PHYSICAL, CHEMICAL AND MICROBIOLOGICAL CHARACTERIZATION OF THE BOTTOM SEDIMENTS OF THE VOLYN REGION LAKES AND THE POSSIBILITIES OF THEIR USE IN MUD TREATMENT

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INTRODUCTION

In the course of studying and researching the recreational resources of the Western Polissia of Ukraine, it becomes clear that the region has a high recreational and balneological potential due to natural medical and health resources, which include areas with a favorable microclimate, aesthetic landscapes, lake complexes and their shores, forests, mineral water sources and deposits of healing mud, etc. The presence of modern sanatorium-resort facilities and tourist infrastructure creates significant prerequisites for the development of recreation and medical tourism capable of meeting the medical and preventive needs of the population. There is growing popularity of various massages, wraps, applications, etc. using peloids in sanatoriums, cosmetic and SPA centers. Of particular scientific interest in this aspect are sapropel therapeutic muds, the balance reserves of which in the Volyn region rank first in Ukraine (geological reserves are estimated at almost 70 million tons).

1. Classification and economic value of sapropel

Sapropel (Greek sapros – rotten, pelos – mud) is an organo-mineral colloid bottom sediment of lakes with an organic matter content of at least 15 %, as well as inorganic components of a biogenic, chemogenic and terrigenous nature¹. Sapropels in their natural state are multicomponent polydisperse systems. They have three main components: water (from 60 % to 97 %), the ash part (sand, clay, carbonates, phosphates, silica, iron compounds, etc.) and organic matter of a very complex and heterogeneous composition (must not be less than 15 %)². Sapropel belongs to renewable natural resources. The processes of its accumulation continue at the present time, and for many reservoirs they are of a progressive nature³.

 $^{^1}$ Ільїн Л. В. Озерознавство: укр.-рос сл. Поняття і терміни. Луцьк : РВВ «Вежа» Волин. нац. ун-ту ім. Лесі Українки, 2001. 112 с.

 $^{^2}$ Ільїн Л. В. Озерні відклади. Екологічна енциклопедія : у 3 т. / редкол.: А. В. Толстоухов (гол. ред.) та ін. Київ : ТОВ «Центр екологічної освіти та інформації», 2008. Т. 3: О–Я. С. 17.

³ Ільїн Л. В., Мольчак Я. О. Озера Волині. Лімнолого-географічна характеристика. Луцьк : Надстир'я, 2000. 140 с.

According to the classification, sapropels are divided into three types: biogenic, clastogenic, and mixed. The types, in turn, are divided into classes of sapropels: organic, siliceous, organo-silicate, silicate, carbonate and iron. The composition of the organic and mineral parts, their ratio and origin are reflected in the name of the species. A total of 14 species are distinguished⁴. There are given quantitative indicators of ash content, calcium and iron oxide content, organic matter composition for each type of sapropel, as well as the typological characteristics of the water body in which a certain type of sapropel accumulates are determined.

Depending on the diagnostic and typological characteristics of organomineral raw materials, the main directions of sapropel use are distinguished: biogenic types of sapropel can be used as organic fertilizer, feed additives (except peat), therapeutic mud, for the production of building materials, adhesive resins; clastogenic species (organo-silicate classes) it is recommended to use the qualities of fertilizers and therapeutic muds; mixed types of sapropel are recommended for use as a feed additive for animals and as an ameliorant to neutralize acidic soils. In recreation, sapropel is used as therapeutic mud and cosmetic preparations. Low-ash organic sapropels containing amino acids and carboxylic acids, mineral macro- and microelements, and physioactive humic substances are used⁵.

Sapropel in its natural state has a jelly-like appearance. Their color is black, brown, gray, dark olive, gray-yellow, bluish and pink to red. Sapropel usually has no smell, only some varieties smell of hydrogen sulfide. The reaction of the sapropel medium is from weakly acidic to weakly alkaline (pH = 4.2-8.2). Their physical properties: density – 1.4–2.7 g/cm³; specific surface – 1100–3200 m²/kg; natural humidity – 72–98 %; moisture content – 78–87 %; volumetric weight – kg/m^3 ; dispersion – 50–250 µm; hydrolytic 1090-1170 30-50 mg. eq/100 g; absorption capacity - 60-75 mg.eq/100 g; the amount of exchange bases - 90-200 mg. eq/100 g; degree of saturation with bases -64–80 %⁶. The similar composition and properties of sapropel significantly reduce their chemical influence during procedures, determining the therapeutic effect of sapropel mainly due to their thermal effect. When evaluating the medicinal and other properties of sapropels, their physical state and chemical composition are most important, the biological components of peloids are of greatest interest to balneologists. These are vitamins, amino acids, trace elements, humic substances,

 $^{^4}$ Справочник ресурсов сапропеля Украины. Кн. 1. Волынская область. Киев : ГГП «Севукргеология», 1994. 194 с.

⁵ Ільїн Л. В. Лімнокомплекси Українського Полісся. У 2-х т. Т. 2: Регіональні особливості та оптимізація. Луцьк : PBB «Вежа» Волинського національного університету імені Лесі Українки, 2008. 400 с.

 $^{^6}$ Справочник ресурсов сапропеля Украины. Кн. 1. Волынская область. Киев : ГГП «Севукргеология», 1994. 194 с.

enzymes that are derived from microorganisms⁷. Compared to other therapeutic muds, they have higher plasticity, heat capacity, slow heat transfer, convenience of storage, transportation and the possibility of application without special knowledge and skills⁸.

