UNIVERSITY
OF LATVIA

Summary of
Doctoral Thesis

Riga, 2020

Karina Stankeviča

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

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

Scientific advisors:
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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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INTRODUCTION

Sapropel is one of the important national natural resources of Latvia. The volume of sapropel the lakes of Latvia is estimated at approximately 500 million tons (with 60% moisture). These organogenic lake sediments are formed during postglacial or the Holocene (last 11,000 years) and accumulated in the aquatic environment of the lake and are essential resources both in economic as well as natural history and in terms of nature protection. In this respect, it is essential to improve our 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 is useful and partially renewable earth resources formed during the Quaternary period. 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., 2017).

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.

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.

he 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.

he 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.

Description of methodology

In order to achieve the goal of the dissertation and fulfil the set tasks, the author has used methods that can be divided into three groups:

Geospatial data analysis – allows a general description of the lakes and sapropel in Latvia, as well as detailed characterization of the catchment basins of the studied lakes.

Paleolimnological and sapropel composition studies – allow characterization of the accumulation and changes in the composition of sapropel over time, taking into account the development and climate of the lake. Paleolimnological studies include carbon and lead dating, identification of pollen and spores, macro- and microfossils, and, for individual samples, malacofauna. The methodology includes loss-on-ignition analysis, determination of the elemental composition, the total amount of metallic elements and humic substances.

All data were subjected to statistical analysis – Pearson correlation, principal component analysis, and scatter plots.

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

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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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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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Patent

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

1 LITERATURE REVIEW

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 (Lopatin, 1983; Lopotko, 1974). Formation of sapropel is highly dependent on the processes in the lake, and the sapropel sediment formation 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). The composition and properties of sapropel in different deposits are very various; it is determined by the productivity of the specific water body, physiographic conditions, hydrological regime, surface runoff and lakebed characteristics, as well as climatic conditions. Freshwater sediments with an organic matter content higher than 15% are generally considered to be sapropel; if the content of organic matter is lower, then these sediments are assessed as highly ashy lake sediments. Sapropel differs from peat in its fine structure, environmental reaction, amount of organic matter, forming organisms and amount of humic substances.

Organic rich deposits in water bodies, including sapropel, appeared after the glacier retreat. In the Baltic countries, it happened 12-15 thousand years ago (Zelcs and Markots, 2004). Massive sapropel formation in this region took place in the Holocene (11,700 cal BP) up to 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).

Formation of uniform terminology and classification of lake sediments is burdensome because each interested science field has developed its own classification and lists of terms, which corresponds to the direction, objectives and particular aims of an individual research mērķiem (Braks, 1971; Lundquist, 1927; Titov, 1950). When evaluating sapropel as a resource, more appropriate classifications are based on the composition of sapropel (BSSC Institute, 2010; Kireicheva and Khokhlova, 1998; Pidoplichko and Grishchuk, 1962).

Three main ingredient sources for freshwater sapropel formation take place. The main source is dead organisms of a lake and its catchment area – 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).

Sapropel contains both chemically unbound and bound minerals – carbonates, silicates, iron hydroxide, etc. Unbound mineral matter is assessed as sapropel fibres. Minerals that are chemically bound to organic substances form complexes of complex biologically active substances in sapropel. Depending on the location of the deposit, sapropel can vary significantly in both the degree of mineralization (ash content) and the composition of organic matter and mineral content – these are essential parameters that determine the potential for the use of sapropel deposits.

Sapropel has a broad range of possible application ways in various fields of national economics (Figure 1), among which agriculture currently takes the most significant part.

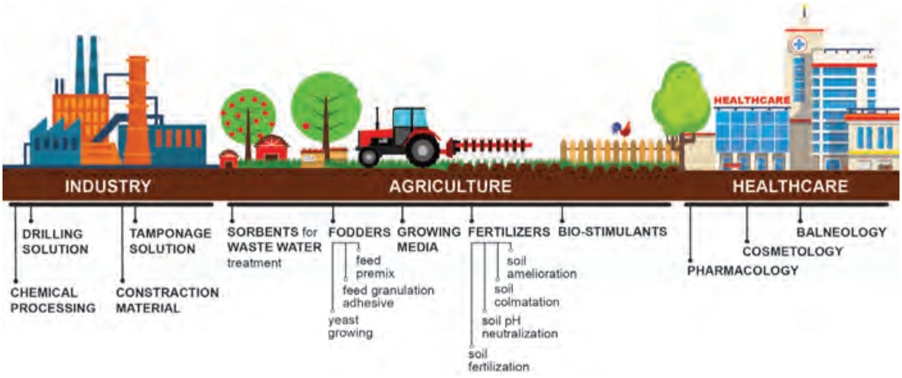


Figure 1. **Options for application of sapropel in the fields of national economics** (author's work out)

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 driven sapropel extraction and utilization to development of a cost-effective, sustainable and well-grounded market niche.

