from 10.6 to 14.1%. A small amount of *Carpinus* appears. Increase in *Picea*, reaching 15.6%. Throughout the zone, *Salix* decrease, but *Ericaceae* increase. At the end of the zone, decrease of *Poaceae* and *Cyperaceae*, but an increased amount of aquatic plants – *Potamogeton*. *Equisetum* and *Sphagnum* increase in the zone	Mixed forest with broadleaves
260-300 *8,800-9,300*	Pd III	*Pinus – Picea* In LPAZ III interval, a sharp decrease in *Betula* to 5% is observed, as well as in *Ulmus*, *Tilia* and *Quercus*. Significant increase characteristic for coniferous pollen values reaching 20% for *Pinus* and 15% for *Picea*. *Chenopodiaceae* and *Urtica* represent ruderal plants	Coniferous forest area of grasslands
300-340 *9,300-10,300*	Pd II	*Betula – Pinus* *Betula* slightly decrease in the upper part of the zone to 25%. *Pinus* increase to 19.2%, *Alnus* varies from 1.5 to 4.7% and *Corylus* 4-7.7%. *Ulmus* appear and increase to 9%, *Ericaceae* and *Linaceae* appear. *Cyperaceae* is up to 3%, *Poaceae* over 1.7%, maintaining a constant curve and reaching the highest values. Ruderal herbs represent *Artemisia*, on average of 2.4%, *Plantago* 0.5%. Herb pollen reaches up to 20%, pointing on the open area around the lake. Spores are represented by *Polypodiaceae*, *Sphagnum* and *Equisetum*	Pine-birch forests with elm and hazel, broad areas of meadows, partly overflowing
340-400 *10,300-11,700*	Pd I	*Betula* In LPAZ I interval, *Betula* dominate and reach 66%, coniferous are represented by *Pinus*, on average of 20%, *Alnus* on average of 5%. Shrubs are represented by *Salix*, on average 1-3%. Herb pollen reaches 10-15%, mainly represented by grass *Poaceae* – 6.4%, *Artemisia* and *Chenopodiaceae* – 1.3%. Aquatic plant pollen mainly are represented by *Menyanthes* and *Nymphaea*	Birch forest stands with some coniferous and broad areas of grasslands
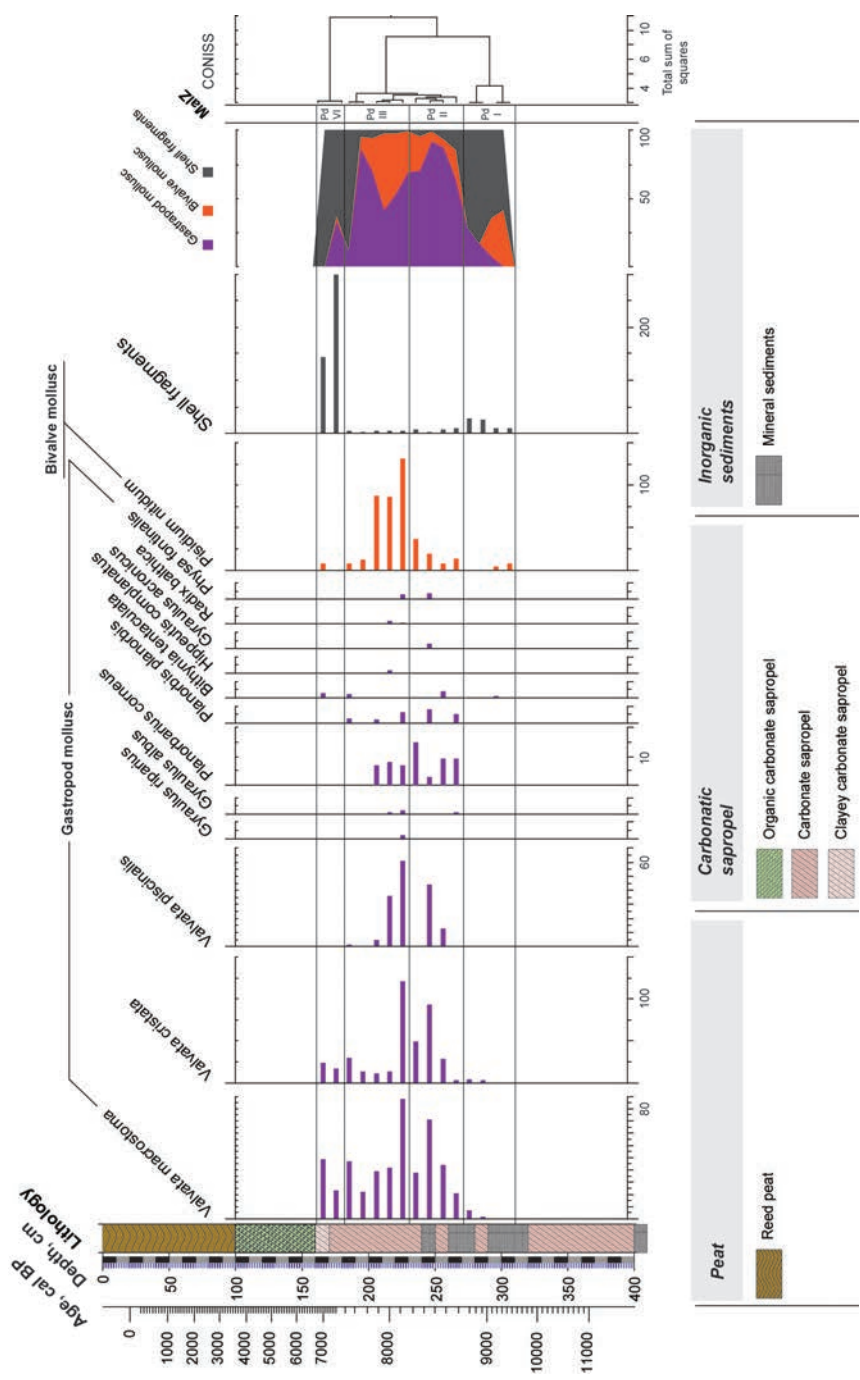
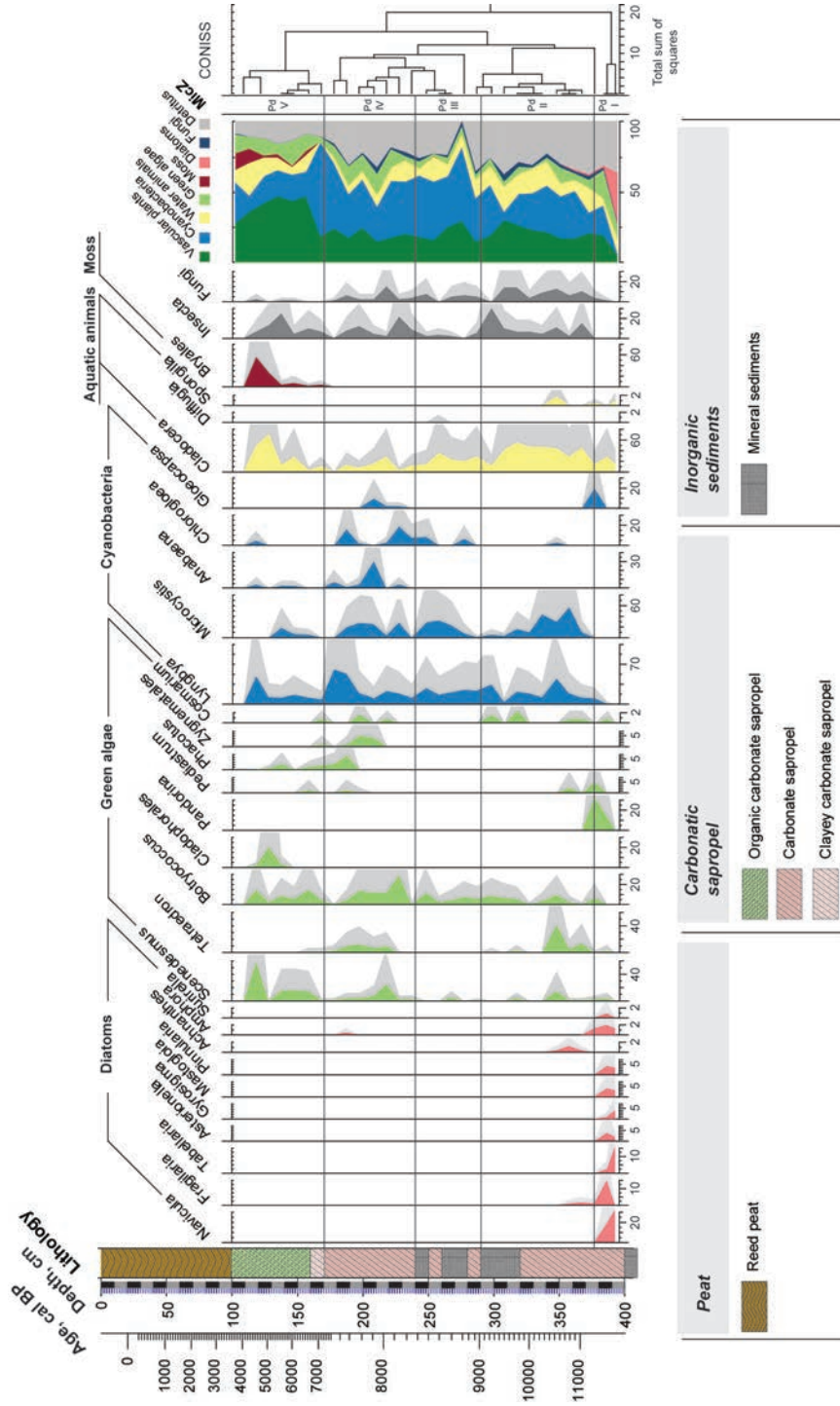*Figure 14.* **Malacofossil diagram of sediments at Lake Padelis**

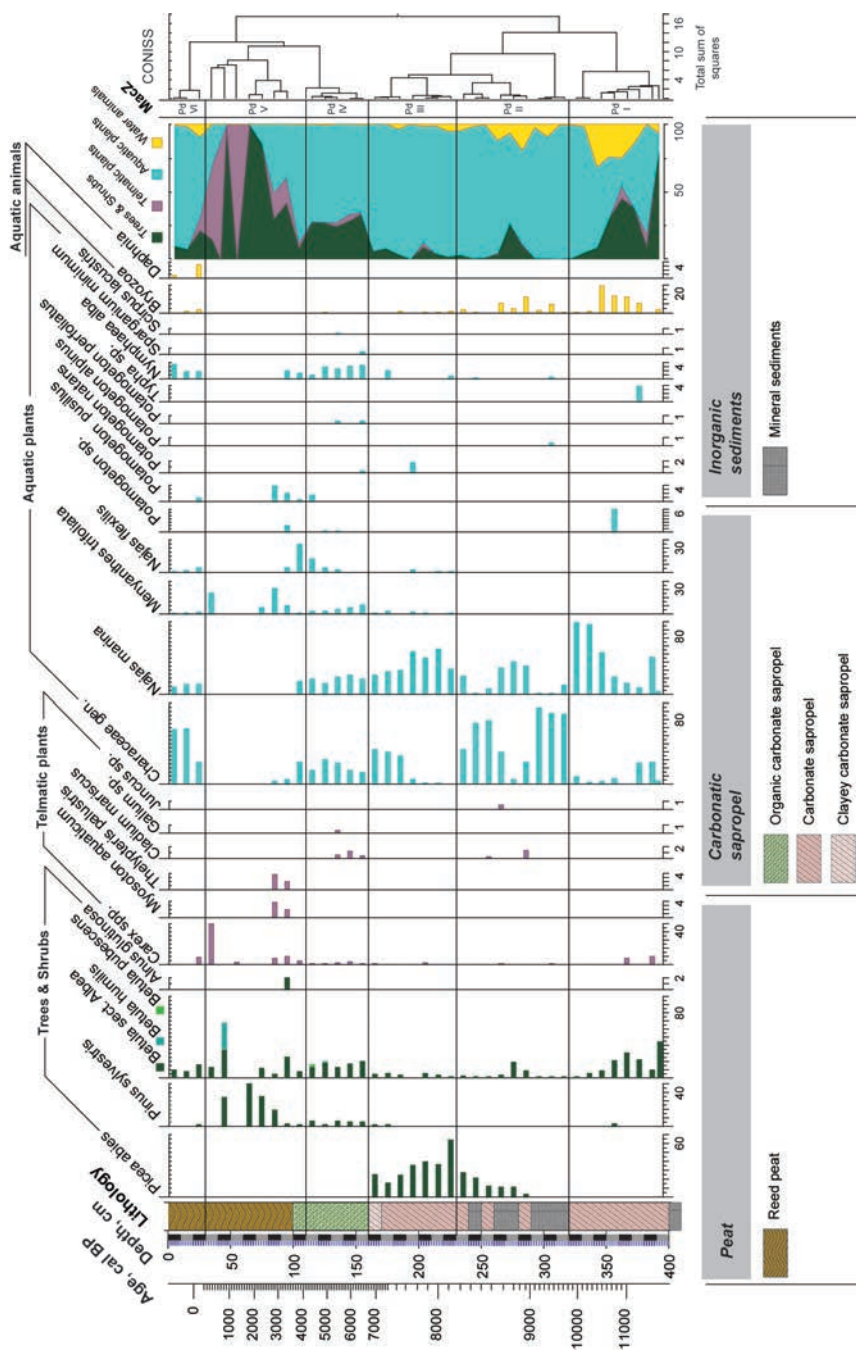*Figure 15.* **Microfossil diagram of sediments at Lake Padelis**

Figure 16. **Macrofossil diagram of sediments at Lake Padelis**

Figure 17. **Pollen diagram of sediments at Lake Padelis**

3.2.4 Lake Pilcine

Microfossils

Five microfossil assemblage zones (MicZ-Pc) were established in Lake Pilcine (Table 19; Figure 18). Microfossils in Lake Pilcine are represented by algae (diatoms, green algae and cyanobacteria), *Insecta*, *Fungi*, vascular plants and aquatic animals.

Table 19

Description of microfossil zones at Lake Pilcine

Depth (cm), Age (cal BP)	MicZ	Description and vegetation type	Sedimentary environment
90-200 *1,300-3,700*	Pc V	*Diatoms – Anabaena* The total amount of vascular plant remains decrease and compose, on average, 25% of all microfossils. The amount and species diversity of diatoms (*Melosira, Aulacoseira, Tabellaria, Cyclotella, Cymbella*) rapidly increase, as well as green algae: *Zygnema* and *Desmidae*. Amounts of aquatic animals decrease and become unstable	Increase in water level Mesoeutrophic lake
200-255 *3,700-4,900*	Pc IV	*Anabaena – Insecta* Diatoms *Cilliata* and *Fungi* disappear. Amounts of green algae decrease. Remains of cyanobacteria *Anabaena* dominate. A high amount of *Insecta*, few pikes of aquatic animals like *Spongilla* and *Cladocera*, and cyanobacteria *Lyngbya*	Low water level, organic-rich and low transparency water
255-295 *4,900-5,700*	Pc III	*Insecta – Pediastrum – Melosira* The remains of *Insecta* dominate in the zone. *Fungi* decreases but are still found. From green algae dominates *Pediastrum* sp. Diatoms are presented with a high amount of *Melosira*, and few of *Pinnularia* and *Aulacoseira*. In the upper part of the zone, aquatic animals *Ciliata* decrease but remains of *Cladocera* increase	Still warm water, a decrease of water level, eutrophication processes slowing down
295-370 *5,700-6,900*	Pc II	*Anabaena – Vascular plants* Increase in *Anabaena*, decrease f vascular plants, but they still compose more than 50% of all microfossils. Green algae and diatoms are found in small amounts, the same as *Insecta*. Marks of *Fungi* are found	Increase in organic matter amount in the water, a decrease of water transparency
370-400 *6,900-7,400*	Pc I	*Vascular plants* A high amount of vascular plants, more than 70% of all microfossils. Other forms as cyanobacteria and diatoms are present	Intensive overgrowing processes

Macrofossils

Six macrofossil assemblage zones (MacZ-Pc) were established in Lake Pilcine (Table 20; Figure 19). Macrofossils in Lake Pilcine are represented by trees (*Picea, Pinus, Betula, Alnus*) and shrubs (*Juniperus, Rubus, Frangula*), ruderal plant remains, as well as remains of aquatic plants and animals, and cultivated plants in upper 40 cm of sapropel layer.

Table 20

Description of plant macrofossil zones at Lake Pilcine

Depth (cm), Age (cal BP)	MacZ	Description and vegetation type	Sedimentary environment
90-130 1,300-2,200	Pc V	*Linum – Potamogeton – Carex – Betula* Various species of pondweed (*Potamogeton gramineus, P. natans* and *P. perfoliatus*) remains increase. Plants with big floating leaves *Nuphar luteum* and *Nymphaea alba* occur. The species number of telmatic plants (*Carex, Persicaria sp., Comarum palustre, Rumex sp., Taraxacum officinale, Linum sp., Lycopus europaeus, Andromeda polifolia*) increase. Plenty of ruderal plants as *Chenopodium album, Raphanus raphanistrum, Spergula arvensis* and seeds of cultivated plant flax (*Linum usitatissimum*) start to occur. These seeds indicate intensive agriculture activity near the lake	Intensive agriculture activity near the lake Water depth ≤100 cm
130-240 2,200-4,600	Pc IV	*Aquatic animals – Carex – Betula* Generally, aquatic animals (*Bryozoa* and *Hydroptilidae*) dominate. Aquatic plants are presented with *Trapa natans, P. natans, N. luteum* and *Typha sp.* Telmatic plants like *Lycopus europaeus, Carex spp., C. virosa* occur regularly. Littoral plant belt with *Typha, Scirpus lacustris, Alisma plantago aquatic, Equisetum* becomes wider. Leaves of hypnum moss together with remains of marsh plant *Andromeda polifolia* occur regularly. This zone is the first one with *Daphnia* occurrence	Intensive lake overgrowing processes Water depth 30-100 cm
240-330 4,600-6,200	Pc III	*Betula pubescens – Bryozoa – Hydroptilidae* In all zone fragments of *Betula pubescens, Bryozoa* statoblasts and *Hydroptilidae* larval cases are found. A small amount of *Picea* abies and *Pinus* needles is signed. In the upper part of the zone, aquatic plants as *Potamogeton acutifolius* and *P. natans, Trapa natans, Nuphar luteum* appear. The total amount of remains is paltry and consist of plants' detritus and zooplankton's chitin	Slight water level decrease 30-100 cm

Table 20 (continued)

Description of plant macrofossil zones at Lake Pilcine

Depth (cm), Age (cal BP)	MacZ	Description and vegetation type	Sedimentary environment
330-370 6,200-6,900	Pc II	*Bryozoa – Hydroptilidae – Betula sect. Albae* Appears aquatic plant *Potamogeton praelongus* and *Potamogeton natans*, coastal water plant *Menyanthes*, telmatic plants *Cicuta virosa*, *Carex* and fragments of *Equisetum* culm. Fragments of *Betula sect. Albae* and *Picea abies*, *Bryozoa* statoblasts, *Hydroptilidae* larval cases occur abundantly. The total volume of detritic remains rapidly increases. In sediments, quartz sand grains and rounded off pieces of wood are found in small amounts, as well as a few charcoals. Plenty of larval cases of the hydroptilid *Orthotrichia* and *Bryozoa* statoblasts occur	Intensification of lake overgrowing processes Increase in water depth up to 100-200 cm
370-400 6,900-7,400	Pc I	*Bryozoa – Picea – Carex* Slightly occur remains of *Bryozoa* statoblasts, some *Hydroptilidae* larval cases in the upper part of the zone, and marks of *Carex* nuts are present. Fragments of washed in the lake *Picea* needles from coastland are found as well	Slight indications of overgrowing start to appear Water depth 30-100 cm

Pollen

Pollen analysis was carried out for 4 m long lake sediment core from a small eutrophic overgrowing lake, Lake Pilcine. The surroundings of the lake are uninhabited and mostly covered with forests, and there are no inflow-out-flow streams in the lake. Therefore, it was expected to obtain the results revealing natural vegetation development without human influence. The data based on changes in pollen composition and fluctuations of them allowed subdividing five local pollen assemblage zones (LPAZ) in pollen percentage diagram revealing vegetation changes in the lake and its surroundings (Table 21; Figure 17).

Pollen composition from Lake Pilcine lake sediment section reflects vegetation development in the area since 7,400 cal BP (the Middle Holocene). The lowest part of samples from the section was taken from sandy sediments rich with pollen, which reflects vegetation composition during the Holocene climatic optimum when a composition of deciduous trees *(Betula, Alnus, Corylus)* dominated in the forest and their maximum reached broadleaved trees, mainly *Tilia* and *Ulmus*.

The obtained data reveal that prevalence of coniferous in forest composition took place since the end of the Middle Holocene when significantly decreased *Alnus, Corylus* and broadleaved trees. In the upper subdivided LPAZ V, pollen composition indicates mixed forest distribution in the area during the last 2,500 cal BP with a significant amount of coniferous. Even though the area is practically uninhabited, the presence and fluctuating amount of cultivated plants (*Secale cereale* and *Triticum*) and ruderal plants in LPAZ V point out on human existence.