2. Reserves and prevalence of sapropel

Deposits of lacustrine sapropel in Ukraine were actively studied by specialists of the Kyiv Geological Exploration Expedition. Detailed purposeful research was determined by the plans for reclamation development of Polissia which required the implementation of permanent active water and runoff monitoring of the lakes. As of January 1, 2021, 308 sapropel deposits were registered in Volyn (190), Rivne (37), Sumy (55), Kharkiv (22), Chernihiv (2) and Kyiv (2) regions⁹. However, today sapropel remains an undemanded raw material. In Ukraine, mining is carried out at only three deposits, two of them in the Volyn region and one in the Kyiv region¹⁰.

According to the stock materials of the Geoinform Ukraine National Research Institute in the Volyn region, 103 sapropel deposits were covered by detailed exploration, exploration and evaluation work was carried out on 87 deposits. By origin, sapropel of mixed types is most abundant: organo-calcareous, calcareous, organo-ferrous and calcareous-ferrous. The total number of balance reserves of this type was 42736.0 thousand tons, or 62.0 % of all. 14273.7 thousand tons (20.7 %) of sapropel of the clastogenic type (organo-sand and organo-clay class) were explored in the Volyn region. Sapropel of the biogenic type is the least common in lakes. A total of 11882.6 thousand tons, or 17.3 %, of sapropel of mixed-algal, peaty, zoogenous-algal and diatom species were explored in the Volyn region 11.

The largest reserves of sapropel have been discovered in lakes Tur (6518.0 thousand tons) and Volyanske (1373.0 thousand tons) of Ratniv district, Lyubiaz (4040.0 thousand tons) of Lyubeshiv district, Luka

⁷ Ільїна О. В., Пасічник М. П., Пасічник Н. В. Озерний сапропель Волинської області: ресурси та перспективи використання у рекреаційно-курортній діяльності. *Географія та туризм.* 2016. Вип. 35. С. 115–124.

⁸ Струс О. Є., Половко Н. П., Малоштан Л. М., Яценко Е. Ю. Дослідження протизапальних та репаративних властивостей екстрактів сапропелю родовища Прибич. збірник наукових праць співробітників Національного університету охорони здоров'я України імені П. Л. Шупика. Вип. 23. Кн. 4. 2014. С. 392−398.

⁹ Пасічник М. П., Ільїн Л. В., Хільчевський В. К. Сапропелеві рекреаційно-туристичні ресурси озер Волинської області. Луцьк : Волиньполіграф, 2021. 172 с.

¹⁰ Пасічник М. П. Озерні родовища сапропелю Рівненської області та перспективи їх використання. *Географія та туризм.* 2018. Вип. 45. С. 133–141.

¹ Ільїн Л. В. Лімнокомплекси Українського Полісся. У 2-х т. Т. 2: Регіональні особливості та оптимізація. Луцьк : PBB «Вежа» Волинського національного університету імені Лесі Українки, 2008. 400 с.

(3078.0 thousand tons)) and Lutsymer (2025.0 thousand tons) of Shatsk district, Synove (1639.0 thousand tons) and Pishchane (1134.0 thousand tons) of Starovyzhiv district, Yagodynske (1932.0 thousand tons) and Ostrivyanske (1128.0 thousand tons) of the Lyuboml administrative district¹².

3. Physico-chemical and microbiological properties of sapropel

To study the material composition and properties of the solid and liquid phases of lake sapropel, we selected reference deposits. The research was mainly carried out in the lake deposits of the Shatsk National Nature Park (Karasynets, Krymne, Lynovets, Luky, Lutsymer, Moshne, Ozertse, Oleshno, Ostrivyanske, Peremut, Pisochne, Prybych, Pulemetske, Svityaz, Somynets and Chorne Velyke). Important factors in the selection of reference objects were the level of their geological study and recreational and tourist development. The study of deposits located in the Shatsk district has a special scientific value since in the Volyn region a project is being implemented to create a resort of state importance on the basis of the Shatsk Lakeland (decision of the Volyn regional council dated 04.07.2016 No. 4/10)¹³. The lakes located within the Shatsk National Nature Park are considered by many experts as benchmarks¹⁴. They are described in numerous cycles of monographs and in published scientific literature^{15, 16, 17, 18, 19}.

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¹² Ільїна О. В., Пасічник М. П., Пасічник Н. В. Озерний сапропель Волинської області: ресурси та перспективи використання у рекреаційно-курортній діяльності. *Географія та туризм.* 2016. Вип. 35. С. 115–124.

¹³ Пасічник М. П., Ільїн Л. В. Гідромінеральний потенціал проектованого курорту державного значення «Шацьк». *Туризм: наука, освіта, практика*: матеріали Міжнародної науково-практичної конференції з нагоди 5-ої річниці створення кафедри туризму та готельно-ресторанної справи у Національному університеті водного господарства та природокористування (м. Рівне, 15−17 березня 2018 р.) / редкол.: проф. В. С. Мошинський та ін. Рівне : видавець О. Зень, 2018. С. 244–246.

¹⁴ Khilchevskyi V. K., Pasichnyk M. P., Ilyin L. V., Zabokrytska M. R. and Ilyina O. V. Hydrographic characteristics of the Shatsk Lakes according to the EU Water Framework Directive. Conference Proceedings, 15th International Conference Monitoring of Geological Processes and Ecological Condition of the Environment, 2021, Vol. 2021. P. 1–5.

¹⁵ Khilchevskyi V., Ilyin L., Pasichnyk M., Zabokrytska M., Ilyina O. Hydrography, hydrochemistry and composition of sapropel of Shatsk Lakes. *Journal of Water and Land Development*. 2021. № 54. P. 184–193.

¹⁶ Каліновський Д. І., Ільїн Л. В. Донні відклади природних водойм Волинської області та перспективи їх використання у рекреації. *Культура народов Причорноморья*. 2009. Вип. 176. С. 120–122.

¹⁷ Ільїна О. В., Пасічник М. П. Озеро Прибич: лімнолого-геохімічний аналіз. Науковий вісник Херсонського державного університету. Географічні науки. 2016. Вип. 5. С. 75–80.

