

Freshwater sapropel (gyttja): its description, properties and opportunities of use in contemporary agriculture

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Abstract. Sapropel (gyttja or dy) is a type of fine-grained and loose sediments, rich in organic matter, deposited in freshwater bodies. Properties of sapropel and quite wide possibilities of extraction makes it as an important natural resource that can be used predominantly in agriculture, horticulture, forestry, farming. Sapropel and its processing products are environmentally friendly, non-toxic, with a definite content of nutrients. The aim of the current paper was to gather the available information about the sapropel properties and its application in agriculture as soil fertilizer or soil amendment, indicating the efficiency and possible ways amounts of application. Another reason why the investigation of sapropel is important in the Baltic States and northern Europe is its wide distribution and availability in freshwater bodies that leads to find out new ways of extraction and bioeconomically-effective utilization of this highly valuable natural resource, obtainable in economically significant amounts, with high opportunities of its use in agriculture. Contemporary agriculture strongly desiderates in new products of high effectivity enhancing soil and crop productivity and quality hand in hand with sustainable development and careful attitude to the nature and surrounding environment.

Key words: lake sediments, humic substances, organic fertilizer, soil amendment, natural resources.

INTRODUCTION

Sapropel, also called as ‘gyttja’ or ‘dy’, is a renewable natural resource, which can be found as the quaternary freshwater organic sediments that accumulate due to the deposition of remains of aquatic plants and animals, mixed with mineral components. Sapropel is a unique geological formation occurring at the bottom of a waterbody throughout its existence (Lopotko, 1974; Lopatin, 1983; Bambalov, 2013). Sapropel formation 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, 2005).

Various freshwater sediments, including sapropel, are widely distributed in many waterbodies of the world. The most intensive formation and accumulation of sapropel is characteristic to the temperate zones of Asia and Europe (Russia, Scandinavian Peninsula, France, Germany, Poland, the Baltic States, Belarus and Ukraine), and the continent of America in the Great Lakes region (Canada and USA) (Shtin, 2005).

Sapropel deposits in waterbodies appeared after the glacier retreat. In the Baltic countries it happened 12–15 thousand years ago (Braks, 1971). Massive sapropel formation in this region took place in the Holocene (12 000 yr BP – present), and because of that, it is not only a valuable natural resource, but also a material evidence for studies of the past climate changes (Yu & McAndrews, 1994; Axford et al., 2009; Stančikaitė et al., 2009; Heikkilä & Seppä, 2010; Ozola et al., 2010; Grimm et al., 2011; Klavins et al., 2011; Stankevica et al., 2015).

Sapropel can be of autochthonous origin, if its accumulation takes place due to the lake biomass deposits; and also of allochthonous origin, where sediments accumulate a large amount of humic substances, which enter the lake from the surrounding areas and marshes (Cranwell, 1975; Largin, 1991; Golterman, 2004). Sapropel of autochthonous origin with maximum organic matter content is considered to be more valuable, since the initial biomass, its biochemical degradation and transformation into sapropel organic substances does not create polycyclic aromatic hydrocarbons, such as benzopyrene, which is characteristic to soil, peat and particularly coal humic substances (Dmitriyeva, 2003).

Basic composition of sapropel consists of three components: minerals of allochthonous origin, inorganic components of biogenic origin, and organic matter arising from remains of plants and animals existing in the lake and its surroundings (Stankeviča, 2011).

Wide distribution of sapropel and versatility of application possibilities makes these organic sediments as an important strategic natural resource. It is used in agriculture, horticulture and forestry as an organic fertilizer and soil conditioner, in farming, for example, as an additive in farm animal feeds. Besides that, sapropel is a suitable raw material for the chemical and construction industry as well as it is applicable in medicine or cosmetology as a therapeutic mud and can be used as a raw material for the production of coagulants.

The aim of the current paper was to gather the available information about the sapropel properties and its application in agriculture as soil fertilizer and soil filler in recultivated or eroded areas, indicating the effectivity and possible ways and amounts of application. Another reason why the investigation of sapropel is important in the Baltic States and northern Europe is its wide distribution and availability in freshwater bodies that leads to find out new ways of extraction and bioeconomical utilization of this highly valuable natural resource. Until now, peat is the main natural resource widely applicable in agriculture as a growth medium, substrate and soil additive (atsauce); however, the use of peat in many countries will be restricted in near future, thus giving a way for development of new soil amendments using alternative resources among which sapropel can be mentioned.

It should be noted that intensive investigation of sapropel was performed during the middle of 20th century, especially in the countries of eastern Europe (e.g., Russia, Belarus, Latvia, Lithuania). Thus the current paper summarizes historical data and scientific information that has been published locally, but which is valuable for the sapropel research and economic efficiency evaluation nowadays in larger scale.

CHARACTERISTICS AND CLASSIFICATION OF SAPROPEL

Sapropel is a type of fine-grained and loose sediments, rich in organic matter, deposited in waterbodies. In petrology, the term ‘sapropelic coal’ denotes the sediments that are formed in the aquatic environment from the remains of macrophytes. The term ‘sapropel’ is often used to designate mainly dark-coloured sediments, rich in organic carbon (Emeis, 2009).

