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# APPLICATION OF DEEP WATER BLACK SEA SEDIMENTS (SAPROPELS) FOR NEUTRALIZATION OF SOIL ACIDITY AT DIFFERENT TYPES OF ACIDIC SOILS

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**Abstract**

*The Black sea sediments (sapropels) neutralize the acidity of Cinnamonic pseudopodzolic soil (Planosol) from pH 4,87($H_2O$) in an amount 1-7 g/kg incubated sapropels from 6.33 to 7.26 pH after 1-4 months incubation. In an amount 10-30 g/kg - from 7.12 to 8.01 pH after 1-4 months incubation. At Brown forest soil (Distric Cambisol), area Beglika from pH 4.42($H_2O$) in an amount 1-7 g/kg sapropels pH changes to 5.26-6.02 units after 1-4 months incubation period. In an amount 10-30 g/kg - from 5.68 to 6.76 pH after 4 months incubation. At Brown forest soil (Distric Cambisol), areaNova Zagora, from pH 5.19($H_2O$) in an amount 1-7 g/kg sapropels pH changes from 6.52 to 6.98 pH after 4 months incubation. In an amount 10-30 g/kg - from 6.82 to 7.23 pH after 4 months incubation.*

**Key words:** *Black sea sapropels, soil acidity, neutralization, cinnamonic pseudopodzolic soil (Planosol), Brown forest soil (Distric Cambisol)*

**Abreviations:** *CPS - Cinnamonic pseudopodzolic soil (Planosol)*

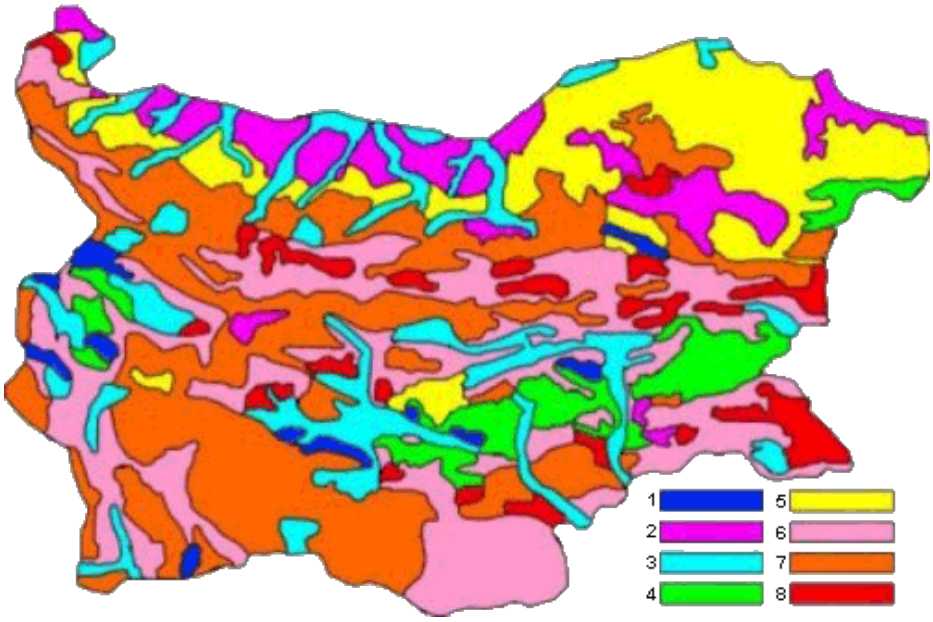
*BFS-B - Brown forest soil, (Distric Cambisol) area Beglika*

