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PALEOCRYOGENESIS AND SOIL FORMATION

THE EFFECT OF CRYOGELS ON THE PHYSICAL PROPERTIES OF SOIL AND PLANTS IN THE COURSE OF A FIELD EXPERIMENT

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Cryostructurization of top soil with aqueous polymer solution has been demonstrated to result in the increase of the part of coarse fractions and the amount of water-stable aggregates in aggregate composition; the angle of the natural soil slope increases from 7 to 45°. All this suggests increased resistance of cryostructured soil to wind and water erosion. In addition, cryostructurization improves the plant growth, increases the number of microorganisms, and promotes accumulation of humic substances in the soil.

Soil erosion, polymer, cryogel, cryostructured soil, soil microflora, perennial, soil structure

INTRODUCTION

Cryogels based on polyvinyl alcohol (PVA) have been the object of rising interest over the recent years. The method of cryotropic gel formation opens up new prospects for improving the existing materials and for developing new materials meant for different practical usages [*Lozinsky et al., 2008*]. The unique combination of certain properties (durability, biocompatibility, stability, and inertness) of the biological media and environmental safety, as well as the relative simplicity of the technology of their production, allow us to consider cryogels a new type of polymer systems, interesting both for fundamental research and for applied science. Over the recent years, these gels have been widely used as materials in biomedicine and in biotechnologies, as well as in the food industry [*Lozinsky, 2002*].

In addition, cryo structuring of soil may be applied to its protection from erosion and desertification, as well as to improvement of plant survivability under adverse conditions of the environment (temperature, moisture content, etc.) [*Altunina et al., 2012*].

The scope of degradation of the soil and plant cover make the scientists focus their attention on the condition of the soil cover of the Earth, which is the crossing point of all the energy and mass exchange flows on the planet and which performs important biosphere and ecosystem functions: life sustenance and maintenance of biodiversity and of the current function of all the structural components of the biosphere – atmosphere, hydrosphere, and lithosphere. Special investigations of the said functions are provided in numerous papers [*Eliseev and Cheverev, 2008; Kovda, 2008; Sokolov et al., 2010*]. The area of the entire soil cover of the Earth, naturally and historically formed in the course of the Earth's evolution, is about 13 billion hectares [*Dobrovolsky, 2002*], with about 4 billion hectares used in the world agriculture. The latter soils are often subject to erosion; in most cases, they are characterized by reduction of the amount of organic matter, reduction of their biological fertility, and change in the type of the biological cycle [*Gendugov and Glazunov, 2009*].

Soil destruction resulting from water erosion and deflation is manifested in different forms: formation of rain channels and ravines, ablation and drift of the fertile layer of soil from the fields, dust storms and, as a result, uncontrolled Aeolian deposits – sand-dunes, sand-drifts, etc. These phenomena occur across vast areas in the world. 31 % land is subject to water erosion, and 34 % land is affected by wind erosion. Up to 60 billion tons of soil material is ablated into the world ocean every year.

The damage inflicted by erosion and deflation to agriculture is manifested not only by soil destruction but also by the evacuation of nutrients from them – N, K, P, Ca, Mg. On the global scale, erosion takes away from the soil cover of fields and pastures 60 times more nutrients than their annual inflow with the fertilizer. Productivity of eroded soils reduces by 35–80 % [*Kretinin, 2006*]. At the current stage of agricultural production, protection of soils from erosion, preservation of the vegetative cover, and protection of the environment from contamination are the most important problems faced by the world agriculture [*Eliseev, 2007*].