Table 21

Description of local pollen assemblage zones at Lake Pilcine

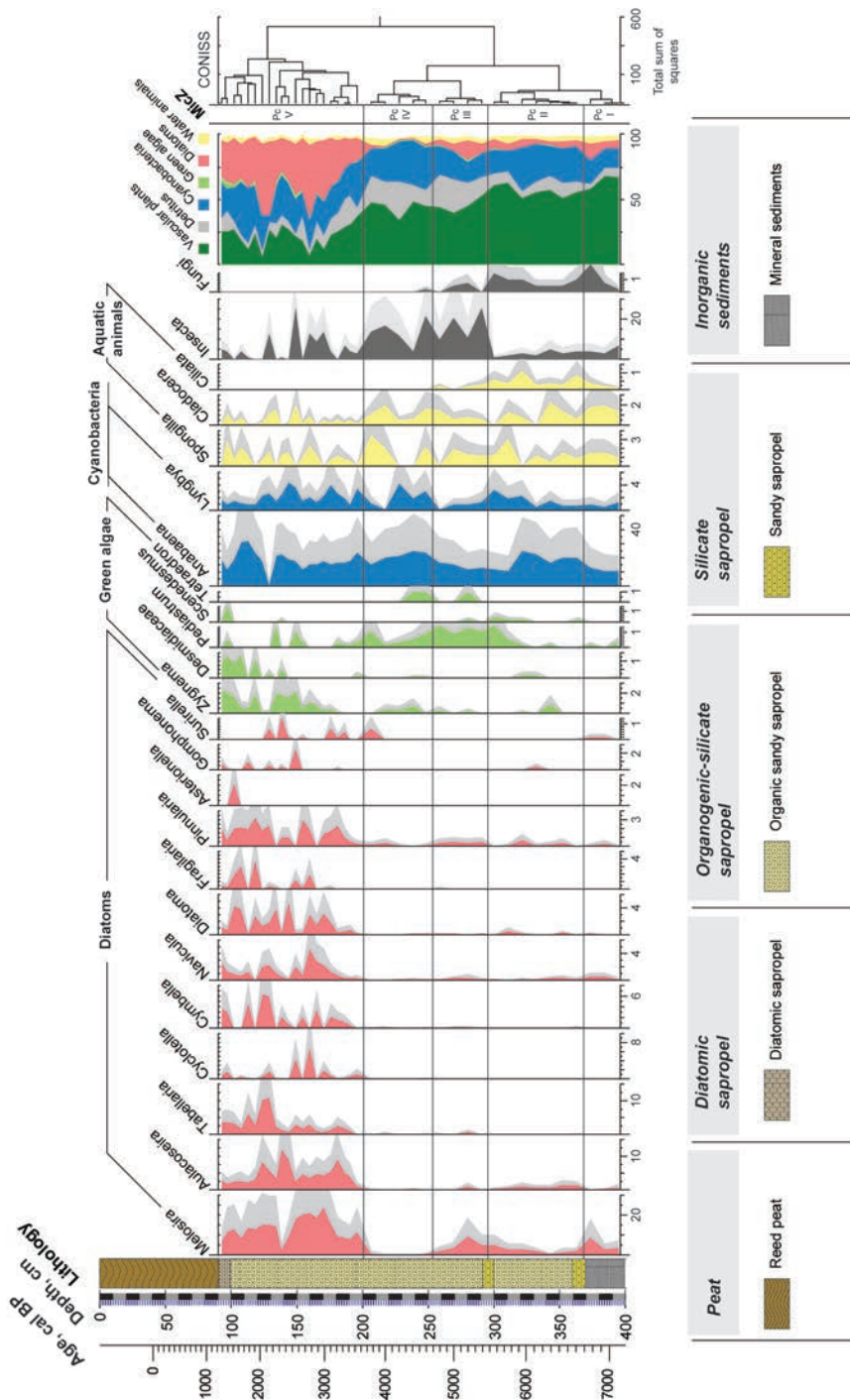| Depth (cm), Age (cal BP)	LPAZ	LPAZ description	Vegetation type in the area
90-140 *1,300-2,400*	Pc V	*Pinus – Betula – Picea* Coniferous tree pollen dominates in the zone: *Pinus* reaches 38.3%, and *Picea* increases to 25.8%. Values of *Betula* pollen vary 15-30.2%, broadleaved tree pollen are in small numbers and decrease in comparison with lower depth interval. In herb pollen composition, *Poaceae* and *Cyperaceae* prevail reaching 3.6%. Values of cultivated plants (*Secale cereale* and *Triticum*) and ruderal plants are fluctuating	Mixed forest with a predominance of coniferous with grasslands and agricultural land
140-200 *2,400-3,700*	Pc IV	*Betula – Pinus – Picea* *Betula* increases, reaching 24.1%, while *Alnus* is gradually decreasing from 15 to 5%. A slight increase in *Pinus* and *Picea* is evident, and significant fluctuation values of them are observed in the entire zone. Pollen of *Corylus*, *Ulmus*, *Quercus* and *Tilia* range only 1-2%. A significant increase in the amount of *Poaceae*, *Urtica*	Mixed forest with birch, alder, pine and spruce
200-290 *3,700-5,600*	Pc III	*Alnus – Tilia – Quercus – Picea* High values of *Alnus* (30%) and *Corylus* reaching 15 %. Broadleaved pollen still at high values, which are composed by an initial increase in *Quercus* and *Tilia* pollen, while *Ulmus* pollen significantly decrease. Presence of herb and aquatic plant pollen is fragmentary. *Betula* still in low values, as well as *Pinus* and *Picea*	Broadleaved forest with alder, hazel and spruce, areas of grasslands
290-360 *5,600-4,700*	Pc II	*Alnus – Ulmus – Tilia* *Tilia, Ulmus, Alnus* and *Corylus* reach their maximum. Herb pollen significantly increases, especially the amount of ruderal plant and aquatic plant pollen. *Betula* still in low values, a gradual increase in *Pinus* and *Picea* pollen up to 10%	Broadleaved forest with grasslands
360-400 *4,700-7,400*	Pc I	*Alnus – Corylus – Ulmus – Tilia* *Alnus* and *Corylus* dominate, *Tilia* and *Ulmus* gradually increase in a range from 1.2% to 6.2%. A small amount of *Betula* and *Pinus* pollen	Broadleaved forest with alder, hazel, areas of grasslands

Figure 18. **Microfossil diagram of sediments at Lake Pilcine**

Figure 19. **Macrofossil diagram of sediments at Lake Pilcine**

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Figure 20. **Pollen diagram of sediments at Lake Pilcine**

3.2.5 Lake Pilvelis

Microfossils

Seven microfossil zones (MicZ-Pv) were established in Lake Pilvelis (Table 22; Figure 21), based on visual and statistical evaluations of algae and remains of aquatic animals and vascular plant. Microfossils are represented by four algae groups (cyanobacteria, green algae, diatoms and desmidiales), vascular plants, aquatic animals, fungi and moss. The genus of algae and aquatic animals was detected.

Table 22

Description of microfossils zones at Lake Pilvelis

Depth (cm), Age (cal BP)	MicZ	Description and vegetation type	Sedimentary environment
00-90 *before present-2,300*	Pv VII	*Higher plants – Anabaena – Aquatic animals* Higher plants increase in the upper part of the zone from 23% to 64%. The average amount of *Anabaena* increases to 21%. The amount of aquatic animals increases reaching on average 20%. Remains of *Scenedesmus, Pediastrum* and *Tetraedron* are found in small amounts, *Botryoccoccus* disappear in the upper part of the zone	Increase in water level, eutrophication proceeds
90-140 *2,300-5,800*	Pv VI	*Higher plants – Aquatic animals* In the upper part of the zone, *Lyngbya* disappears. *Anabaena* decreases from 26 to 7%. Increase in the number of green algae remains up to 3% and still is mainly represented by *Botryoccoccu*. Remains of *Scenedesmus, Pediastrum* and *Tetraedron* appear in a tiny amount. Aquatic animals are mainly represented by *Cladocera* (on average 8%), *Spongilla* increases to 6%. Distribution of *Insecta* chitin is irregular. The average amount of higher plants decreases reaching 30%	Intensive eutrophication, low water level, colder conditions
140-200 *4,200-5,800*	Pv V	*Higher plants – Anabaena* The average total of remains of higher plants is 40%. Cyanobacteria mainly are represented by *Anabaena*; the average incidence in the zone is 30%. *Lyngbya* decreases on average to 3%. Green algae are represented by a small amount of *Botryoccoccus*. Detritus still decrease (on average to 20%). Aquatic animals decrease in the upper part from 10 to 4%, remains of *Spongilla* appear	Continuing decrease in water transparency, intensification of eutrophication, oxygen saturation in the ground layer decreases

Table 22 (continued)

Description of microfossils zones at Lake Pilvelis

Depth (cm), Age (cal BP)	MicZ	Description and vegetation type	Sedimentary environment
200-240 *5,800-6,100*	Pv IV	*Anabaena – Lyngbya* *Lyngbya* continues to decrease to 15%, but *Anabaena* increase from 18 to 25%. Increased detritus (30%) and remains of total higher plants (average 25%). A small amount of *Chlorogloea*. *Scenedesmus* decrease to 3%. The total amount of green algae decrease. Insignificant increase in aquatic animals. Detritus decrease to 30-25%	Continuing decrease in water transparency, the rapid beginning of eutrophication
240-320 *6,100-8,200*	Pv III	*Lyngbya – Anabaena* *Lyngbya* still dominates, but gradually decreases in the upper part of the zone from 60 to 33%. Increase in *Anabaena* (10%). *Chlorogloea* decreases. *Scenedesmus* vary from 5 to 8%. Detritus increase in the upper layer of the zone to 33%	Decreased water transparency
320-390 *8,200-10,000*	Pv II	*Lyngbya – Scenedesmus* Cyanobacteria dominate; blue-green benthic algae *Lyngbya* gradually increase from 1 to >60% in the upper part of the zone. Detritus decrease from 80 to 20%. A small amount of plankton blue-green algae such as *Chlorogloea* and, at the end of the zone, some remains of *Microcystis*. Irregular distribution of *Anabaena*. Remains of green algae are represented by *Scenedesmus* (1-10%) and a small amount of *Tetraedron* and *Pediastrum*. A small number of aquatic animals and higher plants	Clear water rich in nutrients
390-400 *10,000-10,100*	Pv I	*Diatoms – Desmidia – Spongilla* A high amount of diatoms and *Spongilla*. Some remains of *Desmidia*	Clear, cold, soft water

Macrofossils

The macrofossil diagram for Lake Pilvelis was divided into six plant macrofossil zones (MacZ-Pv) (Table 23; Figure 22). The variety of plant species in the lake is reduced: 23 plant forms were established, although species were not detected for 4 forms of plants.

Table 23

Description of local plant macrofossil zones at Lake Pilvelis

Depth (cm), Age (cal BP)	MacZ	Description and vegetation type	Sedimentary environment
00-90 *before present-2,300*	Pv V	*Potamogeton – Nymphaea alba – Characeae* Dominant species are *Potamogeton natans, Nymphaea alba* and *Characeae*. *Daphnia* and *Bryozoa* occur in small amounts. The total number of macrophytes species is increasing for remains of aquatic plants	Intensification of eutrophication processes Water depth 3≤100 cm
90-180 *2,300-5,700*	Pv IV	*Betula – Picea – Characeae* A small amount of *Characeae* oogonia, *Potamogeton pussillus* and *Typha sp.* seeds. A rapidly increased amount of *Daphnia* ephippia. Increase in *Picea* needles and seeds, and remains of aquatic plants, also *Hypnum* leaves, especially in the interval 110-130 cm	Beginning of lakeshore area overgrowth and the start of eutrophication Water depth 30-100 cm
180-240 *5,700-6,100*	Pv III	*Betula* Dominate *Betula sect. Albae* nutlets. A small amount of aquatic and telmatic plants, aquatic animals. Some *Cristatella mucedo* statoblasts. Increase in the amount of *Hypnum* leaves	Decreased water transparency, Water depth 30-100 cm
240-320 *6,100-8,200*	Pv II	*Najas flexilis – Characeae – Potamogeton pussillus* A large amount of *Characeae* oogonia, *Potamogeton pussillus* and especially *Najas flexilis* seeds. Unequally increased number of *Cristatella mucedo*. Seeds of coastal plants are not found	Clear water Water depth 100-200 cm
320-400 *8,200-10,100*	Pv I	*Najas marina – Najas flexilis – Typha – Carex* *Najas marina*, *Najas flexilis* and *Typha*, *Carex* and *Characeae* oogonia regularly occur. The high amount of *Betula sect. Albae* and bryozoans *Cristatella mucedo*. Tree-plant leaves and fragments of twigs, aquatic plant remains are in a small amount. Seldom *Carex* nutlets and *Characeae* oogonia, many *Betula sect. Albae* nutlets. Chitin fragments of zooplankton and several *Hypnum* leaves and culms in the very lower part of the section (390-400 cm).	Clear water Water depth 100-200 cm

Pollen

Pollen analysis was carried out for 4.0 m long sediment sequence of Lake Pilvelis represented mainly by different types of sapropel, except the bottom layer of the analyzed section, which consists of mineral sediments (fine sand). The pollen diagram prepared according to the obtained results showed fluctuations of pollen curves, which reflect changes in pollen composition pointing on vegetation dynamics in the surroundings of the lake. It allows subdivision of six statistically significant local pollen assemblage zones (LPAZ-Pv) (Table 24; Figure 23). The environmental conditions and vegetation dynamics during the sediment accumulation in Lake

Pilvelis were reconstructed based on the changes in pollen spectra and characteristics of sediment composition, as well as radiocarbon dating results.

The reconstructed regional vegetation changes and data of absolute age of sediments revealed that organic-rich sapropel was accumulated in Lake Pilvelis since the Early Holocene, before 10,100 cal BP, and is continuing until today. During this time, different types of sapropel with larger or smaller mineral admixtures were deposited. The sediments contain pollen, which composition reflect changes in vegetation and landscape in the surroundings of the lake.

Table 24

Description of local pollen assemblage zones at Lake Pilvelis

Depth (cm), Age (cal BP)	LPAZ	LPAZ description	Vegetation type in area
00-90 *before present-1,900*	Pv VI	*Betula – Pinus – Poaceae* *Betula* dominates and reaches from 29 to 42.2%, *Pinus* 26.3% and *Picea* increase to 16% in the zone, the number of broadleaved trees decreases. The prevalence of Poaceae increase reaching 2.6%, and a decrease of Cyperaceae. The zone ends with an increase in herbaceous: Asteraceae, Solanaceae and Apiaceae. Values of cultivated plants as *Secale cereale* in the zone interval reach about 1.5%	Mixed tree forest with grasslands and agricultural area
80-160 *1,900-4,900*	Pv V	*Alnus – Quercus – Fraxinus* *Betula* is reaching 34.1%, *Alnus* 29.4%, *Corylus*, *Ulmus* and *Tilia* in the range 3 -5%, while the maximum values reach *Quercus* (8.9%) and *Fraxinus* (6.1%). In the middle of the zone, *Fagus* appears, reaching up to 0.5%. At the end of the zone, *Corylus* decreases, but *Carpinus* increases. A slight increase in *Pinus* and *Picea* is evident, a decrease in Poaceae amount, but around 0.4% of Cyperaceae pollen increase is noted. Pollen dispersion for *Artemisia*, *Ranunculus* and Apiaceae increase. The number of aquatic plants decreases for Nymphaceae and *Potamogeton*; the same trend is for *Equisetum* and *Sphagnum*	Mixed tree forest with a significant presence of oak and ash
160-230 *4,900-6,100*	Pv IV	*Tilia –Ulmus – Corylus – Alnus – Picea* Continues dominance of broadleaved *Corylus*, the average incidence in the whole zone is 17.8%. *Alnus* and *Fraxinus* increase at the end of the zone, but the amount of *Betula* decreases. Constant values retain *Tilia* and *Quercus* in the range of 4-7.3%. *Ulmus* varies from 10.6 to 14.1%. A small amount of *Carpinus* appears. Increase in *Picea* reaching 15.6%. Throughout the zone, *Salix* decreases, but Ericaceae increase. At the end of the zone, decrease of Poaceae and Cyperaceae, but an increased amount of aquatic plants *Potamogeton*. *Equisetum* and *Sphagnum* increase in the zone	Broadleaved forest with spruce

Table 24 (continued)

Description of local pollen assemblage zones at Lake Pilvelis

Depth (cm), Age (cal BP)	LPAZ	LPAZ description	Vegetation type in area
230-310 6,100-8,000	Pv III	*Alnus – Ulmus – Corylus* Betula pollen has a quite stable number of and varies 27-30%. *Corylus*, in general, reaches 18.5-20%, except for the middle part of the zone, where the number of hazel pollen decrease to 2%. The number of broadleaved tree pollen significantly increase pointing on their part in the forest composition: *Tilia* pollen reaches 5.2%. *Quercus* gradually increases in the range from 1.2% to 6.2%. *Alnus* and *Ulmus* are above 5.8%. *Picea* pollen remains in the range of 2.4-5.3%, while *Pinus* reduces to 9%	Broadleaved forest with alder, hazel, grasslands
310-360 8,000-9,300	Pv II	*Pinus – Betula – Ulmus* Amount of *Pinus* pollen increases to 29.2%, while *Betula* decreases in the upper part of the zone to 25%. *Picea* retains a stable incidence with 6%, *Ulmus* increases to 9%, *Alnus* varies from 1.5 to 4.7% and *Corylus* from 7 to 17.7%. Ericaceae and Cyperaceae appear and reach up to 3%, Poaceae over 1.7%, maintaining a constant curve and reaching the highest value. Ruderal herbs represented by *Artemisia*, on average of 2.4%, *Plantago* 0.5%. Herb pollen in total reaches up to 20%, pointing on open landscape area around the lake. Spores are represented by Polypodiaceae, *Sphagnum* and *Equisetum*	Pine-birch forest with elm and hazel, broad areas of grasslands, partly overflowing
360-400 9,300-10,100	Pv I	*Betula* In pollen spectra composition of the zone interval, *Betula* dominates and reaches 66%. Tree pollen is also represented by coniferous, mainly by pine *Pinus* which on average reach 20 %, less represented spruce *Picea* 2-10%. Other tree pollen is in a small amount. Hazel *Corylus* average is around 5%. Shrubs represented by *Salix* on average 1-3%. Herb pollen reaches 10-15%, mainly is represented by grass Poaceae – 6.4% and sedge Cyperaceae – 1.3%. Aquatic plant pollen is mostly represented by *Nymphaea* and Potamogetonaceae	The area is surrounded by birch forest stands with some coniferous and broad areas of grasslands

The results of pollen analysis reflect the changes in regional vegetation and indicate that the organic-rich deposits were accumulated Lake Pilvelis since the Early Holocene, before 10,100 cal BP, and continue to accumulate until today. During this time, different types of sapropel with larger or smaller admixtures of mineral matter were deposited. Sediments contain pollen, which characterizes the changes in the composition of vegetation in the surroundings of the lake.

Proportions between the tree and shrub or arboreal (AP) and herb or nonarboreal (NAP) pollen indicate that area around the lake was partly opened; a grassland-forest
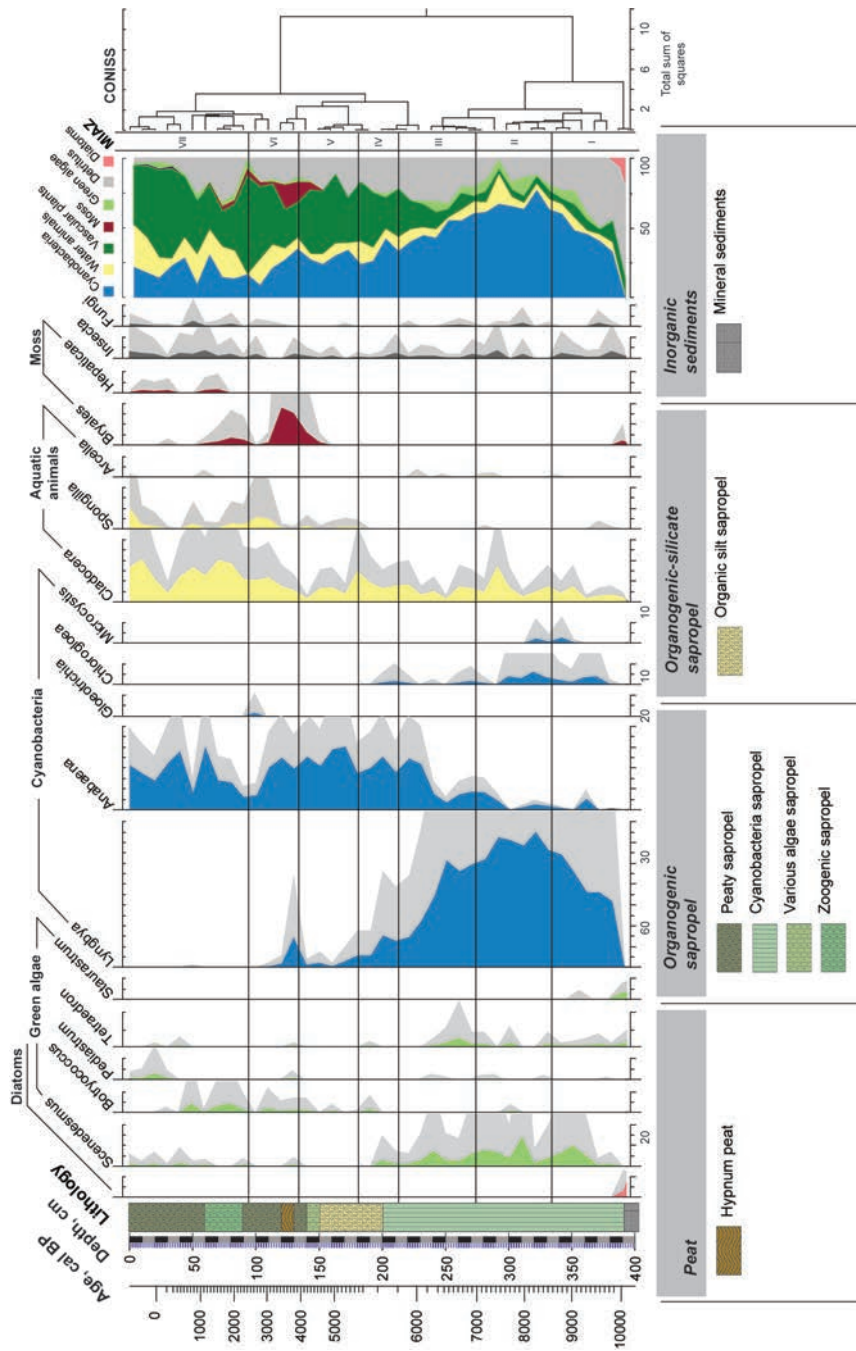
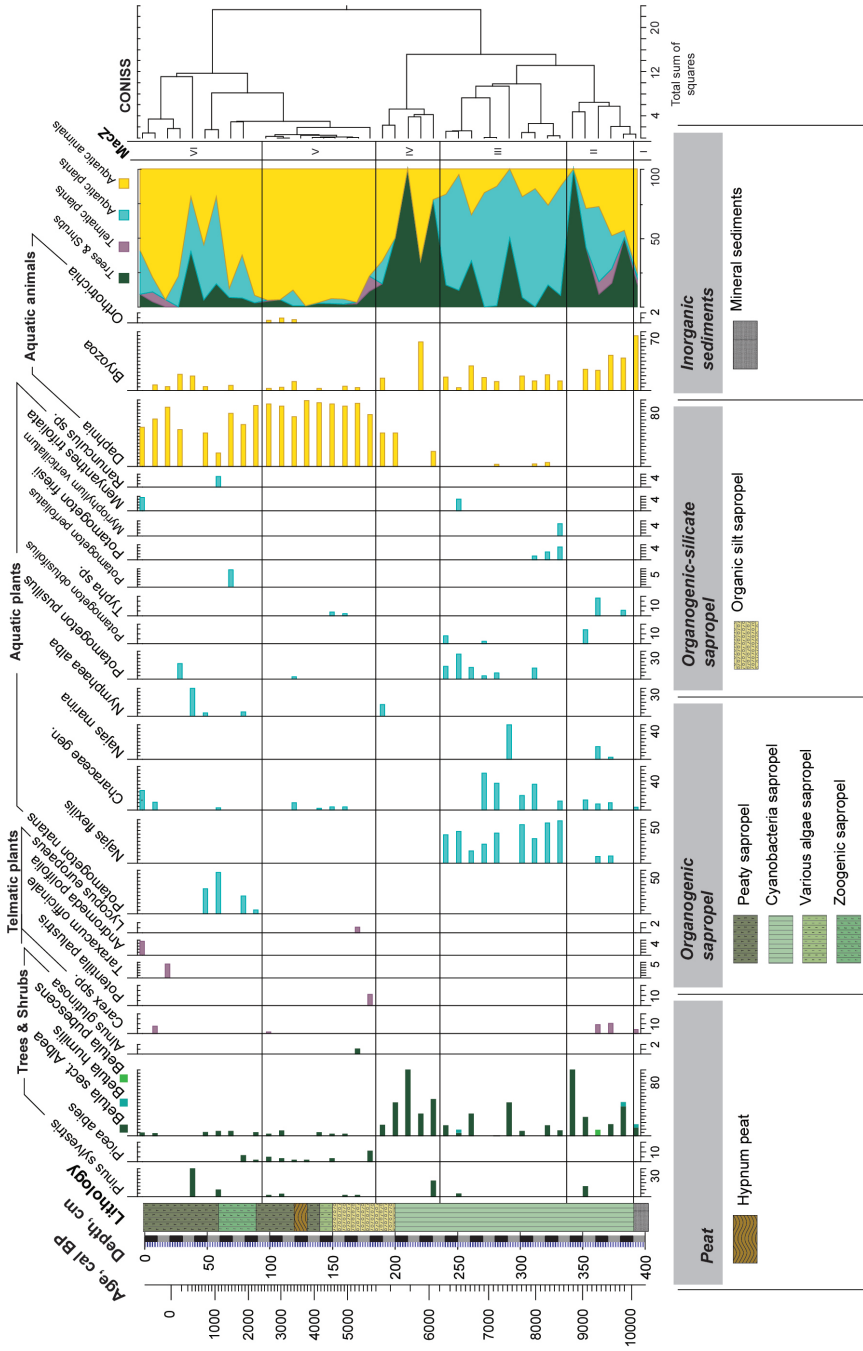*Figure 21.* **Microfossil diagram of sediments at Lake Pilvelis**

