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**Dimitar Dimitrov<sup>1</sup>, Petko Dimitrov<sup>1</sup>, Veselin Peychev<sup>1</sup>,  
Krasimira Slavova<sup>1</sup>****APPLICATION OF NATURAL NANOSIZED MATERIALS  
(NANO-FOSSILS) FROM THE BLACK SEA  
TO AGRICULTURE, NANOTECHNOLOGIES  
AND NEW MATERIALS**

*The deep sea organic mineral sediments (DSOMS) (sapropelic, diatomic and coccolithophoridic) of the Black Sea are built mainly of nano-sized materials, which can be applied in the modern nanotechnologies and material sciences. They are applicable in re-cultivation of acidic soils polluted with heavy and radioactive elements. The supplement stimulates the growth of the plants. From 1984 to 2004, a series of experiments have been carried out on different agricultural plants. In the article the results of these experiments are considered.*

During the last years deep sea organic mineral (sapropelic, diatomic and coccolithophoridic) sediments (DSOMS) of the Black Sea have been profoundly studied with a main goal to use these sediments as a complex raw material for multipurpose allocation (Dimitrov et al. 1999; Дегадюк и др., 2000, Шнюков, Клещенко, Куковская, 2003; Шнюков, Зиборов, 2004, Димитров, Георгиев, Димитров, 2006). Deep sea organic-mineral sediments are widespread along the continental slope and on the abyssal seafloor and are practically inexhaustible in supplies.

Except for the sapropel, the high carbonate coccolithophoridic silt can be also considered as an independent product. They lie directly in the upper layer of the seafloor and have a thickness of up to 50 cm. A nanosize is characteristic of the numerous phyto- and zooplankton nano-fossils species such as coccolithophora (*Emiliana huxleyi*) built of amorphous carbonate skeletons and diatomic algae (*Rizolenia calcar-avis*, *Chaetoceras*, etc.) built of silicate ( $\text{SiO}_{2\text{amorf.}}$ ) skeletons.

The occurrence of “pure” diatomic accumulations on the Black Sea seafloor has been known quite recently. A diatomic field with significant thickness, which exceeds 7 m, is known in the regions of the barrier Bosphorus-Black Sea zone. A similar field is situated in the Danube canyon.

The value of the soil cover is continuously increasing at the present stage of the development of the human society because of its active interference with Nature.

It is well known that the ecological status of the cultivated lands in our country has been significantly deteriorated during the last 20 years. About 40% of the cultivated lands area are degraded or in process of degradation, above

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8 million hectares are eroded (the humic layer is dragged down), about 3 million hectares are over-damped, etc. Vast cultivated areas are salted in the Devnia lowland, the valley of the Maritza River, the Stara Zagora fields and some others. More than 4 million hectares are subjected to acidic impact.

On the one hand Bulgarian cultivated lands are subjected to destruction as a result of irreversible urban and demographic processes. On the other hand they are destroyed by excessive applying of artificial fertilizers and pollution with heavy and radio-active metals. The conditions of the cultivated lands are the same in the almost all Eastern European and Arabian countries. The countries of the EC pay a special attention to natural organic and ecological fertilization although the usage of non-organic mineral fertilizers is limited. It is known that the organic matter in the soil is a nourishing environment for the microorganisms which influence favorably on the growth of plants. In the form of alkaline salts of the humic acids, the organic substance (OS) stimulates the growth of plants, increases the amount and improves the quality of the yields. Besides, OS improves the soil structure, retains moisture and does not allow to escape nourishing salts and microelements from the soil.

During 1982–1985 a number of experiments have been carried out in the Pushkarov Institute and the Wheat and Sunflower Institute in town of General Toshevo to utilize DSOMS for agro-chemical and agro-biological purposes.

The experiments upon spropels performed in 1985 at the Pedology Institute showed that applying 2% spropel in acid soils with pH 5.6 became the soils almost alkaline — pH 7.8. Importing spropels increased by 30% of the wheat biomass (Table 1). Increasing the amount of the raw material (>2%) does not improve the indicators implying that the applied amount of 2% is the optimal (Table 1) [9].