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.

2 MATERIALS AND METHODS

2.1 Study area and particular research sites

Data derived from the surveys of complex geological exploration expeditions carried out in Latvia over the decades were used to design a Freshwater Sapropel Database (GEO-Konsultants, 1995, 1996, 1997, 1998a, 1998b, 1999; Latvijas Geologija, 1994; Latvgeologija 1991a, 1991b, 1992), as well as other sources (Braks et al., 1967, Leinerte, 1988). Freshwater Sapropel Database 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 the database, there are 2,200 lakes in Latvia. Until now, searching of sapropel has been carried out in 1,286 lakes – up to 55% of all lakes in Latvia (Figure 2).

To characterize the detailed impact of environmental conditions on the properties and possible applications of different types of sapropel – organogenic, carbonate and clastic – and interaction of them with climatic changes and lake development stages, three lakes located in Latgale Upland were chosen (Figure 2) – Lake Padelis, Lake Pilcine, Lake Pilvelis. The preliminary data of primary deposit types of sapropel and their characteristic were obtained analyzing the Lake Sapropel Deposit Passports (GEO-Konsultants, 1998b).

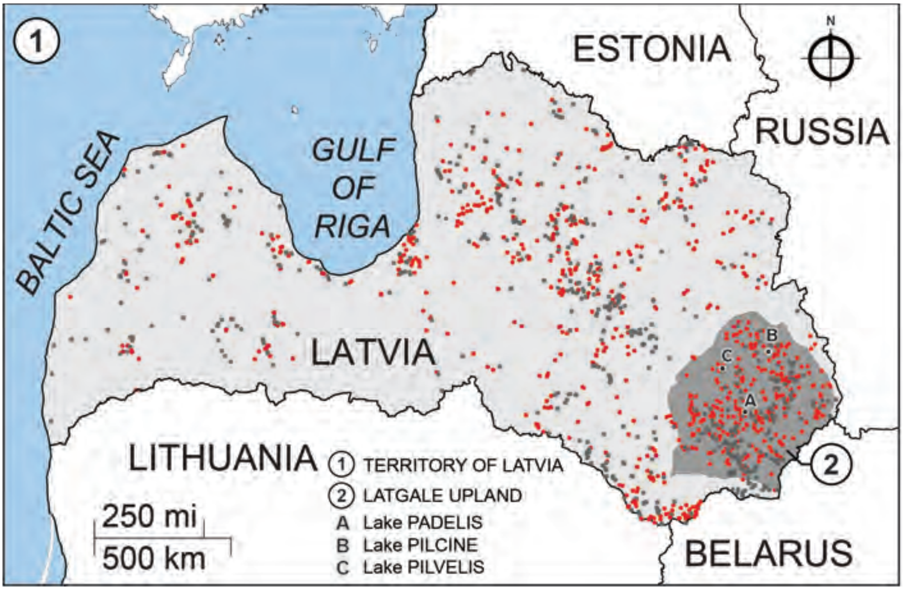


Figure 2. **(1) Location of the studied sites in the territory of Latvia: red points – industrially significant sapropel deposits, grey points – sapropel deposits without industrial significance; (2) Latgale Upland nature areas with the location of particular study sites: A - Lake Padelis, B - Lake Pilcine, C - Lake Pilvelis**

2.2. Sapropel database

Elaborated Freshwater Sapropel Database 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 waterbody 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, which was 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 waterbody 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).

2.3. Analytical methods and age detection of sediments

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 1.

The age was determined for sapropel of Padelis, Pilcine and Pilvelis lakes: in layers deeper than 1 m, dating of conventional radioactive carbon (14C) isotopes was performed, dating of 210Pb was applied for the top meter of sediments.

Table 1

The number of sapropel subsamples investigated 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	Stankevica et al., 2015
2	Plant macrofossils analysis	30	30	40	Stankevica et al., 2015
3	Microfossils analysis	30	40	40	Stankevica et al., 2015
4	Malacofauna analysis	30	-	-	Miller and Tevesz, 2001
Physical-chemical methods					
5	Bulk density	30	40	40	Grossman et al., 2002
6	Loss-on-ignition (LOI)	30	40	40	Stankevica et al., 2015
7	Elemental composition	15	17	20	Stankevica et al., 2012
8	Content of humic substances	30	30	40	Stankevica et al., 2019
9	Content of metallic element	15	17	25	Stankevica et al., 2020
10	Biogenic phosphorus content	30	30	40	Johengen, 1996
11	Granulometry	-	-	40	Last, 2001

2.4. Statistical analysis of the data

Using the results of the PC-ORD 7 database, as well as the results obtained by the analytical methods, the statistical processing of data was performed, scatter plots were created, Pearson correlation and principal components analysis (PCA) were performed.