In a narrower sense ‘sapropel’ (from Greek, ‘*sapros*’ rotten + ‘*pelos*’ mud) denotes contemporary or subfossil, colloidal sediments of continental waterbodies characteristic with a fine structure, that contains significant quantities of organic matter and remains of microscopic water organisms with a small amount of inorganic biogenic component content and admixture of mineral ingredients, which may include sand, clay, calcium carbonate and other minerals (Korde, 1960; Lācis, 2003).

Usually sapropel is formed in a relatively anoxic environment, as a result of physicochemical and biochemical transformations of lake hydrobionts with the participation of various mineral and organic substances in terrigenous (from Latin, ‘*terrigenus*’ created by land) runoff. The sapropel composition and properties in various fields of deposit are very various, and these differences are determined by the productivity of the particular waterbody, surface runoff characteristics and climatic conditions at the area. In general, sapropel is considered to be the specific freshwater sediments with the organic matter content greater than 15%, otherwise, if organic matter content is lower, such deposits are considered to be the mineral lake sediments (Korde, 1960; Kurzo, 2005).

Peat is a natural resource widely applicable in agriculture as a growth medium, substrate and soil additive (Bohne, 2007); however, the use of peat in many countries, e.g., Switzerland and United Kingdom, will be restricted in near future (Waller & Temple-Heald, 2003), thus giving a way for development of new soil amendments using alternative resources among which sapropel can be mentioned. Sapropel differs from peat, as summed up in Table 1, with its fine structure, reaction, quantity of organic matter, the remains of organisms forming it and the amount of humic substances (Korde, 1960; Lishtvan et al., 1989; Bambalov, 2013).

Table 1. The main differences between natural resources such as peat and sapropel

Indicators	Natural resource	
	Sapropel	Peat
Environment of formation	Relatively anoxic	Anoxic
Place of formation	Lakes, estuaries, rivers	Marshes, bogs
Organic matter content, %	15–85	< 50
Sources forming the organic matter	Aquatic organisms: phytoplankton, zooplankton, vascular water and coastal plants	Marsh plants: deciduous and coniferous trees, bushes, grasses, moss

Formation of a 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 certain aims of an individual research (Lundquist, 1927; Titov, 1950; Kireycheva & Khokhlova, 1998; Schnurrenberger et al., 2003). According to the origin of sediments, they can be divided

into two large groups: 'gyttja' attributed to autochthonous sediments and 'dy' – to allochthonous sediments. Later the German scientist R. Lauterborn extended this classification by adding the term 'sapropel' describing sediments characteristic with hydrogen sulphide odour (Hansen, 1959; Kurzo, 1988). The modern understanding of the term 'sapropel' has been introduced by H. Potonie. Classifying lake sediments, H. Potonie singled out two groups: 'sapropel' – viscous, finely dispersed residue, containing 25–90% organic matter, and mineralized sediments – 'sapropelite', which further can be split according to their mineral components: diatomite, lime, iron and sand (Kurzo et al., 2012).

A more detailed and most often used classification of sapropel has been provided by Pidoplichko & Grishchuk. According to their suggestion, lake sediments can be subdivided into seven types (Pidoplichko & Grishchuk, 1962):

- **Clayey sapropel** is highly mineral; usually it is deposited in lakes naturally; it is pasty, heavy, in grey or grey-blue colour;
- **Calcareous sapropel** characteristic with ash content higher than 35% (including 50–65% CaO); deposits are formed in calcium rich groundwater outflow locations; it is of a grey-green colour, after drying out it forms unbound, whitish-grey mass;
- **Silicate sapropel** has a high ash content – greater than 30% (including SiO₂ >30% and CaO <10%); it is grey-green or green with sand grains and dark-coloured, dense dykes;
- **Mixed sapropel** has very high ash content (about 70–80%); it can contain a large amount of calcium and silicates, silicate and clay or clayey particles and calcium; such mixed lake sediments are formed from plankton organisms. Mineral supply source for this type of sapropel can be ground or surface waters; it can be greyish, dark green, blue-green or greyish-brown;
- **Organic (fine detritus) sapropel** has a low ash content not exceeding 30%. It is green, and with an admixture of humus – greenish-brown. Organic sapropel is formed in waterbodies that do not have large mineral matter inflow;
- **Coarse detritus sapropel** has low ash content. It accumulates in lakes, where in addition to planktonic organisms there are many vascular aquatic plants, whose residues in large quantities remains in sapropel. This sapropel is usually dark green in colour and the higher aquatic plant trace inclusions can be observed therein. It is usually deposited on the other sapropel types and does not form thick layers;
- **Peaty sapropel** is formed when the peat deposits come into a contact with a lake, or results from overgrowing of eutrophic waterbodies littoral. This is the intermediate formation between sapropel and peat, brown in colour and containing a variety of helmatic plants – residues of reeds, sedges, horsetails and other plants. When pulverized, peat sapropel does not smear, nor stain; it is characterized by a very low ash content (8–10%) and high decomposition (around 25–30%). This type of sapropel is deposited in layers between peat and sapropel deposits.

During the 70s of the 20th century, Belarusian scientists developed sapropel classification (Table 2), taking into account the requirements of industry and the principles of sapropel genesis (Yevdokimova et al., 1980). This classification is based on quantitative analysis of seven indicators describing the chemical structure of sediments; each isolated type of sapropel is defined as a raw material for a specific direction of use – this is the most complex sapropel classification. Nowadays this

classification is practically adopted as the Governmental Standards of the Republic of Belarus (BSSCI, 2010).