*Table 1*

**Experiment with wheat and increasing of biomass**

Variants	Biomass in %	Water in %	pH
Controller (0)	5,6	100	5,6
Spropel mud 1%	5,7	102	7,3
Spropel mud 2%	7,2	129	7,6-7,9

Since 1987 experiments have been carried out for growing oil-bearing roses and vines in the Agricultural University in Plovdiv. The first plants transplanted in substratum of perlite and spropel in ratio of 1:1 showed rapid improvement of rooting and stability of the plants. For example, the previous substratum of perlite has resulted in rooting 51 of 100 samples while a spropel mixture — 85 samples [7, 8]. The experiments on perennial plants, vegetable and grain plants indicate great opportunities for applying DSOMS in hydroponics and conservatory production [11, 14]. A patent for an invention (№63868/30.04.2003) has been licensed:

(<http://www.bpo.bg/abstracts/pdf/2003/2003-04-p.pdf>)

Experiments for estimating diatomic-sapropelic mud as a raw material for ceramics have been carried out (filtering elements, fillers of concrete, etc.). The following results have been obtained. The temperature of firing of the raw material is comparatively low (950°C). The ceramics mass produced has a bulk weight (1.2–1.6 kg/cm<sup>3</sup>), high porosity (38–55%), its color is delicate pastel nuances. The compressive strength varies widely (from 52 to 235 kg/cm<sup>2</sup> or 5.1–23 MPa). The high content of alkaline oxides in the raw material implies low temperature of fusibility and this is a favorable precondition for using the material as a component for producing glazes [15].

The deep sea organic mineral (sapropelic, diatomic and coccolithophoridic) sediments (DSOMS) of the Black Sea are built mainly of nanosized materials, which can find application in the modern nanotechnologies and new materials.

The Black Sea DSOMS are currently in a peat stage of their development. Due to the anoxic environment of sedimentary deposition, sediments do not pass the stage of complete decay and in semi-decayed state they are conserved in the hydrogen sulfide zone. Considering the fact that the sapropelic, diatomic and coccolithophoridic layers penetrate within each other and are comparatively homogeneous mixture they are considered as complex organic mineral raw material where the sapropels occupy about 80% of the total volume. DSOMS are valuable not only due to their organic matter but also for their carbonate component and the amorphous silicates. The mineral and organic parts contain micro components such as calcium, magnesium, iron, aluminum, manganese and some others. Concentration of more than 20 micro elements exceeds by many times that in soils, being an important stimulant for the plants growth.

DSOMS are used as a complex fertilizer or as a component together with other mineral stimulants — perlite, zeolite. The sediments excel them in agro-technical properties. Sediments can be used directly in the soil in natural state without additional processing of raw material. Other important advantages are:

unlimited supplies of raw material in the water area, which is located at depths of 200 to 2200 m. The content of the organic matter increases with the increase in depth;

the possible exploitation of the raw material will not have negative consequences on the marine environment. The industrial supplies are located at a great depth within the hydrogen sulfide zone, in which life does not exist. The exploitation will have an ecologically positive effect that will influence, if slowly, on the level of the hydrogen sulfide zone;

the dying flora and fauna of the Black Sea serve as an initial substance for producing DSOMS. As a result of the activities of the anoxic bacteria, the dying flora and fauna pass the transformation process of animal and plant plankton and benthos and form biolithic mineral substance with peculiar physical-mechanical and biogeochemical properties.

In 1997–1998 experiments were performed to study the effect of application of sapropelles for improving of hygroscopic capacity of the soil and neutralization of acidity of acid soil, taken from the area of Zlatosel village.

There were 30 g samples of acid light brown pseudo podzol soil (Planosol) in vessels. The samples were taken from three deep horizons in the area of Zlatosel village (Plovdiv district), with pH being 4,5–4,7. They were mixed with sapropel at amount of 1,0 % and 2,0 %. After pouring on with 30 cm double distilling water, samples were left for incubation. The samples were periodically filled up with distilling water and mixed. During the incubation, the vessels were closed to avoid an access of atmospheric air. After incubation period of 45 days pH of the detached varieties in H<sub>2</sub>O and KCl medium were determined with pH-meter. In parallel it was measured pH values of the control samples from the three horizons and at the sapropels by three replications. Much the humic matter was revealed in all analyzing samples. The experimental data are shown in Table 1. Exchange ions were found in the samples. The results are shown in Table 2.

