
SOIL
PHYSICS

Physicochemical Principles of the Fractal Organization of Soil Colloids

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Abstract—An electron-microscopic study was conducted of gel films collected from aggregates from humus-accumulative horizons of chernozem and soddy-podzolic soils. The aggregates were dried and then capillary-wetted and immersed in water. Solutions obtained by pressing from these soils were also studied. Based on the results obtained, a hypothetical mechanism was proposed for the development of fractal organization of soil colloids, which involves the fixation of micron-size mineral particles in the humus gel and their transformation under the effect of aggressive substances with the formation of colloidal particles of reaction products diffusing in the humus gel. Humus macromolecules contain many polar groups; therefore, the colloidal particles pass some distance and are then fixed on these groups. The greater the distance from a coarse particle in the center of a cluster the smaller the number of colloidal particles capable of traversing it. Therefore, the concentration of colloidal particles decreases when going from the cluster center to its periphery according to an exponential law, which results in the development of the fractal organization in the colloidal soil component. Results of soil studies using the small-angle neutron scattering method were analyzed in terms of the hypothesis proposed.

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INTRODUCTION

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

Methods of scanning and transmission electron microscopy showed that colloidal particles in soils are fixed apart in a gel matrix formed by organic molecules, which is semitransparent for an electron beam.

The results obtained [11, 12, 15] suggest that organomineral soil gels present on the surface of soil particles binding these particles compose soil humus occurring in a gel-like state reinforced by organic and inorganic colloidal particles. In the interaction with water, the reinforced humus gel behaves as many polymers: it swells and increases in volume when absorbing water and shrinks when dried. Different impacts on the soil affect the state of the reinforced polymer humus gel, which induces changes in the soil properties.

However, these studies are complicated by problems of isolating the structures studied in undisturbed state. Experiments confirmed the existence of a reinforced humus gel in soils, but they provide no unambiguous

proof of the absence of other types of gel structures in soils [3].

An electron-microscopic study of soil solutions showed that colloidal particles are arranged in space on a substrate to form structures very similar to fractal clusters [11]. This suggested that soil colloids have a fractal structure. Nonetheless, no unambiguous conclusion on the fractal organization of soil colloids can be drawn, because similar structures could be generated during the preparation of soil samples for electron-microscopic study.

Methods should be found to directly observe the colloidal structures in soils rather than study separate fragments of colloidal formations isolated from soils subjected to external impacts. These methods include small-angle scattering of neutrons and X-rays [8].

Small-angle neutron scattering studies [13, 14] confirmed the supposition about the fractal organization of colloids in soils. However, the physicochemical mechanism of this distribution of colloidal particles in the humus gel matrix was not clear.

The aim of this work was to elucidate the mechanism of fractal organization in soil colloids.

EXPERIMENTAL

The effect of the soil type on the fractal organization of soil colloids was studied in samples of a typical chernozem (Kursk oblast), a leached chernozem (Kuban region), a brown forest soil (Popova Island, Primorskii krai), light chestnut and dark chestnut soils (Volgograd oblast), and a krasnozem (Chakva, Georgia) taken from the archive of the Department of Soil Physics and Reclamation, as well in samples of a soddy-podzolic soil from the Prioksko-Terrasnyi Biosphere Reserve, a peat soil from the Yakhroma River floodplain, and a solonetz.

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

Mandelbrot [18] showed that when predried and then capillary-wetted aggregates taken from the illuvial horizons of some soils were placed into water, a film formed on the surface of the water. We supposed that these films are formed from gel-layer fragments separated from the surface of soil particles during drying of the aggregates; hence, they should also be observed for samples taken from the humus-accumulative horizons, where gels are formed by humus molecules. Experiments performed with the aggregates taken from the humus-accumulative horizons of different soils confirmed this supposition [16].

Thus, in the electron microscopic study of gel films released when predried and then capillary wetted aggregates were placed in water, undisturbed soil gels could be isolated and relatively complete information on their structure could be acquired.