Figure 22. **Macrofossil diagram of sediments at Lake Pilvelis**

Figure 23. **Pollen diagram of sediments at Lake Pilvelis**

landscape with birch forest and some coniferous stands existed around the lake during the Early Holocene. The pollen spectra, showing some decrease in the warmth-demanding plant pollen content and increase in birch before the start of broadleaved forest distribution during the Holocene Thermal Maximum, indicate a slight climate cooling. It is supported by some decrease in the quantities of warmth-demanding plant pollen and an increase in the number of corroded and re-deposited pollen along to slight increase in mineral matter in sediments, which probably is related to the lakeshore.

3.2.6 Similarities of environmental formation conditions in studied lakes

In order to determine the environmental factors that directly affect the formation and properties of sapropel, the development of sapropel during the formation of sapropel was reconstructed by biological analyzes of three studied lakes: Padelis, Pilcine and Pilvelis.

Sapropel sediments were formed in Lake Padelis since ~11,700 cal BP (Figure 24) when the lake became mesotrophic. It is reflected by microfossils, which show the extinction of diatom species, and by an increase in macrofossils, which are dominated by the remains of the mesotrophic species *Najas marine*. Up to ~3,600 cal BP, carbonate-type sapropel was formed in the lake, but up to ~6,700 cal BP, a carbonate-type sapropel with high ash content. During this time, the sapropel layers alternate with the interlayers of mineral sediments. Three sedimentary environment zones can be identified in the lake during the formation of these sediments.

During the 9,800-11,700 cal BP, cold, hard, clear water with high calcium content was in the lake. The catchment area of the lake was dominated by birch stands with broad overflowing meadows.

During 8,200-9,800 cal BP, water level fluctuations occur in the lake. It is indicated by the intermediate layers of mineral sediments in carbonate sapropel. Water is still transparent and alkaline, but warmer than before. In the catchment area, pine-birch stands are replaced by mixed forests with broadleaves. 8,200 cal BP in all biological proxies is marked as a change in the species composition of the organisms. The cold episode known as the 8.2 ka BP cold event and the most extreme cold event after the Younger Dryas was detected in different sedimentary environments. This event concurred with the Bond event 5b and continued approximately from 8.6 (8.3) to 8.1 ka BP (Wanner *et al.*, 2011).

During 6,700-8,200 cal BP, the water hardness and transparency of the lake decrease, the amount of dissolved organic matter and nutrients in the water increase. Broadleaved forests with spruce grow in the lake sediment basin. These marks indicate that the climate is warm and humid at this time. The content of organic matter in sapropel is rapidly increasing. From 6,700 to 3,600 cal BP lake organogenic carbonate sapropel begins to form. At the study site, the water depth that time becomes shallower than 100 cm. The amount of dissolved organic matter in the water increases, the hardness of the water decreases, however, the content of Ca in the water, compared to other studied lakes, remains in high concentrations, as evidenced by the Ca content in sapropel – 134 g/kg. The ash content of sapropel

becomes lower than 7%, and the amount of carbonates decreases rapidly from an average of 15% to 0.5%. In the lake catchment area dominates mixed forest with a significant admixture of deciduous trees with grassland and agricultural land.

After 3,600 cal BP, sapropel is no longer formed at the studied area of the lake, instead comes fen type reed peat. Analysis of macrofossils reveals that, in the last century, the water level of the lake has risen and in the upper 30 cm layer of sediments contain plant remains that usually are growing under lake conditions (*Characeae, Najas* and *Nymphaea*).

Figure 24. **Comparison of biological zones characterizing sedimentary environment during the development of Lake Padelis**

Reconstruction of the environment during Lake Padelis shows that under the particular climate conditions in the freshwater lake with clear water sapropel begins to form with high profitability and high carbonate content. Carbonates have entered the lake from the catchment area. When the climate becomes milder, the overgrowth of the lake intensifies and the ash content of sapropel starts to decrease, and the concentration of organic matter increases. Remains of cyanobacteria are the main constituents of organic matter in these sediments. When the catchment area of Lake Padelis became paludified, and the hydrological regime of the lake changed, the content of carbonates and minerals decreased rapidly. The concentration of ash in

sediments decreases to 7%, while organic matter increases up to more than 93% of dry matter. In organogenic carbonate sapropel, the number of cyanobacteria in organic matter decreases and the remnants of organisms characteristic to eutrophic lakes (*Cladocera* and *Bryales*) appear. Remains of molluscs disappear, indicating that pH of sediments becomes neutral, which determines the dissolution of mollusc shells, indicating a drastic change in the chemical composition of the lake water. After 3,600 cal BP, the water depth at the lake site becomes so shallow that reed peat begins to form at the studied place of the lake. Conditions for sapropel formation are no more favourable, and peat formation starts when the water depth becomes suitable for the growth of telmatic plants. At the site of intensive plant growth, residues begin to accumulate, becoming oxidized, consuming dissolved oxygen and nutrients; water transparency decreases, the water warms up easily; thus the conditions become unsuitable for the development of algae and aquatic animals.

In Lake Pilcine, at the study place, sapropel begins to form only since 6,900 cal BP (Figure 25). It was determined by the location of the lake above sea level and the geological and geomorphological conditions of the catchment area. Lake Pilcine is inter-hilly water body of glacial origin, which is on higher elevation (183 m ASL) than other studied lakes (156 m ASL), and sedimentation of Lake Pilcine was affected by the admixture of bedrock debris in the deposits of the catchment area. Water level changes were determined approximately at the same period in Lake Kuzu in Latvia (Terasmaa *et al.*, 2013) and Lake Juusa in Estonia (Punning *et al.*, 2005), as well as in Lake Sloboda in Belarus (Zhukhovitskaya *et al.*, 1998).

Changes of the lake biota communities could be induced not only by water level changes but also by temperature anomalies during 6,600 to 6,400 cal BP. The entire sapropel layer of Lake Pilcine is represented by organogenic-sandy sapropel with the

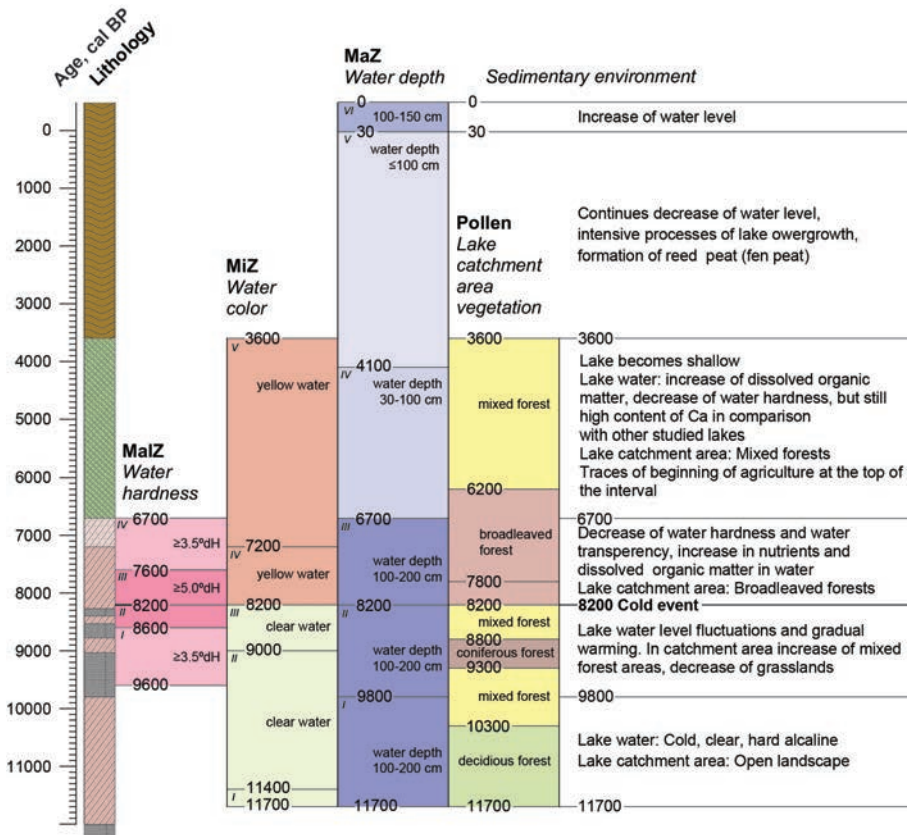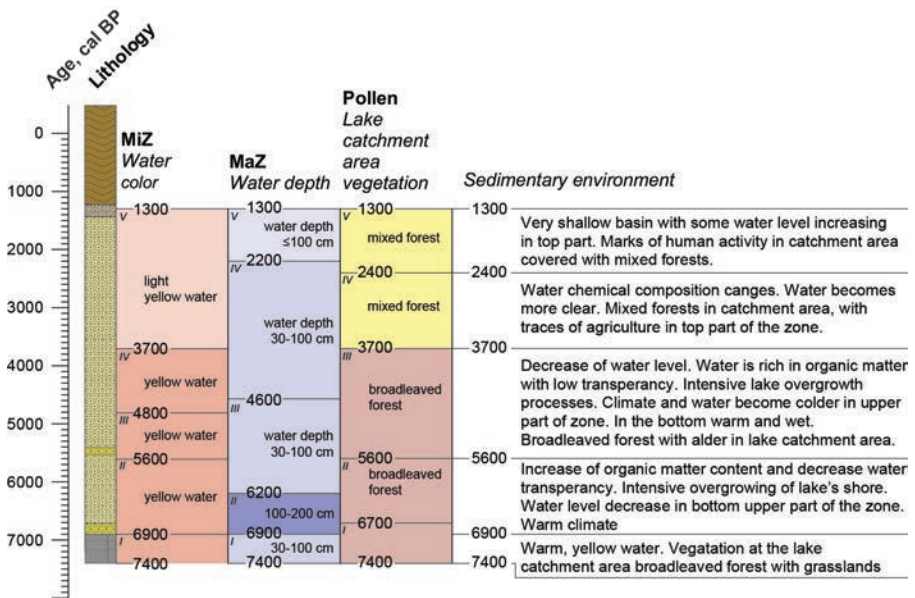*Figure 25.* **Comparison of biological zones characterizing sedimentary environment during the development of Lake Pilcine**

sandy sapropel interlayer accumulated during ~5,400 cal BP. The declining water level in Lake Pilcine is indicated by a sharp increase in *Insecta* and *Bryales*. Although the type of sapropel remains unchanged, the chemical composition of the water in the lake changes dramatically in ~3700 cal BP, when different species of diatoms appear in the microfossils composition. *Anabaena* is prevailing, and the species composition points to the eutrophic lake. Peat begins to form in the lakes Padelis and Pilvelis around this time. Peat in Lake Padelis is forming until the present, but the lake's macrofossils have shown a slight rise in water levels only in the last century. Peat is formed in Lake Pilvelis only 400 years after the predominantly peaty sapropel settles in the lake. Such drastic changes in the composition of microfossils in all three lakes indicate a transient drought event. According to the literature (Stivrins *et al.*, 2014), the short dry event is also recorded in Lake Mazais Svetins located in Rezekne region, and it is detected in many wetlands in Latvia during that time (Kalnina *et al.*, 2019). After 1,300 cal BP, reed peat begins to form in the study area of Lake Pilcine.

Sapropel in Lake Pilvelis started to accumulate since 10,000 cal BP when the presence of *Najas marina* and *Najas flexilis* macrofossils indicates the beginning of eutrophication processes in the lake. Due to favourable conditions for cyanobacteria sapropel in the lake, it was accumulated during 10,000 to 5,800 cal BP. The content of organic matter of this sapropel is higher than 83%, and its organic matter is mostly made up of *Lyngbya* remains. At this time, the water in the lake was transparent and cold. The catchment area was overgrown with grassland that periodically flooded. From 5,800 to 4,500 cal BP, the mineral content increases in sediments and organic-silt sapropel is formed, organic matter of which consists of blue-green alga *Anabaena*. After 4,500 cal BP, the organic content of the lake begins to form. The proportion of organic matter, which is formed by peat-forming plants, indicates the intensification of eutrophication of the lake.

3.3. Distribution, chemical associations and factors influencing the accumulation of metals in sapropel

Knowledge on average content, as well as maximum and minimum values of metallic elements in individual sapropel deposits, helps to understand the variability of sediment composition and properties significant for sapropel applications. For example, sapropel deposits containing a high content of metallic elements can provide nutrients for cultivated plants and soil microorganisms relevant for agriculture. However, such deposits can be toxic to humans if applied for mud therapy and to domestic animals when present in food additives (Vincevica-Gaile and Stankevica, 2018).

The concentration of metallic elements in sapropel samples from Lake Padelis, Lake Pilcine and Lake Pilvelis varies over a wide range (Table 25), indicating that the formation of sediments occurred under various environmental conditions in the water body and its catchment area at different times. Detected variability of metal concentration could be considered as surprisingly high. Among the analyzed metallic elements in the sapropel samples, the highest concentrations were observed for Ca, Fe, Mg, K, Mn, Zn and Na (in the range of 10-10^4 μg/g). Other elements (Cu, Ni, Cr, Pb, Co, and Cd) were present in a concentration of <10 μg/g for each.

Age, cal BP · Lithology · **MiZ** Water color · **MaZ** Water depth · **Pollen** *Lake catchment area vegetation* · *Sedimentary environment*

water depth ≤100 cm

mixed forest

brown water

Intensive lake overgrowing.
Overflowing of bogged shore area.
Marks of human activity in catchment area covered with mixed forests.

1900

2300 — 2300 — 2300

water depth 30-100 cm

brown water

mixed forest

Decrease of water level and transparency.
Beging of lake overgrowing and boging up.
In lake catchment area grow broadleaved forest till ~ 4900 cal BP, after - mixed forests.

4200

4900

broadleaved forest

yellow water

5800 — 5700

6100 — 6100 — 6100 — 6100

water depth 100-200 cm

broadleaved forest

clear water

Clear water rich in nutrients. Water level rise.
Open catchment area with grasslands and pine-birch forests, overflowing.

8200 — 8200 — 8000 — 8200

water depth 100-200 cm

clear water

mixed forest

Clear, cold and soft water.
Open catchmenet area with grasslands and birch stands. In upper part rising inputs of terrigenous material from the catchment area into the lake.

9300 decidious forest

10000 · 10100 · 10100 · 10100

Figure 26. **Comparison of biological zones characterizing sedimentary environment during the development of Lake Pilvelis**

For further assessment of the economical use of studied sapropel, the concentrations of heavy metals were summarized and compared with the data gathered from other sites in Latvia, Belarus, Russia (Kaliningrad Region). The results of the study reveal that studied sapropel sediments cannot be considered as polluted, and detected metal concentrations do not exceed average values found in other places (Table 25).

Analysis of the metal distribution and content in the sediment section and investigation of the lake development provide information on both natural and anthropogenic origins of the metal flow in the lake ecosystem, the drainage conditions, the climatic changes in the region and the changes in the land use in the catchment area during the time of sediment formation (Dean, 1974). The main problem associated with the data interpretation is that the accumulation of metallic elements is affected by various factors (direct impacts within the lake basin and indirect impacts such as metal precipitation with atmospheric precipitation due to transboundary air mass transfer, metal scavenging in stable mineral forms, geochemical impacts of mineral dissolution, *etc.*). Consequently, the source of a particular element may change over time. It induces errors in the evaluation data covering extended time periods. Statistical analysis can be used as a tool for determining the relationship among the element accumulation patterns and identification of the metal accumulation tendencies for the entire sediment accumulation period.

Table 25

**The concentration of metals in sapropel of Lake Padelis, Lake Pilcine and Lake Pilvelis
and other sites of Latvia as well as Belarus and Kaliningrad Region (Russia)**
(GEO-Konsultants, 1998b; Zhukhovitskaya *et al.*, 1998)

µg/g	Ca	Fe	Mg	K	Mn	Zn	Na	Cu	Ni	Cr	Pb	Co	Cd
Lake Padelis													
Mean	230,376	4,654	3,182	171	321	14	163	2.5	1.7	2.8	3.6	1.13	0.06
Max	349,865	12,077	5,757	1,172	570	50	211	8.9	9.1	16.4	7.4	3.18	0.15
Min	11,959	1,550	633	20	70	5	109	0.6	0.3	0.4	1.7	0.31	0.04
Lake Pilcine													
Mean	11,569	10,286	1,702	1,658	174	113	56	25.3	23.6	21.4	6.3	6.08	0.35
Max	20,322	13,802	2,134	2,585	299	179	94	40.9	35.7	46.1	15.2	9.36	0.76
Min	3,938	2,006	1,106	304	41	22	38	3.0	3.2	2.9	0.7	1.04	0.04
Lake Pilvelis													
Mean	9,100	2,536	821	424	109	93	68	12.7	8.8	8.7	6.6	2.89	0.49
Max	13,971	12,216	2,702	2,544	188	198	125	19.8	23.8	44.4	30.9	8.20	0.96
Min	5,405	1,057	492	106	61	46	38	7.6	3.5	2.7	0.6	0.73	0.21
Lakes of Eastern Latvia (115 samples) Lake Eikša, Lielais Kalpes, Maltas, Marinzejas, Pakalnis, Plošu, Rēzeknes, Padelis, Pilcine, Pilvelis, Vēvers, Līducis													
Mean	33,654	8,270	2,081	906	219	112	119	16.7	17.9	20.3	14.7	7.75	0.37
Max	349,865	25,614	8,340	4,940	570	402	390	43.2	35.7	55.4	46.7	13.00	1.66
Min	3,938	1,057	492	20	41	5	11	0.6	0.3	0.4	0.6	0.32	0.04
Lakes of Central Latvia (11 samples)													
Mean						98			19.5	38.6	19.7	7.9	
Max						121			32.0	55.0	39.0	11.9	
Lakes of Western Latvia (15 samples)													
Mean						86			16.3	66.9	19.5	4.8	
Max						170			21.5	191.3	26.1	8.0	
Lakes of Belarus (1492 samples)													
Mean					342	73			13.2	26.0	16.0	7.0	
Max					1,180	233			24.0	40.0		16.0	
Lakes of Kaliningrad Region (38 samples)													
Mean						57			10.6	36.4	17.3	4.8	
Max						181			22.0	81.0	40.2	13	

The chemical element association approach was chosen for the interpretation of statistically significant correlations among the elements of sapropel composition such as total P, elemental composition (C, H, N, O, S), metallic elements, humic substances, mineral and organic matter and carbonates. Geochemical associations merge chemical elements with identical or similar behaviour in hypergenic conditions, as the migration and concentration of element associations in a fixed

environment are defined by one-model factors instead of chemical properties of the elements (Gilucis, 2007). The geochemical association approach is widely used for geochemical atlases in Latvia (Gilucis, 2007), Poland (Lis and Pasieczna, 1995), Lithuania (Kadūnas *et al.*, 1999) and Estonia (Petersell *et al.*, 1997). It is also used for characterisation of water sediments (Jaquet *et al.*, 1982; Leonova and Bobrov, 2012; Marzecova *et al.*, 2011; Panda *et al.*, 2006). The shortage of the geochemical association studies of naturally formed water sediments is that these studies cannot provide an adequate basis for the interpretation of the role of organic matter in the transport and conservation of metallic elements in sediments. Generally, most of the studies are based on statistical data of metals and grain size of mineral matter. This approach is useful in researching mineral sediments in the water. In the case of sapropel, however, incorrect interpretation of data is possible.