According to the ratio between the organic and mineral part, the authors classify sapropel as low ashy (ash content less than 30%) and high ashy (ash content of 31–85%) sapropel. Low ashy sapropel is divided in four types, according to the ratio of humic substances and easily hydrolysable substances associated with the genesis of the proteins in sediments. The first type of sediments contains larger amounts of allochthonous humic material. The other three types of organic sapropel contain humic substances formed of autochthonous material. The sapropel group with high ash content is further categorized into three subtypes based on the chemical analysis of the mineral part: sapropel containing silicon dioxide, carbonate sapropel and mixed sapropel. Taking into account the sapropel composition and properties, the given classification determines the most rational use of sapropel (Braks et al., 1967).

D. Nikolayev's states that the sapropelic organic matter consists of the aquatic organisms, e.g., algae, phytoplankton, zooplankton, higher aquatic animals and plants (Nikolayev, 2003). The proportion of these remains (green algae, cyanobacteria, zooplankton, vascular plants) in sapropel determines the characteristics and quantity of sapropel's organic matter, as well as the fields of its use. For example, sheaths of green algae mainly consist of cellulose (Horne & Goldman, 1994), which is poorly degradable over time, subsequently, sapropel which organic mass proportion consists of green algae is rich in cellulose, but poor in humic substances and minerals. Consequently, this type of sapropel can be rationally used as an adhesive or binder in production of various ecological building materials.

N. Braks definition of sapropel's organic substances can be used when reviewing sapropel from the aspect of chemical technology, in which the organic mass elemental composition is reflected: content of carbon, hydrogen, oxygen, nitrogen and sulphur. The average composition of these elements in sapropelic organic substances is (normalized %): C = 55%; H = 6.7%; N = 2.5%; O = 35.0%, C/H ratio \approx 7.0–8.9 (Braks, 1971).

Studies of sapropel derived from 130 localities in Belarus determined that fluctuations of C, H and N in one type of sapropel depend on its constituent components. Elevated C, but lowered H and N content is characteristic of sediments, which contain 40–60% humic substances and are mainly formed from vascular plants. H and N content increases in sapropel with more zoogenic residues, while C content decreases (Yevdokimova et al., 1980).

Scientists in Latvia revealed that nitrogen content is not directly related to the sapropel mineralization degree, because sapropel with a different ash content has approximately the same amount of nitrogen, but distribution of nitrogen content (also the ash content) in vertical cross-sections of the sediments in different localities differs due to its nature (Braks et al., 1967; Braks, 1971).

Lopotko believes that the maximum concentration of nitrogen is in the pelogenous layer (7.0–7.5% of organic matter) – the layer where active microbiological and biochemical processes take place and large amounts of microorganism protein and nitrogen fixed from the air by cyanobacteria are accumulated (Lopotko & Kislov, 1990).

Table 2. Industrially genetic classification of sapropel (after Yevdokimova et al., 1980)

Type	Form	Label	Diagnostic properties		Utilization	Diagnostic indicators
			A _c , %	Biological composition and oxides, %		
Organic	Peaty	Opr ₁	<30	Thelmatic plants >70	Growth promoters, HS products, fertilizers, production of construction materials	
	Organic, with a high HS content	Opr ₂	<30	Thelmatic and vascular aquatic plants 50–70	Therapeutic mud, biologically active substances, fertilizers	A _c *
	Organic, with a medium HS content	Opr ₃	<30	Diatoms and cyanobacteria	Fillers, drilling solutions, therapeutic mud, fertilizers	
	Organic, with a low HS content	Opr ₄	<30	Green algae –	Binder substances, drilling fluids, therapeutic mud, fertilizers	
Containing silicon dioxide	Silicate (low ash content)	Kp ₁	30–50	Diatoms >90 SiO ₂ /CaO >2 Fe ₂ O ₃ <10	Fertilizers, drilling fluids, production of construction materials, therapeutic mud	
	Silicate (high ash content)	Kp ₂	50–85	Diatoms >90 SiO ₂ /CaO >10 Fe ₂ O ₃ <10	Soil colmatation, tamponage solutions, fertilizers	A _c SiO ₂ /CaO Fe ₂ O ₃
	Autogenous silicate	Kp ₃	30–50	Diatoms >90 SiO ₂ /CaO >2 Fe ₂ O ₃ <10	Growth promoters, therapeutic mud	
	Silicate ferruginous	Kp ₄	>30	Diatoms >90 SiO ₂ /CaO >2 Fe ₂ O ₃ >10	Therapeutic mud	
Carbonate	Carbonate	Kapδ ₁	>30	SiO ₂ /CaO <0.4 Fe ₂ O ₃ <5	Animal feed additives rich in minerals and vitamins, therapeutic mud, soil liming	A _c SiO ₂ /CaO Fe ₂ O ₃
	Carbonate ferruginous	Kapδ ₂	>30	SiO ₂ /CaO 0.4–0.7 Fe ₂ O ₃ >5	Soil liming, tamponage solutions, therapeutic mud	Minerals = = A _c +CO ₂
Mixed	Mixed organic silicate carbonate	CM ₁	>30	SiO ₂ /CaO 0.7–2.0 SiO ₂ /Fe ₂ O ₃ >4 CaO/Fe ₂ O ₃ >3 SO ₃ >10	Fertilizers, construction material production, therapeutic mud	
	Mixed silicate carbonate ferruginous	CM ₂	>30	SiO ₂ /CaO 0.7–2.0 SiO ₂ /Fe ₂ O ₃ 1.0–4.0 CaO/Fe ₂ O ₃ 0.4–3.0 SO ₃ <10	Drilling solutions, construction material production, therapeutic mud	A _c SiO ₂ /CaO SiO ₂ /Fe ₂ O ₃ CaO/Fe ₂ O ₃ SO ₃
	Mixed organic silicate ferruginous	CM ₃	>30	SiO ₂ /CaO 0.7–2.0 SiO ₂ /Fe ₂ O ₃ <1 CaO/Fe ₂ O ₃ <0.4 SO ₃ <10	Therapeutic mud	
	Mixed organic carbonate sulphate	CM ₄	>30	SiO ₂ /CaO 0.7–2.0 SiO ₂ /Fe ₂ O ₃ >1 SO ₃ >10	Therapeutic mud	

