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SOIL PHYSICS

Structure and Properties of Soil Organic–Mineral Gel

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Abstract—Changes in the fractal dimension and scattering intensity of colloidal structures in a chernozem, soddy-podzolic soil, and a krasnozem were studied by small-angle neutron scattering at different temperatures and soil water contents. The character of the neutron scattering by soil colloids indicated that the latter were mass fractals in all of the soils studied; i.e., the colloidal particles were located apart from one another even in dry soils. The obtained results confirmed the supposition about the distribution of colloidal particles in the humus gel matrix. The changes in the fractal parameters of the soddy-podzolic soil and chernozem with increasing water contents were nonmonotonic in character, which indicated complex structural rearrangements of the colloidal component in these soils. From the results obtained, a conclusion was drawn that the destruction of the molecular network of reinforced humus gel occurred upon heating the soils to high temperatures: colloidal particles reinforcing the humus gel began to move and coagulate with the formation of dense aggregates. The electron-microscopic study of gel films released from the predried and then capillary wetted aggregates in water showed that the gel films were nonhomogeneous and included zones of humus gel reinforced by colloidal particles and zones almost free from these particles.

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INTRODUCTION

Experiments on the study of the stickiness, electrical conductivity, enzymatic activity, thermal conductivity, and some other soil properties depending on the duration of the soil–water interaction after addition of water to dry soils confirmed the existence of interactions between soil colloidal particles with the formation of gel structures incorporating the soil solution.

Methods of scanning and transmission electron microscopy, as well as small-angle neutron scattering, showed that colloidal particles in soils are fixed apart in a gel matrix formed by organic molecules.

The results obtained [12, 13, 16] suggest that organic–mineral soil gels present on the surface of soil particles and binding these particles are composed of soil humus occurring in the gel-like state and reinforced by organic and inorganic colloidal particles. In the interaction with water, the reinforced humus gel (**RHG**) behaves as many polymers: it swells and increases in volume when absorbing water, and it shrinks when dry. Different impacts on the soil affect the state of the reinforced humus polymer gel, which results in changes in soil properties.

At the same time, studies of the gel composition [1, 5, 6, 11] indicate that soil gels are structurally nonhomogeneous; therefore, the general concepts of the structure and functioning of soil gels [12, 13, 16] need to be specified and rectified.

It may be supposed that information on the principles of structural rearrangement of soil colloids could be derived from the analysis of changes in the structural organization of soil colloids under the effect of thermal treatment and changes in the soil water content.

EXPERIMENTAL

Small-angle neutron scattering (**SANS**) is a method that can be used to study the structural organization of the whole organic–mineral gel, including internal layers of soil gels without their separation [8]. This method can provide information on the fractal organization of soils, which is an integral characteristic of their colloidal structure [14, 15].

The objects of the study were the humus-accumulative horizons of contrasting soils: a leached chernozem, a soddy-podzolic soil, and a krasnozem. The properties of the soils were described earlier [12]. These soils differed in many parameters, which could provide information on the effect of some soil properties on the structural organization of soil colloids. The specific surfaces of the chernozem and krasnozem exceeded that of the soddy-podzolic soil by an order of magnitude. Hence, the contents of colloidal particles in them were significantly higher than in the soddy-podzolic soil. The krasnozem was enriched in positively charged colloidal particles of iron and aluminum hydroxides compared to the chernozem and soddy-podzolic soil. Humic acids were predominant in the chernozem's humus, and fulvic acids prevailed in the krasnozem and soddy-podzolic soil.

Fractal objects produce a specific scattering pattern when analyzed using the small-angle neutron scattering method: a linear relationship between the scattering intensity and the applied pulse is observed in logarithmic coordinates over a relatively wide pulse range [19]:

$$\log I(k) \sim -x \log k. \quad (1)$$

Measurements were performed using a YuMO small-angle neutron spectrometer installed at a channel of an IBR-2 pulsed reactor at the Joint Institute for Nuclear Research (Dubna). A two-detector system was used; therefore, the range of the scattering vector magnitude Q was from 0.007 to 0.6 Å^{-1} for neutron wavelengths from 0.7 to 5 Å and detector–sample distances of 3.60 and 12.97 m for the first (nearer) and second (farther) detectors, respectively.

The primary data processing was performed using SAS software [9]. The data were normalized to a vanadium reference in order to obtain absolute values of the spectra.

To study the effect of thermal treatment on soil colloids, the air-dry samples were wetted to a near field-capacity level and left to stand for at least two weeks. To study the effect of the soil water content, the air-dry soil samples were wetted to the field capacity, dried to a specific water content, and left to stand in this state for at least two weeks. Toluene was added to the soils to prevent the development of microflora.