To prepare 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–three minutes, the level of water in the Petri dishes was raised, which resulted in the detachment of films from the aggregates and their rising 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.

Samples of soil solutions isolated from the soils wetted to a near field-capacity level by pressing at 10 atm were also studied. The soil solutions were left to stand for 24 h and then 1000 times diluted and applied onto a fresh mica cleavage.

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

The fractal dimensions of the objects studied and the maximum scattering intensity were determined by the small-angle neutron scattering method. For nonfractal objects, peaks corresponding to the size of the sample particles are observed on the scattering curves. The fractal objects produce a specific scattering pattern when analyzed by the small-angle neutron or X-ray

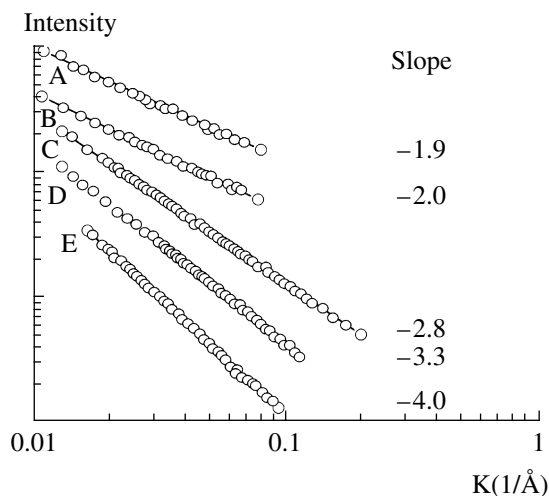


Fig. 1. Scattering data in “rock” coordinates for silicates: (A, B) weakly ramified polymer-like fractal objects; (C) ramified polymer-like objects with fractal mass; (D) loose aggregates from colloidal particles; (E) compact objects with smooth surfaces.

scattering method: a linear relationship between the scattering intensity and the applied pulse is observed in logarithmic coordinates over a relatively wide pulse range (Fig. 1) [17, 19]:

$$\log I(k) \sim -x \log k. \quad (2)$$

For mass fractals, the value of x (the “rock” parameter) coincides with the fractal dimension D ; for surface fractals, $x = 6 - D$.

Measurements were performed using a YuMO small-angle neutron spectrometer with two detectors (Dubna). A two-detector system was used (Fig. 1); therefore, the range of the scattering vector magnitude was from 0.007 to 0.6 \AA^{-1} for neutron wavelengths from 0.7 to 5 \AA and detector–sample distances of 3.60 and 12.97 m for the near and far detectors, respectively.

The test 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 thermobox maintained at 25°C.

Primary data processing was performed using SAS software [9]. The data were normalized to a vanadium reference in order to obtain absolute spectra. The fractal dimension¹ and scattered radiation intensity were recorded.

For better understanding of the advisability of the small-angle neutron scattering method, let us specify its use for soil examination. The method involves the interaction of a neutron beam with soil. Colloid-sized particles scatter neutrons at small angles. When particles interacting with radiation behave as independent radiators, i.e., are separated by a distance larger than the neu-

¹ The “rock” parameter will be hereafter called the fractal dimension for simplicity.

Table 1. Study of humus-accumulative soil horizons by the small-angle neutron scattering method

Soil	Air-dry soil		Soil paste	
	fractal dimension	scattering intensity, cm ⁻¹	fractal dimension	scattering intensity, cm ⁻¹
Soddy-podzolic soil	3.22 ± 0.03	400	2.69 ± 0.03	268
Brown forest soil	3.07 ± 0.02	590	2.64 ± 0.02	483
Leached chernozem	2.90 ± 0.02	200	2.77 ± 0.02	260
Typical chernozem	2.90 ± 0.09	322	2.65 ± 0.09	800
Dark chestnut soil	2.71 ± 0.02	707	2.40 ± 0.02	946
Light chestnut soil	2.97 ± 0.02	500	2.47 ± 0.02	500
Krasnozern	2.82 ± 0.08	1159	2.53 ± 0.02	1205

tron wavelength used, the fractal dimension of the objects is smaller than 3. When the fractal dimension exceeds 3, the colloidal particles are in contact and cannot behave as independent radiators. Hence, the method allows us to confirm or reject the assumption about a distant arrangement of particles in soils [11, 12, 15].