¹⁸ Fesyuk V., Ilyin L., Moroz I., Ilyina O. Environmental assessment of water quality in various lakes of the Volyn region, which is intensively used in recreation. *Visnyk of V. N. Karazin Kharkiv National University, Series "Geology. Geography. Ecology"*. № 52, 2020. P. 236–250.

¹⁹ Khilchevskyi V. K., Pasichnyk M. P., Ilyin L. V., Zabokrytska M. R., Ilyina O. V. Research of the state of lake systems in Volyn region with the use of satellite images. European

The most important properties of lake sediments, which determine their balneological conditions, were studied. These are, first of all, the mass fraction of moisture, specific gravity, plasticity, stickiness, heat capacity, granulometric composition, clogging with particles larger than 0.25×10^{-3} m (per dry substance), the content of organic substances in terms of organic carbon ($C_{\rm org.}$), reaction environment (pH), redox potential (Eh), mineralization and ionic composition of the solution, radioactivity^{20, 21, 22}.

The sapropel of the studied lakes of the region has a high moisture content in its natural state. Its humidity varies widely from 55.0% to 96.0%. At the same time, low moisture values are typical for sapropel with a high ash content (A^c – 70.0–85.0%) and for the lower horizons of sediments, since the moisture content depends on the amount of organic matter and the degree of compaction of sediments. Also, low values are typical for shallow areas of lakes, where coarse-grained material often dominates, and in places adjacent to river estuaries (for example, in the lake sapropel deposit of Lubyaz, the average humidity is 79.0%)²³. The highest values of natural humidity of sediments are characteristic of the upper (pelogen) layer of sediments.

The granulometric composition is determined to reveal the quantitative ratio of the particles that make up the fraction which is necessary for the assessment of physical properties and further classification of raw materials²⁴. The granulometric composition of the studied sapropel deposits indicates that they belong to finely dispersed systems with a predominance of silt-pelitic fractions. The content of colloidal fractions, the most valuable in balneological terms, corresponding to dimensions less than 0.001×10^{-3} m, in sapropel samples from the supporting deposits varies within the range of 4.00-16.00 %, on average -7.00 % (28 samples).

Coarse siltstone fractions, which are represented by size particles $(0.25-0.01)\times 10^{-3}$ m, vary significantly from 4.70 % (sample No. 26, Lake Chorne Velyke) to 42.6 % (samples No. 192, No. 207, Lake Lutsymer) and,

Association of Geoscientists & Engineers. Conference Proceedings, Geoinformatics, 2021, Vol. 2021, P. 1–6.

²⁰ Лечебные грязи (пелоиды) Украины: монография Ч. 1 / Под общей редакцией М. В. Лободы, К. Д. Бабова, Т. А. Золотаревой, Е. М. Никипеловой. Київ: «Куприянова», 2006. 320 с.

²¹ Державний кадастр природних лікувальних ресурсів. Здобутки і перспективи: монографія / за ред. К. Д. Бабова, О. М. Нікіпелової, А. В. Мокієнко. Одеса: Фенікс, 2017. 150 с.

²² Нікіпелова О. М., Солодова Л. Б. Посібник з методів контролю пелоїдів та препаратів на їх основі. Ч. 1. Фізико-хімічні дослідження. Одеса: Укр. НДІ медичної реабілітації та курортології, 2008. 100 с.

²³ Ilyin L. V. Geochemical peculiarities of bottom sediments in polytypic lakes of Ukrainian Polissya. *Limnological Review*. 2002. Vol. 2. P. 155–163.

²⁴ Ilyin L. V., Ilyina O. V. The lake-swamp complexes of Volyn Region. Lakes and artificial water reservoirs-functioning, revitalization and protection. Sosnowiec: University of Silesia, 2004. P. 71–76.

mainly, confined to the upper horizons of sediments. For the pelitic fraction of sapropel with a size of $(0.01-0.001) \times 10^{-3}$ m, the typical range is 8-16%.

The crystalline skeleton, composed of coarse fragments of silicate materials, gypsum, calcite, dolomite, aragonite, organic remains of animal and plant origin, etc., in sapropel deposits is from 13.4 % to 39.8 % (per natural substance). Its maximum values are typical for the sapropel of lakes Lutsymer, Luka (sample No. 105–39.8 %) and Pisochne (sample No. 4–33.7 %). High-quality therapeutic mud should not contain particles larger than 0.25×10^{-3} m, and the total weight of said particles should not exceed 10 % of the weight of raw mud. In the investigated samples of sapropel, the number of particles with a diameter of more than 0.25×10^{-3} m is within the normal range, ranging from 0.035 % to 0.531 % and rarely exceeding 1 %. Sample No. 105 (Luky), in which the number of particles larger than 0.25×10^{-3} m reaches more than 2 %, turned out to be substandard. However, the presence of the mentioned particles in some cases can provide a normal crystalline skeleton of the mud, since their complete absence leads to excessive rarefaction and the inability to keep the shape of the mud application.

The specific gravity of sapropel is an important indicator during balneological assessment and during technological calculations of raw material reserves at the deposit²⁵. The indicator of the specific gravity of sapropel increases during drying while this indicator is more noticeable for mineralized types of sapropel than for organic ones. The structure of the sapropel and the degree of its diagenetic compaction, which mainly depends on the depth of occurrence, affect the specific gravity, as well as the humidity. The specific gravity of the sapropel of the studied lakes increases in accordance with the decrease in the content of organic substances. For example, the sapropel of Lake Somynets has a specific gravity of 1.0305 kg/dm³ with $A^c - 18.24$ %, and the sapropel of Lake Pisochne – 1.0859 kg/dm³, with $A^c - 37.14$ %. The range of specific gravity varies from 1.0294 kg/dm³ (sample No. 41, Lake Karasynets, h – 4.0–4.5 m) to 1.0859 kg/dm³ (sample No. 2, Lake Pisochne, h – 12.0–14.0 m).