The soil samples were placed in Hellma cells with a useful thickness of 2 mm; the beam size was 14 mm. The cells were installed in a thermostat whose temperature varied in a range of 20–90°C. Before the measurements, the samples were exposed at a specified temperature for 10 min.

The electron microscopic study was conducted using a Leo Supra-50 VP scanning electron microscope (Carl Zeiss, Germany).

To prepare the samples for electron microscopy, soil aggregates 3–5 mm in size were placed on filter paper in Petri dishes and the paper was wetted to capillary saturate the aggregates with water. After two to three minutes, the level of the water in the Petri dishes was increased, which resulted in the detachment of films from the aggregates and their rise to the surface of the water. The films were then placed onto an atomically smooth surface of freshly split mica by contacting it with the film-containing water surface.

Carbon was evaporated onto the samples thus prepared and dried (a Univex-300 thermal evaporator, Leybold, Germany).

Changes in fractal dimensions of soil samples determined by the method of low-angle neutron scattering upon changes in the soil temperature

Sample temperature, °C	Scattering intensity at the wavelength of 5 Å, cm^{-1}	Fractal dimension
	Chernozem	
20	765	2.7
35	760	2.73
50	747	2.7
60	745	2.71
70	740	2.71
80	738	2.7
90	720	2.68
60	734	2.7
50	726	2.7
35	729	2.69
20	736	2.7
	Soddy-podzolic soil	
20	235	2.75
35	235	2.81
50	229	2.73
60	230	2.74
70	233	2.75
80	233	2.73
90	235	2.73
60	158	2.72
50	155	2.73
35	161	2.75
20	169	2.76
	Krasnozem	
20	937	2.6
35	900	2.59
50	878	2.59
60	870	2.61
70	856	2.59
80	817	2.63
90	710	2.61
60	680	2.6
50	679	2.6
35	705	2.62
20	723	2.61

RESULTS AND DISCUSSION

The results of studying the effect of temperature on the structure of soil colloids showed (Table 1) that the fractal dimensions of all the soils varied only slightly when the temperature rose to 90°C and then fell to

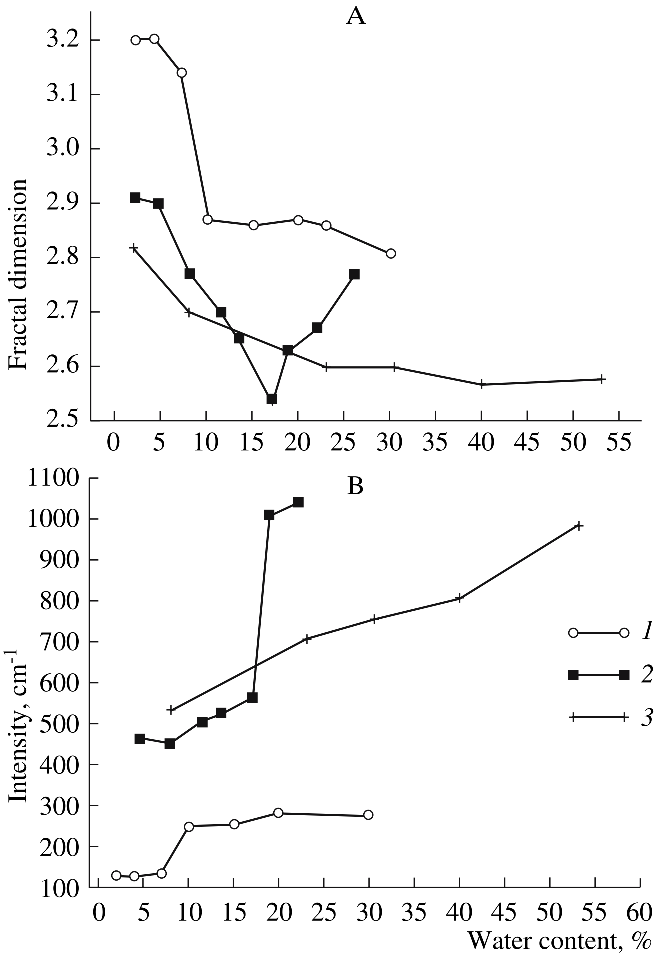

Fig. 1. (A) Fractal dimension and (B) neutron scattering intensity as functions of the soil water content: (*1*) soddy-podzolic soil; (*2*) chernozem; (*3*) krasnozem.