Table 2

**General chemical composition and physical-chemical properties of cinnamonic pseudopodzolic soul (*Planosol*), sapropel and their mixtures**

Horizon depth (cm)	pH		Humus content (%)	CaCO <sub>3</sub> (%)
	in H <sub>2</sub> O medium	in KCl solution		
Control — CPS (planosol)				
A <sub>1</sub> A <sub>2</sub> l(g) 0-10	4,50	3,90	1,21	—
A <sub>2</sub> l(g) 10-28	4,50	4,00	0,48	—
A <sub>2</sub> l(g) 28-40	4,70	3,80	0,31	—
Sapropel				
Sapropel 1	7,28	6,70	6,95	6,20
Sapropel 2	7,25	6,95	6,86	6,22
Sapropel 3	7,20	7,20	6,76	6,18
CPS (planosol) + 1,0 % sapropel				
A <sub>1</sub> A <sub>2</sub> l(g) 0-10	6,4	5,45	1,56	—
A <sub>2</sub> l(g) 10- 28	6,9	6,55	0,54	—
A <sub>2</sub> l(g) 28-40	7,0	6,6	0,37	—
CPS (planosol) + 2,0 % sapropel				
A <sub>1</sub> A <sub>2</sub> l(g) 0-10	7,0	6,55	1,56	—
A <sub>2</sub> l(g) 10-28	7,2	6,80	1,27	—
A <sub>2</sub> l(g) 28-40	7,8	7,00	0,53	—

CPS — cinnamonic pseudo podzol soil.



It has been determined water storage capacity of leached cinnamonic soil (Chromic Luvisol) with mixture of spropels. The 30 g samples of leached cinnamonic soil (Chromic Luvisol) were contained in glasses with volume of 250 cm<sup>3</sup>. They were taken from horizon at a depth of 0–40 cm, with content of spropel being 1,0–5,0%. Samples, including control sample, were poured on with 50 cm<sup>3</sup> distilling water and left for 24 hours storage. The suspensions obtained were mixed and filtrated with preliminary weighed filters (blue band). After filtrating filters were weighed with the analytical balances to determine the water content. The data are presented in Table 3.

Table 3

**Exchange ions content of cinnamonic pseudo podzol soil (*Planosol*) with spropel after 45 days of incubation**

Content of spropel (%)	№	horizon, depth (cm)	Exchange ions (mgcq/100 g)			
			$\Sigma(\text{Ca}^{2+}, \text{Mg}^{2+})$	$\text{Ca}^{2+}$	$\Sigma(\text{Al}^{3+}, \text{H}^+)$	$\text{Mg}^{2+}$
1,0	1	0-10	5,77	4,367	0,05	0,90
	2	10-28	6,13	2,964	0	3,16
	3	28-40	3,87	3,849	0,07	0,02
2,0	4	0-10	6,84	2,655	0	4,18
	5	10-28	7,19	5,973	0	1,22
	6	28-40	5,31	3,894	0	1,42
Control CPS ( <i>Planosol</i> )	7	0-10	31,3	25,0	98,2	6,3
	8	10-28	36,8	17,5	109,3	19,3
	9	28-40	37,5	15,6	96,2	21,9

They show that the change of soil acidity after 45 days incubation period depends on the content of spropel. In the control samples pH varies from 4,5 to 4,7 in H<sub>2</sub>O medium and from 3,90 to 3,80 in KCl solution medium. In the presence of 1,0% spropel pH changes from 6,4 to 7,0 in H<sub>2</sub>O medium and from 5,45 to 6,6 int KCl medium. The 2,0% spropel content increases pH values to 7,0–7,8 and 6,55 to 7,0 in KCl medium respectively. The pH change is related to the content of humus and exchange ions in the samples, containing spropel. The presence of organic carbon and exchange ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) in the spropel improves the buffer ability of the *Planosol* investigated (Table 2, 3, 4) [11].