The researchers of the Institute of Petrochemistry of the Siberian branch of the Russian Academy of Sciences have offered a complex chemical and biological method of fixating moving soils and grounds, presupposing impregnation of their upper layer with the cryogel-forming solution of PVA, with simultaneous seeding of perennial grasses. Fixation takes place after a freezing-thawing cycle when the soil temperatures vary between negative and positive values and cryogel is formed on the soil surface, in the polymer matrix of which there are solid particles of the soil. PVA solutions have been previously shown to have high adhesion to sand and clay grounds and to soils of different composition [*Altunina et al., 2006; Altunina et al., 2010*]. Loose particles of ground or soil cohere into cryo structures, which are resistant to erosion and rather resilient and do not interfere with the growth of plants [*Altunina et al., 2013a,b*]. Cryo structuring of the topsoil performs a protective function for plants at the stage of seed germination and formation of grass sod and influences the number of the labile forms of biophilic macro- and microelements in the soil [*Altunina et al., 2014*]. Plants growing on cryostructured soil have also been shown to increase 2–2.5 times the intensity of photo synthesis and the efficiency of water use, compared to plants growing on common soil [*Altunina et al., 2013c,d*], suggesting their higher adaptability.

The objective of this study was to investigate the influence of cryostructuring of the topsoil on the soil's properties under conditions of a field experiment.

OBJECTS AND METHODS OF INVESTIGATION

The objects of the study were gray forest light loamy soil and polyvinyl alcohol with the average molecular mass of 75 000 and characteristic viscosity of its aqueous solutions $\eta = 0.56$ deciliters/g.

The experiment of cryostructurization of soil under field conditions was conducted in the Tomsk region in 2013. The experimental site consisted of six plots 1 × 1 m seeded by a test culture (tufted hair grass *Deschampsia cespitosa*). The topsoil of the test plots was processed with aqueous 5 % PVA solution by the method of sprinkling at the rate of 2.5 L/1 m^2, and control plots were watered with equal amounts of water. The test was started on April 23. After seeding, the soil temperature dropped to zero values, which allowed a conclusion to be made regarding formation of filled cryogel in the topsoil.

After starting the experiment, no other agronomic measures were taken on the test plots (tillage, watering, etc.). The experiment lasted 130 days. Measurements were made three times, when three independent series of tests were conducted.

During the vegetation period, the temperature of the soil was measured, as well as the microflora population and the scope of the catalase activity. Soil samples were taken for the laboratory tests using a standard technique of sampling [*Vorobyeva, 2006*].

Soil temperature was measured with an electronic thermometer Ama digit ad 17th (Germany) having a remote probe; the probe was immersed in the soil to the depth of 2.5 cm. The measurements were made in 8–9 points on the test and control plots throughout the entire experiment. The measurements were made in the daytime from 1 to 3 p.m in Centigrade (°C) [*Vadyunina and Korchagina, 1986*].

Soil microflora was studied on three main groups of microorganisms participating in ensuring soil fertility: heterotrophic bacteria (ammonifiers), calculated on beef-extract agar-agar (BEA); actinomycetes, calculated on starch-and-ammonia agar-agar. (SAA); and micromycetes calculated on the Chapek agar medium. Their number was determined by seeding dilutions of the soil suspension on respective media and was expressed in colony-forming units (CFU) [*Filatov et al., 2011*]. The number of the cells was recalculated per 1 gram of soil considering the moisture content.

The catalase activity was determined using the gasometric method based on measuring the degradation rate of hydrogen peroxide in its interaction with the soil. Catalase activity was expressed in milliliters of oxygen produced per 1 g of soil during 1 minute [*Khaziyev, 2005*].

At the end of the experiment, the productivity of the tested and control plant communities was compared: the aboveground part of the plants was cut off, and its dry mass was evaluated by the gravimetric method after its frying in the drying cabinet at 60 °C to the constant mass [*Blum, 2005*].

At the end of the experiment, the structure of soil, water resistance of the aggregates, the granulometric and micro aggregate compositions, the angle of the natural soil slope, and the carbon content were identified.

To identify the structure of the soil, a 1 kg soil sample was taken from the soil dried in the laboratory to the dry powder condition and was spread on sieves with the mesh diameter from 10 to 0.25 mm (dry sieving). Each fraction was weighed, and its percentage was calculated.