20°C. The scattering intensity for the soddy-podzolic soil was appreciably lower than for the chernozem and krasnozem, which correlated with the data on the contents of the colloidal particles and the specific surface areas of these soils.

The temperature changes affected the intensity of the scattered radiation. When the chernozem's temperature was increased to 90°C, the intensity of the scattered radiation decreased from 765 to 720 cm^{-1} and did not completely restore upon the temperature decreasing to 20°C. An even more significant decrease in the scattered radiation intensity (from 235 to 158 cm^{-1}) followed by an increase to 169 cm^{-1} was typical for the soddy-podzolic soil; a decrease from 937 to 679 cm^{-1} and an increase to 723 cm^{-1} were observed for the krasnozem.

These results indicate that some colloidal particles become invisible for the SANS method, which can be used for observing particles from 1 to 100 nm in size. Colloidal particles, which predominantly consist of clay minerals, iron and aluminum hydroxides, and silicic acid, cannot dissolve in the water present in the system; hence, they enlarge and their size exceeds 100 nm.

It is notable that aggregation began at 80–90°C, which suggests the fixation of colloidal particles in the structure of humus gel through chemical bonds. It is also notable that the aggregation had an induction period. This was confirmed by the minima of the scattering intensity observed for the soddy-podzolic soil and krasnozem after the temperature decreased from 90 to 60°C. After the breaking of bonds, colloidal particles probably diffused to gaps in the humus matrix, where they interact with one another.

The maximum decrease in the scattering intensity was observed for the krasnozem and soddy-podzolic soil (about 25 and 35%, respectively). For the chernozem, this decrease was no more than 5%, which indicated the higher stability of the humus gel formed by humic acids compared to the fulvic acid-formed gel. The molecules of humic and fulvic acids have similar ends, and the number of polar groups is higher in fulvic acids; therefore, it may be suggested that the humus gel network begins to degrade with increasing temperature: the density of the cross-links decreases, and the mobility of the colloidal particles increases. If the increase in the mobility of the inorganic colloidal particles were limited by the breaking of bonds between the organic molecules of the humus gel and colloidal particles, an opposite situation would be observed: the maximum change in the intensity would be found in the chernozem because of the lower content of polar groups. The data obtained agree with the concepts of the relatively high stability of the chernozem humus.

An increase in the neutron scattering intensity with decreasing temperature was observed for all the soils. This indicated that, first, the aggregation followed a coagulation mechanism rather than a condensation one. Otherwise, the distance between the colloidal particles could not increase with decreasing temperature because of the formation of strong condensation contacts, and, hence, the scattering intensity would not increase. Second, it might be suggested that the close coagulation contacts between the colloidal particles in an aggregate resulted in the aggregate interacting with the neutron beam as a whole unit, because colloidal particles can interact separately with the neutron radiation only when they are located apart from one another.

The study of the effect of the water content on the colloidal structure of the soils showed that a monotonous decrease in the fractal dimension (Fig. 1, A) and a monotonous increase in the scattering intensity (Fig. 1, B) were observed only for the krasnozem. More complex relationships were observed for the soddy-podzolic soil and the chernozem.

The explanation of the results requires considering the nature of the water bonds in soils. It is believed [17] that, at low water contents, water occurs in soils in the adsorbed state on the surface of soil particles. As the water content increases, films of liquid, poorly mobile water are formed on the surface of particles; then, the filling of soil capillaries can begin.

In these terms of perceiving soil as a polydisperse system, the results obtained are difficult to explain. The highest changes in the fractal dimension were observed in the region of film water for the krasnozem and soddy-podzolic soil and covered the region of capillary water for the chernozem. In addition, the nonmonotonic relationships observed for the soddy-podzolic soil and chernozem cannot be explained in all these terms.

When the soil is considered as containing a humus gel reinforced by colloidal particles, its interaction with water proceeds in a different way. As the water content increases, the hydration of active sites in humus molecules and colloidal particles should first occur. The complete hydration (filling of the shrinked RHG) then takes place. The RHG structure and the mutual arrangement of colloidal particles remain almost unchanged. A further increase in the water content entails the swelling of the RHG with inclusion of water in it. These changes in the RHG will cover the region of film water and the beginning of the capillary water region, because fine capillaries can be completely filled with the swelled RHG. The formed colloidal system should have a limited share stress and a high viscosity. In fact, a low mobility of film water was observed, as well as a low mobility of water in capillaries smaller than 10 μm [3, 10]. Shein [17] reported data illustrating the existence of poorly mobile gel layers in capillaries: an abrupt increase in the infiltration coefficient when a specific pressure is exceeded (the excess of the limit share stress of gel structures, their decomposition, and an increase in the effective diameter of capillaries) and the absence of infiltration under low pressures. All these data find their explanation in terms of soil colloids occurring as a reinforced humus gel.