RESULTS AND DISCUSSION

Let us analyze the fractal characteristics observed for soils (Table 1). The value of the fractal dimension for dry soil samples is notable. For most soils, it is lower than 3. The fractal dimension of wet, freshly prepared precipitates of silver bromide and barium sulfate was determined for the control. As was expected, the fractal dimension of the contacting colloidal particles was 3.2–3.3. Consequently, colloidal particles in air-dry soils are located at a distance from one another, which can be explained only by their stabilization in the molecular humus network, because, otherwise, they would come in contact after the removal of water.

In the electron micrographs of films isolated from chernozem and soddy-podzolic soil, there are zones containing inorganic particles (Fig. 2, a–d). Two types of the clusters formed can be distinguished. In one type, the cluster has a nucleus, a micron-size inorganic particle around which colloidal particles are grouped. In the other type, the colloidal particles are grouped in a similar way, but there is no micron-size nucleus. Similar formations are observed in electron micrographs of soil solutions pressed from a chernozem, a soddy-podzolic soil, a krasnozern, and a greenhouse substrate (Fig. 3, a–d). The presence of these clusters in humus films allows reasons to be suggested for the fractal organization of soil colloids.

Let us consider the concept of fractal organization. There is no strict and complete definition of fractals to date [10]. Mandelbrot [18] defined a fractal as follows:

“A fractal is a structure composed of parts that are similar, in some degree, to the whole.” According to Lauwrier [17], a fractal is a geometrical figure in which an identical fragment repeats itself on an ever diminishing scale.

The above definitions denote a significant feature inherent to fractals and observed experimentally: a fractal is self-similar at any scale of observation.

The determination of the fractal dimension D requires that the diameter δ of the covering sets (e.g., the length of the linear standard) tends to zero. In real physical systems, this requirement cannot be met because of natural limitations. Nonetheless, fractal theory can also be applied to physical objects.

In the general case, the number of particles composing an object with fractal dimension D can be found from the following asymptotic relationship [1]:

$$N = \rho(R/R_0)^D, \quad (1)$$

where R is the radius of the object, R_0 is the radius of a particle, and ρ is the packing density of the particles.

The D value in the relationship “number of particles–radius” is called the cluster dimension. All the monomers in the cluster are similar in mass; therefore, the number of particles N is frequently interpreted as the mass and ρ as the mass density. The cluster dimension is called the mass dimension.

The above relationship is important for the analysis of physical objects, because it allows one to determine whether the object is fractal and to find its dimension. It should also be kept in mind that physical fractals have rather a statistical self-similarity, in contrast to mathematical fractals with a regular structure (such as the Kock curve or Serpinsky carpet).

It should be emphasized that a highly porous material with a random pore size distribution is not always fractal in nature. A characteristic feature of a fractal is