3 RESULTS AND DISCUSSION

3.1. Typology, amount and distribution of freshwater sapropel in Latvia

In order to develop research methods using GIS software, as well as to let the information on the lake sapropel resources in Latvia would become available to the public, as well as to identify prospective sapropel industrial deposits, the data needed to be digitized through the development and creation of a digital database.

To assess the economic potential of sapropel, the author offers a definition of sapropel and an adapted freshwater sapropel classification system used in lake sapropel prospecting and geological surveys in Latvia (GEO-Konsultants, 1995; Latvgeologija, 1991a, 1991b, 1992; Latvijas Geologija, 1994): ***freshwater sapropel – subfossil colloidal sediments of continental water bodies with a fine-grained or gelatinous structure, containing significant amounts 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.***

In the proposed **Classification of Freshwater Sapropel,** 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 (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 2).

In terms of sapropel as a resource, it is included into a solid fuel group which also involves peat, wood, lignin (Podgorodetskii et al., 2015); therefore, the author proposes recognized and proven methods to be used for determination of the type of sapropel: detection of ash content (LVS/STK/38, 2011), analysis of Ca and Fe content in dry mass (Vincēviča-Gaile, 2014), detection of microfossils (Stankevica et al., 2015), analysis of granulometry (Last, 2001).

The Freshwater Sapropel Database was designed to systematize and summarize available information on the results of lake sapropel searching works. Compiled data reveals that there are 2,200 freshwater lakes (greater than 3 ha) in Latvia. Up to now, searching of sapropel has been carried out at 1,286 lakes, in 55% of all lakes in Latvia (Figure 2).

The total amount of identified lake sapropel in Latvia is 974,982.2 thsd. m^3 (or 527,938.5 thsd. tons with a moisture content of 60%); from which 712,213.3 thsd. m^3 or 287,746.3 thsd. tons can be assessed as industrially significant sapropel deposits.

Location of lakes in the territory of Latvia is uneven; i.e., a large part of the Zemgale plain is practically absent of lakes – lakes occupy only 0.47% of the area of Zemgale planning region (PReg). In turn, in the counties of Mersrags, Liepaja, Babite, the density of lakes concerning the territory of a county is more than 20%, which is determined by the location of large water bodies – Lake Engure, Lake Liepaja and Lake Babite – in these territories.

Table 2

Sapropel Classification System adapted for Latvia

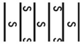
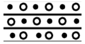
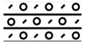
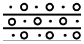
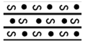
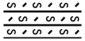
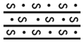
Class	Order	Type	Symbol	Diagnostic marks					Possibilities of use
				Ash, %	g/kg DM		Microfossil and granulometric composition, %		
					Ca	Fe			
Biogenic	Organogenic (O)	Peaty		<30	<60	<140	vascular plants	>35	HS products, growth stimulators, binder, fertilizers
		Zoogenic					animals	>15	Therapeutic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

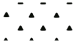
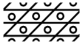
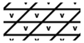
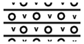
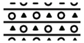
Table 2 (continued)

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			
Silicate	Silicate (Si)	Sandy	▤	65-85	<60	<285	sand	30-50	Soil improvers
		Silty	▤				silt	30-50	
		Clayey	▤				clay	30-50	
Carbonate	Carbonate (C)	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	Fertilizers, soil lime
		Silty carbonate	▨				calcite silt	<20 30-50	
		Clayey carbonate	▨				calcite clay	<20 30-50	
		Carbonate sandy	▦	65-85	60-140	<140	calcite sand	<20 >50	Soil improvers
		Carbonate silty	▦				calcite silt	<20 >50	
		Carbonate clayey	▦				calcite clay	<20 >50	
		Carbonate	▨	<85	>140	<140	calcite	>20	Soil lime, therapeutic mud, feed additives

Table 2 (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			
Mixed	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 (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

Assuming the total territory of planning regions, 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 investigated. 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, in Zemgale PReg in 84 (of total 185) lakes (Table 3).

Table 3

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

	Latgale	Kurzeme	Vidzeme	Riga	Zemgale	Total
PReg area, km^2	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, km^2	475.8	209.9	156.4	126.1	50.4	1018.6
No. of investigated lakes	590	121	356	132	84	1283
Deposit area, km^2	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. m^3	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. m^3	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

In Latgale PReg, the most substantial known total amount of sapropel stocks 414,403.3 thsd. m3 (184,902.9 thsd. t) are located, of which 338,818.3 thsd. m3 (114,769.0 thsd. t) can be counted to the industrially significant sapropel resources, which in volume make up 48.86% of all identified industrially relevant sapropel reserves in the country. Latgale PlReg is followed by Vidzeme PlReg, where industrially significant sapropel reserves make up 27.21% by volume. The smallest sapropel stocks are located in Kurzeme PlReg – 73,117.7 thsd. m3 (53,582.2 thsd. t), of which only 28,723.1 thsd. m3 (16,268.9 thsd. t) are of industrial significance, which is only 4.14% of all industrially relevant sapropel reserves in the country.