Spropel amount of 1,0–5,0% increases the water storage capacity of samples, taken from deep horizon 0–40 cm of leached cinnamonic soil from 3,0% to 24% in relation to the control sample (Chromic Luvisol). The most significant increase in water storage capacity was found when 3,0% of spropel was added according to the correlation soil-spropel. It can be explained by increase

of inner-capillary space in the soil samples, containing sapropel. In fact sapropels improve the soil structure resulted in higher inner-aggregate porosity.

Sapropels neutralize soil acidity of cinnamonic pseudo podzol soil (Planosol) from 4,5–4,7 to 7,0–7,8 pH with insignificant amount of sapropel (1,0–2,0%) and 1,0–5,0 % sapropels improve the water storage capacity of leached cinnamonic soil (Chromic Luvisol) from 3,0% to 24% , in relation to the control samples. Thus sapropels could be used for recultivation of acid soils and for soils with insufficient water storage capacity.

Table 4

**Water storage capacity of leached cinnamonic forest soil (*Chromic Luvisol*) with different amount of sapropel**

Horizon depth (cm)	Sample №	Variants SFPS + sapropel (%)	Water storage Capacity (%) in comparison to Control
0-40	1	1,0	103,4
	2	2,0	112,1
	3	3,0	117,3
	4	5,0	124,4
	5	Control	100

In 1997–1999 it was made a study of the assimilation of Cr, Mo and Mn from tomatoes, cv. “Yana” and peppers, cv. “Albena” after enriching of soil in sapropels. The experiments were carried out on pot plants in plastic houses.

Deep water Black sea sediments (sapropels) represent an ecological natural fertilizer, containing a large spectrum of microelements useful for plants. In the recent decades the studies of changes in the content of the microelements are of a particular interest. Chromium, manganese and molybdenum are the microelements which actively have been assimilated by plants. The formation of plant mass depends on the chromium, manganese and molybdenum supply. These microelements are important for the synthesis of the organic substance in plants, for example, vitamins, and of the metabolism of a number of nutrient elements in a plant organism. In fact, Cr, Mn, Mo take part in a number of important physiological and biological processes.

It have been established for a great number of crops the optimal content of chromium, manganese and molybdenum, its critical level and toxic concentration under which the growth is depressed and the yield declines. A study has been performed to determine the chromium, manganese and molybdenum content in plant material of vegetable crops after application of sapropels as supplement for soils to increase agrobiological properties. Its results show that the chromium content varies in the production of the vegetable crops tomatoes cultivar Jana and peppers cultivar Albena (Table 5) [12]. The highest concentration of chromium was found in the soil contained 0,6 % of sapropels. The chromium content increases with the increase of sapropels in peat composite.

Table 5

**Chromium content in the production of vegetable crops after treatment with sapropel**

Variant	Tomatoes		Peppers	
	Cr mg/kg	% compared to control	Cr mg/kg	% compared to control
Control	13,0	100	15,0	100
0,2	15,0	115,4	15,5	103,3
0,4	17,5	134,6	16,0	106,7
0,6	18,0	138,4	16,5	110,0

The Table 6 shows that the lower content of 10 mg/kg Mo dry mass was found after the treatment with various concentration of sapropels in tomatoes cultivar Jana containing 0,2 % of sapropels [12]. The highest molybdenum content of 12 mg /kg dry was registered when content of sapropels was 0,6 % .

Table 6

**Molybdenum content in the production of tomatoes after treatment with sapropel**

Variant	ISP method	
	Mo mg/kg	% compared to control
Control	8,0	100,0
0,2	10,0	125,0
0,4	11,5	143,7
0,6	12,0	150,0

The content of manganese also varies in plant material after treatment with sapropels (Table 7) [12]. The least manganese variation of 152,5 mg/kg Mn dry mass was determined in a case of 0,2% of sapropels in peat composite. After dressing 0,6% of sapropels the content of manganese was much higher s 177 mg/kg Mn dry mass in tomatoes cultivar "Jana".

Table 7

**Manganese content in the production of tomatoes after treatment with sapropel**

Variant	ISP method	
	Mn mg/kg	% compared to control
Sapropel, %		
Control	144,0	100,0
0,2	152,5	105,0
0,4	176,0	122,2
0,6	177,0	122,9

These results show that the chromium, manganese and molybdenum content in the production of the vegetable crops varies in plant material. The highest concentration of these microelements was found when peat composite contains 0,6% of sapropel. The content of chromium, manganese and molybdenum depends on the biologic features of the species.