The data of element correlation in sapropel from Lake Padelis, Lake Pilcine and Lake Pilvelis revealed major groups of metallic element associations individual for each lake.

Lake Padelis

The element accumulation pattern for the sediments of Lake Padelis discovered three separate well-recognized zones (Figure 27).

The third zone (250-400 cm) characterizes sapropel accumulation from ~11,600 cal BP until ~8,400 cal BP – the period when intensive weathering of calcareous minerals in the lake basin happened, and calcareous sapropel layers in the sediment profile were intermixed with lime layers. For this sediment segment, high content of mineral matter is characteristic and relatively high concentrations of Na, Mg, Ca were found (Figure 13A). Correlation analysis demonstrates that these elements represent the first group of chemical element association and are bound positively with mineral matter and carbonates (except Na), but negative links exist with Cd and organic matter.

For the second zone (190-250 cm corresponding to ~7,700-~8,400 cal BP), decreased concentrations of organic substances and increased concentrations of major elements such as Mg, K, Fe and heavy metals (*e.g.*, Cr, Co, Ni, Cu and Pb) are characteristic. It is not entirely clear what were the sources for such changes, but probably they might be related to the changes of weathering patterns of mineral matter and development of vegetation consuming mineral substances for their development. Biological analysis of sediments does not give any convincing evidence on changes in environment or climate except relatively abundant amounts of molluscs in this period. The remains of molluscs are abundant as well as the diversity of these species in this sediment interval (Figure 14).

The first zone (100-190 cm) characterizes relatively recent (~3,600-~7,700 cal BP) processes. In this sediment segment, the content of organic matter, as well as average concentrations of K, Fe, Cr, Co, Ni, Cu, Cd and Pb, are increasing. At the same time, concentrations of Na, Mg, Ca and Mn are lower in comparison with the average concentrations in the upper zones. Statistically significant correlation shows that the second group of metallic element associations in sapropel of Lake Padelis is K, Cr, Fe, Co, Ni, Cu (Figure 27B) and they are positively bound to each other. Cd has a positive correlation with total P, organic matter and humic substances and negative
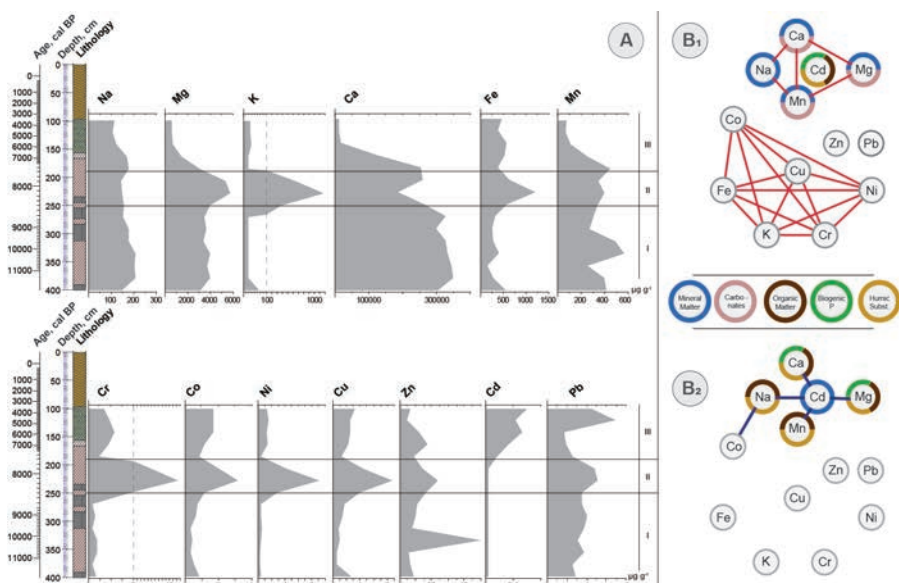
Figure 27. **(A) Distribution pattern of metallic elements in sapropel from Lake Padelis. For the legend of the lithological section, see A; (B) Statistically significant correlation (P>0.01) of elements in sediments from Lake Padelis: (B1) positive correlation, (B2) negative correlation**

correlation with Ca, Na, Mg, Mn and mineral matter. Zn and Pb have stable links with other analyzed elements.

93.45% of the data used in PCA allowed the detection of four factors that can be used to explain the accumulation processes of metallic elements in sapropel from Lake Padelis (Table 26).

Factor 1 (Principal Component 1) in PCA of metal accumulation in Lake Padelis allows explaining 60.49% of analyzed data. Thus, this factor might be considered as the dominant one describing processes which are affecting metal accumulation, especially if compared with the results of PCA for other lakes. Factor 1 has a positive correlation with BD, MM and CB, as well as Na, Mg, Ca, Mn. Factor 1 has a negative correlation with the parameters related to the presence of organic matter in sediments MS, OM, P_{bio} and CHNS, and a metal (Cd). Thus, it can be stated that Factor 1 of PCA describes carbonate-rich terrigenous materials, changes in their intensity, as well as impacts of groundwaters enriched with carbonates and elements associated with them (Ca, Mg and others) (Table 26; Figure 28).

Factor 2 in PCA has a negative correlation with the first group of metallic element associations in Lake Padelis, such as K, Cr, Fe, Co, Ni, Cu. These elements have positive correlations among each other. The source of these elements can be a weathering of mineral matter; therefore, Factor 2 most likely indicates the source of organic matter in the lake.

Factor 3 has a positive correlation with Zn and a negative with Pb. Factor 4 is positively correlated with Pb; however, the relations of these two factors with environmental processes were not identified.

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Table 26

Results of PCA for the characteristic parameters of sapropel from Lake Padelis
(*in italic:* loadings above the critical threshold of 0.413, in bold: above 0.536)

Parameter	Factor 1	Factor 2	Factor 3	Factor 4
Eigenvalues	**16.33**	**6.46**	**1.52**	**0.92**
Total variance, %	**60.49**	**84.41**	**90.02**	**93.45**
Cumulative variance, %	**60.49**	**84.41**	**90.03**	**93.45**
Bulk density (BD), g/cm²	0.8372			
Moisture (MS), %	- 0.9250			
Mineral matter (MM), %	0.9836			
Organic matter (OM), %	- 0.9892			
Carbonates (CB), %	0.9374			
Na, µg/g	0.7721			
Mg, µg/g	0.8777			
K, µg/g		- 0.9757		
Ca, µg/g	0.9705			
Fe, µg/g		- 0.9293		
Cr, µg/g		- 0.9882		
Mn, µg/g	0.8256			
Co, µg/g		- 0.8984		
Ni, µg/g		- 0.9915		
Cu, µg/g		- 0.9687		
Zn, µg/g			0.7828	
Cd, µg/g	- 0.9678			
Pb, µg/g			- *0.5554*	0.5615
Humic substances, %	- 0.7962			
C, %	- 0.9064			
H, %	- 0.9725			
N, %	- 0.9445			
S, %	- 0.9276			
Biogenic phosphorus (P_{BIO}), µg/g	- 0.8542			

Lake Pilcine

Also, the element accumulation pattern for the sediments from Lake Pilcine discovered three separate well-recognized zones (Figure 29A).

For the first zone (200-400 cm corresponding to ~3,700-~7,400 cal BP), high concentrations of K, Fe, Cr, Co, Ni and Cu are characteristic. All these elements represent the main group of element associations in Lake Pilcine and positive bounds among the components and carbonates (Figure 29B).

For the second zone (130-200 cm corresponding to ~2,200-~3,700 cal BP), drop-down of meal concentrations (Na, Mg, K, K, Fe, Cr, Co, Ni, Cu and Zn) from bottom to top of the layer is characteristic, but the concentrations of Mn, Cd and Pb are not
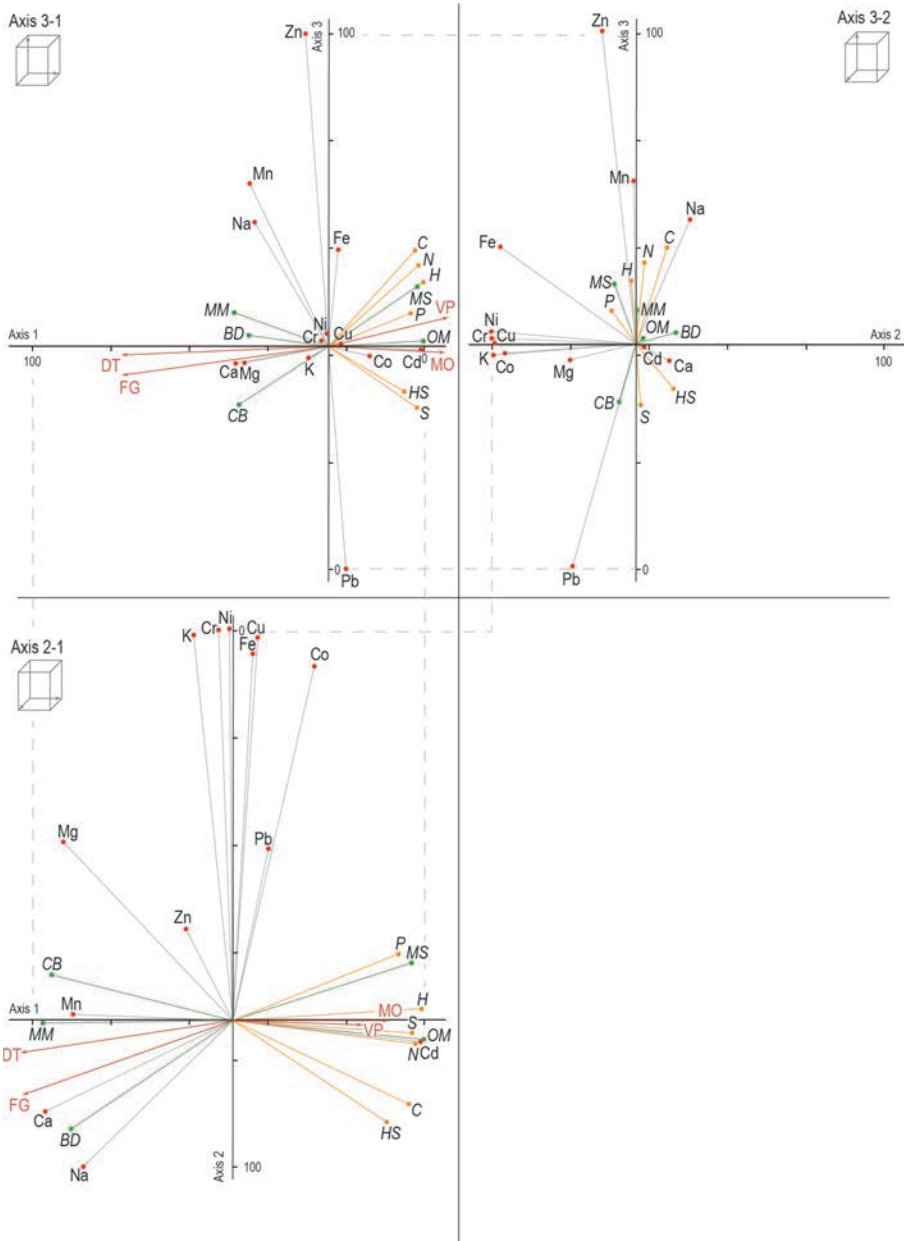
Figure 28. **The ordination of variables representing selected properties and elements detected for sapropel from Lake Padelis on the first three PCA axes**

fluctuating. These three elements form the second group of element association: they have a positive mutual correlation, as well as correlate positively with organic components (organic matter, biogenic P and humic substances).

The third zone (90-130 cm corresponding to ~1,300-~2,200 cal BP), reveal increase in concentrations for all investigated metallic elements. Concentrations
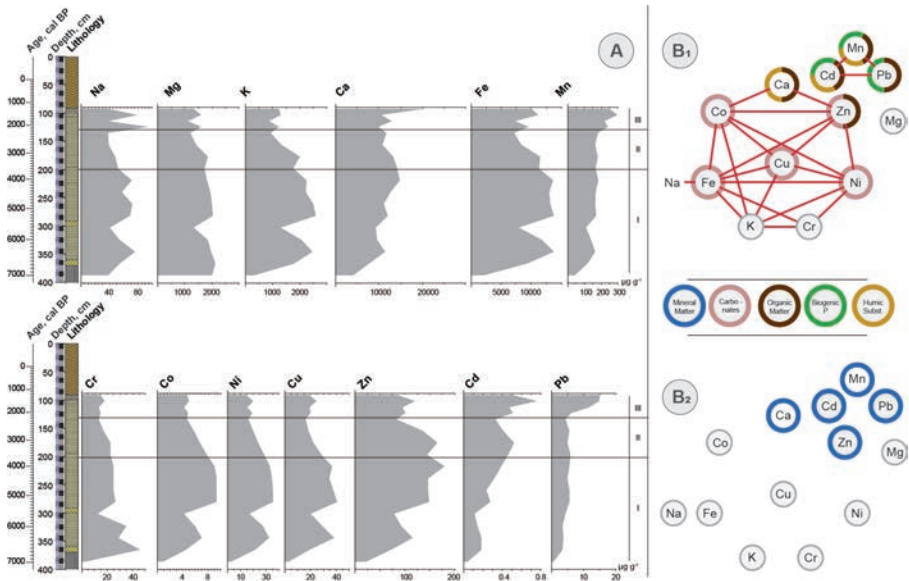
Figure 29. **(A) Distribution pattern of metallic elements in sapropel from Lake Pilcine. For the legend of the lithological section, see B; (B) Statistically significant correlation (P>0.01) of elements in sediments from Lake Pilcine: (B$_1$) positive correlation, (B$_2$) negative correlation**

of Ca, Mn, Cd and Pb reach much higher levels. In the third group of element associations, all elements from the second group are included (Mn, Cd, Pb), as well as Ca and Zn that form the group of metals with a negative correlation with mineral matter.

89.43% of the data used in PCA allowed the detection of four factors that can be used to explain the accumulation processes of metallic elements in sapropel from Lake Pilcine.

Variability of 54.04% of data in PCA can be explained with Factor 1 (Table 27). Factor 1 reveals good correlation with water content, the content of organic matter, the main components of sediment organic matter (CHN), the content of carbonates, biogenic phosphorus P$_{bio}$, as well as two groups of metals: 1) Fe, Co, Ni, Cu with good correlation among them; and 2) Ca, Mn, Zn, Cd and Pb which have a negative correlation with mineral matter, but a positive correlation with organic matter and its components (Figure 30). Studies revealed that in ashes of the sediments from the bottom layer of Lake Pilcine dominates silicates; thus, Factor 1 of PCA could be related to flows of silicate containing mineral matter (*e.g.*, clay particles) from the lake basin, as well as paludification of the lake.

Factor 2 demonstrates positive correlations with metals Mg, K, Cr, Ni, Cu, Co and Fe, but negative correlations with organic components of sediments (humic substances), P$_{bio}$ and metals (Mn and Cd) that correlated positively with the indicators of organic matter. Thus, it can be suggested that factor 2 explains the impact of terrigenous input to the lake. Factor 3 shows a positive correlation with Na and a negative correlation with S in organic substances. Factor 4 demonstrates correlation with humic substances, but its origin so far is hard to identify (Figure 30).

Table 27

Results of PCA for the characteristic parameters of sapropel from Lake Pilcine

(*in italic*: loadings above the critical threshold of 0.482, **in bold**: above 0.606)

Parameter	Factor 1	Factor 2	Factor 3	Factor 4
Eigenvalues	14.050	6.638	1.378	1.186
Total variance, %	54.038	25.531	5.300	4.561
Cumulative variance, %	54.038	79.568	84.868	89.429
Bulk density (BD), g/cm²	- 0.9356			
Moisture (MS), %	0.9315			
Mineral matter (MM), %	- 0.9485			
Organic matter (OM), %	0.9425			
Carbonates (CB), %	0.7727			
Na, µg/g			0.5266	
Mg, µg/g		0.8430		
K, µg/g		0.7687		
Ca, µg/g	0.8350			
Fe, µg/g	**0.7668**	*0.5927*		
Cr, µg/g		0.7139		
Mn, µg/g	**0.7543**	*- 0.4839*		
Co, µg/g	**0.7343**	*0.6015*		
Ni, µg/g	0.6700	0.7342		
Cu, µg/g	0.6855	0.6810		
Zn, µg/g	0.7940			
Cd, µg/g	**0.6385**	*- 0.5738*		
Pb, µg/g	- 0.5987			
Humic substances, %		- 0.7148		0.5455
C, %	0.9325			
H, %	0.9326			
N, %	0.9595			
S, %			- 0.6167	
Biogenic phosphorus (P_{BIO}), µg/g	0.6617	- 0.6765		

Lake Pilvelis

In the element accumulation pattern of sediments from Lake Pilvelis, four separate zones can be observed (Figure 31A):

The first zone (400-390 cm corresponding to ~10,100-11,800 cal BP) is formed from the mineral sediments with high concentrations of Mg, K, Fe, Cr, Co, Ni and Cu, as well as with low concentrations of Ca, Zn and Cd.

For the second zone (270-390 cm corresponding to ~6,800-~10,100 cal BP), the concentrations of Mg, K, Cr, Co, Ni are low, with a tendency to decrease from bottom to top. Also, the concentrations of Fe and Cu are low, but they do not decrease
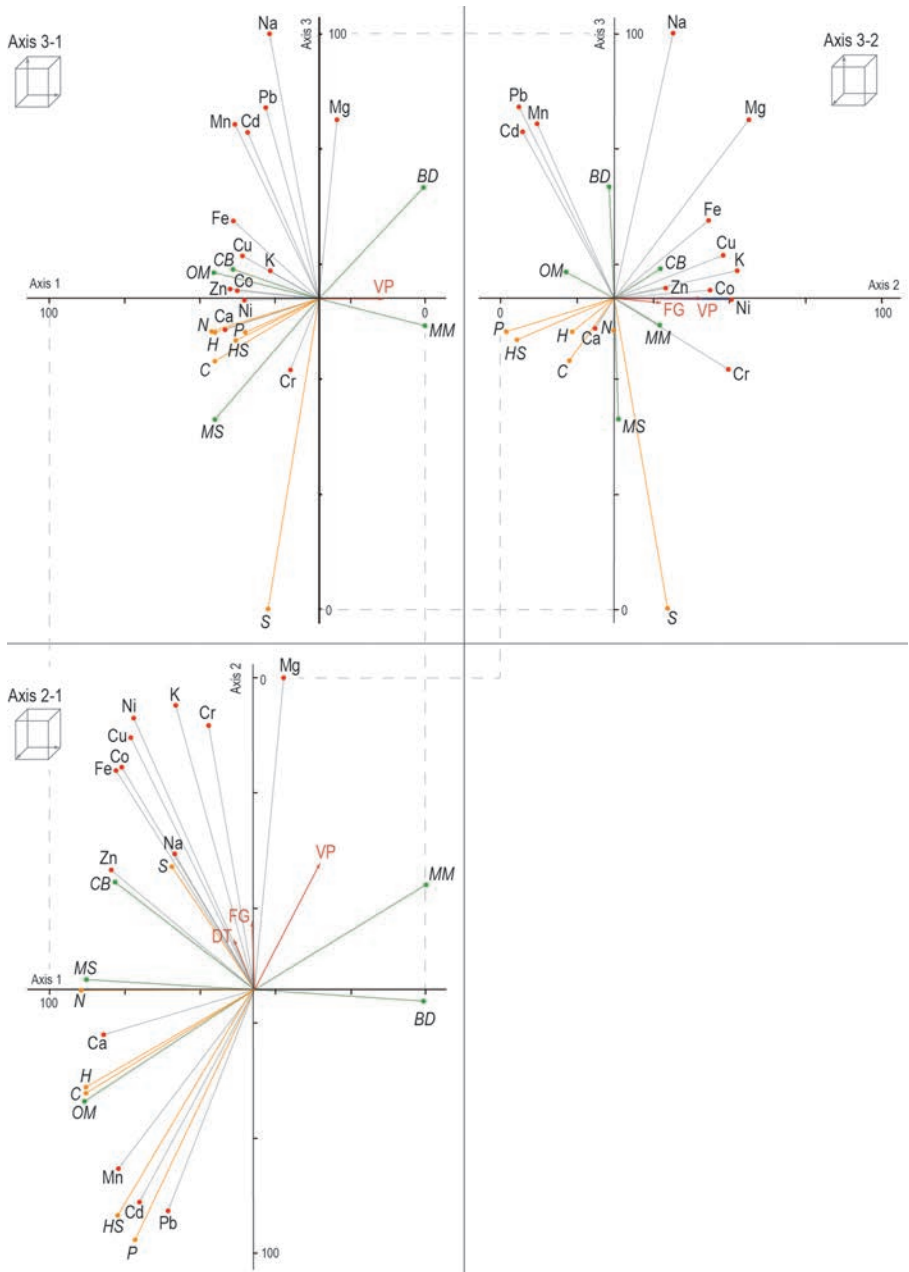
Figure 30. **The ordination of variables representing selected properties and elements detected for sapropel from Lake Pilcine on the first three PCA axes**

gradually from bottom to top. In sapropel of Lake Pilvelis, the first group of metallic element associations consists of metallic elements (K, Mg, Cr, Fe, Co, Ni) bound mutually and with mineral matter. Cu has a positive correlation with a part of the first group's elements like K, Cr, Co and Ni.
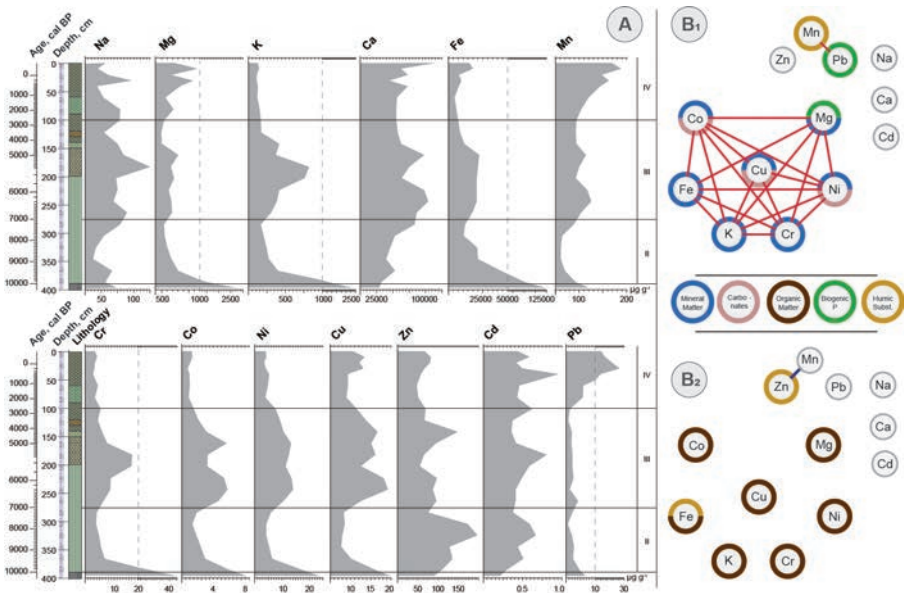
Figure 31. **(A) Distribution pattern of metallic elements in sapropel from Lake Pilvelis. For the legend of the lithological section, see C; (B) Statistically significant correlation (P>0.01) of elements in sediments from Lake Pilvelis: (B₁) positive correlation, (B₂) negative correlation**

For the third zone (100-270 cm corresponding to ~2,600-~6,800 cal BP), the concentrations of Zn, Cd and Pb decrease in comparison to deeper layers, but the concentrations of Na, Mg, K, Ca, Fe, Mn, Cr, Co, Ni, Cu increase. Content of mineral matter in this layer increases indicating that the element input in the lake could be related more to organic matter.