The most valuable with a broader range of uses is organogenic sapropel, which accounts for 18.68% of all sapropel stocks. The most extensive stocks of this sapropel are also located in Latgale PlReg (44.43%) and Vidzeme PReg (23.10%) (Table 4).

Although the area of Kurzeme PReg lakes occupies 1.54% of the region's territory, sapropel stocks are the lowest – the total amount is about 70 million m3, and 47.86% of these resources are silicate sapropel, which has a low potential for use.

Table 4

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 154 million m3, 41% is silicate sapropel and 12% iron-containing sapropel, which also has a low potential for use.

The data reveals that the highest filling coefficient of lakebeds with sapropel is in Latgale PReg (on average 0.61), but the lowest – in Kurzeme PReg (0.54). In other regions, the filling of lakebeds does not differ significantly (0.56-0.60).

3.2. Formation regularities of sapropel deposits in Latvia

Sapropel in lakes of Latvia began to form and accumulate in the Early Holocene, about 11,700 years ago, when the climate became favourable for the development of the lake's fauna and flora. It should be noted that before the Holocene, mainly mineral sediments with a low amount of organic matter were accumulating in the lakes because due to the cold and harsh climate, the production of organic matter in the lakes did not exceed the mineralization.

Studies reveal that sapropel stocks have accumulated mainly in the lakes which lakebeds have formed on the glacigenic, glaciofluvial and glaciolimnic sediments of the Upper Pleistocene Latvian suite (Q_3ltv), which have accumulated as a result of glacial and melting waters. In the lakes formed on Holocene sediments (Q_4), sapropel is accumulating in insignificant amounts. The formation of the sapropel is mainly determined by the conditions of the catchment area, it's surface relief, geological structure, the hydrological and hydrographic regime of the lakes, development of the lake's flora and fauna.

The formation of different sapropel classes depends significantly on the type of sediment in the lake catchment area (Figure 3) and the type of lakebed formation. For example, sapropel of the organogenic class is formed mainly in lakes situated at the boundary of glacigenic and glaciofluvial sediments of the Upper Pleistocene (Q_3), because such lakes are generally shallow offering favourable conditions for the accumulation of organic sediments. It is possible that the water currents in these lakes were too weak to leach organic matter but deep enough to prevent the formation of coastal littoral overgrowth, where low type peat is formed. Sapropel with the predominant silicate mineral component is formed in lakes situated on the Upper Pleistocene glaciolimnic (lgQ_3ltv) sediments. These sediments are rich in SiO_2 and Al_2O_3; they contain large amounts of silicates: quartz, feldspar, mica, etc.

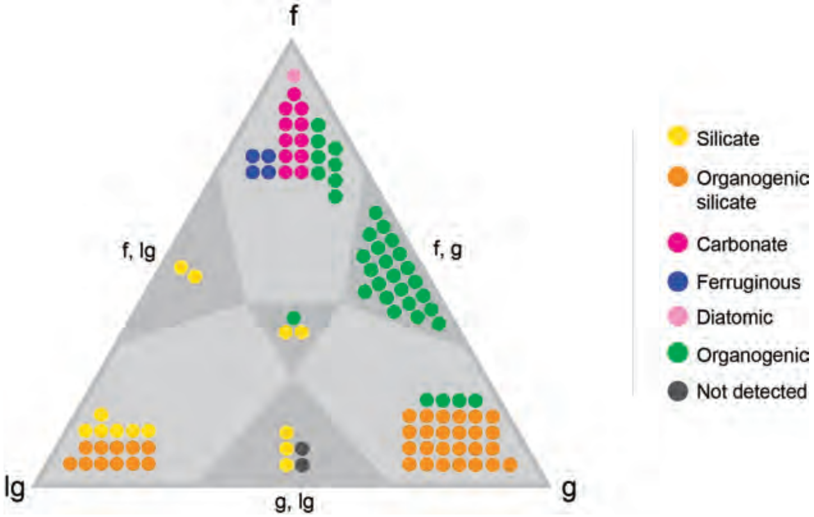


Figure 3. **The percentage (each point is 1%) of distribution of different sapropel deposits in lakes located in the area of the Late Pleistocene deposits: (g) glacigenic deposits (till); (f) glaciofluvial deposits (sand, gravel, pebble); (lg) glaciolacustrine deposits (fine sand, silt, clay)**

Lakes with lakebeds situated on the Upper Pleistocene glaciofluvial (fQ_3ltv) sediments are characterized by the accumulation of various classes of sapropel that do not accumulate in other types of lakes. Such lakes are characterized by large catchment areas, from which carbonates and ferrous minerals were leached, mainly from moraine areas. Organogenic sapropel has accumulated mainly in shallow and eutrophic bays of these lakes.