In many cases traditional methods of nitrogen nutrition lead to a number of unfavorable effects on the environment such as increasing of soil acidity and pollution of plant production with nitrates, especially by using of ammonium nitrate. A part of ammonium nitrogen can't be assimilated because of evaporation due to decomposition of the salt in soil. Nitrates are very movable and reach and pollute the subsoil waters. The presence of nitrates is a general problem for many European regions. In many inhabited areas, the subsoil waters are contaminated by nitrates. In regions of intensive agriculture activities the content of nitrates is more than the permissible of 50 mg/l. The intensive nitrogen nutrition pollutes the environment and plants don't assimilate rationally nitrogen resulting in decrease in yield and worsening quality of plant production.

During the last years sapropelle have become a subject of special research, because of the opportunity for their application in several fields of agriculture, related to the soil fertility. An attempt has been undertaken to study the possibility of optimizing nitrogen nutrition by using of modified granules, containing sapropel as supplementt and covering with water swelling polymeric layer.

In 2002–2003 the tomatoes cultivar "Rila" was studied under plastic houses conditions. Tomato seedlings were planted in two variants, I and II using four replications (4×8 plants). Ammonium nitrate was supplied as nitrogen fertilizer. It was introduced in the form of modified granules by norm of 12 g per plant during the pricking out. In control plants 15 g per plant were generally supplied by triple fertilizing on 26.04 (a week after pricking out of seedlings), on 21–22.05 and after the appearance of first red tomatoes in both investigating years.

The size of granules was 8–10 mm, containing 44% of ammonium nitrate, 30% of the Black sea sapropels as a supplement and 26% of a filler (kaolin). The granules were formed with a rotary plate granulator by spraying 0,5% water solution of polyvinyl alcohol (PVA) in the experiment I and 0,5% water solution of modified polyvinyl (PVA-M) in the experiment II. PVA-M represents acetyl with acetylic anhydride PVA. The rate of acetylating OH-groups was 30%. After drying up granules were covered separately by polymeric layer by treatment with 5,0% water solution of the same polymers.

Tomato plants were formed to phase "fifth bunch" by the equal irrigation regime by drop irrigation system. The harvesting of tomatoes was made in the period of 17.06–30.07. An yield of tomatoes and content of vitamin C were general in comparison to the control experiments. The experimental data are shown in Tables 8, 9 [13].

The median data of tomatoes yield from the two year investigation are shown in Table 8. The general and the early standard yield according to har-



Table 8

**General standard and median yield of tomatoes cv. "Rila" under plastic house conditions by optimizing nitric nutrition**

Variants	Median data of harvestings in 2002–2003 kg								General yield (kg)
	1	2	3	4	5	6	7	8	
I	2,10	5,46	8,70	10,30	11,47	13,00	17,50	12,2	80,73
II	2,05	5,50	7,60	10,20	10,25	12,00	15,30	10,79	73,71
Control	0,800	1,500	2,300	5,800	4,600	7,500	11,200	5,600	70,2

Table 9

**Median data of general and median yield and content of vitamin C of tomatoes, cv. "Rila" (2002–2003)**

Variants	Number of plants	General yield (kg)	Median yield per plant (kg)	% compared to Control	Content of vitamin C mg/kg
I	32	80,73	2,52	115,06	18,99
II	32	73,71	2,30	105,02	19,39
Control	32	70,2	2,19	100	17,78

vestings 1, 2 and 3 to 30.06 (cases I, II) was higher in comparison with the control plants — I 16,70 to II 15, and 15 to 4,60 respectively. The general yield was 80,73 in the case I, 73,71 in the case II and 70,2 in the control experiment. These differences seem to have resulted mostly from the improved assimilation of the ammonium and nitrate nitrogen by the modified granules which form a membrane by swelling of polymer coverings, due to the soil moisture. It leads to regularly assimilation of nitrogen by the tomato plants rhizosphere.