*BFS-N - Brown forest soil, (Distric Cambisol) area Nova Zagora*

## 1. INTRODUCTION

The acidity of the soil medium is an important factor for the soil fertility, because it directly affects the mobility and assimilation of nutrient and non-nutrient elements, related to the growth and development of plants. Most crops grow best in soils with slightly acidic and near neutral (pH 6.0-7.5) reaction. Highly acidic reaction adversely affect them, because increasing the content of mobile forms of aluminum, manganese and other elements, which in small quantities are useful for plants , but in bigger - harmful. At the same time hinders the feeding of plants with such important bio-elements such as calcium, magnesium, phosphorus, molybdenum and others. In our country there are many areas with increased soil acidity, where is necessary to grow important crops. In such cases, the neutralization of soil is a solid reserve for increasing the yield and quality of crop production. The crops respond strongly to high soil acidity, as the most vulnerable are the young, still fragile plants. The most typical symptoms are: changes in the root system, stunted growth, yellow or brown color, the destruction of the tissue that becomes mucous mass, limited formation of lateral roots and root hairs, change the aerial organs - deformation of young leaves which remain small and warped, and in particularly severe cases, the leaves decay firstly at the periphery and the top, and later - completely. With increasing of soil acidity calcium and magnezium carbonates dissolve and wash, leading to destroying of the soil structure, which affects the physical properties of soil. Conditions are unfavorable for root growth. At pH less than 5 was found to significantly reduce the number of small roots of some crops. It is also known that acidic soils are unfavorable for the activity of beneficial aerobic nitrifying bacteria. Nitrogen-fixing bacteria in soil does not grow at pH less 5.5. At pH less than 5.3, aluminum becomes much more accessible and cause toxicity, especially in cereals. (Atanasov, 2006)

Currently, in the country there are about 1.5 million hectares acid soils, of which 67 500 ha are classified as very acidic, which is unfavorable for growing of many economic important crops.(fig.1) Under conditions of active manifestation of the erosion processes, such as waterlogging and soil fertilization with physiologically acidic nitrogen fertilizers, such as ammonium nitrate, ammonium sulfate, are emerging trends to modify the acid-base balance in the soil associated with increased contents of exchangeable $H^+$ and $Al^+$ ions and strongly reduce the content of basic elements such as calcium, magnesium and others.(Koteva et all,1993)




Legend: 1.alkaline, 2.weakly alkaline, 3. slightly alkaline to neutral, 4. neutral; 5.neutral to slightly acidic, 6.slightly acidic, 7 - moderately acidic, 8. acidic.

Fig.1.Location of the places with different values of soil pH in Bulgaria (Agrobiostim)

The liming is a general method for improving the physical and agrochemical properties of the acidic soils, leading to optimized water-aer regyme of soils, especially in black earth. Calcium lime from imported materials coagulate yl particles, protecting them against washing from the arable horizon. To neutralize the toxic soil acidity most commonly used lime meliorants are limestone and dolomite. The main disadvantage of these ameliorants is the lack of buffering capacity, so that they do not provide long-term stabilization of soil reaction - no more than 3 - 4 years. Secondly the cost of liming are significant - 200 lv/da recultivated land and more. Furthermore, in order to be effective lime meliorants must be ground into powder form. The neutralization ability of particles with size more than 0.25 mm is very weak and continues a few years. Powdery meliorants however, create problems in the technology of liming. In practice, for this purpose, are used a centrifugal spray machines of mechanical and pneumatic principles which require the material to be granulated. The presence of minimal moisture according to Nikolov et all, (2010) leads to compacting and congestion of bunkers and augers of the technics. The problem is also present in meliorants storage in warehouses. Moreover because of its decreased solubility in the soil solution, the effect of dolomite application manifests after 2-3 years.

During last years, the deep water Black sea organic-mineral sediments (sapropels) according to Dimitrov et all (1988) in agreement with Shnukov et all (1999) are a subject of special research, because of the opportunities for their application in several aspects of agriculture, related to the soil fertility. The rich organic-mineral composition of sapropels according to Nikolov et all (2011[a], 2011[b] ,2011[c]) make them appropriable as ameliorant and complex fertilizer for soils with unfavourable physico-chemical properties, such as containing heavy metals and for soils with degraded water-air regyme.

The aim of the present study was to establish the optimal quantities of sapropels necessary for recultivation of three type's acidic soils to values over pH 5.5 and near to the neutral medium, which is most favorable for growing of agricultural crops.

## 2. MATERIAL AND METHODS

### *2.1. Elemental analysis*

Sample sapropels, taken from a depth 1200 m was analysed for the content of Si, K, P , Ti , Al, Ca, Na, N and P., as well as some microelements, as Fe, Mn, Mg, Cr, Mo, Cu, and heavy metals Zn, Ni, Pb. They were determined in the form of oxides. An inductively coupled emission spectrometry (Jobni Yvon Emission - JY 38 S. France) was used. The quantitative measuring was carried out with apparatus ICP.