The correlation of sapropel classes with the characteristic values of the lake – the origin of the lake depression, water regime, trophic condition of the lake and the filling of the lakebed with sediments – reveals that in glacigenic lakes all types of sapropel can be formed (Figure 4). These lakes are the oldest in the territory of Latvia because they were formed during the Vistula glacier.

Silicate sapropel in small amounts was also formed in old rivers and lakes situated on eolian sediments. Both old rivers and former river tributaries are peculiar, small and shallow, elongated or arched lakes in river floodplains. Alluvial material is gradually leaching into these lakes, which also provides a mineral component for sediment formation in these lakes. In the areas of the eolian sediments, small elongated lakes are formed between the dunes, where silicate sapropel has accumulated, the composition of which is influenced by eolian sand on the shores of the lakes. Sapropel stocks in both old rivers and eolian lakes are small, and resources are scarce for economically viable industrial extraction.

Sapropel can be formed in lakes with all types of water regime; however, more extensive stocks are found in lakes with runoff and flow-through water regime.

Sapropel is less common in drain-off lakes because stagnant water is poorly saturated with oxygen, has more reduced transparency, and water layers do not mix. Such conditions are not favourable for lake biota and are being replaced by peat-forming plants.

Trophic condition of the studied lakes reveals that modern industrially relevant sapropel deposits were formed in eutrophic and hypereutrophic lakes. In dystrophic lakes, sapropel formation was stopped by swamping, which limited the development of aquatic animals and plants. In oligotrophic and mesotrophic lakes, the thickness of the sapropel layer and the depth of the water makes the extraction of sapropel economically unprofitable. Lakes filled with sapropel more than 50% are considered to be of industrial importance. Analysis of the database revealed that sapropel with a high amount of mineral components (carbonates, silicates) accumulated in lakes during the Early Holocene. Organogenic sapropels, formed in shallow and overgrown lakes, usually were accumulating above it.

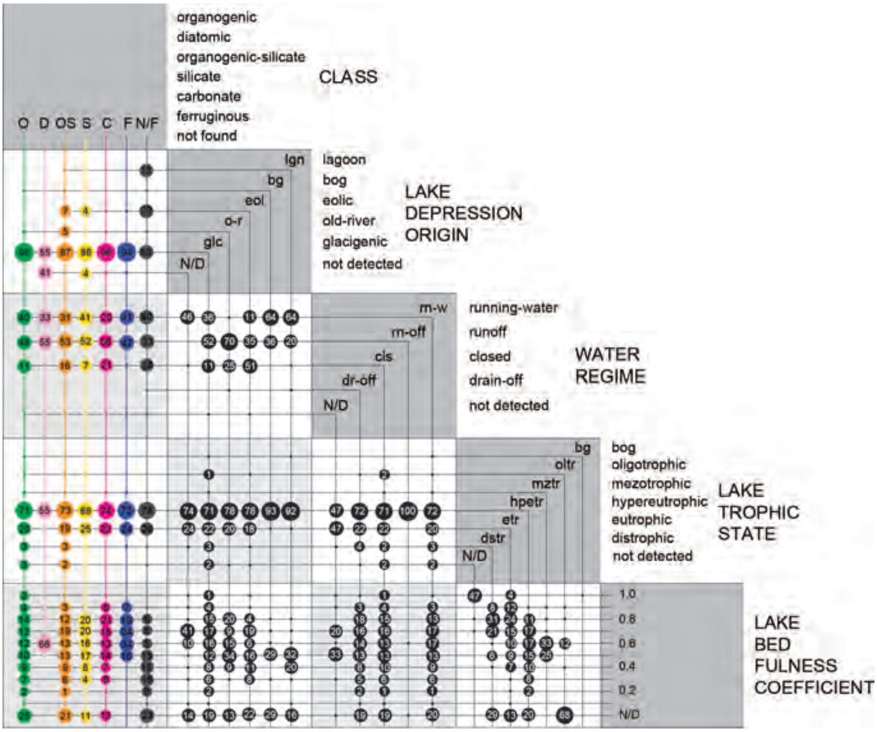


Figure 4. **The percentage of sapropel deposits of different order depending on the lake characteristics**