For the fourth zone (0-100 cm corresponding to ~2,600 cal BP until present), the concentrations of Mg, Ca, Fe, Mn, Cu, Zn and Pb increase in the upper 50 cm. Increase in concentrations of Ca, Mn and Pb leads to suppose that the source of these elements in the upper layer is human impact. The second group of element associations consists of metals (Mn, Zn and Pb) (Figure 31B). Pb has two positive bonds with Mn and total P. Mn has a negative correlation with Zn and a positive correlation with Pb and humic substances. Ca, Na and Cd have no statistically significant correlation with any of the analyzed components.

82.65% of the data used in PCA allowed the detection of four factors that can be used to explain the accumulation processes of metallic elements in sapropel from Lake Pilvelis (Table 28).

The parameters of Factor 1 (Table 28; Figure 32) change depending on the characteristics of sapropel composition, i.e., mineral matter versus organic matter, and this factor represents the input of mineral matter with the inflow from the catchment basin and air, and the productivity of biota in the lake and surrounding areas. Granulometric analysis of mineral particles in sapropel from Lake Pilvelis reveals that the size of mineral grains corresponds to the size of clay particles (0.001-0.0001 mm), which means that the composition of metallic elements in

sapropel is affected mainly by the composition of mineral matter, not by the size of particles.

Factor 2 is strongly positively loaded by Mn, Pb, humic substances and biogenic P and negatively loaded by the depth and Zn, N_{org} and S_{org}. Furthermore, the graphical depiction of statistical component correlation (Figure 32) reveals similar interconnection among these elements, i.e., Mn positively correlates with humic substances and Pb, Zn – with N_{org}. Both these components (Zn, N_{org}) reach the highest

Table 28

Results of PCA for the characteristic parameters of sapropel from Lake Pilvelis
(*in italic:* loadings above the critical threshold of 0.413, **in bold:** above 0.536)

Parameter	Factor 1	Factor 2	Factor 3	Factor 4
Eigenvalues	**14.464**	**5.327**	**2.682**	**1.497**
Total variance, %	**49.875**	**18.369**	**9.247**	**5.164**
Cumulative variance, %	**49.875**	**68.245**	**77.492**	**82.655**
Bulk density (BD), g/cm²	- 0.7116			
Moisture (MS), %	0.8546			
Mineral matter (MM), %	- 0.9542			
Organic matter (OM), %	0.9594			
Carbonates (CB), %	- 0.4957		- 0.4154	- 0.4224
Na, µg/g			- 0.5575	
Mg, µg/g	- 0.8744			
K, µg/g	- 0.9743			
Ca, µg/g			- 0.6678	
Fe, µg/g	- 0.9514			
Cr, µg/g	- 0.9596			
Mn, µg/g		0.8574		
Co, µg/g	- 0.8188		- 0.4142	
Ni, µg/g	- 0.8722			
Cu, µg/g	- 0.6559		- 0.4956	
Zn, µg/g		- 0.7793		
Cd, µg/g	0.4419			
Pb, µg/g		**0.6584**	*0.4561*	
Humic substances, %		0.8432		
C, %	0.8483			
H, %	0.7396			
N, %		- 0.7697		
S, %		- 0.5553		
Biogenic phosphorus (P_{BIO}), µg/g		0.4866	0.4918	- 0.4339
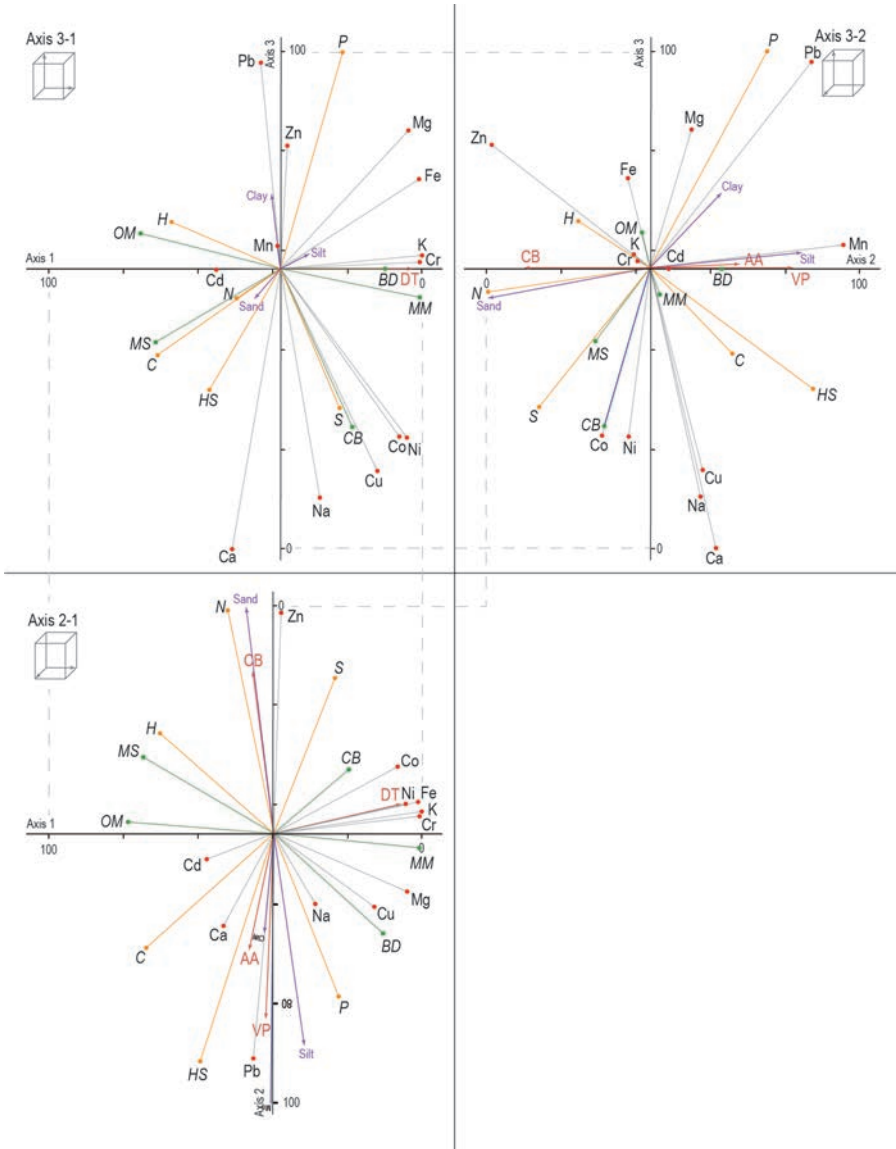
Figure 32. **The ordination of variables representing selected properties and elements detected for sapropel from Lake Pilvelis on the first three PCA axes**

concentration in samples of deeper sediment layers (380-240 cm corresponding to ~9,800-~6,100 cal BP), where the total amount of cyanobacteria has a strong correlation with Zn. Zn and N_{org} correlate negatively with Mn, which was detected in

higher concentration in the upper layers of sediments (0 cm to 100 cm corresponding to approximately last ~2,500 years), similarly to Pb. Such tendencies indicate that the inflow of Mn and Pb is connected with human activity, probably since ~3,200 cal BP. Higher concentrations of these elements in the upper layers of different lakes where for Mn and Pb that are not site-specific elements of the catchment areas; it probably shows that atmospheric pollution could be the main source of Mn and Pb in the lake (Shotyk *et al.*, 1998; Terasmaa *et al.*, 2013; Wolfe and Härtling, 1997).

Negative loadings by carbonates, Na, Ca, Co and Cu and positive loadings by Pb and biogenic phosphorus represent the third factor that can be associated with the changes in the lake catchment area such as lake eutrophication and bogging up of the lake catchment area during which metals were carried in with certain mineral substances.

Carbonates and biogenic P showed negative loading under the fourth factor that is not identified.

Statistically significant correlation shows a positive bond of organic S and cyanobacterial mat remains.

CONCLUSIONS

1. The Sapropel Classification System has been developed and adapted, considering the environmental conditions in Latvia. The classification system is based on the factors influencing the formation of sapropel, the composition and properties of sapropel, as well as the possibilities of its use. It includes information on the application fields of sapropel and expands knowledge on already known uses. The Sapropel Classification System can be applied as a matrix to characterize any sapropel derived in Latvia and identify prospective ways of application.

2. Based on the adapted Sapropel Classification System, the Freshwater Sapropel Database of sapropel resources has been developed, which reveals industrially significant sapropel deposits and their characteristics, the amount and typology of sapropel resources in lakes of Latvia. The database identifies prospective directions for the exploitation of sapropel, which can serve as a tool to support regional development, sustainable and economically justified use of natural resources and lake restoration options.

3. The in-depth complex paleolimnological research carried out in the lakes of the Latgale Upland determined the absolute age, lithological, biological and chemical composition and other parameters regarding lake sediments revealing the development of a lake ecosystem in the Holocene, as well as the nature of sapropel formation. The results allow concluding that in lakes of the Latgale Upland sapropel began to form in the early Holocene, i.e., before 11,700 cal BP. In the sediment profiles of all studied lakes, particular periods in 6,900-6,700 cal BP and 4,200-3,600 cal BP are well-marked when severe climate changes occurred. Obtained data allow identifying the intensity and significance of the anthropogenic impact, primarily indicating the changes in species and chemical composition, revealing the impact of agriculture and forestry on biological processes in lakes.

4. The set of multi-proxy analyses applied for detailed investigation of lake sediment profiles, including detection of P_{org}, elemental composition (C, H, N, O, S), the concentration of metallic elements (Na, K, Ca, Mg, Fe, Mn, Cu, Co, Ni, Pb, Cr, Cd and Zn), the content of mineral part, organic matter (including humic substances) and carbonates, characterizes the peculiarities and extent of sediment formation under the influence of various natural (direct and indirect) and anthropogenic factors, as well as the changes during the lake lifetime. The analysis of sediment chemical composition reflects the nature of geochemical processes in the sediment formation process, which results in the genesis of typical geochemical element associations according to the lake development phase, as well as reveals anthropogenic impact on lake ecosystems and the process of element accumulation.

5. The multi-proxy approach applied for the first time in Latvia to study the biological and chemical composition of lake sapropel in accordance with the developed Sapropel Classification System reveals the determination of optimal use, treatment and processing of sapropel as a natural resource, as well as provides a new understanding of the conditions of lake sediment formation and influencing factors.

6. The results of the research suggest that the potential for sapropel use depends on the conditions of sediment formation, mainly environmental factors and processes that affect the chemical composition of sapropel, including the accumulation of heavy metals during sapropel formation, which confirms the hypothesis.

ACKNOWLEDGMENT

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LATVIJAS UNIVERSITĀTE

ĢEOGRĀFIJAS UN ZEMES ZINĀTŅU FAKULTĀTE

Karina Stankeviča

SAPROPEĻA ĪPAŠĪBU RAKSTURS ATKARĪBĀ NO VEIDOŠANĀS APSTĀKĻIEM UN TĀ IZMANTOŠANAS IESPĒJAS

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Darba zinātniskie vadītāji:
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    Dr. geogr. **Laimdota Kalniņa**

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    2. Prof. *Dr.sc.ing.* **Ainis Lagzdiņš** (Latvijs Lauksaimniecības universitāte)
    3. Asoc. prof. *Dr.biol.* **Gunta Spriņģe** (Latvijas Universitāte)

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    6) Asoc. prof. *Dr.biol.* **Gunta Spriņģe**
    7) Doc. *Dr.geogr.* **Juris Burlakovs**
    8) Doc. *Dr.geogr.* **Oskars Purmalis**, promocijas padomes sekretārs

Promocijas darba aizstāvēšana notiks 2020. gada 30. oktobrī plkst. 11:00 Latvijas Universitātes Ģeogrāfijas un Zemes zinātņu fakultātes Promocijas padomes sēdē Jelgavas ielā 1, 702. telpā, Rīgā.
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Promocijas padomes sekretārs
    Dr.geogr. **Oskars Purmalis**
    Latvijas Universitāte
    Ģeogrāfijas un Zemes zinātņu fakultāte
    Raiņa bulvāris 19, LV-1586, Rīga
    e-pasts: oskars.purmalis@lu.lv

ANOTĀCIJA

Promocijas darbā tika pētītas sapropeļa īpašību un izmantošanas iespēju izmaiņas atkarībā no tā veidošanas apstākļiem, analizējot datus par sapropeļa iegulām visā Latvijā un detalizēti izpētot trīs ezeru (Padēlis, Pilcines ezers un Pilvelis) sapropeļa profilus.

Darba ietvaros tika izveidota saldūdens ezeru sapropeļa GIS datubāze un tika adaptēta sapropeļa tipu klasifikācija, ar mērķi sistematizēt un apkopot datus par sapropeļa pētījumiem visā Latvijā, noteikt kopējos resursa apjomus un veikt izpēti par sapropeļa resursu veidošanās raksturīgām iezīmēm, kā arī izvērtēt iespējamās sapropeļa izmantošanas jomas.

Lai raksturotu sapropeļa uzkrāšanās likumsakarības klimata un vides ietekmē, tika veikta trīs ezeru profilu izpēte, izmantojot multidisciplināru metožu pieeju, kas ietvēra nogulumu profila paleobotāniskā un ķīmiskā sastāva izpēti, kā arī nogulumu vecuma noteikšanu ar iespēju rekonstruēt vides un klimata apstākļus.

Rezultāti atklāj, ka Latvijas ezeros (kuru kopējais skaits ir vairāk nekā 2200) uz doto brīdi apzinātie sapropeļa krājumi ir aptuveni 975 miljoni m^3 jeb 530 tūkst. t (ar mitrumu 60%). Sapropeļa uzkrāšanās ir raksturīga ezeriem, kas veidojušies Augšpleistocēna nogulumos, turklāt sapropeļa tips ir atkarīgs no šo nogulumu rakstura. Sapropeļa iegulas ir raksturīgas glacigēnas izcelsmes ezeriem ar caurteces un noteces ūdens režīmu. Lielāko sapropeļa krājumu apjoms atrodas eitrofos un hipereitrofos ezeros. Sapropeļa veids un sastāvs atšķiras katras iegulas ietvaros un ir atkarīgs no ūdens ķīmiskais sastāva, dziļuma un temperatūras. Jaunākajos nogulumos ir novērotas augstākas metālu koncentrācijas, salīdzinot ar fona līmeni, kas tiek saistīts ar cilvēka darbības ietekmi.

Atslēgvārdi: *saldūdens sapropelis, gitija, sedimentu veidošanās apstākļi, holocēns, metālisko elementu akumulācija, putekšņi, makro- un mikroatliekas, malakofauna, Latvijas ezeri*

SATURS

IEVADS

Sapropelis ir viens no nozīmīgiem Latvijas nacionālajiem dabas resursiem. Tā apjoms ezeros ir vairāk nekā 500 miljoni tonnu (ar mitrumu 60%). Šie organogēnie ezera nogulumi ir veidojušies holocēnā pēdējos 11 000 gados un uzkrājušies ūdens vidē. Sapropelis ir nozīmīgs resurss gan Latvijas ekonomikai, gan ka dabas vēstures izpētes objekts, gan vides aizsardzības ietvaros. Tāpēc ir svarīgi uzlabot zinātnisko un sabiedrības izpratni par procesiem, kas notiek ūdenstilpēs, jo īpaši par faktoriem, kas ietekmē sedimentāciju un sedimentu sastāvu.

Ezera nogulumu zinātniskā izpēte ir aktuāla sekojošu iemeslu dēļ:

1. Ezera nogulumi ir pagātnes dabas arhīvs. Tie atspoguļo klimata, veģetācijas un zemes izmantošanas veidu pārmaiņas pagātnē, tādējādi nogulumu analīzi var izmantot kā instrumentu vides mainības rekonstrukcijai.

2. Nogulumu sastāva izmaiņas ezera attīstības laikā ir cieši saistītas ar to veidošanās vidi, paleoģeogrāfiskajiem un paleoekoloģiskajiem apstākļiem, ieskaitot ezera ūdens līmeņa svārstības, kā arī atklāj dabas notikumus, piemēram, vulkānu izvirdumus, meža ugunsgrēkus un cilvēku ietekmi.

3. Ezera nogulumu daudznozaru pētījumiem ir īpaša nozīme, lai izprastu klimata un vietējās vides izmaiņas laika gaitā, kas ietekmē sedimentācijas procesus un nogulumu īpašības, iemeslus un raksturu.

4. Ezeru nogulumos ir saistīts liels apjoms organiskā oglekļa, slāpekļa un fosfora savienojumu. Tādējādi ezeru nogulumus var uzskatīt par nozīmīgu dabas resursu ar plašu pielietojuma potenciālu. Ezera nogulumu praktiskā izmantošana ir nozīmīga dažādās nozarēs, ieskaitot lauksaimniecību, dārzkopību un mežsaimniecību, kā arī medicīnu vai kosmetoloģiju, kur sapropeli var lietot kā ārstnieciskās dūņas vai kā izejviela ķīmiskajā vai farmaceitiskajā ražošanā.

5. Ezeru nogulumu pētījumu rezultāti ļauj labāk izprast, kādi pasākumi būtu jāņem vērā ezeru ekosistēmas aizsardzībā, īpaši attiecībā uz ezeriem, kuri izzūd intensīvu aizaugšanas procesu un organisko nogulumu uzkrāšanās ietekmē.

Sapropelis ir nozīmīgs organiskā materiāla izejvielu avots. Tas ir daļēji atjaunojams zemes dziļu resurss, kas izveidojies kvartāra periodā. Šajā darbā termins "sapropelis" tiks izmantots, lai aprakstītu iekšzemes saldūdens nogulumus, kas ir bagāti ar organiskām vielām (organisko vielu saturs pārsniedz 15%) un kuri veidojas iekšzemes ūdenstilpēs bioloģisku un ķīmisku procesu rezultātā sadaloties atmirušu augu un ūdens organismu atliekām (Stankeviča *et al.*, 2017).

Promocijas darba hipotēze

Sapropeļa pielietošanas potenciāls ir atkarīgs no tā veidošanās apstākļiem, galvenokārt no ģeoloģiskajiem procesiem un vides faktoriem, kas ietekmē sapropeļa elementu sastāvu, tostarp, smago metālu uzkrāšanos sapropeļa veidošanās laikā.

Promocijas darba mērķis

Izpētīt saldūdens sapropeļa uzkrāšanās apstākļus ūdenstilpēs, metālisko elementu uzkrāšanās rakstūru un sapropeļa veidošanās ietekmi uz tā īpašībām un izmantošanas iespējām.

Promocijas darba uzdevumi

1. Pielāgot saldūdens sapropeļa klasifikācijas sistēmu Latvijas apstākļiem un izpētīt tās izmantošanas iespējas uz atsevišķu Latvijas ezeru piemēra;
2. Novērtēt sapropeļa pielietošanas potenciālu un izpētīt tā izmantošanas iespējas.
3. Izveidot saldūdens sapropeļa resursu datubāzi Latvijas ezeriem un novērtēt sapropeļa izmantošanas iespējas;
4. Veikt sapropeļa sastāva izpēti, izmantojot paleolimnoloģiskās un ķīmiskās izpētes metodes;
5. Analizēt un raksturot uzkrāto sapropeļa nogulumu sastāvu, ņemot vērā ģeoloģisko struktūru, ezera baseina teritorijas reljefu un ezeru ieplakas veidošanās rakstūru.