*A_c – ash content, %

Changes of nitrogen content in vertical sections of sediments as well as other chemical indicators can be used for sapropel layer splitting in certain stratigraphic horizons.

Content of nitrogen in various types of sapropel ranges from 2.7% to 6% of organic substances and 0.5 to 4.0% dry weight. Organic substances of sapropel, which include animal residues, contain more nitrogen (4.4–4.8%) than algae (3.0–4.2%) or peat forming plant residue (2.6–3.5%) (Ponomareva, 2002).

Content of sulphur in sapropelic organic matter ranges from 0.1% to 1.8%, not exceeding 3% in the dry mass, but while industrially preparing and storing sapropel, sulphur compounds are oxidized, thus the acidity increases (Kazakov & Pronina, 1941; Yevdokimova et al., 1980; Lopotko et al., 1983). The highest sulphur concentrations in organic substances are present in the carbonate sapropel (Kireycheva & Khokhlova, 1998).

According to the elemental composition the freshwater sapropel is similar to humus. The sediments of saline lakes contains smaller amount of organic substances (approximately $\geq 10\%$); flora and fauna is poorer in these lakes and mineralization processes are faster (Lishtvan & Lopotko, 1976; Shtin, 2005).

It should be noted that the total content of organic substance in various sapropel types is different: in organic sapropel 70–93% in silicate and carbonate sapropel – 15–70%, in mixed sapropel – 15–70% (Lopotko, 1974; Pidoplichko, 1975; Yevdokimova et al., 1980; Kireycheva & Khokhlova, 1998).

ORGANIC SUBSTANCES OF SAPROPEL

Organic substances of sapropel can be defined in various ways:

- Undissolved remains of hydrobionts and autochthonous colloidal substances, as terrigenous input through runoff. It is the sum of biological and organic components (Baksheyev, 1998; Nikolayev, 2003);
- A complex of low molecular weight organic compounds and biopolymers, and adsorption complexes with minerals (Lopotko et al., 1983).

Sapropel can be defined as an underwater form of humus while the classifying the biolites of organic matter – the sedimentary rocks composed primarily of extinct animals, plants and their life product remnants (Hansen, 1959), but other scientists distinguish soil, peat and sapropel humus, considering them as accumulation forms of organic matter with various origins (Filippov et al., 1969).

Any carbon containing fossil sediments consist of various groups of chemical compounds (Poznyak & Rakovskiy, 1962). Identification of different compound groups extracted from the organic mass of sapropel is based on fractionation methods; therefore, according to these methods several composition variations of individual components have arisen. Poznyak and Rakovskiy (1962) identified following compounds within the sapropelic organic mass:

- Bitumens;
- Water-soluble substances;
- Easily hydrolysable substances (including humic and fulvic acids);
- Cellulose;
- Non-hydrolysable substances.

Similarly Baksheyev (1998) isolated such sapropelic organic substances as bitumens, hydrocarbons, sapropel acids and the non-hydrolysable substances. Comparing the group of chemical compounds in various sapropel samples, it was established that the groups of substances (e.g., humic acids, non-hydrolysable substances), according to their chemical nature from different sites, are not identical and in great extent are dependent on the properties of sapropel forming organisms (e.g., plankton, vascular plants, humic substances) and their transformation conditions (Braks, 1971).

Kireycheva & Khokhlova (1998) in their study of sapropel isolated bitumens and lipids (extracted with non-polar solvents such as benzene, diethyl ether etc.), humic substances (extracted with alkaline solutions), easily hydrolysable substances (extracted after hydrolysis using 2% HCl), difficult hydrolysable substances (extracted after hydrolysis using 80% H₂SO₄) and non-hydrolysable substances (remaining after the sequential extraction of all fractions). Bitumens extracted from sapropel have a larger molecular weight of fatty acids than peat bitumens, and sapropel storage on the field for two months, increases concentration of bitumen in sapropel by 1.5 times (Karpukhin, 1998). Bitumens are organic substances (lipids) that can be extracted from sapropel with a variety of organic solvents. Bitumen composition is characterized by fatty acids, steroids, carotenoids, paraffin, wax and glycerol content (Orlov et al., 1996). Sapropel bitumen components attract particular attention because they have a high bactericidal, bacteriostatic and antioxidant activity. Several studies have focused on the easy and efficient methods to obtain these substances from sapropel (Kireycheva & Khokhlova, 1998; Šire, 2010). Organic substances that have been only slightly altered are composed of peloid bitumen (therapeutic mud), which contain a large number of double bonds and functional groups – carotene, phospholipids, unsaturated fatty acids and alcohols (Fillipov et al., 1969).