According to the dry sieving data, the structure coefficient was calculated using the formula

$$K_{str} = a/b,$$

where K_{str} is the structure coefficient; *a* is the sum of micro aggregates sized from 0.25 to 10 mm, %; *b* is the sum of micro aggregates less than 0.25 mm in diameter and lumps larger than 10 mm, % [*Vorobyeva, 2006*].

The water resistance of the aggregates was determined by the method of wet sieving using a set of sieves with the mesh diameter varying from 10 to 0.25 mm. The weight of the fractions was expressed per cent.

Using the results of dry and wet sieving, the criterion of water resistance of the aggregates was calculated (the A criterion) by the formula

$$\text{A criterion} = C_{\mathrm{wr}}/C \cdot 100,$$

where C is the content of structural fractions sized from 1 to 0.25 mm in the soil obtained by dry sieving, %; C_{wr} is the content of water resistant aggregates sized from 1 to 0.25 mm, % [*Vorobyeva, 2006*].

The granulometric and micro aggregate composition of the soil was determined by the methods proposed by N.A. Kachinsky. Soil preparation for the granulometric and micro aggregate tests was made using a pyrophosphate method with different pyrophosphate concentrations and with different mechanical force applied [*Vadyunina and Korchagina, 1986; Shein and Karpachevsky, 2007*].

Based on the micro aggregate and granulometric tests, the dispersion coefficient and the degree of soil aggregation were calculated. The dispersion coefficient according to Kachinsky (K_d, %):

$$K_d = I_{\mathrm{m}}/I_{\mathrm{g}},$$

where I_{m}, I_{g} are the contents of silt fractions in the micro aggregate and granulometric tests, respectively.

The degree of soil aggregation according to Baver (A_{g}, %):

$$A_{\mathrm{g}} = P_{\mathrm{m}} - P_{\mathrm{g}}/P_{\mathrm{m}},$$

where P_{m}, P_{g} is the content of fractions larger than 0.05 mm in the micro aggregate and granulometric tests, respectively.

Based on the results of the granulometric tests of the soil, specific surface area of the soil particles was determined with a geometric method [*Shein, 2005*].

The angle of the natural soil slope in the control and cryostructured soil samples was determined in the overmoisturized state by slow plate removal [*Vadyunina and Korchagina, 1986*].

The content of carbon in the control and cryostructured soil samples was determined with a titrometric method according to V.I. Tyurin, which consists in oxidation of the carbon contained in the organic matter of the soil with potassium dichromate in the presence of sulfuric acid. Depending on the results of determining carbon of organic compounds, the content of humus was calculated. For this purpose, the value of the mass fraction of carbon expressed as per cent was multiplied by the coefficient equal to 1.724 [*Vorobyeva, 2006*].

The results were processed using the statistical package MS Office Excel 2003.

RESULTS AND DISCUSSION

The anti-erosion resistance of soils depends on a number of their properties, especially water permeability, soil pedality, and water resistance of the soil structure, which are determined by the mineralogic and granulometric composition, as well as by the content of humus. As the silt fraction and humus content increase in soil, its anti-erosion resistance grows, while the high content of the fraction of large dust particles (0.05–0.01 mm) significantly decreases the water stability of the soil structure.

In addition, soil structure is one of the factors of its fertility. In structurized soil, optimal conditions are created for the water, air, and thermal regimes, which, in its turn, ensures microbial activity, mobilization and accessibility of nutrients for plants.

The specific surface area of the soil particles in the soil under study was 44 cm^2/g. After cryostructrization with the PVA solution, the fraction of the aggregates of all fractions larger than 3 mm increased in soil: >10; 10–7; 7–5 and 5–3 mm (Fig. 1). This seems to result from the aggregating action of the PVA solution on the small particles of the soil, which formed micro aggregates, followed by macro aggregates, due to the presence of cryogel.