*2.2. Determination of pH.*

pH values ($H_2O$) of the tested acidic soils and soil-sapropels mixtures were determined with pH meter, model OP-211 /1, (ISO 10390). Additionaly was determinated pH values of the tested soils in solution of 1N KCl.

*2.3. Incubation of sapropels in the investigated soils.*

In banks were set 30 g air dry samples of the tested acidic soils, taken from deep horizon 0 - 40 cm: CPS (*Planosol*) taken from the area of Zlatosel village, region Plovdiv, BFS-B, (*Distric Cambisol*) taken from the area of Beglika village, region Batak and BFS-N (*Distric Cambisol*) taken from the area of Banya village, region Nova Zagora. All samples were mixed with sapropels at amounts as follows: 1 g/kg, 3 g/kg 5 g/kg, 7 g/kg,10 g/kg, 20 g/kg, and 30 g/kg. After pouring on with 30 ml double distilling water, samples were left for incubation. The samples were periodically filled up with distilling water and mixed. During the incubation, the banks were closed to avoid an access of atmospheric air. After incubation period of 1, 2. 3 and 4 months at a temperature 303 K were determined pH of the detached variants in water medium. Parallel were established pH value of sample sapropels used and control samples.

*2.4. Determination of humus content and exchange ions*

The humus content of CPS (Planosol), in sample pure sapropels and in three soil-sapropels mixtures was determined by the method of Turin (Trendafilov et all) The content of exchange ions $Ca^{2+}$, $Mg^{2+}$, $Al^{3+}$ and $H^{+}$ in CPS (Planosol) and in soil-sapropels mixtures was determined by standard method in extract of 1n KCI (Trendafilov et all)

## 3. RESULTS AND DISCUSSION

According to pH of the soil medium, soils are classified as highly acidic - pH 4.1 -5.0, medium acidic - 5.1 to 6.0, slightly acidic - from 6.1 to 6.5, neutral - from 6 6 to 7.0 and from 7.1 to 8.5 - slightly alkaline. Under this classification, taken by us for research two types forest soils - CPS (Planosol) and BFS-B (*Distric Cambisol*) belong to highly acidic soils, as BFS-N (*Distric Cambisol*) belongs to medium acidic soils.

Table 1. Chemical composition of Black sea sapropels.

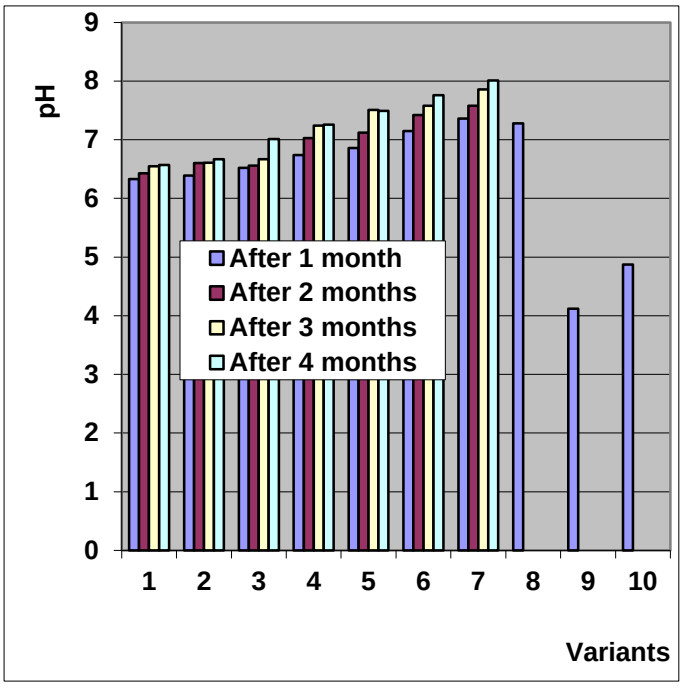
Content of N, P, humus, micro- and macroelements