The average specific gravity for sapropel deposits of the Volyn region, based on the results of the analysis of 26 samples, is 1.0561 kg/dm³. Regardless of the composition (the content of organic matter, limestone, silica, and other components), a close relationship between specific mass and moisture is observed. In this way, the universal dependence "density – humidity" is confirmed, which is characteristic of all water-saturated clastic sedimentary rocks, regardless of the composition and type of structural connections.

²⁵ Порядок здійснення медико-біологічної оцінки якості та цінності природних лікувальних ресурсів, визначення методів їх використання. *Збірник нормативно-директивних документів з охорони здоров'я*. 2003. № 9. С. 72–91.

Plastic-viscous properties of peloids are usually determined by shear stress and stickiness. The most optimal shear stress of sapropel peloids is in the range of 50-750 Pa. Sapropel mud of low humidity (shear stress - more than 600-800 Pa) must be diluted with water or oil before use. On the contrary, at high humidity and shear stress less than 100 Pa, preliminary dehydration is necessary²⁶. The shear stress index in the sapropel deposits of the Volyn region varies widely from 102 Pa to 776 Pa (samples No. 21 and No. 23 of the Chorne Velyke Lake deposit). For the sapropel of Pisochne Lake, the average value is 324 Pa, for the sapropel of the Chorne Velyke Lake deposit – 431 Pa, for the Karasynets Lake deposit – 364 Pa, for the Somynets Lake deposit – 506 Pa. The average value of shear stress for the sapropel of the region, based on the results of the analysis of 26 samples, is 401 Pa. Stickiness is an additional balneotechnical indicator of the rheological properties of sapropel. Determining the amount of stickiness comes down to measuring the force required to tear off a brass disk stuck to its surface from the healing mud. According to the results of research by specialists of Ukrainian Research Institute of Medical Rehabilitation and Resortology of the Ministry of Health of Ukraine in sapropel deposits of Volyn lakes, stickiness varies within insignificant limits, from 518.38 Pa (Lake Oleshno) to 678.56 Pa (Lake Pulemetske). Such indicators determine the possibility of using peloids for mud applications, that is, they confirm the ability of sapropel to stay on the body of a recreationist.

Organic carbon is the most reliable indicator of the total content of organic substances in sapropel deposits. Content of $C_{\text{org.}}$ (per dry matter) varies in a fairly high interval, from 4.88% in the mineral deposits of Lake Svityaz to 43.56% in the peaty sapropel of Lake Oleshno. High concentrations are typical for organic types of sapropel. For sapropel peloids of high quality this indicator should not be less than 10.0%.

The indicator that characterizes the content of organic substances in sapropel is loss during burning (LDB). When sapropel is heated to a temperature of 900 °C, its mass decreases due to the removal of water, humus, carbon dioxide, adsorbed gases, and chlorides²⁷. The maximum losses during roasting were recorded in the sediments of the Karasynets Lake deposits, 85.53 % (sample No. 40), Somynets Lake – 81.76 % (sample No. 52) and Pisochne Lake –76.28 % (sample No. 4). High LDB values indicate a decrease in the mineral component in sapropel deposits, i.e. higher concentrations of

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 $^{^{26}}$ Лечебные грязи (пелоиды) Украины : монография Ч. 1 / под общей редакцией М. В. Лободы, К. Д. Бабова, Т. А. Золотаревой, Е. М. Никипеловой. Киев : «Куприянова», 2006. 320 с

²⁷ Нікіпелова О. М., Солодова Л. Б. Посібник з методів контролю пелоїдів та препаратів на їх основі. Ч. 1. Фізико-хімічні дослідження. Одеса: Укр. НДІ медичної реабілітації та курортології, 2008. 100 с.

organic matter. The change of LDB with the depth of deposits shows the nature of sedimentation (dominance of allochthonous or autochthonous component). The optimal value of LDB for sapropel peloids is more than $50\%^{28}$.

 $\begin{tabular}{ll} Table 1 \\ Separate balneological properties of sapropel peloids \\ from the deposits of Shatsk Lakes^{29} \\ \end{tabular}$

Lake deposit	Humidity, %	Ac, %	Hd	Ећ, мВ	Corg., %	Shear stress, Pa	Stickiness, Pa	Specific heat capacity, kJ/ (kg×K)	Clogging with particles >0.25×10 ⁻³ m
Pisochne	96,2	38,9	6,5	-60	26,5	161,46	527,64	4,06	0,235
Svityaz	73,6	83,5	7,2	-15	4,88	412,84	610,96	3,31	0,189
Pulemetske	92,9	52,6	6,6	-55	16,8	196,20	678,56	3,95	0,262
Oleshno	92,2	15,9	6,5	-75	43,5	208,46	518,38	3,93	0,046
Prybych	96,1	10,8	7,0	-80	29,7	294,30	606,33	4,06	0,035

The specific heat capacity of mud is the amount of heat required to heat 1.0 kg of peloids by 1 K (kJ/kg×K)³⁰. For the sapropel of the Volyn region, the heat capacity index varies from 3.31 kJ/kg×K in the sapropel of Lake Svityaz to 4.08 kJ/kg×K in the Pisochne deposit. As you know, water has a higher heat capacity than minerals of the solid phase, therefore, with an increase in the humidity of sapropel, the thermal properties increase, and with a decrease, they decrease. The high thermal properties of sapropel determine its balneological use. The table 2 shows the minimum, maximum, and averaged values of the specific heat capacity of sapropel of the studied deposits.

²⁸ Пасічник М. П., Ільїн Л. В., Хільчевський В. К. Сапропелеві рекреаційно-туристичні ресурси озер Волинської області. Луцьк : Волиньполіграф, 2021. 172 с.