Lopotko with colleagues (1992) in their studies determined that sapropel has a low bitumen content of 2–7% of the organic mass, but Poznyak & Rakovskiy (1962), extracting bitumens with gasoline and alcohol-benzene mixture, obtained them in amount 4.3–9.9%. In low ash and medium ash sediments bitumen quantities usually do not exceed 5%, rarely they can reach 6.0–8.1% of the organic mass (Ponomareva, 2002). Bitumen content in sapropel is lower than in peat; sapropel bitumens predominantly consist of saturated compounds. Sapropel bitumens differ from the peat bitumens with lower acidity level and lower saponification that indicates a content of neutral character compounds – hydrocarbons (Kazakov & Pronina, 1941).

Sapropel is characterized by low carbohydrate amount, because during the sapropel formation there is an active decomposition of the carbohydrates to carbon dioxide and humification (formation of the humic substances in the reactions of amino acid condensation). An average quantity of hemicellulose in organic matter of sapropel is 6–25%, but cellulose – 1–8% (Pidoplichko & Grishchuk, 1962). Sapropel components contain 1–2% of cellulose. Sapropel carbohydrate complex consists of ≥80% of hemicellulose; therefore it can be used in production of animal feed additives and fertilizers applicable in agriculture and horticulture (Lopotko et al., 1992).

Composition and properties of sapropel humic substances are determined by their most important features such as biological activity, biochemical stability, binding ability etc. Depending on the content and the specific relationship of humic substances, sapropel that is brought into soil may variously affect biochemical processes, soil structure

formation resulting in quality of agricultural products. Sapropel humic substances differ from the soil humic substances with a higher carbon/hydrogen ratio and absence of saturated aromatic rings (Orlov et al., 1996). Humic substances of sapropel are more reduced and possess a greater activity than soil humic substances. Humic substances of sapropel consist from humic acids, fulvic acids and humine. Extraction of humic substances from sapropel minerals and organic compounds is usually performed according to the classical scheme of Tyurin, which is used for studying the chemical composition of soils (Orlov et al., 1996). Investigated sapropel samples are decalcified to remove carbonates. Although this method is simple, natural polymer dissolution and deposition do not enable a complete elimination of all low molecular weight components (carbohydrates, alcohols, amino acids), therefore, depending on the investigated object and purposes, this scheme is often modified (Karpukhin, 1998; Kireycheva & Khokhlova, 1998).

Humic acids is the largest group of organic substances. They are usually extracted from the sediments with alkaline solvents and precipitated into an acid environment (pH 1–2). The dark brown colour is characteristic to humic acids. In humic acids of fen and raised peat the amount of carbon ranges from 57.7% to 64.2%, while hydrogen from 4.3% to 5.4% (Kazakov & Pronina, 1941). Humic acids of sapropel differ from the peat in the sense of elemental composition as follows: the hydrogen content is higher than that of peat humic acids, which indicates the presence of fatty acids. Y. Kazakov (1950) stated that higher content of nitrogen in sapropel humic acids testifies to humin like compounds – melanoids, generated by the condensation of protein decomposition substances (amino acids and substances formed as a result of carbohydrates destruction). Types of sapropel humic substances vary in elemental composition, content of functional groups and fragments, which are determined by sapropel forming substances, and the humification conditions of the particular reservoir (Stepanova, 1996).

Valuable finding indicates the presence of water-soluble vitamins in sapropel: ascorbic acid (C), B group vitamins – thiamine (B1), riboflavin (B2), pantothenic acid (B5), pyridoxine (B6), folic acid (B9) and cyanocobalamin (B12). Large quantities of fat-soluble vitamins – tocopherol (E), vitamins D and P were also found (Shtin, 2005). Sapropel containing cyanocobalamin (vitamin B12), which is concentrated in the upper layer (up to 1 m) of sediments, has a high value to be applied as a livestock feed additive. Experimental studies show that vitamin B12 is synthesized by many microorganisms in mud sediments, it plays an important role in protein exchange and other processes, but as many vitamins are not stable substances, refrigeration or long storage of sapropel reduces the cyanocobalamin content (Letunova, 1958).