When the water content in the soddy-podzolic soil attained a level of 7–8%, its RHG was expanded and the distances between the reinforcing colloidal formations (colloidal particles and their aggregates of colloidal size) increased. This was confirmed by an increase in the fractal dimension (Fig. 1, A), which could be interpreted as an increase in the average distance between the colloidal objects dispersing the neutron radiation. It is notable that the structural rearrangement in the soddy-podzolic soil occurred in a very narrow range of water content. An increase in the scattering intensity was observed in the same water content range (Fig. 1, B), which indicated an increase in the amount of colloidal particles apparently formed during the disintegration of aggregates.

A more complex tendency was observed for the chernozem. First, the fractal dimension increased (and the scattering intensity also increased slightly) with increasing water content (Fig. 1). Hence, the RHG swelled, the average distance between the formations of colloidal size (particles and aggregates) increased, and a minor part of the aggregates disintegrated into colloidal particles or aggregates of colloidal size. At a water content of about 17%, an inflection was observed in the fractal dimension curve (Fig. 1, A), as well as a jump in the scattering intensity (Fig. 1, B), which could be attributed to the disintegration of aggregates to colloidal particles at this water content and a decrease in the average distance between the scattering particles.

In the krasnozem, a decrease in the fractal dimension and an increase in the intensity were observed with increasing water content (Fig. 1), which indicated a swelling of the RHG with increasing distance between the scattering colloidal formations, the amount of which continuously increased due to the disintegration of aggregates. However, the swelling of the RHG, which increased the distance between the particles, prevailed over the disintegration of aggregates, which increased the amount of colloidal formations and decreased the average distance between them.

Our experiments provided information on the changes in soil colloids; however, they, as well as the earlier studies [12, 13, 16], did not allow the direct visual observation of gel structures in soils, and the methods used only indirectly characterized their structure and behavior. The experiments confirmed the existence of reinforced humus gel in soils, but they provided no unambiguous evidence for the absence of other gel structures in soils [14].

Grossman and Lynn [18] showed that when predried and capillary wetted aggregates taken from the illuvial horizons of some soils were placed in water, a film was formed on the water surface. The authors studied these films and showed that these were particles of clay minerals several microns to tens microns in size linked by an inorganic gel. This conclusion was based on the fact that the organic gel could not be oxidized with hydrogen peroxide.

We supposed that similar films form from the gel layer fragments detached from the surface of soil particles during the drying of aggregates; hence, they should also be observed for samples taken from humus-accumulative horizons, where gels consist of humus molecules. Experiments performed with aggregates taken from the humus-accumulative horizons of different soils confirmed this supposition.

Thus, an electron-microscopic study of gel films formed when predried and then capillary wetted aggregates were placed in water allowed us to isolate soil gels in the unchanged form and to acquire relatively complete information on their structure.

The typical microstructure of the films isolated from soddy-podzolic soil is presented in Fig. 2. These films are analogous to the films that we isolated from the chernozem and those isolated by Grossman and Lynn from illuvial soil horizons [18]; they represent a gel reinforced by mineral particles of micron size.

In high-magnification images, it can be seen that gel films include zones of two types. In one case, particles