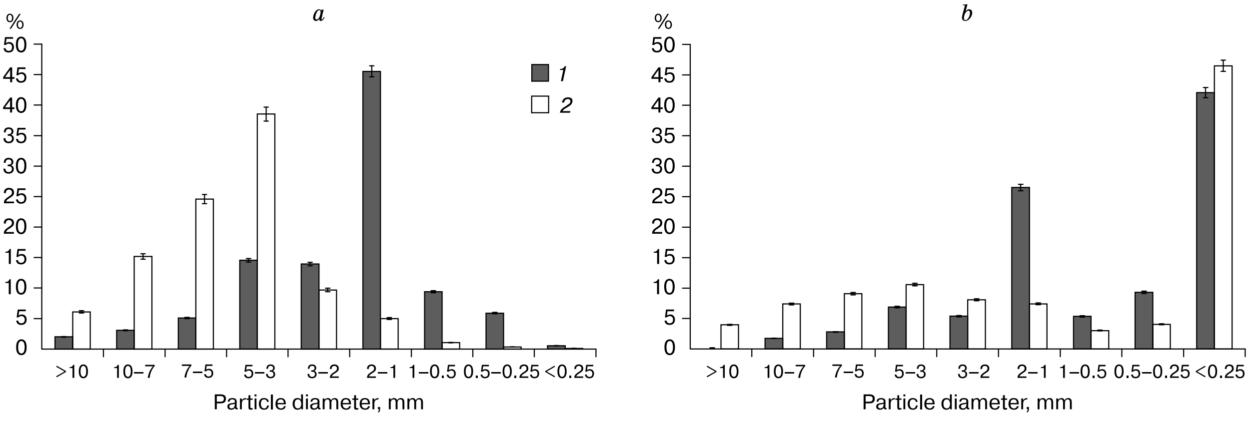

Fig. 1. Results of analyzing the structure of control soil (*1*) and cryostructured soil (*2*):
a – dry sieving; *b* – wet sieving.

In natural conditions, the silt fraction plays the main role of a connector between dusty and sandy basic soil particles, ensuring durability and stability of the soil aggregates.

In unstructured soils subject to erosion, a cryogel-forming solution is capable of organizing separate particles: after the freezing-thawing cycles, the particles glued by the polymer solution prove to be built in into 3D spatial cellular cryogel matrix, which has high mechanical durability and water resistance, increasing the erosion resistance of soil.

After soil fractioning with dry and wet sieving, the structure coefficient was calculated (K_{str}) and the water stability criterion (the A criterion) of the soil aggregates. K_{str} of the control soil was equal to (38.2 ± 0.4), that of cryostructured soil was (15.4 ± 0.3). This is caused by the increase in the fraction of soil particles with the diameter exceeding 10 mm (Fig. 1, *a*). Although after cryogel introduction K_{str} decreases 2.5 times, i.e., reduction in soil structuring occurs, erosion processes are thus prevented (deflation, ablation, etc.).

The water stability criterion (A criterion) of the control soil sample without cryogel was equal to (96 ± 2) %, and in the soil with cryogel it was (516 ± 3) %. Thus, cryostructured soil had very good water stability, while the control soil had satisfactory water stability. Hence, there emerge aggregates in the cryostructured soil, which have respective bonds among the particles composing an aggregate and are capable of resisting external impacts and of ensuring water stability.

The granulometric composition plays an essential role in the physical, mechanical, water, air, thermal, and other agronomic properties of soil. When using the pyrophosphate method, significant change in the granulometric composition of soil in horizon A1 was observed, caused by incomplete destruction of aggregates: compared to the control samples, the content of the sandy fractions increased (0.05–1 mm), and the fraction of the fine and medium-sized dust decreased (0.01–0.001 mm) (Fig. 2, *a*).