CHEMICAL COMPOSITION OF MINERAL SUBSTANCES IN SAPROPEL

Mineral components of sapropel are important for the characteristics of sediment type and application potential in agriculture. Formation process of mineral components in the bottom sediments is associated with sedimentation of terrigenous runoff minerals as well as organic and chemical deposition of mineral ions dissolved in a lake waterbody. Usually terrigenous runoff minerals are quartz (SiO_2), dolomite ($\text{CaMg}(\text{CO}_3)_2$), silicates and aluminosilicates (e.g., feldspar, hydromica, chlorites, kaolinite). Biochemical processes lead to the accumulation of calcite and aragonite (carbonates of Mg, Ca, Sr, Ba, Fe, Mn), pyrite (FeS_2), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hematite (Fe_2O_3), marcasite (FeS_2)

and vivianite into the sapropel of a watercourse (Korde, 1960; Krasov et al., 1986; Lopotko & Yevdokimova, 1986; Wetzel, 2001).

Among the iron minerals the brown oxides are prevalent – iron(III) oxyhydroxides, hydrogoethite (FeOOH), more rarely – iron pyrite and phosphates, rarely – siderite (FeCO₃). Iron heptahydrate minerals are typical of the lower part of the sapropel layer, where siderite and part of the iron phosphates are formed. This happens due to the decomposition of organic matter and any reduction conditions resulting thereof. Iron phosphates, as well as the brown iron oxides are common in all genetic types of sapropel – content of iron phosphate increases with the decrease of carbonates. Content of these phosphates in carbonate sapropel is about 0.4%, in mixed sapropel – 0.8%, but in sapropel containing silica – 1.4%. Calcium phosphates in sapropel occur in the form of apatite, iron phosphates – in the form of vivianite (Krasov et al., 1986). The total amount of iron in sapropel constitutes 2–18%, rarely as much as >25%. The iron generally enters the sediments in the form of colloidal organo-mineral compounds together with the clay particles. Fe₂O₃ in organic sapropel typically constitutes 4.9%, in sapropel containing silicon dioxide – 5.6%, carbonate – 4.7%, mixed sapropel – 8.4%, but sometimes this figure may reach 30–50% of the ash volume (Shtin, 2005). Large quantities of iron, especially in mobile forms, have suppressing influence on the plants (Yevdokimova et al., 1980). Intensive mineral depletion takes place in aquatic environment, and thereby the quantity of iron mobile forms increases, and may represent up to 80% of the total iron mass (Lopotko et al., 1983). Iron compound reduction and mobility decreases in the process of drying and ventilating in the air, and a part of hydrated forms transit into crystals. Mobile iron compounds do not exceed 1% in air-dry samples (Yevdokimova et al., 1980; Lopotko & Yevdokimova, 1986).

At the integrated level the mineral composition of sapropel is evaluated according to the ashiness (composition/content of ash). The greatest part of the ash is made up by iron and calcium phosphates – within the ash composition in the form of the stable oxide there are not less than one 1% of the following compounds: SiO₂, Fe₂O₃, Al₂O₃, CaO, MgO, Na₂O, K₂O, P₂O₅ (Yevdokimova et al., 1980). Russian, Lithuanian and Latvian scientists consider sediments with ash content greater than 85% to be the lake sediments with a high ash content (Nikolayev, 2003).

The correlations of silicon component accumulation in various types of sapropel showed that the silicon enters sapropel in form of suspension from the remains of diatoms and accumulate in bacteria; the major component of the ash characteristic to organic sapropel is SiO₂, while other silicon compounds are present in very small quantities. Significant differences of silicon compounds in the ash of organic sapropel were not determined (Lopotko & Yevdokimova, 1986; Kireycheva & Khokhlova, 1998). Mixed sapropel contains a slightly larger quantity of ash, but its content is identical to that of the organic sapropel when SiO₂ dominates in ash. If the mixed sapropel contains carbonates, then CaO+MgO content is 7.9% to 16.6%, but the ash content of such sapropel can reach 60%. Silicate sapropel contains silicon oxide in free form – quartz and quartz in the form of various silicates and aluminosilicates, and the content ranges from 30.3% to 70% (Kurzo, 1988). Diatoms sapropel contains amorphous silicic acids, which are more available to plants (Lopotko, 1974), but the abundance of silicon does not have a toxic effect on plants (Nikolayev, 2003).

The main mineral component of carbonate sapropel is calcium carbonate. The mineral form of calcium is dolomite, clayey-ferruginous carbonate aggregates and

biogenic calcite. Carbonates (about 20–50% of the total content) are present as amorphous and colloidal compounds, which have an organic origin and a high degree of mobility (Yevdokimova et al., 1980). CaO content of carbonate sapropel may reach 90%, but in organic sapropel – 0.4% to 5.25% of ash. Mixed sapropel contain 0.9–12.5% of CaO, but silicate sapropel – 1.2–12.3% of dry matter, on average in different sapropel types CaO content ranges from 0.7% to 37% of dry matter.

Calcite precipitation in eutrophic waterbodies is promoted by the photosynthesis of plants, which bind CO₂, and organisms (molluscs, small barnacles) that during their lifetime accumulate calcium in the cells. As the amount of sulphate in water increases, reduction of sulphate may occur, resulting in calcareous sediments. The presence of calcium in the watercourse accelerates the decomposition of organic matter and increases the calcium content of the sediments (Stable, 1986). Due to increased acidity which is caused by larger CO₂ content in the organic matter degradation process, carbonates may also fail to deposit (Nikolayev, 2003).

Aluminium content of sapropel changes within the range from 0.3% to 11%, usually it is within 2–4% range and its higher concentrations can be found in silicate sapropel, as it contains clay minerals. The studies of sapropel in Belarus did not reveal the presence of amorphous forms of aluminium, which are highly toxic to plants (Kurzo, 1988; Wetzel, 2001).