Promocijas darba novitāte

– Multiparametru metodes pieeja sapropeļa sastāva analīzē;
– Tika noteikts:
  ▪ Makroelementu un smago metālu uzkrāšanās raksturs sapropelī;
  ▪ Vides faktoru ietekme uz sapropeļa veidošanos;
  ▪ Sakarību identificēšana starp sapropeļa veidošanos un sastāvu.
– Izstrādāta sapropeļa resursu izpētes metodoloģija, izmantojot mūsdienīgas izpētes metodes;
– Veikta sapropeļa sastāva un ģeoloģiskās veidošanās apstākļu mijiedarbības izpēte, kas pielietojama resursu izmantošanas prognozēšanai.

Metodoloģijas raksturojums

Lai sasniegtu promocijas darba mērķi un izpildītu izvirzītos uzdevumus, autore izmantojusi metodes, kuras var iedalīt trīs grupās:

Ģeotelpiskā datu analīze – ļauj vispārīgi raksturot ezerus un sapropeli Latvijā, kā arī detāli raksturot pētāmo ezeru sateces baseinus.

Paleolimnoloģiskie un sapropeļa sastāva pētījumi – ļauj raksturot sapropeļa uzkrāšanās un sastāva izmaiņas laikā, ņemot vērā ezera attīstību un klimatu. Paleolimnoloģiskie pētījumi ietver oglekļa un svina datējumus, putekšņu un sporu, makro- un mikroatlieku, kā arī atsevišķiem paraugiem malakofaunas identificēšanu. Sapropeļa sastāva izpētē ietilpst karsēšanas zudumu analīze, elementsastāva, metālisko elementu kopējā daudzuma un humusvielu apjoma noteikšana.

Visiem datiem tika veikta statistikā analīze – Pīrsona korelācija, galveno komponentu analīze un izkliedes diagrammas.

Promocijas darba rezultātu aprobācija

Promocijas pētījuma rezultāti ir aprobēti 23 zinātniskās publikācijās, no kurām 12 ir indeksētas SCOPUS un Web of Science zinātniskās literatūras datu bāzēs, apspriesti 24 ziņojumos starptautiskās zinātniskās konferencēs, 17 referātos vietēja mēroga konferencēs Latvijā; izstrādāts 1 patents.

Zinātniskās publikācijas:

1. **Stankevica, K.**, Vincevica-Gaile, Z., Klavins, M., Kalnina, L., Stivrins, N., Grudzinska, I., Kaup, E. (2020). Accumulation of metals and changes in composition of freshwater lake organic sediments during the Holocene. *Chemical Geology, 539*, 119502, https://doi.org/10.1016/j.chemgeo.2020.119502 (SCOPUS; Web of Science)

2. **Stankevica, K.**, Vincevica-Gaile, Z., Klavins, M. (2019). Role of humic substances in agriculture and variability of their content in freshwater lake sapropel. *Agronomy Research, 17*(3), 850-86, https://doi.org/10.15159/AR.19.094 (SCOPUS; Web of Science)

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5. Purmalis, O., **Stankeviča, K.** (2017). Radiolokācijas pielietošana sapropeļa iegulu izpētē [Sapropel deposits exploration using radiolocation approach]. Kļaviņš, M. (Red.) *Kūdra un sapropelis – ražošanas, zinātnes un vides sinerģija resursu efektīvas izmantošanas kontekstā* (132-137 lpp.). Rīga: Latvijas Universitāte.

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7. **Stankeviča, K.**, Kļaviņš, M., Kalniņa, L. (2017). Sapropeļa definīcija un klasifikācijas iespējas [Sapropeľs definition and classification options]. Kļaviņš, M. (Red.) *Kūdra un sapropelis – ražošanas, zinātnes un vides sinerģija resursu efektīvas izmantošanas kontekstā* (165-168 lpp.). Rīga: Latvijas Universitāte.

8. **Stankevica, K.**, Vincevica-Gaile, Z., Muter, O., Klavins, M. (2016). Physiological response of bacteria consortium to the presence of intact and autoclaved freshwater sapropel (gyttja) derived in the eastern Latvia. In Méndez-Vilas, A. (Ed.), *Microbes in the Spotlight: Recent Progress in the Understanding of Beneficial and Harmful Microorganisms* (pp. 110-115). Boca Raton: BrownWalker Press.

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13. **Stankevica, K.**, Vincevica-Gaile, Z., Muter, O. (2014). Microbial community analysis of sapropel (gyttja) derived from small overgrowing lakes in the eastern Latvia. In J. Truu, U. Kalnenieks (Eds.), *Soil ecosystem health and management of contaminated sites: Special issue of the 2nd Conference of Baltic Microbiologists* (pp. 66-82). Tartu: Tartu University.

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Patents

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1. PĒTĪJUMA TEORĒTISKAIS PAMATOJUMS

Sapropelis ir organogēni nogulumi, kuri uzkrājušies ūdens vidē, stāvošās vai lēni caurtekošās ūdenstilpēs, veidojušies no ūdensaugu un dzīvnieku organismu atliekām, kā arī no ūdenstilpē esošām vai no sateces baseina ienestām minerālo vielu daļiņām (Lopatin, 1983; Lopotko, 1974). Sapropelis ir zemes dziļu resurss, kas pēc tā ieguves daļēji un lēni atjaunojas. Sapropeļa veidošanās ir atkarīga no procesiem, kas norit ūdenstilpēs, un tā veidošanās norisinās vielu un enerģijas cirkulācijas pārrāvumu dēļ (Kurzo, 1988). Dažādu atradņu sapropeļa sastāvs un īpašības ir ļoti atšķirīgas; to nosaka konkrētās ūdenstilpes produktivitāte, fizioģeogrāfiskie apstākļi, hidroloģiskais režīms, virszemes noteces un gultnes īpatnības, kā arī klimatiskie apstākļi. Par sapropeli pieņemts uzskatīt saldūdens nogulumus ar organisko vielu saturu augstāku par 15%; ja organisko vielu saturs ir zemāks, tad šie nogulumi tiek dēvēti par augsti pelnainiem ezera nogulumiem. No kūdras sapropelis atšķiras ar smalku struktūru, vides reakciju, organisko vielu daudzumu, veidotājorganismiem un humusvielu daudzumu.

Baltijas valstu teritorijā nogulumi ar organisko vielu piemaisījumu, tai skaitā sapropeli, sāka veidoties pirms 12-15 tūkstošiem gadu (Zelčs and Markots, 2004), ledājam atkāpjoties un klimatam kļūstot siltākam. Masveida sapropeļa veidošanās norisinās holocēnā (no 11 700 kal.g.p.m.) līdz mūsdienām (Heikkilä and Seppä, 2010; Klavins *et al.*, 2011; Ozola *et al.*, 2010; Stančikaitė *et al.*, 2009, 2015; Stankevica *et al.*, 2015; Stivrins, 2015; Stivrins *et al.*, 2014, 2015, 2019; Terasmaa *et al.*, 2013).

Vienotu terminu un klasifikācijas ieviešana ezeru nogulumiem ir sarežģīta, jo katra zinātnes nozare ir izveidojusi savu terminoloģiju un klasifikāciju, kas atbilst tās pētījumu virzienam un mērķiem (Braksh, 1971; Lundquist, 1927; Titov, 1950). Izvērtējot sapropeli kā resursu piemērotākas klasifikācijas ir balstītas uz sapropeļa sastāvu (BSSC Institute, 2010; Kireicheva and Khokhlova, 1998; Pidoplichko and Grishchuk, 1962).

Sapropeļa sastāvā ietilpst trīs izcelsmes veidu vielas. Galvenais avots ir organismu atliekas no ezera teritorijas – planktons, bentoss un makrofīti. Otrs avots ir alohtonas izcelsmes organiskas, minerālas vielas un organiski-minerālais materiāls, kas tiek ienests ezerā ar gaisa plūsmām, nokrišņiem, noteci un gruntsūdeņiem. Trešā vielu grupa ir tās, kas nogulsnējas ezera pamatnē ķīmisku un fizikāli-ķīmisko procesu rezultātā (Bambalov, 2013).

Organisko vielu komplekss ir sapropeļa svarīgākā sastāvdaļa, kas veido organisko komponentu summu. Tās var iedalīt molekulāros organiskos savienojumos (proteīni, ogļhidrāti, humīnskābes, vitamīni un enzīmi) un hidrobiontu neizšķīdušās atliekās, kuras satur celulozi, fosforu, kāliju un kalciju (Stankeviča un Klaviņš, 2013).

Sapropelis satur gan ķīmiski nesaistītas, gan saistītas minerālvielas – karbonātus, silikātus, dzelzs hidroksīdu u.c. Nesaistītas minerālvielas tiek pieskaitītas pie sapropeļa balastvielām. Minerālvielas, kas ķīmiski saistītas ar organiskajām vielām, sapropelī veido sarežģītu bioloģiski aktīvo vielu kompleksu. Atkarībā no atradnes vietas sapropelis var būt stipri atšķirīgs gan pēc mineralizācijas pakāpes (pelnu satura), gan organiskās masas grupu sastāva un minerālvielu satura – šie ir būtiski parametri, kas nosaka sapropeļa iegulu izmantošanas potenciālu.
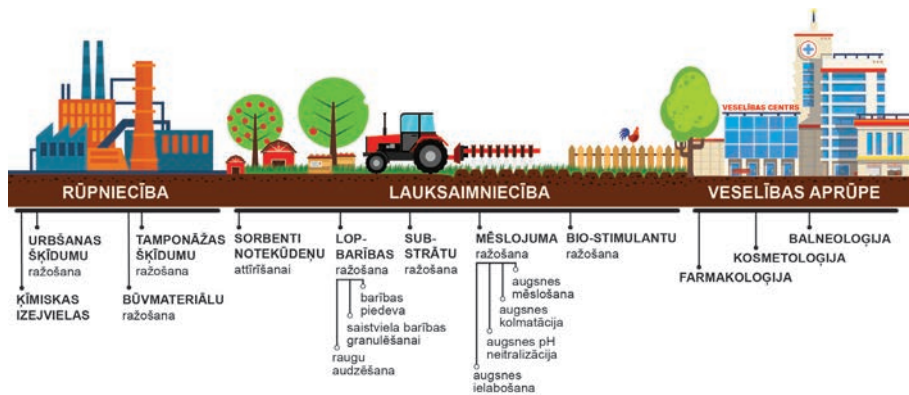
1. attēls. **Sapropeļa izmantošanas iespējas**

Sapropelim ir plašas izmantošanas iespējas (1. attēls). To var izmantot praktiski jebkurā tautsaimniecības jomā, taču tā lielā dažādība un zemais izpētes līmenis traucē racionāli iegūt gaidāmos rezultātus.

Latvijā sapropeli plaši izmanto lauksaimniecībā kā mēslojumu un lopkopībā kā dzīvnieku barības piedevu, taču apzinātās sapropeļa izmantošanas iespējas ir daudz plašākas un ietver arī šādas sfēras:

–   Lauksaimniecība un lopkopība – kaļķošana, mēslojums, vitamīnu-minerālā barība, zaļā masa;
–   Būvniecības un celtniecības industrija:
    ▪   saistviela celtniecības kompozītmateriāliem, piemēram, skaidu plāksnēm;
    ▪   saistviela siltumizolācijas kompozītmateriāliem, piemēram, siltumizolācijas plāksnēm;
    ▪   sapropeļbetons;
    ▪   poru materiāls celtniecības materiāliem, piemēram, drenu caurulēm un ķieģeļiem.
–   Ķīmiskā rūpniecība – plastmasas, fenoli, šķīdinātāji, amonjaks, eļļas, lakas, parafīns, metilspirts;
–   Kalnrūpniecība (zemes dziļu derīgo izrakteņu ieguve):
    ▪   flotācijas reaģents rūdas bagātināšanai;
    ▪   viskozitātes samazinātājs urbšanas darbos;
–   Enerģētika – cietais kurināmais, šķidrais kurināmais, kokss, gāze;
–   Medicīna un veterinārā medicīna – ārstnieciskās dūņas un aplikācijas, ārstnieciskie ūdeņi un preparāti, farmaceitiskie materiāli.

2. MATERIĀLI UN METODES

2.1. Pētījuma teritorija un detalizētās izpētes vietas

Darba ietvaros izveidotā **saldūdens sapropeļa resursu datubāze** satur informāciju par ezeriem un purviem, kas bija iekļauti kompleksās ģeoloģiskās izpētes ekspedīciju pārskatos (GEO-Konsultants, 1995, 1996, 1997, 1998a, 1998b, 1999; Latvijas Geologija, 1994; Latvgeologija, 1991a, 1991b, 1992), kā arī citos avotos (Braksh *et al.*, 1967; Leinerte, 1988). Sapropeļa datubāze tika izveidota, lai raksturotu sapropeli kā Latvijas nacionālo stratēģisko resursu, noteiktu tā daudzumu un izvietojumu valstī, kā arī identificētu noteicošos vides faktorus sapropeļa atradņu veidošanai. Pēc sapropeļa datubāzes datiem, Latvijā ir 2200 ezeri. Līdz šim sapropeļameklēšana ir veikta 1286 ezeros, kas atbilst apmēram 55% no visa Latvijas ezeru skaita (2. attēls).
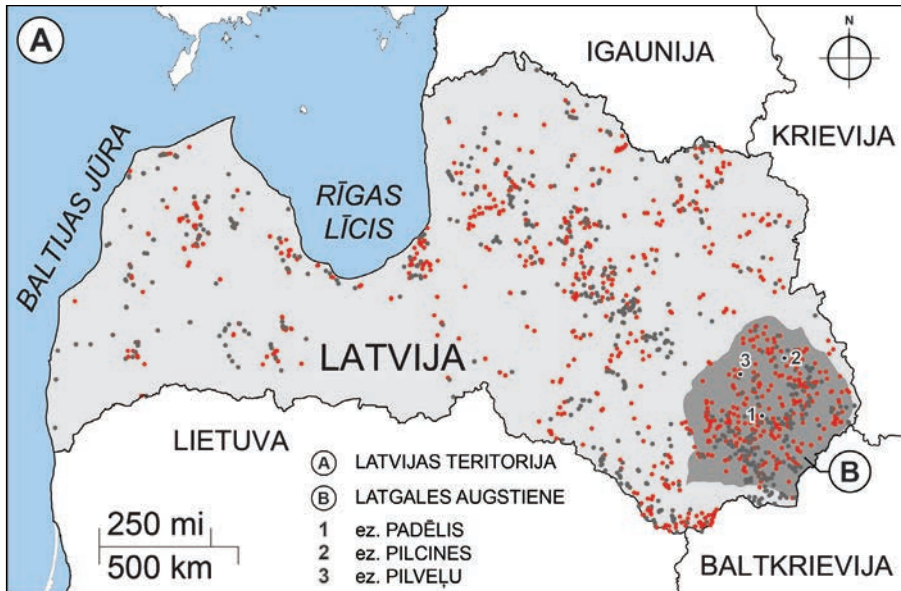
2. attēls. **(A) Izpētes vietu izvietojums Latvijas teritorijā: sarkanie punkti – rūpnieciski nozīmīgas sapropeļa atradnes, pelēkie punkti – sapropeļa iegulas, kas netika atzītas par rūpnieciski nozīmīgām; (B) Latgales augstiene ar detāli pētītām sapropeļa iegulām izvēlētajos ezeros: 1. Padēlis, 2. Pilcines ezers, 3. Pilvelis**

Lai detalizēti raksturotu vides apstākļu ietekmi uz dažāda tipa – karbonātiska, klastiska un organogēna – sapropeļa īpašībām, sastāvu un izmantošanas iespējām, raksturojot klimatu un ezera attīstības stadijas, tika izvēlēti trīs ezeri, kas atrodas Latgales augstienē (2. attēls) – Padēlis, Pilcines ezers un Pilvelis. Sākotnējie dati par sapropeļa iegulām un to raksturojumu tika iegūti izmantojot saldūdens sapropeļa pases (GEO-Konsultants, 1998b).

2.2. Sapropeļa datubāze

Sapropeļa datubāze ir sagatavota ĢIS vidē ESRI Shapefile formātā LKS-92 TM koordinātu sistēmā ar mēroga noteiktību 1:5 000 un UTF-8 rakstzīmju kodējumu, un

sastāv no diviem slāņiem. Ezeru poligona slānis tika izveidots par pamatu izmantojot ĢIS Latvija 10.2 brīvpieejas datubāzes ūdenstilpju slānī (Envirotech, 2013). Izveidotajā slānī ir iekļauta informācija par datubāzes objekta – ezera – parametriem, kas tika iegūti no kompleksās ģeoloģiskās izpētes ekspedīciju datiem, kā arī *www.ezeri.lv* datubāzē publicētas informācijas.

Ezeri, kas nebija iekļauti ĢIS Latvija ūdenstilpju slānī, tika ievietoti no jauna izveidotā slānī, kombinējot datus no ortofoto un lielmēroga topogrāfiskajām kartēm (ORTOFOTO 3 NIR, 2009; TOPO 10K PSRS, 1963).

2.3. Analītiskās metodes un sedimentu vecuma noteikšana

Ezeru sapropeļa bioloģiskā un ķīmiskā sastāva izpētei tika izmantota multiparametru metodes pieeja, kas ļauj raksturot sastāva izmaiņas visa sapropeļa profilā un saistīt tās ar ezera attīstības un vides faktoru izmaiņām. Paraugu apjoms, vieta un analīžu metodes ir uzskaitītas 1. tabulā.

1. tabula

Sapropeļa paraugu skaits, kas tika izmantoti sapropeļa sastāva analīzei ar dažādām analītiskām metodēm

Nr.	Analītiskā metode	Paraugu skaits ezeros			Atsauce uz izmantoto analītisko metodi
		Padēlis	Pilcines	Pilvelis	
Bioloģiskas metodes					
1	Sporu-putekšņu	30	30	40	Stankevica *et al.*, 2015
2	Augu makroatlieku	30	30	40	Stankevica *et al.*, 2015
3	Mikroatlieku	30	40	40	Stankevica *et al.*, 2015
4	Malakofaunas	30	-	-	Miller and Tevesz, 2001
Fizikāli-ķīmiskas metodes					
5	Vielas blīvums	30	40	40	Grossman *et al.*, 2002
6	Karsēšanas zudumu analīze	30	40	40	Stankevica *et al.*, 2015
7	Elementsastāvs	15	17	20	Stankevica *et al.*, 2012
8	Humusvielu daudzums	30	30	40	Stankevica *et al.*, 2019
9	Metālu kopējais daudzums	15	17	25	Stankevica *et al.*, 2020
10	Biogēnā fosfora daudzums	30	30	40	Johengen, 1996
11	Granulometriskā analīze	-	-	40	Last, 2001

Padēļa, Pilcines un Pilveļu ezeru sapropelim tika veikta vecuma noteikšana: slāņos, kas dziļāki par 1 m tika veikta konvencionālā radioaktīvā oglekļa (^{14}C) izotopu datēšana, virsējam nogulumu metram ^{210}Pb datēšana.

2.4. Datu statistiskā apstrāde

Izmantojot PC-ORD 7 datubāzes rezultātus, kā arī analītisko metožu iegūtos rezultātus tika veikta datu statistiskā apstrāde, izveidotas izkliedes diagrammas, veikta Pīrsona korelācija un galveno komponentu analīze (PCA).

3. REZULTĀTI UN DISKUSIJA

3.1. Saldūdens sapropeļa tipoloģija, daudzums un izplatība Latvijas teritorijā

Lai attīstītu inovatīvas resursu izpētes metodes, izmantojot ĢIS programmatūru, kā arī lai informācija par ezeru sapropeļa resursu izvietojumu un krājumiem Latvijā kļūtu pieejama sabiedrībai, turklāt lai tiktu apzinātas perspektīvas sapropeļa rūpnieciskās iegulas, datus bija nepieciešams digitalizēt, izstrādājot un izveidojot digitālo datubāzi.

Jaunu datu pievienošanai, kā arī papildināšanai izstrādātajā datubāzē ar mērķi novērtēt sapropeļa izmantošanas ekonomisko potenciālu, autore piedāvā **sapropeļa definīciju** un **pielāgoto saldūdens sapropeļa klasifikācijas sistēmu**, ko ezeru sapropeļu atradņu meklēšanas darbos un krājumu novērtēšanā izmantoja derīgo izrakteņu ģeoloģiskās izpētes ekspedīcijās Latvijā (GEO-Konsultants, 1995; Latvgeologija, 1991a, 1991b, 1992; Latvijas Geologija, 1994).

Piedāvātā sapropeļa definīcija: *saldūdens sapropelis ir subfosili, koloidāli kontinentālo ūdenstilpju nogulumi ar smalkgraudainu vai želejveida struktūru, kas satur 15% un vairāk organisko vielu, kuras veido ūdens augu organismu atliekas ar pārsvarā nelielu neorganiskas izcelsmes komponentu saturu*.

Autores izstrādātā **saldūdens sapropeļa klasifikācija** organiskos nogulumus iedala *Tipā, Klasē* un *Veidā* pēc pelnu (Ac) procentuālā satura sausnā, Ca un Fe kopējā satura (g/kg sausnas), mikroatlieku un mineraloģiskā sastāva (2. tabula).

Sapropelis kā resurss ir ietverts cietā kurināmā grupā, kurā ietilpst kūdra, koks, lignīns (Podgorodetskii *et al.*, 2015), tāpēc sapropeļa veida noteikšanai autore piedāvā izmantot pasaulē atzītas un pārbaudītas metodes: pelnu satura noteikšana (LVS/ STK/38, 2011), Ca un Fe kopējais saturs sausnā (Vincēviča-Gaile, 2014), mikroatlieku analīze (Stankevica *et al.*, 2015), granulometriskā sastāva noteikšana (Last, 2001).

Saldūdens sapropeļa datubāze tika izstrādāta, lai sistematizētu un apkopotu pieejamo informāciju par ezeru sapropeļa meklēšanas darbu rezultātiem. Pēc iegūtajiem datiem Latvijā ir 2200 ezeri, kas lielāki par 3 ha. Līdz šim sapropeļa meklēšana ir veikta 1286 ezeros (ap 55% no visiem Latvijas ezeriem) (2. attēls).

Kopējais apzinātais ezeru sapropeļa apjoms visā Latvijas teritorijā sastāda 974 982,2 tūkst. m³ (527 938,5 tūkst. t ar mitrumu 60%), no tiem par rūpnieciski nozīmīgiem sapropeļa krājumiem ir atzīstami 712 213,3 tūkst. m³ jeb 287 746,3 tūkst. t.