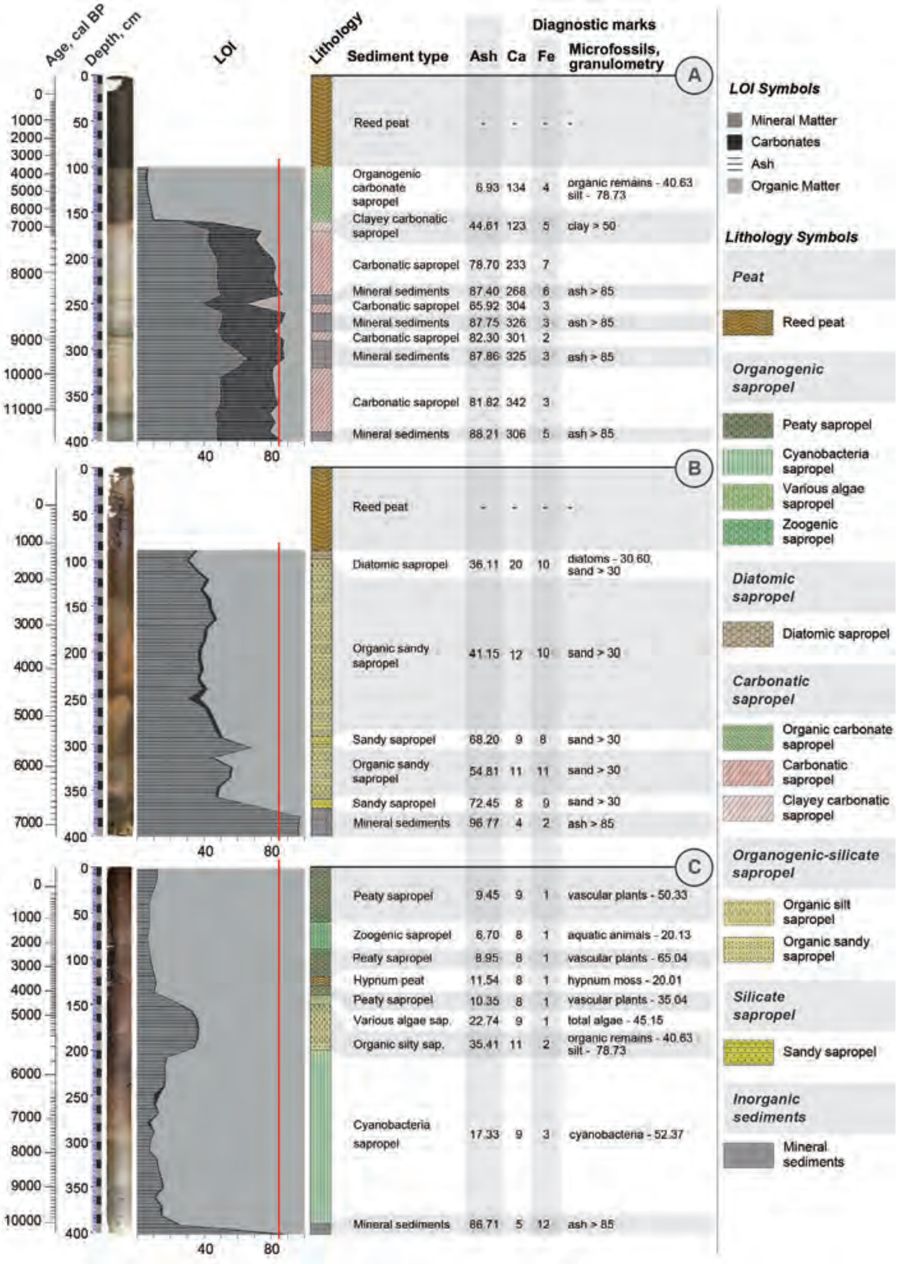
3.3. Reconstruction of environmental and lake conditions during the sapropel formation

When studying climate or environmental change, sediment classification is less important than in the studies of sapropel as a mineral. The parameters of a resource must be strictly defined in search work, as well in legislation and use. Therefore, in order to approbate adapted Freshwater Sarpopel Classification and to reconstruct environmental factors that directly affect sapropel formation and properties in the studied lakes (Padelis, Pilcine and Pilvelis), sediment composition (lithology) of these lakes was determined using the requirements of classification (Table 2). Summarized results of the study reveal that a carbonate sapropel deposit has formed in Lake Padelis, an organogenic-silicate deposit in Lake Pilcines and an organogenic sapropel deposit in Lake Pilvelis (Figure 5).

In Lake Padelis, sapropel had begun to form since the early Holocene before 11,700 cal BP, when the lake became mesotrophic. It is reflected in the composition of microfossils – during this time, diatoms disappear, but in macrofossils a mesotrophic specie Najas marine increases. 8,200 cal BP is well reflected in sediments, the time when spruce-birch forests in the catchment area of the lake are replaced by mixed forests. Up to 3,600 cal BP, carbonate sapropel is formed in the lake; up to 6,700 cal BP carbonate sapropel layers alternated with mineral sediment interlayers. Already before 3,600 cal BP, the amount of carbonates and mineral matter rapidly decline, organogenic sapropel starts to form, a lot of coastal plant debris appears, the lake begins to overgrow rapidly.