LIVING ORGANISMS IN SAPROPEL AND THEIR ROLE IN BIOLOGICAL ACTIVITY

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

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

Regarding living organisms in sapropel, range of substances transformation are carried out, not only formation of sapropel sediments, but also regeneration and preservation of sediment properties over time. Microorganisms are involved in the mineralization and synthesis of organic substances in sapropel; it determines the

presence of various gases (e.g., hydrogen sulphide, ammonia, methane) and their quantity in sediments. Biochemical substances formed by microorganisms in biological processes also determine some physically chemical properties of sapropel. Sediments like sapropel are tended to accumulate biologically active and antibacterial substances, which are of a great importance in balneology, as well as in agriculture and soil recultivation perspectives.

USE OF SAPROPEL IN AGRICULTURE

Sapropel has a very wide range of possible application ways in broad spectrum of fields of national economics (Fig. 1), among which agriculture currently takes the greatest part. Sapropel can be applied widely, from a 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 cost-effective, sustainable and well-grounded perspective market niche development.

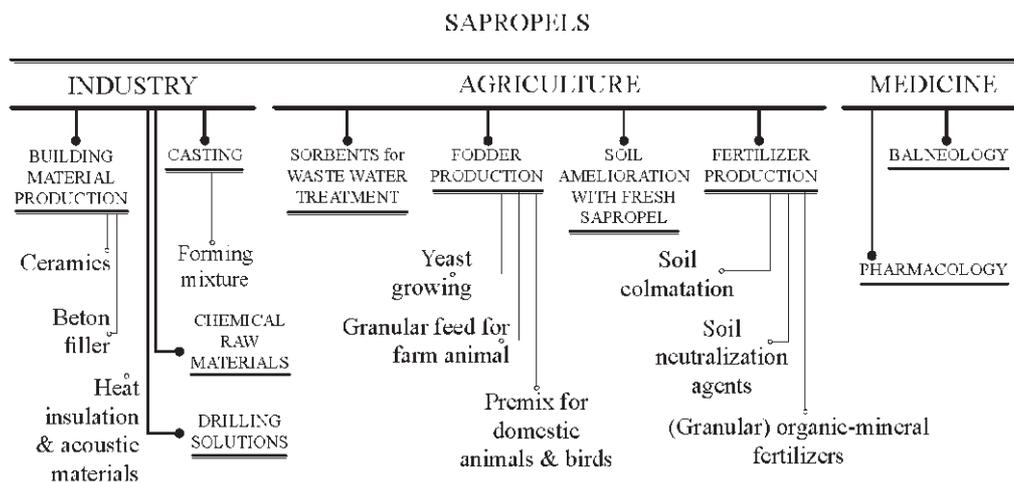


Figure 1. Application options of sapropel in fields of national economics (authors' workout, according to Kurzo, 2005).

Among the possible applications of sapropel, animal feed production already is an existing field. Sapropel alkali extracts, similarly to lignite and peat extracts, contain 40% humic substances. Improvement of animal feed mixtures' efficiency using sapropel has been extensively studied in Lithuania and Belarus during the second half of the 20th century. Sapropelic feed additives improve operation of animal liver and stomach, blood formation and circulation, reduces the occurrence of diseases and increases resistance of animal health to adverse environmental conditions (Lishtvan & Lopotko, 1976; Soldatenkov, 1976; Yevdokimova et al., 1980; Shtin, 2005). The most valuable type of sapropel for use in feed additives is deemed to be the organic sapropel, because it contains enough high concentration of proteins, vitamins, enzymes and other biologically active substances, but studies conducted in Lithuania have showed that

almost all types of sapropel can be used in a production of feed additive (Soldatenkov, 1976; Kurzo, 2005).

Currently increasing popularity is attributed to feed additives of sapropelic humus such as sodium humate. These humic formulations enhance the oxidation processes in animal body, i.e., helps to increase and accumulate proteins in blood and body mass, increases the formation of erythrocytes in the red bone marrow, improves synthesis of vitamin A and other vitamins, normalizes metabolism and is effective in the treatment of toxicities (Shtin, 2005).

Another highly important application way of sapropel in agriculture is its use for preparation of soil substrates or growth media. Major criteria in this respect is content of organic matter and balance of pH in sediments (Semakina et al., 2001). Sapropel as soil substrate can be used in form of mixtures with peat, sludge and any kinds of composted biowaste (Kurzo, 2005; Yongoing et al., 2010). Some authors suggest also supply of mineral fertilisers to improve the application potential of sapropel (Skromanis et al., 1989). Most widely the possibilities of sapropel application in soil substrates or soil amendments have been tested in Belarus, where actual applications of sapropel in agriculture reached 1.5 million tons per year (Kurzo, 2005).

According to the data provided by Kurmysheva (1988), keeping sapropel on the field for two months the quantity of bitumen increases twice, but storing the sapropel in settling tanks for one year the amount reduces by 1.5–2 times. However, in case of sapropel stored in the settling tanks the analysis of samples from upper layer revealed the increase of bitumen quantity 6.0–7.6%, and these changes are analogous to the sapropel that is stored on the field and where over time appropriate microflora developed as well. Storing sapropel in settling tanks for five years, the amount of bitumen increased, but did not reach the initial scores. Multiple freezing and refreezing of sapropel did not significantly influence the quantity of bitumen fractions (Kireychева & Khokhlova, 1998).