²⁹ Звіт про науково-дослідну роботу «Виявлення природних лікувальних ресурсів на території рекреаційної зони Шацьких озер та їх прогнозна оцінка». Одеса. : ДУ «УкрНДІМРтаК», 2017. 177 с.

³⁰ Нікіпелова О. М., Ніколенко С. І., Солодова Л. Б. Щодо проекту показників безпечності лікувальних грязей (пелоїдів). *Праці Одеського політехнічного університету*. 2013. Вип. 2 (41). С. 205–208.

Table 2

Specific heat capacity of sapropel of the Shatsk lakes, kJ/ (kg×K)

(compiled based on the stock materials of the Geoinform of Ukraine)

Lake	Indicator for the deposit						
deposit	minimum	maximum	average				
Karasynets	3.93	3.93	3.93				
Krymne	3.77	4.06	3.93				
Luky	3.93	3.93	3.93				
Moshne	3.77	4.06	3.91				
Ozertse	3.77	4.02	3.97				
Ostrivyanske	3.93	4.02	3.97				
Peremut	3.81	4.06	3.93				
Pisochne	3.89	4.08	4.02				
Pulemetske	3.31	3.89	3.77				
Somynets	3.56	3.93	3.77				
Lucymer	3.77	4.06	3.89				
Chorne Velyke	3.72	3.89	3.77				

The pH indicator. The studied sapropel deposits are characterized by a significant range of environmental reaction indicators (pH) from alkaline to acidic $(pH=8.49-4.70)^{31}$. The maximum alkalinity is observed in sapropels of lakes where the carbonate type of sedimentation prevails: Lake Krymne (pH-8.49) and Lake Chorne Velyke (pH-8.20). The extreme values of pH in the sediments of the same lake sometimes differ significantly, mostly not by the area of the lake, but in the stratigraphic section and depending on the layer-by-layer occurrence of different types of sapropel. The largest amplitude of fluctuations was recorded in lakes Prybych (pH-3.05) and Moshne (pH-2.86).

In the sapropels of the Karasynets, Krymne, Peremut, Pulemetske, Somynets and Chorne Velyke lakes, a weakly alkaline environment (≥7.0 pH) can be observed, and in the lakes Lutsymer, Moshne, Pisochne and Prybych – slightly acidic (≤7.0 pH). A low amplitude of pH values is characteristic of the sapropel of the Karasynets, Lutsymer, Peremut, and Pulemetske lakes. However, we associate this with the low level of scientific and geological study of these deposits.

Redox potential (Eh) characterizes the state of balanced redox systems in sediments, the existence of which is due to the presence of chemical compounds containing elements with variable valence³². The studied sapropels are characterized by negative Eh values, from -15 mV (Lake Svityaz) to -80 mV

³¹ Ilyin L. V. Geochemical peculiarities of bottom sediments in polytypic lakes of Ukrainian Polissya. *Limnological Review*. 2002. Vol. 2. P. 155–163.

³² Лечебные грязи (пелоиды) Украины: монография Ч. 1 / под общей редакцией М. В. Лободы, К. Д. Бабова, Т. А. Золотаревой, Е. М. Никипеловой. Київ: «Куприянова», 2006. 320 с.

(Lake Prybych), which indicates the superiority of reduction processes in the sediments and favorable conditions for sulfate reduction (which is confirmed by the data of microbiological analyzes: the number of sulfate-reducing bacteria reaches 102–105 CFU/1g of sapropel substrate).

The sapropel of the Volyn lakes has a negligible content of hydrogen sulfide: from 0.004 % (Lake Svityaz) to 0.006 % (Lake Pulemetske, Lake Prybych), which is significantly lower than the therapeutically active concentration (0.1 % per natural substance). All sediment samples are sulphide-free.

4. Sanitary and microbiological condition of bottom sediments of lakes

Sapropel microflora of some lake deposits. In 2017, specialists of Ukrainian Research Institute of Medical Rehabilitation and Resortology of the Ministry of Health of Ukraine studied the number of microorganisms of individual taxonomic and ecological and physiological groups in sapropel of lake deposits of the Volyn region (Table 3). In sapropel samples, saprophytic bacteria – producers of catalase – were isolated. Their greatest distribution was observed in the sediments of Pulemetske and Oleshne lakes. Gramnegative bacteria Pseudomonas fluorescens were detected only in sediments of Lake Pisochne in the amount of 7.8×103 CFU/1 g of sapropel.

 $\begin{tabular}{ll} Table 3 \\ Sapropel microflora of individual Shatsk lakes, CFU/1 g$^{33} \\ \end{tabular}$

Calcated annual	Sample number and lake						
Selected groups microorganisms	№ 1 Svityaz	№ 2 Pulemetske	№ 3 Pisochne	№ 4 Oleshne	№ 5 Prybych		
Saprotrophic bacteria	torrential growth	1.2×104	torrential growth	1.2×104	torrential growth		
Fluorescent pseudomonad	0	0	7.8×103	0	0		
Microorganisms that absorb organic nitrogen	1.5×104	1.5×104	1.5×104	1.5×104	1.5×104		
Fat-splitting microorganisms	7.5×102	7.2×102	0	1.6×102	102		
Oligocarbotrophic bacteria	2.8×103	5.2×103	5.2×103	2.0×104	2.5×102		
Heterotrophic bacteria	3.2×103	0	0	3.2×103	3.8×103		
Iron oxidizing	0	102	102	3.3×103	102		

 $^{^{33}}$ Звіт про науково-дослідну роботу «Виявлення природних лікувальних ресурсів на території рекреаційної зони Шацьких озер та їх прогнозна оцінка». Одеса. : ДУ «УкрНДІМРтаК», 2017. 177 с.