| Chemical composition of Black sea sapropels | | | | |
|---|---|---|---|---|
| $Cr_2O_3$ (g/t) | $MoO_3$ (g/t) | ZnO (g/t) | MnO (g/t) | $PbO_2$ (g/t) |
| 50.0 | 36.4 | 65.8 | 383.4 | 28.2 |
| CuO (g/t) | NiO (g/t) | P (g/kg) | N (g/kg) | Humus (g/kg) |
| 36.6 | 49.8 | 9.6 | 25.4 | 68.6 |
| $SiO_2$ (g/kg) | $TiO_2$ (g/kg) | $Al_2O_3$ (g/kg) | FeO (g/kg) | MnO (g/kg) |
| 397.6 | 7.0 | 117 | 45.6 | 0.40 |
| MgO (g/kg) | CaO (g/kg) | $Na_2O$ (g/kg) | $K_2O$ (g/kg) | Loss (g/kg) at 1273 K |
| 26.8 | 154.6 | 21.3 | 18.3 | 199.7 |

The data from the elemental analysis of sapropelles are shown at table № 1. The content of macro- and microelements was established, calculated as oxides. The results obtained show that the content of calcium - 154,6 g/kg , calculated as CaO is more than its content in the most soil types. The content of some other basic elements as Mg, Mn, Fe, as well as some other necessary for the plants micro elements as Cr, Mo, Cu etc. exceeds their content in various soils. The humus content is 68, 6 g/kg, due to a presence of dead organic matter in the sapropeloide bottom sediments. Another important advantage of sapropeloide sediments according to Dimitrov (2010) is their sterility, due to their forming in non-living hidrogen sulphide zone on the sea bottom.

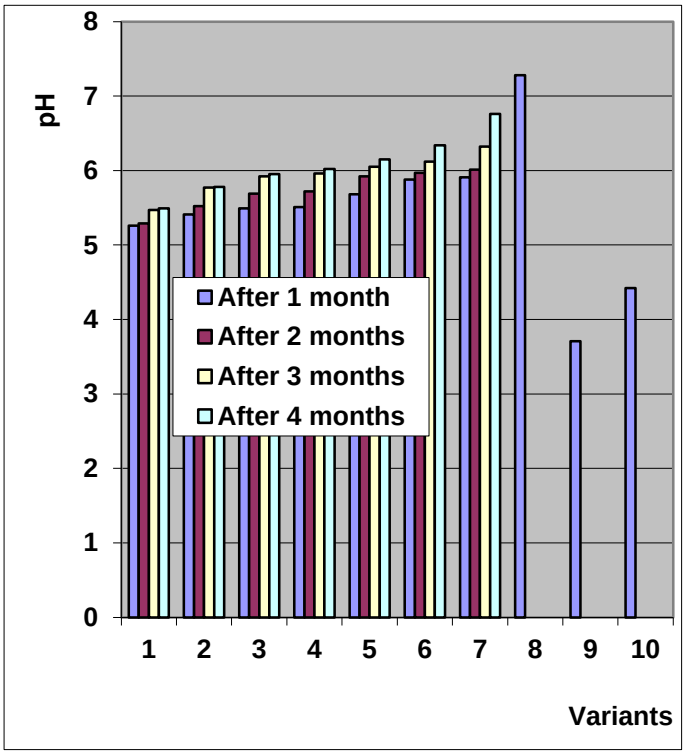
Table 2. Exchange ions and humus content in CPS (*Planosol*) and CPS - sapropels mixtures

| Soil-sapropels samples | Exchange ions after a month of incubation, mgeq/100g | | | | Humus g/kg |
|---|---|---|---|---|---|
| | $Ca^{2+}$ | $Mg^{2+}$ | $\sum(Ca^{2+},Mg^{2+})$ | $\sum(Al^{3+},H^{+})$ | |
| CPS + 10 g/kg | 3.7 | 1.6 | 5.3 | 0.06 | 8,3 |
| CPS + 20 g/kg | 4.2 | 2.3 | 6.5 | 0 | **11.** |
| CPS + 30 g/kg | 4.6 | 2.9 | 7.6 | 0 | **12.7** |
| (CPS) Control | 19.4 | 15.8 | 35.2 | 101.2 | 6.7 |




**Legend: 1**.1.0 g/kg, **2**.3.0 g/kg, **3**. 5 g/kg**, 4**. 7 g/kg , **5**.10 g/kg, **6**.20 g/kg**, 7**. 30 g/kg sapropels, **8**.Sapropels, **9**.Control (KCl) **10**.Control ($H_2O$)