Latvijas teritorijā ezeru izvietojums ir nevienmērīgs; lielā daļa Zemgales līdzenuma ezeru praktiski nav – ezeri aizņem tikai 0,47% no Zemgales plānošanas reģiona (PlR) platības. Savukārt Mērsraga, Liepājas, Babītes novados ezeru blīvums attiecībā pret novada teritoriju ir lielāks par 20%, ko nosaka lielu ūdenstilpju – Engures, Liepājas un Babītes ezera – izvietojums šajās teritorijās.

Attiecībā pret kopējo teritoriju, lielākais ezeru izvietojuma blīvums ir Latgales PlR (3,27%), tam seko Kurzemes (1,54%), Rīgas (1,21%) un Vidzemes (1,03%) PlR.

Saldūdens sapropeļa klasifikācija

Tips	Klase	Veids	Apzīm.	Pelnai-nība, %	g/kg sausna Ca	g/kg sausna Fe	Mikroatliekas, mineroloģiskais sastāvs, %, %		Izmantošanas iespējas
Biogēns	Organogēns (O)	Kūdrains					vaskulārie augi	>35	humusvielu preparāts, augšanas stimulators, saistviela, mēslojums
		Zoogēns					dzīvnieki	>15	ārstnieciskās dūņas, mēslojums, bioloģiski aktīvo vielu avots, ķīmiskās pārstrādes izejviela
		Dažādaļģu		<30	<60	<140	aļģu summa	>45	
		Zilaļģu					zilaļģes	>35	saistviela, urbšanas šķīdums, ārstnieciskās dūņas, mēslojums
		Zaļaļģu					zaļaļģes	>35	
	Kramaļģu (Kr)	Kramaļģu		<65	<60	<140	kramaļģes	>35	augšanas stimulators, ārstnieciskās dūņas, mēslojums
Silikātu	Organogēni-silikātisks (OS)	Organogēni- smilšains					organic remains sand	40 >30	mēslojums, ārstnieciskās dūņas, urbšanas šķīdums, ķīmiskās pārstrādes izejviela
		Organogēni-aleirītisks					organic remains silt	40 >30	
		Organogēni-mālains		30-65	<60	<140	organic remains clay	40 >30	
		Kramaļģu-smilšains					diatoms sand	<20 >30	ārstnieciskās dūņas, ķīmiskās pārstrādes izejviela
		Kramaļģu-aleirītisks					diatoms silt	<20 >30	
		Kramaļģu-mālains					diatoms clay	<20 >30	

Diagnostikas pazīmes

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Saldūdens sapropeļa klasifikācija

Tips	Klase	Veids	Apzīm.	Diagnostikas pazīmes						Izmantošanas iespējas
				Pelnai-nība, %	g/kg sausna		Mikroatliekas, minerologiskais sastāvs, %, %			
					Ca	Fe				
Silikātu	Silikātu (Si)	Smilšains		65-85	<60	<285	smilts	30-50		augsnes ielabotājs
		Aleirītisks					aleirīts	30-50		
		Mālains					māls	30-50		
		Organogēni-karbonātisks		<30	60-140	<140	org. atl.*	40		mēslojums, dzīvnieku barības piedeva, ķīmiskās pārstrādes izejviela
							kalcīts	<20		
		Smilšaini-karbonātisks		30-65	60-140	<140	kalcīts	<20		mēslojums, augsnes kaļķošanas materiāls
							smiltis	30-50		
		Aleirītiski-karbonātisks					kalcīts	<20		
							aleirīts	30-50		
	Karbonātu (Kar)	Mālaini-karbonātisks					kalcīts	<20		
							māls	30-50		
		Karbonātiski-smilšains		65-85	60-140	<140	kalcīts	<20		augsnes ielabotājs
							smiltis	>50		
		Karbonātiski-aleirītisks					kalcīts	<20		
							aleirīts	>50		
Karbonātu		Karbonātiski-mālains					kalcīts	<20		
							māls	>50		
		Karbonātisks		<85	>140	<140	kalcīts	>20		kaļķošanas materiāls ārstnieciskās dūņas, barības piedeva

Saldūdens sapropeļa klasifikācija

Tips	Klase	Veids	Apzīm.	Pelnai-nība, %	g/kg sausna Ca	g/kg sausna Fe	Mikroatliekas, mineroloģiskais sastāvs, %, %	%, %	Izmantošanas iespējas
	Dzelzi saturošais (Dz)	Organogēni-dzelžains		<65	<60	140-285	limonits	5-10	mēslojums
		Karbonātiski-dzelžains		<65	60-140	140-285	limonits	5-10	augsnes kaļķošanas materiāls, ārstnieciskās dūņas
		Dzelžaini-karbonātisks		<85	>140	140-285	limonits	5-10	augsnes kaļķošanas materiāls
		Dzelžains		<85	<140	>285	limonits	>10	netiek izmantots
	Sēru saturošais (Se)	Sēru saturošais		<85	<140	<140	sulfīdi	>10	netiek izmantots
Jauktais	Jauktais (J)	Organogēni silikātu karbonātisks		<30	60-140	<140	silikāti kalcīts sulfīdi	<10	mēslojums, urbšanas šķīdums, ārstnieciskās dūņas
		Silicate karbonātiski dzelžains		<30	60-140	140-285	sulfīdi	<10	urbšanas šķīdums, saistviela, ārstnieciskās dūņas
		Organogēni silikātu dzelžains		<30	<140	140-285	sulfīdi	<10	ārstnieciskās dūņas
		Organogēni karbonātiski sēru saturošais		<30	60-140	<140	sulfīdi	>10	ārstnieciskās dūņas

Sapropeļa resursu meklēšanas darbi vispilnīgāk veikti Latgales PlR, kur no 958 ezeriem ir izpētīti 590 ezeri jeb 61,58%, Kurzemes PlR no 395 ezeriem sapropeļa meklēšanas/izvērtēšanas darbi veikti 121 ezerā, Vidzemes PlR no 583 ezeriem 356 ezeros, Rīgas PlR – 132 (244) ezeros, Zemgales PlR – 84 (185) ezeros (3. tabula).

3. tabula

Informācija par sapropeļa atradnēm un kopējiem sapropeļa krājumiem Latvijā

	Latgale	Kurzeme	Vidzeme	Rīga	Zemgale	Latvija
PIR teritorijas platība, km²	14,564.9	13,598.5	15,251.2	10,440.1	10,734.2	64,588.9
Kopējais ezeru skaitss	958	393	583	244	185	2363
Ezeru kopējā platība, km²	475.8	209.9	156.4	126.1	50.4	1018.6
Sapropeļa atradņu skaits	590	121	356	132	84	1283
Sapropeļa atradņu platība, km²	457.1	164.1	144.9	107.9	37.9	911.3
Sapropeļa atradņu izpētes pakāpe, %	61.58	30.63	61.06	54.09	45.40	54.30
Apzināto sapropeļa krājumu apjoms, tūkst. m³	414,403.3	73,117.7	240,741.2	154,415.0	92,305.0	974,982.2
Apzinātie sapropeļa resirsi, tūkst. ᵗ	184,902.9	53,582.2	141,035.1	109,199.2	39,219.1	527,938.5
Rūpnieciski nozīmīgo sapropeļa krājumu apjoms, tūkst. m³	338,818.3	28,723.1	188,643.7	76,456.0	60,714.0	693,355.1
Rūpnieciski nozīmīgo sapropeļa resursi, tūkst. t	114,769.0	16,268.9	96,946.9	37,189.8	13,848.4	279,023.0

Latgales PlR ir pieejams vislielākais apzinātais kopējais sapropeļa krājumu apjoms 414 403,3 tūkst. m³ (184 902,9 tūkst. t), no kuriem 338 818,3 tūkst. m³ (114 769,0 tūkst. t) ir pieskaitīti pie rūpnieciski nozīmīgiem sapropeļa resursiem, kas pēc apjoma veido 48,86 % no visiem apzinātajiem rūpnieciski nozīmīgajiem sapropeļa krājumiem valstī. Aiz Latgales PlR seko Vidzemes PlR, kura apzināti rūpnieciski nozīmīgi sapropeļa krājumi pēc apjoma veido 27,21 %. Vismazākie sapropeļa krājumi ir Kurzemes PlR – 73 117,7 tūkst. m³ (53 582,2 tūkst. t), no kuriem rūpnieciski nozīmīgi ir tikai 28 723,1 tūkst. m³ (16 268,9 tūkst. t), kas ir tikai 4,14% no visiem rūpnieciski nozīmīgiem sapropeļa krājumiem valstī.

Vērtīgākais ar plašākām izmantošanas iespējām ir organogēnas klases sapropelis, kura kopējais apjoms ir 18,68% no visiem sapropeļa krājumiem. Arī šī sapropeļa lielākie krājumi atrodas Latgales PlR (44,43%) un Vidzemes PlR (23,10%) (4. tabula).

Kaut gan Kurzemes PlR ezeru platība aizņem 1,54% no reģiona teritorijas, sapropeļa krājumi ir viszemākie – kopējais apjoms ir ap 70 milj. m³, turklāt 47,86% šo resursu sastāda silikātu sapropelis, kam ir zems izmantošanas potenciāls.

Sapropeļa resursu sadalījums pēc apjoma Latvijas plānošanas reģionos

Plānošanas reģions	O	Kr	OS	Si	Kar	Dz
Latgales	80 924,6	-	265 253,3	43 628,6	19 794,8	4 797,0
Kurzemes	4 819,1	320,0	23 686,9	34 997,2	7 271,9	2 022,6
Vidzemes	42 080,0	3 187,0	109 753,8	11 241,3	8 265,3	66 213,8
Rīgas	19 984,0	-	35 327,0	63 172,0	17 335,0	18 597,0
Zemgales	34 330,0	794,0	51 276,0	1 917,0	3 720,0	268,0
Kopā Latvijā	18 2137,0	4 301,0	485 296,9	154 956,1	56 386,9	91 898,4

Arī Rīgas PlR, kur kopējais sapropeļa apjoms ir lēsts ap 154 milj. m^3, 41% ir silikātu un 12% dzelzi saturošs sapropelis, kam arī ir zems izmantošanas potenciāls.

Dati liecina, ka ezerdobju visaugstākais aizpildījuma koeficients ar sapropeli ir Latgales PlR (vidēji 0,61), bet viszemākais – Kurzemes PlR (0,54). Pārējos reģionos ezerdobju aizpildījums būtiski neatšķiras un ir 0,56-0,60.

3.2. Sapropeļa veidošanās likumsakarības Latvijas teritorijā

Sapropelis Latvijas ezeros sāka veidoties un uzkrāties agrajā holocēnā apmēram pirms 11 700 gadu, kad klimats kļuva labvēlīgs ezera faunas un floras attīstībai. Jāatzīmē, ka pirms holocēna ezeros uzkrājās galvenokārt minerāli nogulumi ar mazu organisko vielu daudzumu, jo aukstā un bargā klimata dēļ, organisko vielu produkcija ezeros nepārsniedza mineralizāciju.

Pētījumos konstatēts, ka sapropeļa krājumi galvenokārt uzkrājušies ezeros, kuru ezerdobes ir veidojušās uz augšpleistocēna Latvijas svītas (Q$_3$*ltv*) glacigēnajiem, glaciofluviālajiem un glaciolimniskajiem nogulumiem, kuri uzkrājušies ledāja un tā kušanas ūdeņu darbības rezultātā. Ezeros, kas veidojušies uz holocēna nogulumiem (Q$_4$) sapropelis uzkrājas nenozīmīgos daudzumos. Sapropeļa veidošanos galvenokārt nosaka sateces baseina apstākļi, tā virsmas reljefs, ģeoloģiskā struktūra, ezeru hidroloģiskais un hidrogrāfiskais režīms, ezera floras un faunas attīstība.

Dažādu sapropeļa klašu veidošanās ir būtiski atkarīga no nogulumu veida ezera sateces baseinā (3. attēls) un ezerdobes veidošanas tipa. Piemēram, organogēnās klases sapropelis veidojas galvenokārt ezeros, kas veidojušies uz augšpleistocēna (Q$_3$) glacigēno un glaciofluviālo nogulumu robežas, jo šādi ezeri parasti ir sekli, kas labvēlīgi ietekmē organisko nogulumu uzkrāšanos. Iespējams, ka šajos ezeros ūdens straumes bijušas pārāk vājas, lai izskalotu organisko materiālu, tomēr pietiekami dziļas, lai tajos neveidotos piekrastes litorāles aizaugumi, kuros veidojas zemā tipa kūdra. Sapropelis ar dominējošo silikātu minerālo komponentu veidojas ezeros, kas veidojušies uz augšpleistocēna glaciolimniskajiem (lgQ$_3$*ltv*) nogulumiem. Šie nogulumi ir bagāti ar SiO$_2$ un Al$_2$O$_3$, satur lielu daudzumu silikātu: kvarcu, laukšpatu, vizlu u.c.
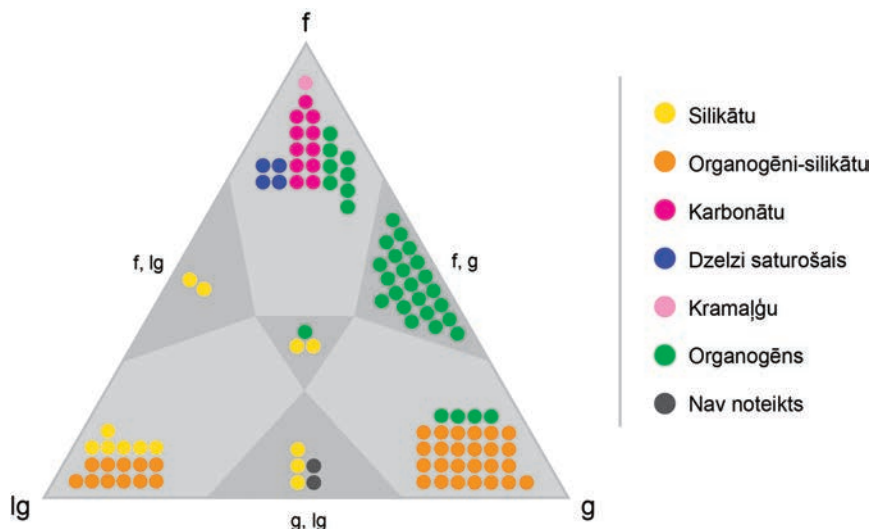
3. attēls. Sapropeļa klašu veidošanās likumsakarības atkarībā no augšpleistocēna (Q_3)
nogulumu veida, uz kuriem veidojies ezers

Ezeriem, kuru ezerdobes izveidojušās uz augšpleistocēna glaciofluviālajiem (fQ₃ltv) nogulumiem, ir raksturīga dažādu klašu sapropeļa uzkrāšanās, kas neuzkrājas cita veida ezeros. Šādiem ezeriem ir raksturīgas lielas sateces baseina teritorijas, no kurām noteces rezultātā pārsvarā no morēnas apgabaliem, tika ieskaloti karbonāti un dzelzi saturoši minerāli. Organogēnais sapropelis šādos ezeros ir uzkrājies galvenokārt seklos un eitroficētos ezera līčos.

Sapropeļa klašu korelācija ar ezera raksturojošajiem lielumiem – ezera ieplakas izcelsmi, ūdens režīmu, ezera trofisko stāvokli un ezera gultnes piepildījumu ar nogulumiem – atklāj, ka glacigēnas izcelsmes ezeros pārsvarā veidojas visi sapropeļa veidi (4. attēls). Latvijas teritorijā šie ezeri ir vecākie, jo veidojušies Vislas apledojuma ledāja darbības laikā.

Silikātu tipa sapropelis nelielos daudzumos veidojās arī vecupju un uz eolajiem nogulumiem esošajos ezeros. Gan vecupju, gan bijušo upju pietekās veidojas savdabīgi, mazi, sekli, iegareni ezeri, kuru sateces baseini atrodas upju palienēs. Šajos ezeros pakāpeniski ieskalojas aluviālais materiāls, kas arī veido minerālo komponentu šo ezeru nogulumiem. Eolo nogulumu apgabalos starp kāpām izveidojas mazi iegareni ezeri, kuros uzkrājies silikātu sapropelis, kura sastāvu ietekmē eolās smiltis ezeru krastos. Gan vecupju, gan eolo ezeru sapropeļa krājumi ir nelieli, un resursi ir mazvērtīgi ekonomiski izdevīgai rūpnieciskai ieguvei.

Sapropelis veidojas ezeros ar visa veida ūdens režīmu, tomēr lielāki krājumi ir ezeros ar noteces un caurteces ūdens režīmu. Sapropelis ir retāk sastopams beznoteces ezeros, jo stāvošs ūdens ir vāji piesātināts ar skābekli, tam ir sliktāka caurredzamība un nenotiek ūdens slāņu sajaukšanās. Šādi apstākļi nav labvēlīgi ezeru biotai un to aizstāj kūdru veidojošie augi.

Pētāmo ezeru trofiskais stāvoklis parāda, ka mūsdienu rūpnieciski nozīmīgās sapropeļa iegulas ir izveidojušās eitrofos un hipereitrofos ezeros. Distrofajos ezeros sapropeļa veidošanos apturēja pārpurvošanās, kas limitēja ūdens dzīvnieku un
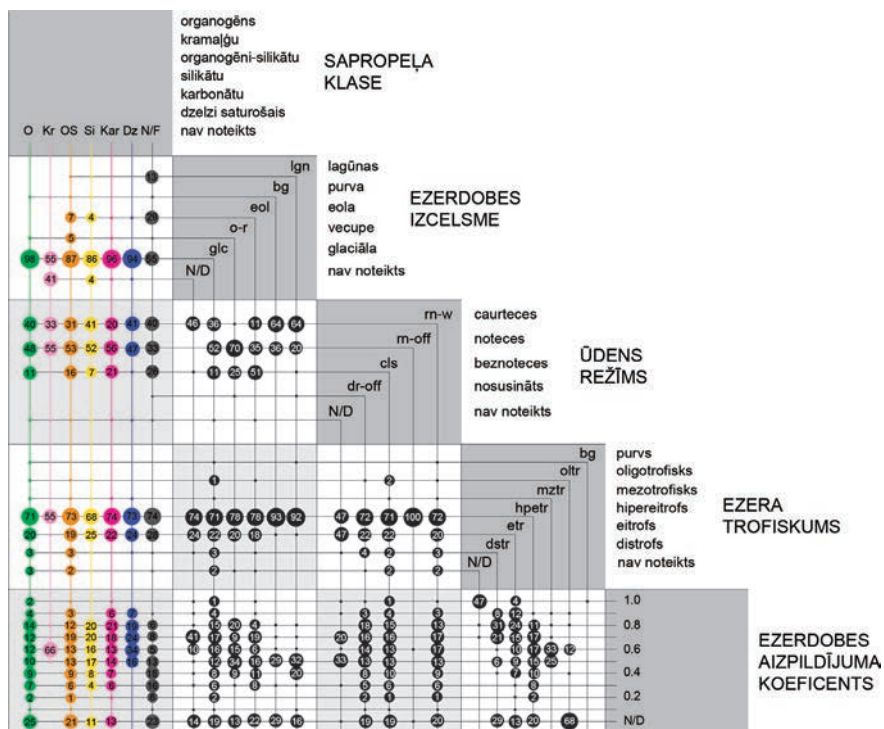
4. attēls. **Sapropeļa klašu procentuālais sadalījums atkarībā no ezera īpašībām**

ūdens augu attīstību. Oligotrofos un mezotrofos ezeros sapropeļa slāņa biezums un ūdens dziļums padara tā ieguvi ekonomiski neizdevīgu. Par rūpnieciski nozīmīgiem tiek atzīti ezeri ar piepildījumu lielāku par 50%. Datubāzes analīze atklāj, ka agrajā holocēnā ezeros uzkrājās sapropelis ar augstu minerālās komponentes daudzumu (karbonātu, silikātu). Virs tā parasti uzkrājušies organogēno sapropeļu veidi, kas veidojas seklos un aizaugušos ezeros.

3.3. Vides un ezera attīstības rekonstrukcija sapropeļa veidošanās laikā

Pētot klimata vai vides izmaiņas nogulumu klasifikācija ir mazāk svarīga nekā pētot sapropeli kā derīgo izrakteni. Resursa parametriem ir jābūt stingri definētiem gan meklēšanas darbos, gan likumdošanā un izmantošanā. Tāpēc, lai aprobētu promocijas darbā izstrādāto un adaptēto sapropeļa klasifikāciju un rekonstruētu vides faktorus, kas tieši ietekmē sapropeļa veidošanos un īpašības darbā pētītajos ezeros (Padēlis, Pilcine un Pilvelis), šo ezeru sapropeļa profilu nogulumu sastāva (litoloģijas) noteikšana tika veikta izmantojot saldūdens sapropeļa klasifikācijas tabulu (2. tabula). Apkopotie pētījuma rezultāti atklāj, ka Padēļa ezerā ir izveidojusies karbonātiskā sapropeļa iegula, Pilcines ezerā – organogēni-silikātu sapropeļa un Pilveļu ezerā – organogēnā sapropeļa iegula (5. attēls).