In all samples of sapropel, the presence of bacteria that assimilate organic nitrogen (1.5×104 CFU/ 1 g) is well expressed. The microbiological role of fat-splitting microorganisms consists in the formation of fatty acids and CO₂. The most of them are in the mineralized sapropels of the Svityaz and Pulemetske lakes – 7.5×102 CFU/1 g. The number of oligocarbotrophic bacteria is the largest in organic types of sapropel and ranges from 2.5×102 CFU/1 g (Prybych Lake) to 2.0×104 CFU /1 g (Oleshne Lake). Heterotrophic bacteria – producers of amino acids were found only in samples sapropel from lakes Svityaz (3.2×103) CFU/1 g). of (3.2×103 CFU/1 g) and Prybych (3.8×103 CFU/1 g). Iron-oxidizing bacteria are not numerous and well expressed only in the peaty sapropel of Lake Oleshne $(3.3\times103 \text{ CFU/1 g})$.

The maximum number of microorganisms is observed in the upper horizons of sapropel deposits which is due to the presence of readily available organic substances. As the depth of sapropel deposits increases, the intensity of sulfate reduction increases tenfold, and the number of ammonifying and heterotrophic microorganisms decreases dramatically (up to 100 times) already at a depth of 2.0 m. In this way, various ecological and trophic groups of microorganisms of sapropel deposits participate in the transformation of organic and mineral compounds of mud, enriching it with biologically active substances. A variety of specific microflora of sapropel is the basis of its antibacterial properties.

The sanitary-epidemiological condition of sapropel deposits was assessed based on the results of sanitary-bacteriological analyzes of the bottom sediments of supporting lake sapropel deposits. The complex of sanitary and bacteriological research was carried out in accordance with the criteria given in the "Instructions" and includes the determination of: total microbial count, titer of bacteria of the *Escherichia coli* group, titer *Clostridium perfringens*, pathogenic *Staphylococcus*, *Pseudomonas aeruginosa* and *Enterococcus*. Additionally, salmonella was detected. The research was conducted on samples of the surface layer (0.0–0.1 m) of lake sediments, collected between October 15–21, 2018.

At the time of the research, the sanitary-microbiological condition of sapropel samples taken from Pisochne and Moshne lakes was satisfactory and within normal limits. Total microbial number varied from 0.2×10^{-4} to 0.4×10^{-4} . The presence of *Escherichia coli* bacteria in the said samples of sapropel indicates fecal contamination of the reservoir. *Pathogenic staphylococcus*,

³⁴ Порядок здійснення медико-біологічної оцінки якості та цінності природних лікувальних ресурсів, визначення методів їх використання. *Збірник нормативно-директивних документів з охорони здоров'я*. 2003. № 9. С. 72–91.

Pseudomonas aeruginosa, Enterococcus, and Salmonella were not detected in any of the samples (Table 4).

Table 4
Sanitary and microbiological state of sapropel deposits of lakes of the Volyn region, 2018³⁵

	Lake sapropel deposit, sample number and sediment sampling depth					
Microbiological indicators	Pisochne, № 14C, h – 1,5 m	Moshne, № 15C, h – 1,0 m	Peremut, № 16C, h – 2,0 m	Somynets, № 17C, h – 0,5 m		
Total microbial numbers, CFU·g ⁻¹	$0,2 \times 104$	$0,4 \times 104$	$0,2 \times 104$	$0,2 \times 104$		
Escherichia coli, CFU/10 g	> 10	> 10	> 10	> 10		
Clostridium perfringens, CFU· (0.1 g) ⁻¹	> 0,1	> 0,1	> 0,1	> 0,1		
Staphylococcus, CFU· (10 g) ⁻¹	ı	I	_	-		
Pseudomonas aeruginosa, CFU· (10 g) ⁻¹	-	=	-	_		
Coli forms, CFU· (10 g) ⁻¹	-	-	-	-		
Enterococcus, CFU· (10 g) ⁻¹	_		_	_		
Salmonella, CFU/25 g	=	=	=	=		

Note: "-" is not detected.

The bactericidal effect of sapropel was determined in relation to a test culture of *Escherichia coli* with an infectious dose of 10–6 CFU/1 cm³ according to the method used by specialists of the Ukrainian Research Institute of Medical Rehabilitation and Resortology of the Ministry of Health of Ukraine³⁶. The antimicrobial activity of sapropel against Escherichia coli was observed in daily dynamics until the complete death of the test culture. The research was conducted in the laboratory of soil microbiology of the Volyn branch of the State institution "Institute of Soil Protection" (Lutsk). The bactericidal index of peloids was calculated using the formula that takes into account the logarithm of the colony-forming units of *Escherichia coli* inhibited by sapropel extract, as well as the time during which the death of the test culture occurred. If the indicator is $100.0 \% \ge BIP \ge 50.0 \%$, the sample was assessed as highly bactericidal, if $49.0 \% \ge BIP \ge 39.0 \%$ – moderately bactericidal, and if $38.0 \% \ge BIP \ge 1.0 \%$ – low bactericidal. BIP was

³⁵ Пасічник М. П., Ільїн Л. В., Хільчевський В. К. Сапропелеві рекреаційно-туристичні ресурси озер Волинської області. Луцьк: Волиньполіграф, 2021. 172 с.

³⁶ Порядок здійснення медико-біологічної оцінки якості та цінності природних лікувальних ресурсів, визначення методів їх використання. *Збірник нормативно-директивних документів з охорони здоров'я*. 2003. № 9. С. 72–91.

determined on samples of sapropel deposits collected on October 15–21, 2018 (Table 5).