**Fig.1**. Neurtalization of CPS (Planosol) with sapropels




**Legend: 1**.1.0 g/kg, **2**.3.0 g/kg, **3**. 5 g/kg**, 4**. 7 g/kg , **5**.10 g/kg, **6**.20 g/kg**, 7**. 30 g/kg sapropels, **8**.Sapropels, **9**.Control (KCl) **10**.Control ($H_2O$)

**Fig.2**. Neurtalization of BFS-B (Distric Cambisol) with sapropels

The data for the content of exchange ions and humus in CPS(*Planosol*) and some soil-sapropels mixtures after a month of incubation show that the sea sapropels increase the content of humus in CPS from 6.7 to 8.3-12.7 g/kg depending on the amount of sapropels. The pH values in the soil samples depend on the content of humic and fulvo acids in the form of alkaline salts, because they increase the buffering capacity of soils – the most important factor to stabilize soil pH. Parallel to increasing of basic exchange ions decrease the content of $Al^{3+}$ and $H^{+}$ - from 103,23 mgeq/100g in CPS to 0,06 in an amount 10 g/kg sapropels to absence of these ions by more higher concentrations.(table.2)

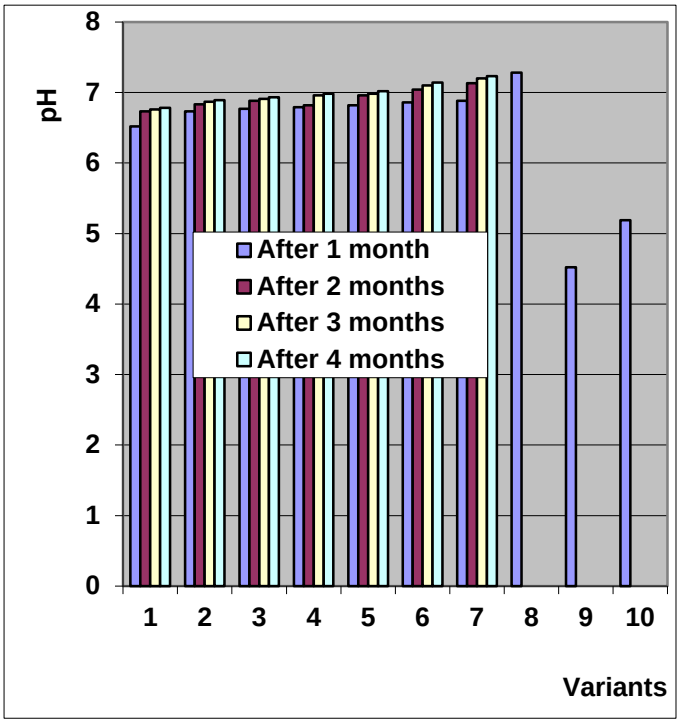
Figure 1 shows data for the pH of sample CPS, sapropels and CPS–sapropels mixtures. The most significant change comes one month after incubation of sapropels in the soil. After the first month pH increased insignificantly - from 0.1 to 0.6 pH units for the next three months of incubation. For variants 1 and 2 with 1,0 g/kg and 3,0 g/kg sapropels, values close to neutral medium (pH 6.57 to 6.67) were reached only after 4 months incubation period and this trend is maintained and variant 3 (5,0 g/kg sapropel), as the pH reached 7.0 units. Under variant 4 (7,0 g/kg sapropel), the same value was reached after 2 months incubation period, and after four months reached 7.26 pH units. Variant 5 (10 g/kg sapropel) pH value reaches 6.86 units after 1 month and four months after the pH was already in the weakly alkaline medium - 7.5 units. In variants 6 and 7 (10-30 g/kg) pH reaches values of more weakly alkaline medium of the first month and 7.15 - 7.36 pH units. After four months of incubation the corresponding values for pH were 7.76 to 8, 01 units. The data from fig.1 show that even in minimum quantities - 1 – 3 g/kg sapropels neutralize soil acidity to values close to neutral medium – pH 6,5 - 6,7%.