According to the micro aggregate analysis, after cryostructuring the content of fine aggregates decreased in the soil (to 0.25 mm), while the fraction of large aggregates (0.25–1 mm) increased (Fig. 2, *b*). The dispersion coefficient of the control soil was (18.3 ± 0.5) %, and that of the experimental soil was (11.7 ± 0.4) %. The degree of aggregation in the control and cryostructured soils was (22.3 ± 0.3) and (28.7 ± 0.5) %, respectively. That means, that the cryostructured soil had a high degree of micro structuring, while the control soil had a good degree of micro structuring. A higher degree of aggregation of the experimental soil indicated increased water stability of the structural elements in the course of the experiment.

The natural slope angle is another indicator of erosion resistance: this is the highest possible degree of the angle formed by the stable dry soil slope with the horizontal surface. The natural slope angle (the repose angle) depends on the granulometric composition and the shape of the soil particles. The greater the natural slope angle is, the more stable is the surface in relation to external impacts. For the control soil, the natural slope angle was 7°, while for the cryogel-processed soil, it was 45° (6.4 times higher), both at the beginning and at the end of the vegetation season (130 days after). Thus, cryostructured soil had high erosion resistance.

To ensure growth and development of plants, one of the most essential environmental factors is the temperature regime of the soil, which determines the intensity of biological, chemical, physical, and bio-

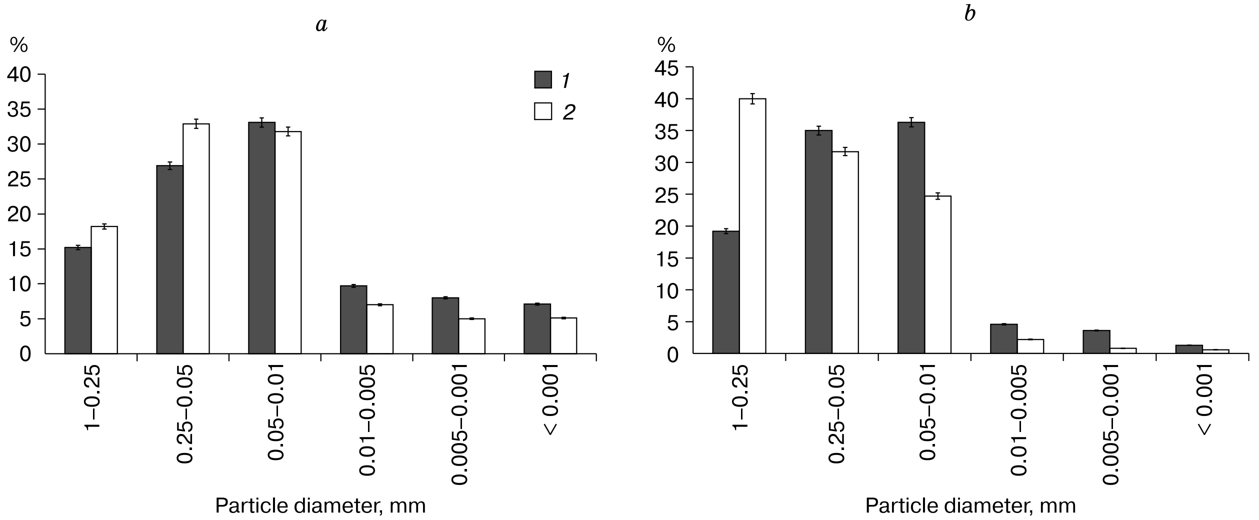

Fig. 2. Results of analyzing the granulometric (*a*) and microaggregate (*b*) composition of control soil (*1*) and cryostructured soil (*2*).

chemical processes in the soil. The temperature regime is determined both by the external conditions (the current weather) and the thermal physical qualities of soil itself (the heat absorbing capacity, the thermal capacity, and thermal conductivity of soil). Temperature measurements during a vegetation season in the experimental and control soils showed cryostructurization of top soil to cause soil temperature increase in the daytime by 0.5–1.7 °C at the depth of 2.5 cm (the minimum depth of impregnation of topsoil with the aqueous solution of PVA) (Fig. 3).