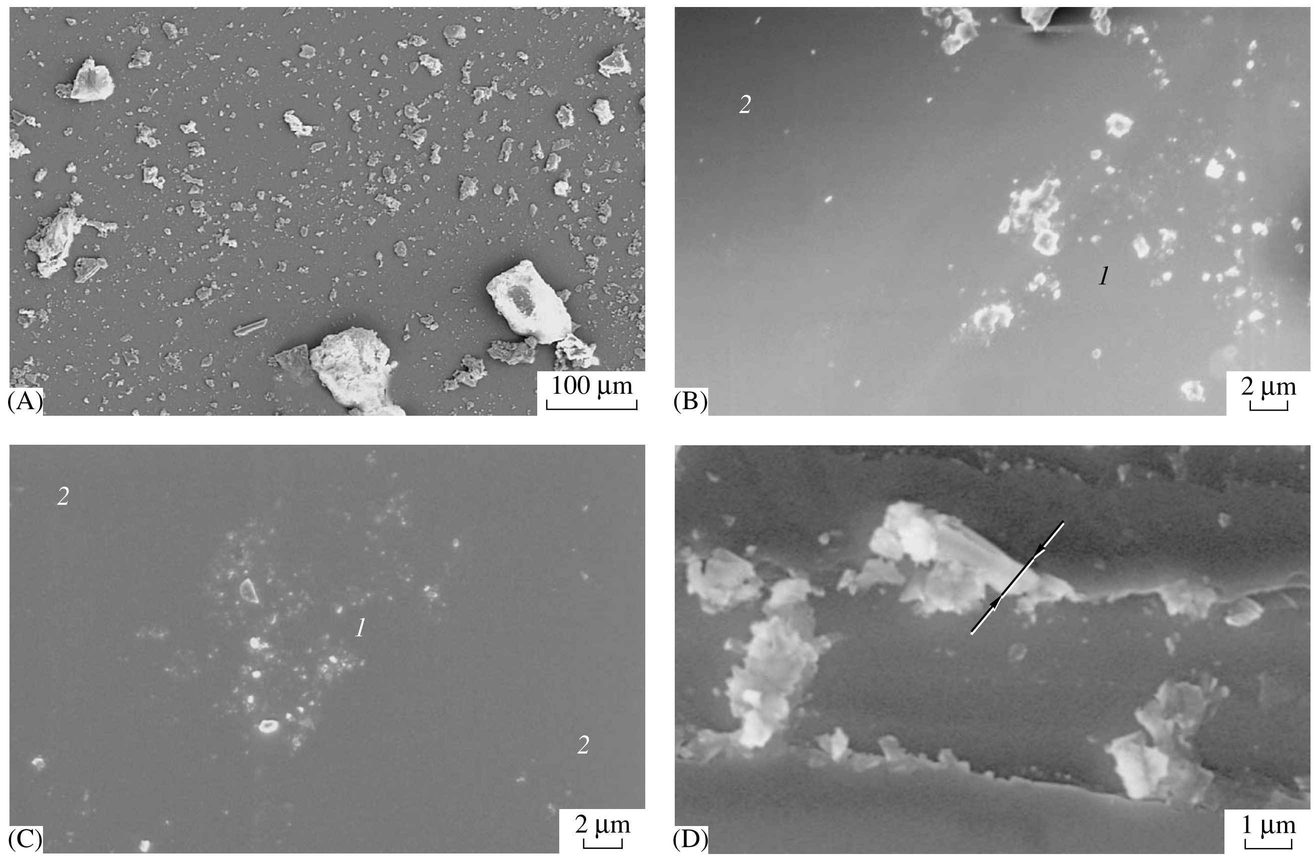

Fig. 2. Electron micrographs of films on a mica substrate isolated from the surface of soil aggregates: (A) soddy-podzolic soil, magnification ×500; (B) soddy-podzolic soil, magnification ×10000; (C) chernozem, magnification ×10000; (D) chernozem, magnification ×25000; (*1*) humus gel zones reinforced by colloidal particles; (*2*) humus gel zones free from colloidal particles.

several tens of nanometers in size are located in the close vicinity of one another or are concentrated around microparticles in the humus gel matrix (Fig. 2, *1*). These are expected results, because many authors [2, 4, 7] observed gels of colloidal particles around inorganic microparticles. In particular, when clay mineral particles in water were treated with dyes, a transparent layer with an increased concentration of dye was observed around these particles [7]. This phenomenon was explained by the presence of a gel shell formed by colloidal particles around a clay-mineral microparticle.

In the other case, humus gel films usually located between the microparticles contain almost no or significantly lower concentrations of nanoparticles (Fig. 2, *2*).

In the study of films from the chernozem, areas were found where films were broken and curved (Fig. 2, D). This allowed us to estimate their thickness at about 0.7 μm.

The analysis of microparticle surface images showed that the microparticles enter into the film; i.e., the humus gel is located on their surface, as we noted earlier [13].

CONCLUSIONS

1. The destruction of the molecular network of the reinforced humus gel occurs upon heating soils to high temperatures. Colloidal particles reinforcing the humus gel begin to move and coagulate with the formation of dense aggregates more 100 nm in size.

2. Their interaction with water results in the complex rearrangement of soil colloidal structures. The disintegration of aggregates into smaller colloidal formations occurs simultaneously with the swelling of the humus gel reinforced by colloidal particles and their aggregates.

3. The results of studying gel films indicate that the organic–mineral soil gel is heterogeneous; it includes zones of humus gel reinforced by colloidal particles and zones of humus gel almost free from the reinforcing colloidal particles. Therefore, it may be concluded that the humus gel linking the zones containing micro- and nanoparticles plays the leading role in the formation of soil gels in the humus-accumulative soil horizons.

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