In previous investigation it was established that spropels decrease the soil acidity to optimal value for the most of the vegetable crops parameters. Table 9 shows the median yield per plant (kg) and the percentage of improved yield compared to control. In the case I and II the increase was 15% and 5,02 respectively in comparison with the control observations. The content of vitamin C varies from 17,78 mg/kg in control experiment to 18,99 mg/kg in the case II and 19,39 mg/kg in the case I. The data could be explained by correlation dependence between yield mass and content of the vitamin tested. Beside this spropels increased the resistance of tomato seedlings against low temperatures, because of higher content of dry mass, compared to control plants.

The application of modified granulates, containing spropelles and water swelling polymers PVA, PVA-M, improve the nitrogen nutrition by tomatoes cv. Rila under plastic house condition. It leads to higher early and standard yield, independently on decreasing nutrient norm.

In granules with more amfifilyc polymer (PVA-M) the biggest yield was registered.

This method of nutrition is recommended to decrease nitrates in vegetable crops. An ecological effect is expected to be realized because of regulating entry of nitrogen by granules.

Oil bearing rose "Kazanlika" is the most important and essential perfume oil crop in Bulgaria. Unfortunately the rose plantations decrease in the last decades, leading to decline rose oil production. The main method for seedlings production is the rooting of rose clips in various substrates in greenhouse conditions. There are two technologies of seedlings production — rooting of green clips by spraying in peat-perlite substrate and rooting of ripe clips without spraying. The first method is more effective but requires more investments. The second method decreases the percentage of rooted clips in comparison with the first one.

The Black sea deep water sapropels are an object of special research in recent time because of their rich composition and opportunities for application in different aspects of agriculture. Research activities have been undertaken to improve the technology of rooting Kazanlika oil-bearing rose by ripe clips and by using Black Sea sapropels in the substrate composition.

During 1997-1998 in Plovdiv Agriculture University it was studied the effect of the Black Sea sapropelles application to stimulation of the rooting and the median growth of rooting Kazanlika oil-bearing rose. The experiment was carried out under plastic house conditions. In September–October on the beds with a width of 80 cm the clips of Kazanlika oil-bearing rose were applied for rooting. The experiment was carried out with two substrates enriched in sapropel. A variant I represents perlite + 3,0% of sapropel and a variant II — peat — perlite substrate in relation of 1:1+3,0% sapropel. For comparison two etalon substrates were used s balcanin-zeolite substrate and mineral mixture for tomatoes. The number of the examined clips in all variants was 80. The beds were supplied with water regularly for supporting of moisture substrate. After six months the percent of rooted clips and their growth were calculated. The experimental data are shown in Table 10 [4].

It was found an influence of sapropel on rooting of oil-bearing rose clips. Two variants of substrates containing sapropel were investigated. When substrates were represented by perlite, enriched in 3,0% of sapropel, the percent of rooted clips was 90, being by 5-10% more than the etalon substrates, but the median growth was low - 6,04 cm, because of lower nutrient ability of this substrate in comparison with the other substrates. In the second substrate containing peat/perlite in relation of 1:1 and enriched in 3,0% of sapropel the percent of rooted clips was 95, which is 10-15% more than in the etalon substrates. The median growth of rose plants in the variant II was 21,76 cm that is 3,58 cm more than in the mineral mixture for tomatoes and 11 cm more than in the balcanin/zeolite substrate.

The stimulation effect on the rooting of the clips can be explained by the rich content of microelements and organic stuffs in the sapropels. It is known that they take an active part in a number of important physiological and biological processes of plants, including the rose clips risogeneses and related to it growth of rose plants.

The data analysis shows that sapropels stimulate the risogeneses of oil-bearing rose clips and can be applied by seedlings production of "Kazanlika" oil-bearing rose. 3 mass% of sapropel in peat-perlite substrate increases median growth of clips from 3,6% to 11,0% in comparison to the other substrates investigated.