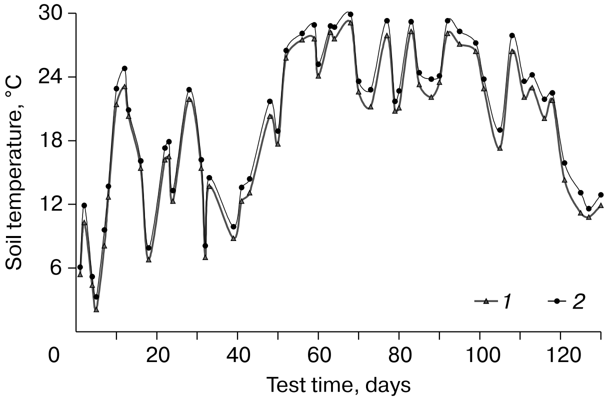

Fig. 3. Temperature change in control soil (*1*) and cryostructured soil (*2*) throughout the experiment.

Many processes occurring in soil are related to activity of the soil micro flora: firstly, this is circulation of biogenic elements, transformation of organic and mineral compounds, synthesis of enzymes, vitamins, amino acids, auxins, and chelates [*Filatov et al., 2011*].

The experiment results showed the amount of soil micro flora to grow in cryostructured soil. Its original amount varied in the range of $0.5{\cdot}10^6$–$2{\cdot}10^6$ CFU/g of soil. During the experiment, the number of microorganisms in the cryostructured soil exceeded the control figures 3–5 times (Fig. 4). It is known from literature that polyvinyl alcohol gels are inert and are not subject to destruction by bacteria and enzymes [*Koptilova et al., 2011*]. Therefore it is unlikely that polyvinyl alcohol in soil could have served as a nutritive substrate. Rather, increase in the number of microorganisms may be related to more intense growth of plants, the root extracts of which they use. The positive influence on the soil micro flora may also be related to the mulching action of the polymer film on the soil surface, which stabilizes its water and temperature regimes [*Altunina et al., 2014*].

The study of the enzymatic activity of the cryostructured soil has shown that the catalase activity did not essentially differ from that in the control soil but in certain intervals of time it exceeded the control figures by 4–8 %.

Improvement of the environmental condition of the soil due to termination of the wind and water erosion, stabilization of the temperature regime, and increase of the water-retaining quality of the substrate