Bactericidal index of sapropel of the Volyn region³⁷

Lake deposit Humidity, % pH Escherichia coli, day Bacterial peloids, %

№	deposit	Humidity, %	рн	coli, day	peloids, %
1 ^B	Prybych	94,72	6,23	7	86
2^{B}	Chorne Velyke	95,56	8,17	10	60
3^{B}	Krymne	71,82	8,49	10	60
4^{B}	Pisochne	81,13	6,42	8	75
5 ^B	Moshne	79,22	6,28	7	86

Sample

The results of the study show that all samples of lake sediments are highly bactericidal by the value of BIP (BIP >50.0%). The fact of complete death of the *Escherichia coli* test culture was recorded during 7–10 days (on average almost 9 days). The fastest complete death of *Escherichia coli* was observed in samples of organic sapropel species No. 11B (Lake Prybych) and № 15B (Lake Moshne) – on the 7th day, the bactericidal index, calculated according to the method, was 86%. The test culture dying process lasted the longest in the sapropel samples of the Chorne Velyke and Krymne lakes³⁸.

We measured the natural radioactivity of the territory adjacent to the lake deposits with the ECOTEST TERRA MKS-05 dosimeter. In the places where the bottom sediments were collected and the territories adjacent to the deposits, the radiation background was in the range of 0.07–0.11 $\mu Sv/h$ (or 7–11 $\mu R/h$). It should be noted that the level of natural radioactivity did not exceed the natural background of the region, which, according to the data of the Volyn Regional Laboratory Center of the Ministry of Health of Ukraine, is 10–13 $\mu R/h$ and the requirements of the state hygienic standard "Radiation Safety Standards of Ukraine", according to which the dose load should not exceed 1 mSv/year (0.114 $\mu Sv/h$) 39 .

Table 5

 $^{^{37}}$ Пасічник М. П., Ільїн Л. В., Хільчевський В. К. Сапропелеві рекреаційно-туристичні ресурси озер Волинської області. Луцьк : Волиньполіграф, 2021. 172 с.

³⁸ Пасичник М. П. Сапропелевые лечебные грязи Волынской области Украины. Wschodnioeuropejskie Czasopismo Naukowe. 2020. № 1 (53), С. 26–30.

³⁹ Ільїн Л. В., Громик О. М. Уміст радіонуклідів у лімносистемах Західного Полісся (на прикладі водойм зони радіоактивного забруднення Волинської області). *Науковий вісник Волинського національного університету імені Лесі Українки. Географічні науки.* 2012. № 18. С. 4–10.

CONCLUSIONS

The sapropel of the investigated support deposits with an organic matter content of more than 50.0 % is mostly homogeneous, retains good plasticity and stickiness in a wide moisture range, and has high specific heat values. In particular, the natural humidity of lake sediments is in the range of 55.0–96.0 %; clogging with particles with a diameter of more than 0.25×10^{-3} m does not exceed 2.0 %; losses during burning reach 85.53 %; specific gravity ranges from 1.0294 kg/dm^3 to 1.0859 kg/dm^3 ; the shear stress varies within 102-776 Pa, and the stickiness is not lower than 518.38 Pa; heat capacity reaches $4.02 \text{ kJ/(kg}\times\text{K)}$; the reaction of the environment varies from weakly alkaline to weakly acidic (pH -8.49-4.70); redox potential - reducing (from -15 mV to -80 mV); organic carbon is present in amounts from 4.88 % to 43.56 % on dry matter. According to the microbiological conditions the sapropel of the Volyn lakes, in most cases, meets the epidemiological requirements. Confirmed bactericidal properties against *Escherichia coli* (BIP -60-86 %).

The bottom sediments of the lakes of the Volyn region meet the regulatory requirements established for therapeutic muds and are classified as freshwater, sulfide-free sapropel peloids of various degrees of mineralization – organic ($A^c - <30.0\%$), organo-mineral silicate or carbonate class ($A^c - 30.0-50.0\%$) and mineralized ($A^c - >50.0\%$).

Sapropel healing mud has high plasticity, heat capacity, slow heat transfer, convenience of storage, transportation and the possibility of application without special tools and skills at home.

Further research of sapropel deposits is connected with the preparation and implementation of the state target program for the infrastructure modernization of the sanatorium-resort complex of the region, with the creation of an integrated management system for the use of natural resources, stabilization and improvement of the ecological state of the surrounding natural environment, as well as with the organization of monitoring on the territory of resorts and natural healing facilities – health resources. Preservation and rational use of lake sapropels, study and development of other deposits will contribute to their further involvement in the sanatorium-resort industry.

SUMMARY

The aim of the paper is to evaluate the resources of lake's sapropel in Volyn region suitable for use in the recreational and health resort activities as therapeutic peloids. The publication gives data on quantitative characteristics of sapropel resources in Volyn region. Examined the prospects of using Lake's sapropel area in health resort activity. The analysis shows that the Volyn region has significant reserves of sapropel suitable for use in the recreational and health resort activities.

The practical significance is the possibility of using systematic material of lake's sapropel in Volyn region, as a key factor in the development of curative tourism in the region. Materials of the article could be used to promote and popularize the therapeutic sapropel in Volyn region on the market of recreational and health services.