Table 10

**Median growth and percent of rooted oil-bearing rose clips in nutrient substrate enriched in sapropel**

Variants	Number of clips	Substrate Composition	Median growth of rose clip, cm	Rooted clips (%)
I	80	perlite + 3 mass.% sapropel	6,04	90
II	80	peat : perlite 1:1+3 mass % sapropel	21,76	95
Etalon I	80	Balcanin-zeolite substrate	10,75	80
Etalon II	80	Mineral mixture for tomatoes	18,18	85

The attempts are well-known to produce diatomite from the continental slope of California, where tests of airlift system were carried out during the 60<sup>s</sup> of the last century. The airlift systems have operated for 10 years with an annual production of 1 million tons at a tentative price of 42–45 USD per ton. The content of water in sapropels reaches 70–80% and 1 m<sup>3</sup> of the raw material with a volume weight of 1.12–1.25 g/cm<sup>3</sup> produces the 300–400 kg dry mass. The consistency of DSOMS is semi-fluid to soft plastic and can be easily maintained. The depths of production are from 200 m to 2200 m that creates totally new conditions for the yielding equipment. Corrosion should be taken into account under conditions of 20–22‰ saline waters and the aggressive action of the hydrogen sulfide should be paid attention as well. The foundations of developing technologies for extracting sapropels were laid down in Bulgaria during the 80<sup>s</sup> of the 20<sup>th</sup> century, when the first articles on the sapropel properties were published [1, 9, 15]. In 1988 the Bulgarian Academy of Science funded a project "Development of technique and technology for producing deep sea organic-mineral sediments from the Black Sea bottom" [4]. A review and analysis of the existing technologies were made. The airlift system was estimated as the most suitable for the Black Sea. A grab or dredge technology was considered to be applicable for production of small amounts of material for semi-industrial and technological purposes. The estimation of automatic underwater shuttles with autonomic performance showed that they were too expensive but considerably safer. However, such equipment can be put into operation after organizing its production. Later, when the valuable properties of the sapropels become known, a number of technological developments appeared in NIPI Ocean-mash from Ukraine and in some other leading scientific institutes of the world [5]. A production complex using grab technology will weigh about 1500–2000 tons. It can be placed on a ship with a length of 200 m, width of 20–25 m and displacement of 20–25 000 tons. The optimum productivity of the techno-



logical equipment under the conditions of the Black Sea is 300m<sup>3</sup>/h or about 1 million m<sup>3</sup>/per year. At a tentative price of 45 USD per ton, the annual production at wholesale prices will be about 45 million USD. Depending on the market demand, one or several production complexes will be developed. The tentative price of the whole complex (a ship and technological equipment) will be 18–20 million USD.

#### General conclusions:

1. The natural nanosized materials — high carbonate coccolithophoridic silt — can be applied in the production of carbonate glass in the cement industry, for slack lime of acid soils.

2. The Black Sea deep sea sapropel sediments are an important potential raw material for multi-purpose utilization. In the areas of agriculture and natural environment, the expected results are: production and use of the nanosized natural materials (nano-fossils) affecting directly the environment and agricultures such as greenhouse production, etc. They can be applied for recultivating acid, poor in micro-elements and demolished soils, as well as for enriching substrates and recultivating lands polluted with heavy and radio-active metals. The supplement stimulates the plants growth, accelerates the ripening, increases the yield, neutralizes the acidity of the soils and increases their moisture. They are a competitive raw material to the non-organic mineral fertilizer. A patent for invention N63868/30.04.2003 is licensed.

3. It is expected that the diatomic nano-fossils can be also used in the area of IT: using super pure SiO<sub>2amorf.</sub> for producing materials that are in line with the global trends in these areas such as optic cables, chips, highly energetic amorphous glasses, nutrient for producing artificial piezoquartz, optics, etc.

1. Велев, В., П. Димитров, М. Файер. Строеж и състав на холоценските сапропелоиди от западната част на Черно море // Океанология, 1992. — С. 58–63.

2. Дегадюк Е. Г., Дегадюк С. Е., Черный, Е. П. И др. Агрономическая ценность сапропеловых и кокколитовых илов Черного моря и вопросы техногенной безопасности. В: Геология Черного и Азовского морей. Киев, 2000. — С. 164–174.

3. Димитров, Д., Г. Георгиев, П. Димитров. Некоторые результаты применения глубоководных органогенно-минеральных осадков дна Черного моря для агробιολογических целей. Геология и полезные ископаемые мирового океана, № 1. — 2006.