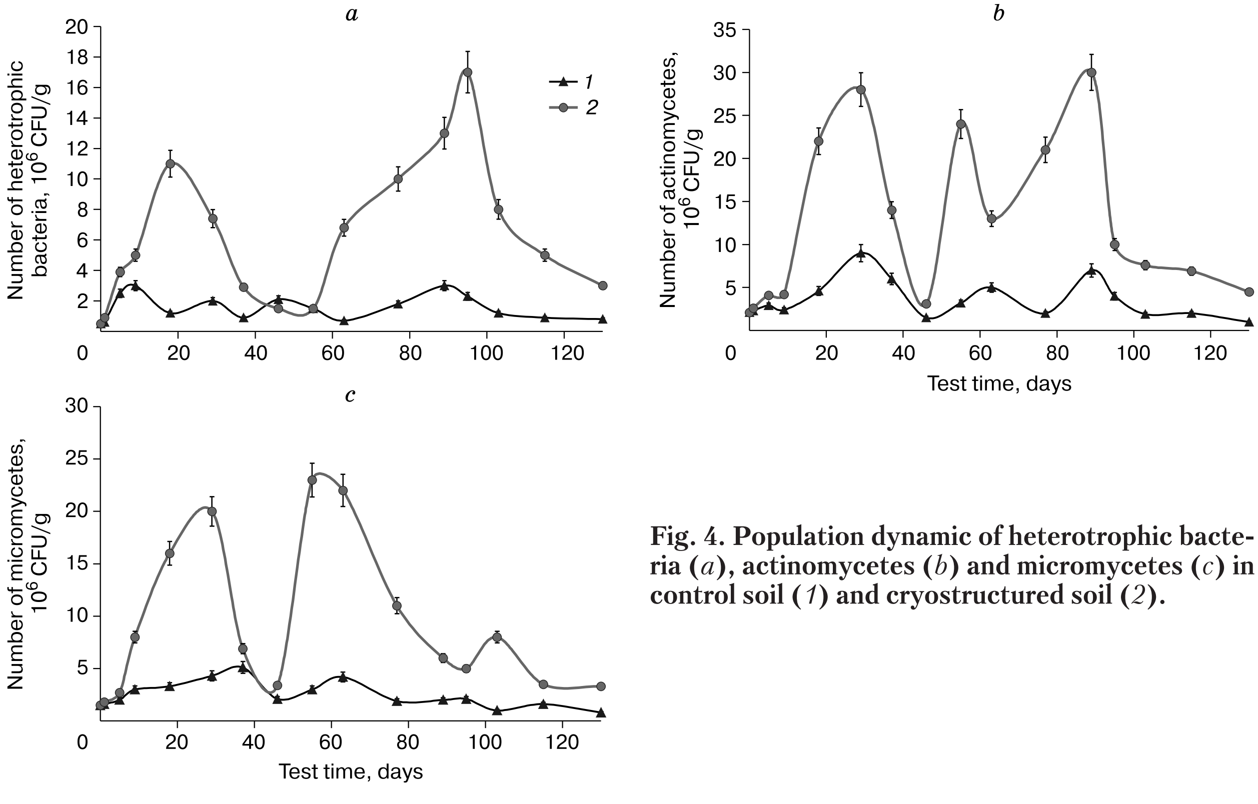

Fig. 4. Population dynamic of heterotrophic bacteria (*a*), actinomycetes (*b*) and micromycetes (*c*) in control soil (*1*) and cryostructured soil (*2*).

create favorable conditions for plant vegetation. Positive influence of cryostructurization of top soil upon productivity of the plant population has been demonstrated: the dry top plant weight in the control soil at the end of the vegetation season was 4.62 g, in the experimental soil it was 5.22 g (13 % higher).

The content of the humic substances in soil is one of the main indicators of soil fertility. At the end of the vegetation season, the content of carbon in the control soil was 3.46 %, and that in the cryostructured soil was 4.06 %. The cryogel-forming solution contains organic polymer; therefore, the content of carbon in the experimental soil minus the fraction of PVA was 3.76 %, which corresponds to the fraction of humic substances of 6.48 % (in the control soil, it was 5.97 %). This may be caused by its more active formation from the organic remains under the influence of the soil micro flora with increased productivity of the grass stand or by reduction in the migration of the organomineral soluble complex due to the water insulating qualities of the cryogel.

CONCLUSION

It has been shown that physical characteristics of cryostructured soil change: in the aggregate state, the fraction of the aggregates larger than 3 mm in diameter increases, the number of water-resistant aggregates grows, and the coefficient of water dispersion of the soil decreases (in the control soil it is (18.3 ± 0.5) %; in the experimental soil it is (11.7 ± 0.4) %); the degree of aggregation rises (in the control soil it is (22.3 ± 0.3) %, in the experimental soil it is (28.7 ± 0.5) %), and the natural slope angle reaches 45°.

In the course of the experiment, changes in the functioning of the microbial and plant communities are noted: the amount of micro flora in the experimental soil throughout the vegetation season exceeded the control data 3–5 times, while the productivity of the plant community grew by 13 %.

Thus, cryostructuring of gray top soil has positive influence on the erosion resistance of the soil, its fertility, the number of microorganisms in it and the plant growth, which may be used for practical purposes.

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