References

- 1. Fesyuk V., Ilyin L., Moroz I., Ilyina O. Environmental assessment of water quality in various lakes of the Volyn region, which is intensively used in recreation. *Visnyk of V. N. Karazin Kharkiv National University, Series* "Geology. Geography. Ecology". № 52, 2020. P. 236–250.
- 2. Ilyin L. V. Geochemical peculiarities of bottom sediments in polytypic lakes of Ukrainian Polissya. *Limnological Review*. 2002. Vol. 2. P. 155–163.
- 3. Ilyin L. V., Ilyina O. V. The lake-swamp complexes of Volyn Region. Lakes and artificial water reservoirs-functioning, revitalization and protection. Sosnowiec: University of Silesia, 2004. P. 71–76.
- 4. Khilchevskyi V. K., Pasichnyk M. P., Ilyin L. V., Zabokrytska M. R. and Ilyina O. V. Hydrographic characteristics of the Shatsk Lakes according to the EU Water Framework Directive. Conference Proceedings, 15th International Conference Monitoring of Geological Processes and Ecological Condition of the Environment, 2021, Vol. 2021. P. 1–5.
- 5. Khilchevskyi V. K., Pasichnyk M. P., Ilyin L. V., Zabokrytska M. R., Ilyina O. V. Research of the state of lake systems in Volyn region with the use of satellite images. European Association of Geoscientists & Engineers. Conference Proceedings, Geoinformatics, 2021, Vol. 2021. P. 1–6.
- 6. Khilchevskyi V., Ilyin L., Pasichnyk M., Zabokrytska M., Ilyina O. Hydrography, hydrochemistry and composition of sapropel of Shatsk Lakes. *Journal of Water and Land Development*. 2021. № 54. P. 184–193.
- 7. Державний кадастр природних лікувальних ресурсів. Здобутки і перспективи : монографія / за ред. К. Д. Бабова, О. М. Нікіпелової, А. В. Мокієнко. Одеса : Фенікс, 2017. 150 с.
- 8. Звіт про науково-дослідну роботу «Виявлення природних лікувальних ресурсів на території рекреаційної зони Шацьких озер та їх прогнозна оцінка». Одеса : ДУ «УкрНДІМРтаК», 2017. 177 с.
- 9. Ільїн Л. В. Лімнокомплекси Українського Полісся. У 2-х т. Т. 2: Регіональні особливості та оптимізація. Луцьк : PBB «Вежа» Волинського національного університету імені Лесі Українки, 2008. 400 с.
- 10. Ільїн Л. В. Озерні відклади. Екологічна енциклопедія: У 3 т / Редкол.: А. В. Толстоухов (гол. ред.) та ін. Київ : ТОВ «Центр екологічної освіти та інформації», 2008. Т. 3: О-Я. С. 17.

- 11. Ільїн Л. В. Озерознавство: укр.-рос сл. Поняття і терміни. Луцьк : РВВ «Вежа» Волин. нац. ун-ту ім. Лесі Українки, 2001. 112 с.
- 12. Ільїн Л. В., Громик О. М. Уміст радіонуклідів у лімносистемах Західного Полісся (на прикладі водойм зони радіоактивного забруднення Волинської області). *Науковий вісник Волинського національного університету імені Лесі Українки. Географічні науки*. 2012. № 18. С. 4–10.
- 13. Ільїн Л. В., Мольчак Я. О. Озера Волині. Лімнолого-географічна характеристика. Луцьк : Надстир'я, 2000. 140 с.
- 14. Ільїна О. В., Пасічник М. П. Озеро Прибич: лімнолого-геохімічний аналіз. *Науковий вісник Херсонського державного університету*. *Географічні науки*. 2016. Вип. 5. С. 75–80.
- 15. Ільїна О. В., Пасічник М. П., Пасічник Н. В. Озерний сапропель Волинської області: ресурси та перспективи використання у рекреаційно-курортній діяльності. *Географія та туризм.* 2016. Вип. 35.
 - C. 115-124.
- 16. Каліновський Д. І., Ільїн Л. В. Донні відклади природних водойм Волинської області та перспективи їх використання у рекреації. *Культура народов Причорноморья*. 2009. Вип. 176. С. 120–122.
- 17. Лечебные грязи (пелоиды) Украины : монография Ч. 1 / под общей редакцией М. В. Лободы, К. Д. Бабова, Т. А. Золотаревой, Е. М. Никипеловой. Киев : «Куприянова», 2006. 320 с.
- 18. Нікіпелова О. М., Ніколенко С. І., Солодова Л. Б. Щодо проекту показників безпечності лікувальних грязей (пелоїдів). *Праці Одеського політехнічного університету*. 2013. Вип. 2 (41). С. 205–208.
- 19. Нікіпелова О. М., Солодова Л. Б. Посібник з методів контролю пелоїдів та препаратів на їх основі. Ч. 1. Фізико-хімічні дослідження. Одеса : Укр. НДІ медичної реабілітації та курортології, 2008. 100 с.
- 20. Пасичник М. П. Сапропелевые лечебные грязи Волынской области Украины. *Wschodnioeuropejskie Czasopismo Naukowe*. № 1 (53), 2020. С. 26–30.
- 21. Пасічник М. П. Озерні родовища сапропелю Рівненської області та перспективи їх використання. *Географія та туризм.* 2018. Вип. 45. С. 133–141.
- 22. Пасічник М. П., Ільїн Л. В. Гідромінеральний потенціал проектованого курорту державного значення «Шацьк». Туризм: наука, освіта, практика : матеріали Міжнародної науково-практичної конференції з нагоди 5-ої річниці створення кафедри туризму та готельноресторанної справи у Національному університеті водного господарства та природокористування (м. Рівне, 15–17 березня 2018 р.) / редкол.: проф. В. С. Мошинський та ін. Рівне : видавець О. Зень, 2018. С. 244–246.

- 23. Пасічник М. П., Ільїн Л. В., Хільчевський В. К. Сапропелеві рекреаційно-туристичні ресурси озер Волинської області. Луцьк : Волиньполіграф, 2021. 172 с.
- 24. Порядок здійснення медико-біологічної оцінки якості та цінності природних лікувальних ресурсів, визначення методів їх використання. *Збірник нормативно-директивних документів з охорони здоров'я*. 2003. № 9. С. 72–91.
- 25. Справочник ресурсов сапропеля Украины. Кн. 1. Волынская область. Киев : ГГП «Севукргеология», 1994. 194 с.
- 26. Струс О. €., Половко Н. П., Малоштан Л. М., Яценко Е. Ю. Дослідження протизапальних та репаративних властивостей екстрактів сапропелю родовища Прибич. Збірник наукових праць співробітників Національного університету охорони здоров'я України імені П. Л. Шупика. Вип. 23. Кн. 4. 2014. С. 392–398.

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