4. Димитров, П., П. Василев Дълбоководни органогенно-минерални утайки от дъното на Черно море и технологии за техния добив. Варна, 1988. ИО БАН, 95.

5. Шнюков Е., Зиборов А. Минеральные богатства Черного моря. НАНУ, Киев. — 2004. — 278 с.

6. Шнюков Е., Клещенко С., Куковская Т. Сапропелевые осадки Восточной и Западной впадин Черного моря. Геофиз. журнал, 2003., т. 25. — № 2. — С. 100–122.

7. Dimitrov P., Dimitrov D.. On the possibilities of utilizing the organogenic mineral sediments as a natural ecologic fertilizer for recultivation of contaminated soils. — Second international conference on marine industry, 28 September — 2 October 1998, Varna, 1998. Bulgaria.

8. Dimitrov, P., Nikolov N., Dimitrov D. 1998. Application of the Black Sea bottom sediments for natural ecological fertiliser, recultivation of exhausted solis. // The Energy Resources of the Black Sea, 21–22 September 1998, Batumi, Georgia.

9. Dimitrov, P., N. Nikolov, D. Dimitrov, P. Petrov. Application of Black Sea Bottom Sediments Natural Ecological Fertiliser, Recultivation of Exhausted Soils. Geology and mineral resources of the Black Sea, Kyiv, 1999. — P. 182–189.



10. *Dimitrov D., V. Peychev, P. Dimitrov.* Nontraditional resources from Bulgarian economical zone in the Black Sea. Intern Conf. "Global Changes and problems", Sofia (in press), 2007.

11. *Nikolov, N., N. Artinova, D. Dimitrov, P. Dimitrov, D. Solakov.* Possibility of Application of Black Sea Sediments (Sapropels) for Neutralization of Soil Acidity and Increasing of Hygroscopic Capacity of the Soils. Assessment of the Black sea sedimentary system since the last glacial extreme. Abstracts. 23–26 October 2004, Varna, Bulgaria.

12. *Nikolov, N., M. Kamburova, D. Dimitrov, P. Dimitrov, D. Solakov, V. Peychev.* Studying of the accumulation of Cr, Mo and Mn from tomatoes and paprika after introduction of Sapropels in the soil. Assessment of the Black sea sedimentary system since the last glacial extreme. Abstracts. 23–26 October 2004, Varna, Bulgaria.

13. *Nikolov, N., D. Cholakov, C. Yamakova (Moskova), D. Dimitrov, P. Dimitrov, D. Solakov.* Studying of the Influence of Sapropels on the Increasing of the Yield of Tomatoes in Plastic houses / Assessment of the Black sea sedimentary system since the last glacial extreme. Abstracts. 23–26 October 2004, Varna, Bulgaria.

14. *Nikolov, N., C. Yamakova (Moskova).* Application of Black sea sapropels for increasing of the rooting and the growth of oleaginous rose rooting clips / Assessment of the Black sea sedimentary system since the last glacial extreme. Abstracts. 23–26 October 2004, Varna, Bulgaria.

15. *Razvigorova M., T. Budinova, V. Velez, S. Valcheva.* Geochemical and petrographical analyses of Holocene Sapropels of The Black Sea / I European Coal conference, 1997.— Geology. — P. 411–419.

Глибоководні мінеральні осадки дна Чорного моря (сапропелеві, діатомові та кокколитофоридові мули) можуть бути успішно застосовані в сучасних технологіях і виробництві нових матеріалів. Вони можуть використовуватися як добриво для вирощування різних с/г культур, а також для рекультивациі кислих і забруднених ґрунтів. Із цією метою в період 1984–2004 рр. у Болгарії проведено серії дослідів. У статті подано їх результати.

Глибоководные органо-минеральные осадки дна Черного моря (сапропелевые, диатомовые и кокколитофоридовые илы) успешно могут применяться в современных технологиях и производстве новых материалов. Они могут использоваться как удобрение для выращивания различных с/х культур, а также для рекультивации кислых и загрязненных почв. С этой целью в период 1984–2004 гг. в Болгарии проведены серии экспериментов. В статье рассмотрены результаты этих экспериментов.