Figure 2 shows data for the pH of samples BFS-B, sapropels and BFS-B-sapropels mixtures. The most significant change comes after a month incubation of sapropels in the studied samples. After the first month pH increased in borders 0.2 to 0.9 pH units for the next three months of incubation. For variants 1 and 2 with 1, 0 g/kg, 3,0 g/kg and 5 g/kg sapropels, the pH values 5.49 to 5.95 were reached after 4 months incubation period. The pH value near to neutral medium - 6.34 was reached after 4 months incubation in variant 6 with 20 g/kg sapropel – 6.34. The maximum value - 6.76 pH units after 4 months incubation

was reached in variant 7 with 30 g/kg incubated sapropels, because the starting pH value of BFS-B is strongly acidic – pH 4.42($H_2O$) and 3.71 respectively in 1N KCl.

Figure 3 represents the data for samples pH of BFS-N, sapropels and BFS-N-sapropels mixtures. The starting pH of BFS-N was 5.19 in water medium (4.52 in 1N KCl). The result obtained show that in variants 1, 2, 3 pH reached neutral medium after a month of incubation in borders 6.52 – 6.77. The difference of pH values between these variants and the following – 4-7 is insignificantly – about 0.2 pH units. The pH value increased weak during the next three monts and reached 6.78 – 7.23 in all soil-sapropels samples.

The sea sapropels has a neutral reaction – 7. 28 pH units, but the main reason for the change of pH in the incubation with the acid soils should be noted activation of exchange bases, leading to an increase in pH in the neutral medium after the period of incubation.




**Legend: 1**.1.0 g/kg, **2**.3.0 g/kg, **3**. 5 g/kg**, 4**. 7 g/kg , **5**.10 g/kg, **6**.20 g/kg**, 7**. 30 g/kg sapropels, **8**.Sapropels, **9**.Control (KCl) **10**.Control ($H_2O$)

**Fig.3**. Neurtalization of BFS-N (Distric Cambisol) with sapropels

The change of pH is related to the content of humus and exchange ions at the samples, containing sapropels. The presence of organic carbon and exchange ions ($Ca^{2+}$, $Mg^{2+}$) at the sapropels composition, improve the buffer ability of the investigated soils. Furthermore in aqueous medium the pH values of the tested soils was determinated in solution of 1N KCI, to establish the hidden soil acidity, due to ion exchange between $H^+$ and $K^+$. In the presence of a certain amount of potassium salts in the tested soils, this acidity is also evident, and must be taken into account. It was established that the difference between the event and further activated hidden acidity of the three type soils is between 0.6 to 0.7 pH units.

The amount of sapropels which should be invested to correct the soil acidity depends on the type of culture to be grown. Most crops according to Terziev et all (2006) grow in neutral and weak acidic medium. The optimum soil pH (6.5 to 7.5) was achieved at amounts 10 g/kg, 20 g/kg and 30 g/kg, as the second and third valies are recommended because of the fact that with sapropels in the soil are also imported some nutrients - macro-, micro elements and humic substances, which according to Arancon et all (2006) have an important impact on the plants physiology. Higher concentrations over 30 g/kg according to Nikolov (2011**[b]**) are not desirable because the alcaline medium hindered mineral nutrition of plants, because of reducing the amount of absorbable forms of macro and micronutrient elements.

## 4. CONCLUSIONS

Sapropels neutralize the soil acidity by the tested CPS (Planosol) from 4.87 to neutral and weak alkaline medium, depending on the content of incubated sapropels. About the first type of BFS (Distric Planosol), area Beglika, because of the low starting pH ($H_2O$) - 4, 42, the necessary amount of sapropels for reaching of neutral medium has to be 20 - 30 g/kg, by 4 months incubation period. At BFS (Distric Planosol), taken from the area of Banya village, region Nova Zagora, pH changes to neutral medium (6.52-6.88) after the first month of incubation at all used amounts of sapropels – from 1.0 to 30 g/kg.

The results obtained show that, even with minor amounts of incubated sapropels – 1-10 g/kg, pH of the studied soils changes significantly to values near to weak acidic or neutral medium, which is favorable for plants growing. The amounts 10-30 g/kg are recommended, because the most active biochemical substrates on which plants respond best are humic- and fulvo acids of natural origin. The study shows that sapropels could be used for recultivation of acidic soils and for their enriching with some useful for the plants nutrient elements.

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