The entire sapropel deposit in Lake Pilcine is formed by organogenic-sandy sapropel with an interlayer of sandy sapropel which started to form only in 6,900 cal BP. At that time, the amount of organic matter in the sediments of Lake Padelis was rapidly increasing, indicating a decrease in the catchment area of the lake and fluctuations in the water level. Water level changes have been 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).

Although the type of sapropel in Lake Pilcine since 3,700 cal BP did not change, a rapid increase of diatoms (Melosira, Aulacoseira, Tabellaria, Cyclotella, Cymbella) and green algae (Zygnema, Desmidae) was observed in microfossils, indicating changes in the chemical composition of water. Around this time, peat begins to form in Lake Padelis and Lake Pilvelis. A layer of peat in Lake Pilvelis is formed about 400 years ago, later mainly peaty sapropel is formed. In Lake Padelis, peat is forming up; however, at a depth of ~40 cm the composition of macrofossils reveals an increase in water level. Such changes in the biological composition of sediments in all three lakes indicate a short period of drought. Similar climatic changes are also indicated by the data derived in another lake in Latvia – Lake Mazais Svetins (Stivrins et al., 2014) and many bogs in the territory of Latvia (Kalnina et al., 2019). Before 1,300 cal BP reed peat begins to form in Lake Pilcine.



				Diagnostic marks
Sediment type	**Ash**	**Ca**	**Fe**	**Microfossils, granulometry**
A				
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
B				
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
C				
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

Figure 5. **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)**

In Lake Pilvelis, sapropel has been accumulating since 10,000 cal BP, with the onset of rapid eutrophication processes, as indicated by the macrofossils of Najas marina and Najas flexilis. From 10,000 to 5,800 cal BP, the lake had favourable conditions for the accumulation of cyanobacteria sapropel. The organic matter content of these sediments is higher than 83%, consisting mainly of blue-green algae Lyngbya remains. At that time, the lake water was clear and cold. Meadows were formed in the catchment area, and they were periodically flooded. From 5,800 to 4,500 cal BP, the amount of mineral matter in the sediments increases and organogenic-aleurytic sapropel is formed, the organic residues of which are formed mainly by the blue-green algae Anabaena sp. After 4500 cal BP, organic sapropel with an increased amount of peat-forming plant residues and a 10 cm thick interlayer of peat accumulates in the lake indicating the intensification of lake eutrophication and fluctuations in the water level.

Environmental and lake development and reconstruction of sapropel formation allow concluding that the type of sapropel is closely 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 periods (Figure 6). When the lake ecosystem is still able to perform self-control, the periods of cold and drought are not reflected in the change in the type of sapropel, but appear in the changes in the composition of organic matter-forming organisms – the composition of macro- and microfossils. As the lake catchment becomes swampy and shrinking, it no longer provides a large amount of leaching of mineral components, 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. In the littoral zone of the lake, the formation of sapropel is replaced by the formation of peat, which is caused by the rapid development of peat-forming plants.

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

To determine the intended use of sapropel, it is essential to understand the variability and properties of sediment content. High values of metallic elements can be a decisive factor when using sapropel as a fertilizer, whereas it becomes a negative factor indicating possible toxicity when used as a feed additive.

The distribution and content of metallic elements in the sediment profile provide information on both anthropogenic and naturally occurring flows of metallic elements in the lake ecosystem, runoff regime of a lake, regional climate change, and land-use change in the catchment area during the sediment formation (Dean, 1974).

The concentration of metallic elements in sapropel samples from Lake Padelis, Lake Pilcine and Lake Pilvelis varies over a wide range (Table 5), indicating that the formation of sediments occurred under various environmental conditions during a long period in the water body and its catchment area. Among the analysed metallic elements in the sapropel samples, the highest concentrations were observed for Ca, Fe, Mg, K, Mn, Zn, and Na (in the range of 10-104 µg/g). Other elements (Cu, Ni, Cr, Pb, Co, and Cd) were present in concentrations of <10 µg/g for each.