Another field of recently developed sapropel application is a production of liquid sapropel-based fertilisers and sapropel extracts containing a complex of biologically active substances, predominantly taking into account content and specifics of humic substances (Diskovska et al., 2011; Ferdman et al., 2011). Sapropel extracts and mixtures containing humic substances can be obtained using extraction with alkaline solutions and dispersion technologies. Recent studies have demonstrated high efficiency of such formulations for various crop cultures and extension of application options (Pastukh & Popov, 2007; Ferdman et al., 2011; Bunere et al., 2014). For example, laboratory tests implemented at the Department of Environmental science in the University of Latvia involved cultivation of radish in hydroponics where liquid fertilizer of humic acids derived from sapropel was tested. Investigating the efficiency of liquid fertilizer at various concentrations, it was detected that humic acids in concentration of 5 mg L⁻¹ lead to increase of radish root dry mass by 94%, but dry mass of foliage increased by 1.5 times, in addition with double increase of total chlorophyll content in comparison to the control samples. Parallel experiments were performed using suspension of raw sapropel and water at various concentrations, recalculating to the amount of humic substances. Obtained results revealed lower efficiency, i.e., dry mass of radish roots increased only by 62% (Bunere et al., 2014). Efficiency of raw sapropel application can be influenced by several factors such as chemical state of humic substances as they might present in other forms than salts, as well as a deficiency of K⁺

ions that stimulate seed germination and plant development (Ponomareva, 2002). Ponomareva (2002) conducted two years long field experiment cultivating crops and fertilizing them only three times during a vegetation period using a liquid containing 0.01% potassium saponin humates. Results indicated an increase in a crop yield for tomato cultivars (30–35%), potato (20–25%), cucumber (45–50%), sweet pepper (25–35%), sugar beet (25–45%), wheat (30–35%). Besides the crop yield increase, application of potassium saponin humates elevated crop resistance against several plant diseases such as peronosporosis, *Botrytis cinerea*, bacteriosis and verticilliosis (Ponomareva, 2002).

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

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

Group 2 – saponin with organic matter content from 10% to 50% is used for production of complex mineral fertilizers, which are rich in lime, phosphoric acid, total nitrogen and organic matter;

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

Notable results in practical performance of soil fertilization using saponin were achieved in 1954–1955 in Latvia at the Bulduri Horticultural Technical College (Vimba, 1956). Comparable field experiments were accomplished using saponin, manure and saponinite as fertilizers in light sandy soil for cultivation of potatoes, cabbages and carrots. Results indicated increase of crop yield in favour of saponin (Table 3).

Table 3. Impact of saponin, saponinite and manure application as fertilizers on crop yield (Vimba, 1956)

Crop	Fertilizer*	Yield, (cnt ha ⁻¹)	Yield, (%)
Potatoes	Control	207	100
	Manure	255	123
	Saponin	334	160
	Saponinite	292	141
Cabbage	Control	360	100
	Manure	580	160
	Saponin	630	175
Carrots	Control	441	100
	Manure	595	135
	Saponin	618	140
	Saponinite	618	140

*Fertilizer was applied at concentration 30 t ha⁻¹; control – without fertilizer

Experiments showed that using saponin in humic soil pots, and replacing the humic soil with saponin, early cabbage seedlings in saponin pots developed much better and were stronger than the seedlings in the usual humus pots. Besides saponin, in tests also

sapropelite (containing about 25% of organic matter) derived from the Lielupe River (Latvia) was used. Compared with control, applications of sapropelite increased the carrot yield by 40%, potatoes yield by 41% and cucumber yield by 60% (Vimba, 1956).

Another, ten years long, study done by Lithuanian scientist using carbonate sapropel revealed that sapropel addition to soil may change not only soil acidity but also can increase moisture level of soil as well as total porosity, independently from meteorological conditions. After all fertilizer treatments was not detected changes in soil density. Use of carbonate sapropel as soil fertilizer can improve soil physical properties better than limestone applications. Data analysis of crop productivity changing season by season increased in higher level after applications of carbonate sapropel applications in comparison with limestone due to sapropel's mineral content and plant nutrition potential (Daugvilienė, 2014).

The most rational use of sapropel would be distribution within the industry and agriculture. Economic value of this natural resource can increase by applying more valuable types of sapropel in the chemical industry, but those with higher rate of mineralization in subfields of agriculture.

CONCLUDING REMARKS

Agriculture, including forestry, horticulture, conventional and organic, domestic and industrial, food and feed crop cultivation, urban gardening, and also animal breeding and soil recultivation after intensive exploitation are among the most important and perspective spheres of sapropel application potential. Contemporary agriculture strongly desiderates in new products of high effectivity enhancing soil and crop productivity and quality hand in hand with sustainable development and careful attitude to the nature and surrounding environment. Sapropel is a natural resource obtainable in economically significant amounts, and in this time of shortage of resources worldwide, it has to be exploited at utmost appropriate way, giving benefits for both, economics and environment.

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