Vecums, kal g.p.m.
Dziļums, cm
LOI
Litoloģija
Nogulumu veids
Ac Ca Fe

Diagnostikas pazīmes

Mikroatliekas, granulometrija

(A)

LOI simboli

- Mineralvielas
- Karbonāti
- Pelni (Ac)
- Organiskas vielas

Litoloģijas simboli

Kūdra

Grīšļu kūdra

Nogulumu veids	Ac	Ca	Fe	Mikroatliekas, granulometrija
Grīšļu kūdra	-	-	-	-
Organogēni-karbonātisks sapropelis	6.93	134	4	organiskas atliekas - 40.63 silt - 78.73
Mālaini-karbonātisks sap.	44.61	123	5	māls > 50
Karbonātisks sap.	78.70	233	7	
Minerālie nogulumi	87.40	268	6	pelni > 85
Karbonātisks sap.	65.92	304	3	
Minerālie nogulumi	87.75	326	3	pelni > 85
Karbonātisks sap.	82.30	301	2	
Minerālie nogulumi	87.86	325	3	pelni > 85
Karbonātisks sap.	81.82	342	3	
Minerālie nogulumi	88.21	306	5	pelni > 85

(B)

Nogulumu veids	Ac	Ca	Fe	Mikroatliekas, granulometrija
Grīšļu kūdra	-	-	-	-
Kramaļģu sapropelis	36.11	20	10	kramaļģes - 30.60; smilts > 30
Organogēni-smilšains sapropel	41.15	12	10	smilts > 30
Smilšains sapropelis	68.20	9	8	smilts > 30
Organogēni-smilšains sapropelis	54.81	11	11	smilts > 30
Smilšains sapropelis	72.45	8	9	smilts > 30
Minerālie nogulumi	96.77	4	2	pelni > 85

(C)

Nogulumu veids	Ac	Ca	Fe	Mikroatliekas, granulometrija
Kūdrains sapropelis	9.45	9	1	vaskulāri augi - 50.33
Zoogēns sapropelis	6.70	8	1	ūdens dzīvnieki - 20.13
Kūdrains sapropelis	8.95	8	1	vaskulāri augi - 65.04
Hypnum kūdra	11.54	8	1	hypnum sūnas - 20.01
Kūdrains sapropelis	10.35	8	1	vaskulāri augi - 35.04
Dažādaļģu s.	22.74	9	1	aļģu summa - 45.15
Organogēni-aleirītisks s.	35.41	11	2	organiskas atliekas - 40.63 aleirīts - 78.73
Zilaļģu sapropelis	17.33	9	3	zilaļģes - 52.37
Minerāli nogulumi	86.71	5	12	pelni > 85

Organogēns sapropelis

- Kūdrains sapropelis
- Zilaļģu sapropelis
- Dažādaļģu sapropelis
- Zoogēns sapropelis

Kramaļģu sapropelis

- Kramaļģu sapropelis

Karbonātu sapropelis

- Organogēni-karbonātisks sap.
- Karbonātisks sapropelis
- Mālaini-karbonātisks sapropelis

Organogēni-silikātisks sapropelis

- Organogēni-aleirītisks sap.
- Organogēni-smilšains sap.

Silikātu sapropelis

- Smilšains sap.

Ar organiskām vielām nabadzīgi nogulumi

- Minerālie nogulumi

5. attēls. (**A**) **Padēļa ezera** (**B**) **Pilcines ezera** (**C**) **Pilveļu ezera nogulumu profila raksturojums: vecums, dziļums, karsēšanas zuduma rezultāti, litostratigrāfija un nogulumu veids, izmantojot autores adaptēto saldūdens sapropeļa klasifikāciju**

Padēļa ezerā sapropelis ir sācis veidoties kopš agrā holocēna pirms 11 700 kal.g.p.m, kad ezers kļūst mezotrofs. To atspoguļo mikroatliekas, kuru sastāvā šajā laikā pazūd kramaļģes, un starp makroatliekām palielinās mezotrofās sugas *Najas marine* daudzums. Nogulumos labi iezīmējas 8200 kal.g.p.m. – laiks, kad ezera sateces baseinā egļu-bērzu mežus nomaina jauktie meži. Līdz 3600 kal.g.p.m. ezerā urbuma vietā veidojas karbonātiskais sapropelis, līdz 6700 kal.g.p.m. karbonātu sapropeļa slāņi mijās ar minerālo nogulumu starpslāņiem, bet jau pirms 3600 kal.g.p.m. strauji samazinās karbonātu un minerālu daudzums, sāk veidoties organogēnais sapropelis, parādās daudz piekrastes augu atliekas, sākas strauja ezera aizaugšana.

Visu sapropeļa iegulu Pilcines ezerā veido organogēni smilšainais sapropelis ar smilšaina sapropeļa starpslāni, kas sāka veidoties tikai 6900 kal.g.p.m. Ap šo laiku Padēļa ezera nogulumos strauji palielinās organisko vielu daudzums, norādot uz ezera sateces baseina teritorijas samazināšanos un ūdens līmeņa svārstībām. Ķūžu ezerā Latvijā (Terasmaa *et al.*, 2013), Juusa ezerā Igaunija (Punning *et al.*, 2005), kā arī Sloboda ezerā Baltkrievijā (Zhukhovitskaya *et al.*, 1998) arī tika noteiktas ūdens līmeņa svārstības. Kaut arī sapropeļa tips Pilcines ezerā kopš 3700 kal.g.p.m. nemainās, tomēr mikroatlieku sastāvā strauji pieaug kramaļģes (*Melosira, Aulacoseira, Tabellaria, Cyclotella, Cymbella*) un zaļaļģes (*Zygnema, Desmidae*), norādot uz ūdens ķīmiskā sastāva maiņu. Ap šo laiku Padēļa un Pilveļu ezeros sāk veidoties kūdra. Pilveļu ezerā kūdras slānis veidojies pirms apmēram 400 gadiem, vēlāk veidojas galvenokārt kūdrainais sapropelis. Padēļa ezerā kūdra veidojas līdz mūsdienām, tomēr ~40 cm dziļumā makroatlieku sastāvs uzrāda ūdens līmeņa celšanos. Šādas izmaiņas nogulumu bioloģiskajā sastāvā visos trijos ezeros norāda uz īslaicīgu sausuma periodu. Līdzīgas klimatiskās izmaiņas atklāj arī dati no Mazā Svētiņu ezera (Stivrins *et al.*, 2014) un daudziem purviem Latvijas teritorijā (Kalnina *et al.*, 2019). Pirms 1300 kal.g.p.m. Pilcines ezerā sāk veidoties niedru kūdra.

Pilveļu ezerā sapropelis sāk uzkrāties kopš 10 000 kal.g.p.m., sākoties straujiem eitrofikācijas procesiem, uz ko norāda *Najas marina* un *Najas flexilis* makroatliekas. No 10 000 līdz 5800 kal.g.p.m. ezerā bija labvēlīgi apstākļi zilaļģu sapropeļa uzkrāšanās procesam. Šo nogulumu organisko vielu saturs ir lielāks par 83%, ko galvenokārt veido zilaļģu *Lyngbya* atliekas. Šajā laikā ezera ūdens bija dzidrs un auksts. Sateces baseinā veidojās pļavas, kuras periodiski applūda. No 5800 līdz 4500 kal.g.p.m. nogulumos palielinās minerālvielu daudzums un veidojas organogēni-aleirītiskais sapropelis, kura organiskās atliekas veido galvenokārt zilaļģes *Anabaena* sp. Pēc 4500 kal.g.p.m. ezerā uzkrājas organiskais sapropelis ar paaugstinātu kūdru veidojošo augu atlieku daudzumu un 10 cm biezu kūdras starpslāni – tas norāda uz ezera eitrofikācijas intensificēšanos un ūdens līmeņa svārstībām.

Vides un ezera attīstība, un sapropeļa veidošanās rekonstrukcija ļauj secināt, ka sapropeļa tipam ir cieša saistība ar ezerā nonākošo minerālo komponenti, ūdens sateces baseina lielumu un aizaugšanu, ūdens ķīmisko sastāvu un dziļumu, kā arī aukstuma un sausuma periodiem (6. attēls). Kad ezera ekosistēma vēl spēj veikt paškontroli, aukstuma un sausuma periodi neatspoguļojas sapropeļa tipa izmaiņā, bet uzrādās organisko vielu veidotājorganismu sastāva izmaiņās – makro- un mikroatlieku sastāvā. Ezera sateces baseinam pārpurvojoties un samazinoties, tas vairs nenodrošina lielu daudzumu minerālkomponentu ieskalošanos, ūdens režīms kļūst pārāk lēns, lai aizskalotu ezerā veidoto organisko materiālu, ezerā sāk veidoties organiskais sapropelis. Ezera litorāles zonā sapropeļa veidošanos aizstāj kūdras veidošanās, ko izraisa kūdras veidotājaugu strauja attīstība.
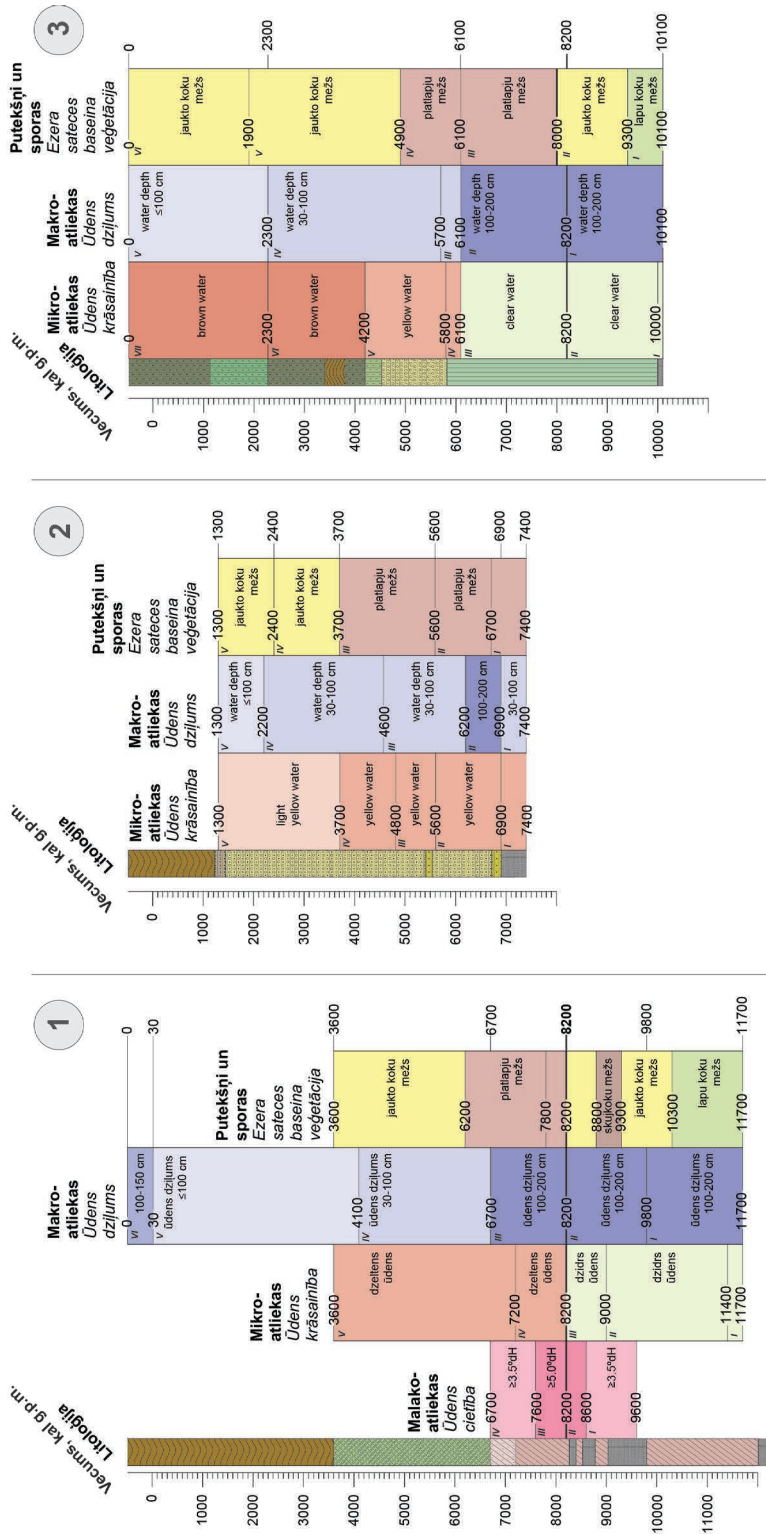
6. *attēls*. Biologisko komponenšu salīdzinājums Padēļa, Pilcines un Pilveļu ezeros. Litoloģijas simbolus skat Attēls 5

3.4. Metālisko elementu saturs un faktori, kas ietekmē to uzkrāšanos sapropelī

Lai noteiktu, kādam izmantošanas veidam sapropelis ir pielietojams, ir svarīgi saprast nogulumu satura mainību un īpašības. Metālisko elementu satura augstas vērtības var būt pozitīvs radītājs izmantojot sapropeli kā mēslojumu vai negatīvs, jo tas kļūst toksisks, izmantojot to kā dzīvnieku barības piedevu.

Metālisko elementu sadalījums un saturs nogulumu profilā sniedz informāciju gan par antropogēnām, gan dabiskas izcelsmes metālisko elementu plūsmām ezera

5. tabula

Kopējais metālu saturs sapropelī dažādos Latvijas, Baltkrievijas un Krievijas ezeros
(pētījuma dati; GEO-Konsultants, 1998b; Zhukhovitskaya et al., 1998)

µg/g	Ca	Fe	Mg	K	Mn	Zn	Na	Cu	Ni	Cr	Pb	Co	Cd
Padēļa ezers													
Vid	230376	4654	3182	171	321	14	163	2,5	1,7	2,8	3,6	1,13	0,06
Max	349865	12077	5757	1172	570	50	211	8,9	9,1	16,4	7,4	3,18	0,15
Min	11959	1550	633	20	70	5	109	0,6	0,3	0,4	1,7	0,31	0,04
Pilcines ezers													
Vid	11569	10286	1702	1658	174	113	56	25,3	23,6	21,4	6,3	6,08	0,35
Max	20322	13802	2134	2585	299	179	94	40,9	35,7	46,1	15,2	9,36	0,76
Min	3938	2006	1106	304	41	22	38	3,0	3,2	2,9	0,7	1,04	0,04
Pilveļu ezers													
Vid	9100	2536	821	424	109	93	68	12,7	8,8	8,7	6,6	2,89	0,49
Max	13971	12216	2702	2544	188	198	125	19,8	23,8	44,4	30,9	8,20	0,96
Min	5405	1057	492	106	61	46	38	7,6	3,5	2,7	0,6	0,73	0,21
Ezeri Latvijas austrumu daļā (115 paraugi) Eikša, Lielais Kalpes, Maltas, Marinzejas, Pakalnis, Plošu, Rēzeknes, Padelis, Pilcine, Pilvelis, Vēvers, Līducis													
Vid	33654	8270	2081	906	219	112	119	16,7	17,9	20,3	14,7	7,75	0,37
Max	349865	25614	8340	4940	570	402	390	43,2	35,7	55,4	46,7	13,00	1,66
Min	3938	1057	492	20	41	5	11	0,6	0,3	0,4	0,6	0,32	0,04
Ezeri Latvijas centrālajā daļā (11 paraugi)													
Vid						98		19,5	38,6	19,7	7,9		
Max						121		32,0	55,0	39,0	11,9		
Ezeri Latvijas ziemeļu daļā (15 paraugi)													
Vid						86		16,3	66,9	19,5	4,8		
Max						170		21,5	191,3	26,1	8,0		
Ezeri Baltkrievijā (1492 paraugi)													
Vid					342	73		13,2	26,0	16,0	7,0		
Max					1180	233		24,0	40,0		16,0		
Ezeri Kaļiņingradas reģionā (38 paraugi)													
Vid						57		10,6	36,4	17,3	4,8		
Max						181		22,0	81,0	40,2	13		

ekosistēmā, ezera noteces režīmu, klimatiskajām izmaiņām reģionā un izmaiņām zemes izmantošanā sateces baseinā nogulumu veidošanās laikā (Dean, 1974)

Metālisko elementu koncentrācija sapropeļa paraugos no Padēļa, Pilcines un Pilveļu ezeriem svārstās plašā diapazonā (5. tabula), norādot uz to, ka nogulumu veidošanās notika dažādos vides apstākļos ūdenstilpē un tās sateces baseinā ilgā laika periodā. Starp analizētajiem metāliskajiem elementiem sapropeļa paraugos visaugstākās koncentrācijas tika novērotas Ca, Fe, Mg, K, Mn, Zn un Na (10-104 µg/g). Citu elementu (Cu, Ni, Cr, Pb, Co un Cd) koncentrācija tika konstatēta zem 10 µg/g.

Lai novērtētu, vai pētāmajam sapropelim nav paaugstināts metālisko elementu saturs, tas tika salīdzināts ar sapropeli no citiem Latvijas, Baltkrievijas un Krievijas ezeriem (5. tabula).

Galvenā datu interpretācijas problēma ir tā, ka metālisko elementu uzkrāšanos ietekmē dažādi faktori (tiešā ietekme ezera sateces baseinā un netiešā ietekme, piemēram, saistīta ar gaisa masas pārrobežu pārnesi, metālisko elementu saistīšanu stabilās minerālu formās, minerālu šķīšanas ģeoķīmisko iedarbību utt.). Līdz ar to noteikta elementa avots laika gaitā var mainīties. Tas izraisa kļūdas vērtēšanas procesā, kad dati aptver ilgākus laika periodus. Statistisko analīzi var izmantot kā instrumentu, lai noteiktu sakarības starp elementu uzkrāšanās modeļiem un identificētu metālu uzkrāšanās tendences visā nogulumu veidošanās periodā.

Metālisko elementu koncentrāciju mainība un metālu Pīrsona korelācija uzrāda, ka pozitīvas korelācijas saites visu trīs pētāmo ezeru nogulumos ir starp sešiem metāliem: Co, Cu, Ni, Fe, K, Cr. Šie metāli veido pelitofīlo elementu asociāciju. Šos elementus sorbē māla daļiņas vai arī tie ietilpst māla minerālu kristāliskajos režģos un, līdz ar to, to transportu nodrošina minerālvielas un karbonāti. Otra metālu grupa ir atšķirīga katra ezera ietvaros.

Galveno komponentu analīze kā galveno faktoru visos ezeros uzrāda metālu uzkrāšanās sakarību ar minerālo komponentu, kas nonāk ezerā no sateces baseina ar noteci, caurteci vai gruntsūdeņiem. Padēļa ezerā tie ir ar karbonātiem bagāti terigēnie nogulumi, Pilcines ezerā – silikātu saturošu minerālvielu plūsmas, bet Pilveļu ezerā – minerālvielu ienese no sateces baseina un gaisa.

SECINĀJUMI

1. Izstrādāta un Latvijas vides apstākļiem adaptēta Sapropeļa klasifikācijas sistēma, kas ir balstīta uz sapropeļa veidošanos ietekmējošiem faktoriem, sapropeļa sastāva un īpašībām, kā arī izmantošanas iespējām. Tā ietver informāciju par sapropeļa izmantošanas iespējām un paplašina zināšanas par jau zināmiem pielietojumu veidiem. Sapropeļa klasifikācijas sistēmu var izmantot kā matricu sapropeļa raksturošanai un perspektīvo pielietojuma jomu identificēšanai.

2. Balstoties uz adaptēto Sapropeļa klasifikācijas sistēmu, izstrādāta Saldūdens sapropeļa resursu datubāze, kas atspoguļo rūpnieciski nozīmīgās sapropeļa iegulas un to raksturojumu, sapropeļa resursu apjomu un tipoloģiju Latvijas ezeros. Datubāze nosaka perspektīvos sapropeļa izmantošanas virzienus, kas var kalpot kā instruments reģionālās attīstības atbalstam, ilgtspējīgai un ekonomiski pamatotai dabas resursu izmantošanai un ezeru rekultivācijai.

3. Latgales augstienes ezeros veiktā padziļinātā kompleksā paleolimnoloģiskā pētījumā noteikts ezera nogulumu absolūtais vecums, litoloģiskais, bioloģiskais un ķīmiskais sastāvs un citi parametri, kas atklāj ezeru ekosistēmas attīstības gaitu Holocēnā, kā arī sapropeļa veidošanās raksturu. Pētījuma rezultāti ļauj secināt, ka Latgales augstienes ezeros sapropelis sāka veidoties jau agrā Holocēnā, pirms 11 700 kal.g.p.m. Visu pētīto ezeru nogulumos labi iezīmējas laiks 6900-6700 kal.g.p.m. un 4200-3600 kal.g.p.m., kad notika izteiktas klimata izmaiņas. Iegūtie dati ļauj identificēt antropogēnās ietekmes intensitāti un nozīmīgumu, primāri liecinot par sugu un ķīmiskā sastāva izmaiņām, atklājot lauksaimniecības, mežsaimniecības ietekmi uz bioloģiskiem procesiem ezeros.

4. Multiparametru metodes pieeja detalizētai ezeru nogulumu profilu izpētei, ietverot P_{org}, pamatelementu (C, H, N, O, S), metālisko elementu (Na, K, Ca, Mg, Fe, Mn, Cu, Co, Ni, Pb, Cr, Cd un Zn), minerālvielu un organisko vielu (tostarp humusvielu), karbonātu satura noteikšanu, raksturo nogulumu sastāva veidošanās īpatnības un apjomu dažādu dabisku (tiešu un netiešu) un antropogēnu faktoru ietekmē, kā arī ezera pastāvēšanas laikā radušās izmaiņas. Nogulumu ķīmiskā sastāva analīze atspoguļo ģeoķīmisko procesu raksturu nogulumu veidošanās procesā, kas rezultējas ar tipisku ģeoķīmisku elementu asociāciju ģenēzi atbilstoši ezera attīstības fāzei, kā arī atklāj antropogēno ietekmi uz ezeru ekosistēmām un elementu akumulācijas procesu.

5. Latvijā pirmo reizi izmantotā multiparametru metodes pieeja ezeru sapropeļa bioloģiskā un ķīmiskā sastāva izpētei saskaņā ar izstrādāto Sapropeļa klasifikācijas sistēmu atklāj sapropeļa kā dabas resursa optimālas izmantošanas, apstrādes un pārstrādes iespējas noteikšanu, kā arī sniedz jaunu izpratni par ezeru nogulumu sastāva veidošanās apstākļiem un tos ietekmējošiem faktoriem.

6. Pētījumā iegūtie rezultāti ļauj secināt, ka sapropeļa pielietošanas potenciāls ir atkarīgs no nogulumu veidošanās apstākļiem, galvenokārt no vides faktoriem un procesiem, kas ietekmē sapropeļa ķīmisko sastāvu, tostarp, smago metālu uzkrāšanos sapropeļa veidošanās laikā, kas apstiprina darbā izvirzīto hipotēzi.

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