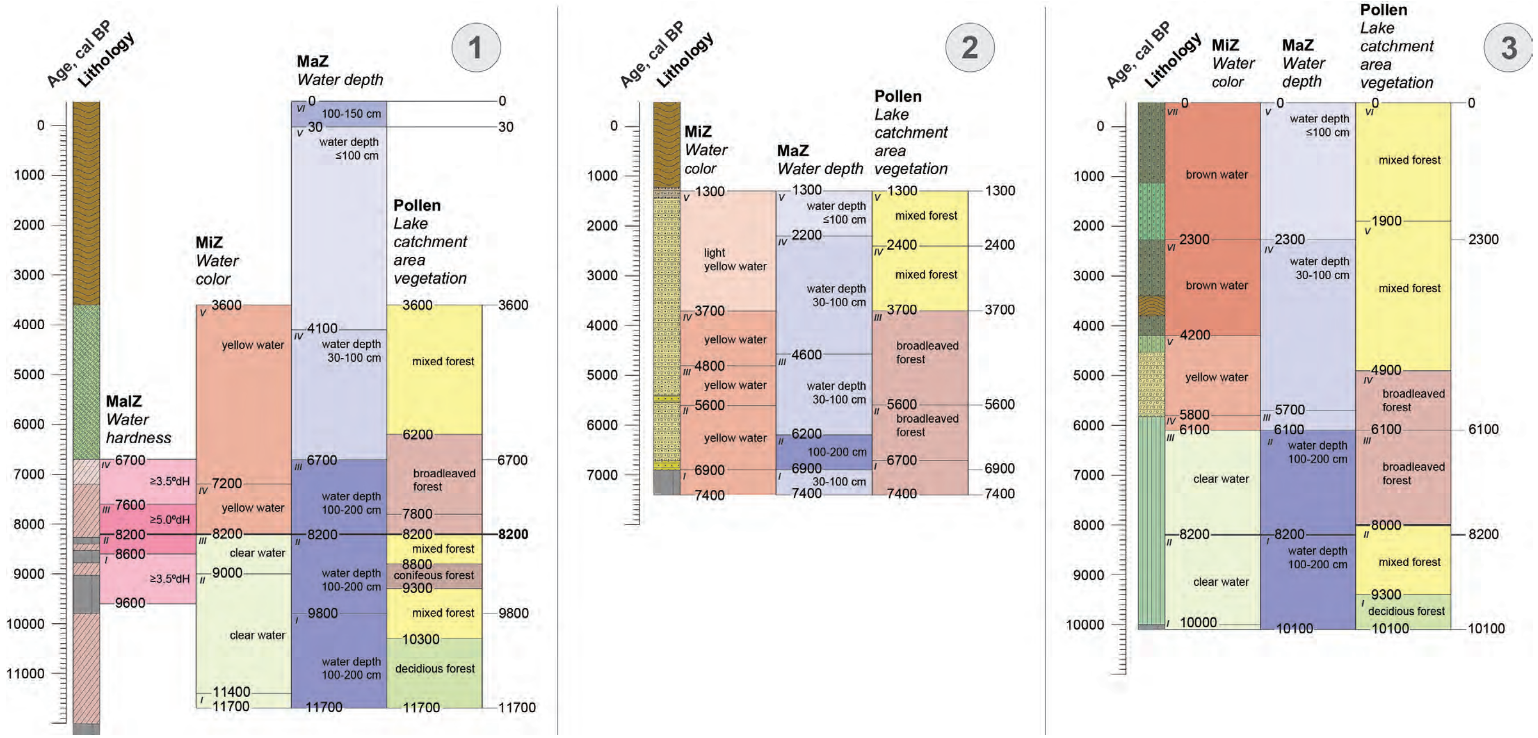


Figure 6. **Comparison of bioproxies in (1) Lake Padelis, (2) Lake Pilcine, (3) Lake Pilvelis**

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	

To assess whether the studied sapropel does not have a high content of metallic elements, the data were compared with element concentration in sapropel from other lakes in Latvia, Belarus and Russia (Table 5).

The main problem in data interpretation is that the accumulation of metallic elements is influenced by various factors (direct effects in the lake catchment and indirect effects such as transboundary air mass transfer, binding of metallic elements to stable mineral forms, geochemical effects of mineral dissolution, etc.). Consequently, the source of a particular element may change over time. It leads to errors in the evaluation process when the data cover more prolonged periods. Statistical analysis can be used as a tool to determine the relationships between element accumulation patterns and to identify trends in metal accumulation throughout the sedimentation period.

The variability of metallic element concentrations and the Pearson correlation of metals revealed that positive correlation bonds exist in the sediments of all three studied lakes between six metals: Co, Cu, Ni, Fe, K, Cr. These metals form an association of pelitophilic elements. These elements are sorbed by clay particles or are part of the crystalline lattice of clay minerals and, therefore, they are transported by minerals and carbonates. The second group of metals is different within each lake.

PCA as the main factor in all lakes reveals the correlation of metal accumulation with the mineral component entering the lake from the catchment area with runoff, flow-through or groundwater. In Lake Padelis they are carbonate-rich terrigenous sediments, in Lake Pilcine – streams of silicate-containing minerals, and in Lake Pilvelis – mineral input from the catchment basin and air.

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.

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