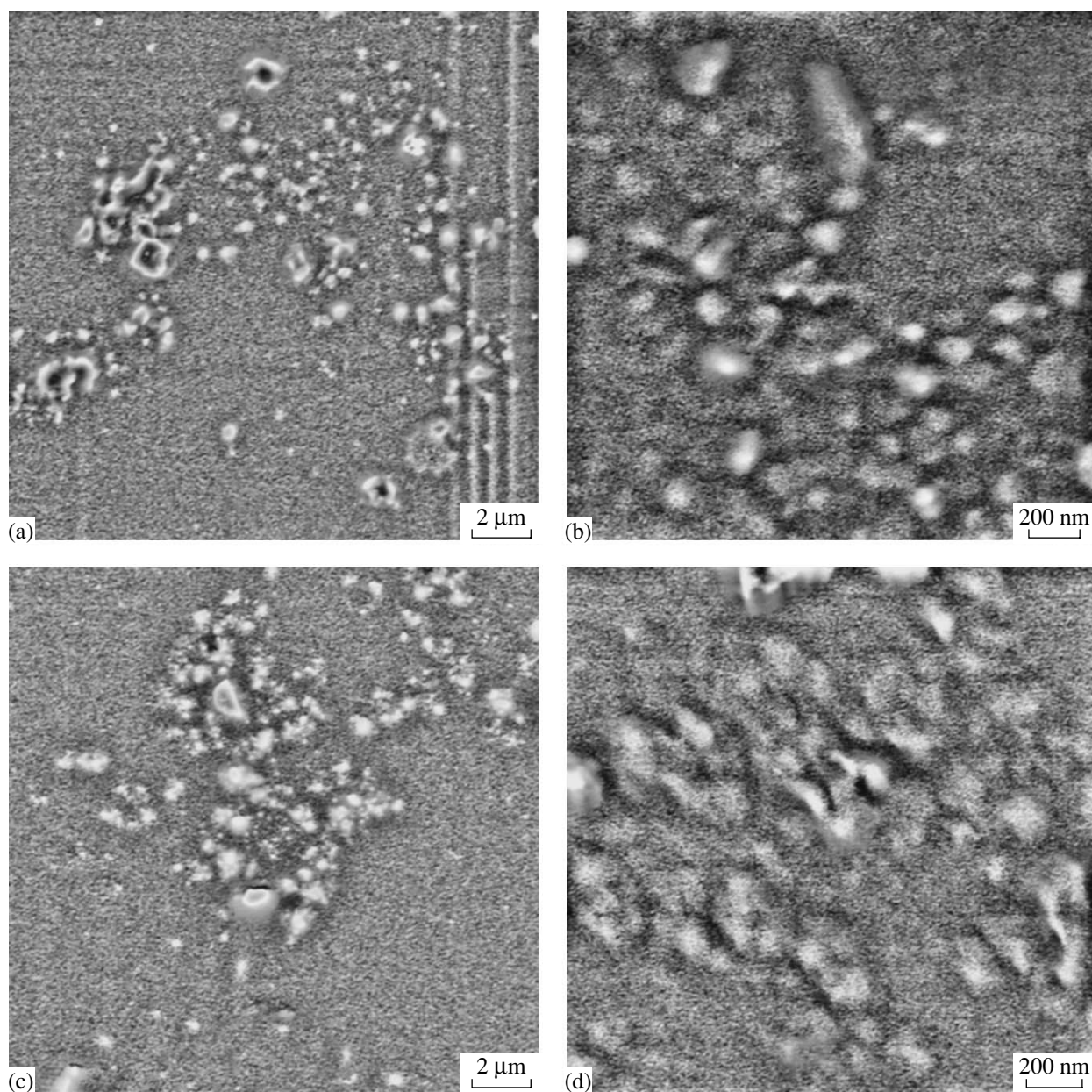


Fig. 2. Electron micrographs of films isolated from aggregates of (a, b) soddy-podzolic soil and (c, d) a chernozem on a mica support.

that its density decreases with increasing size according to a power law.

This is the principle of the method for determining the fractal dimension of objects from micrographs [22]. A cluster is selected in a micrograph; its center is found, and concentric circles with increasing radius R are drawn. The number of particles (if they are similar in size) or the area of the particles belonging to the cluster analyzed is calculated within each circle. For fractal objects, the number of these objects or their area N depends on the circle radius R according to a power law (Eq. (1)).

Some points important for understanding fractal organization should be noted. First, it is known that the surface of many minerals is covered by a gel film composed of colloidal particles resulting from mineral weathering under the effect of external factors [2, 5, 17]. In particular, when the effect of dyes on particles of clay minerals in water was studied by optical spectroscopy, a transparent layer with an increased concentration of dye was observed around the particles [17]. Second, it is known that ions, molecules, and colloidal particles can diffuse in polymer gels [3]. Third, mineral particles are fixed in the humus gel of soils [11, 12, 15].

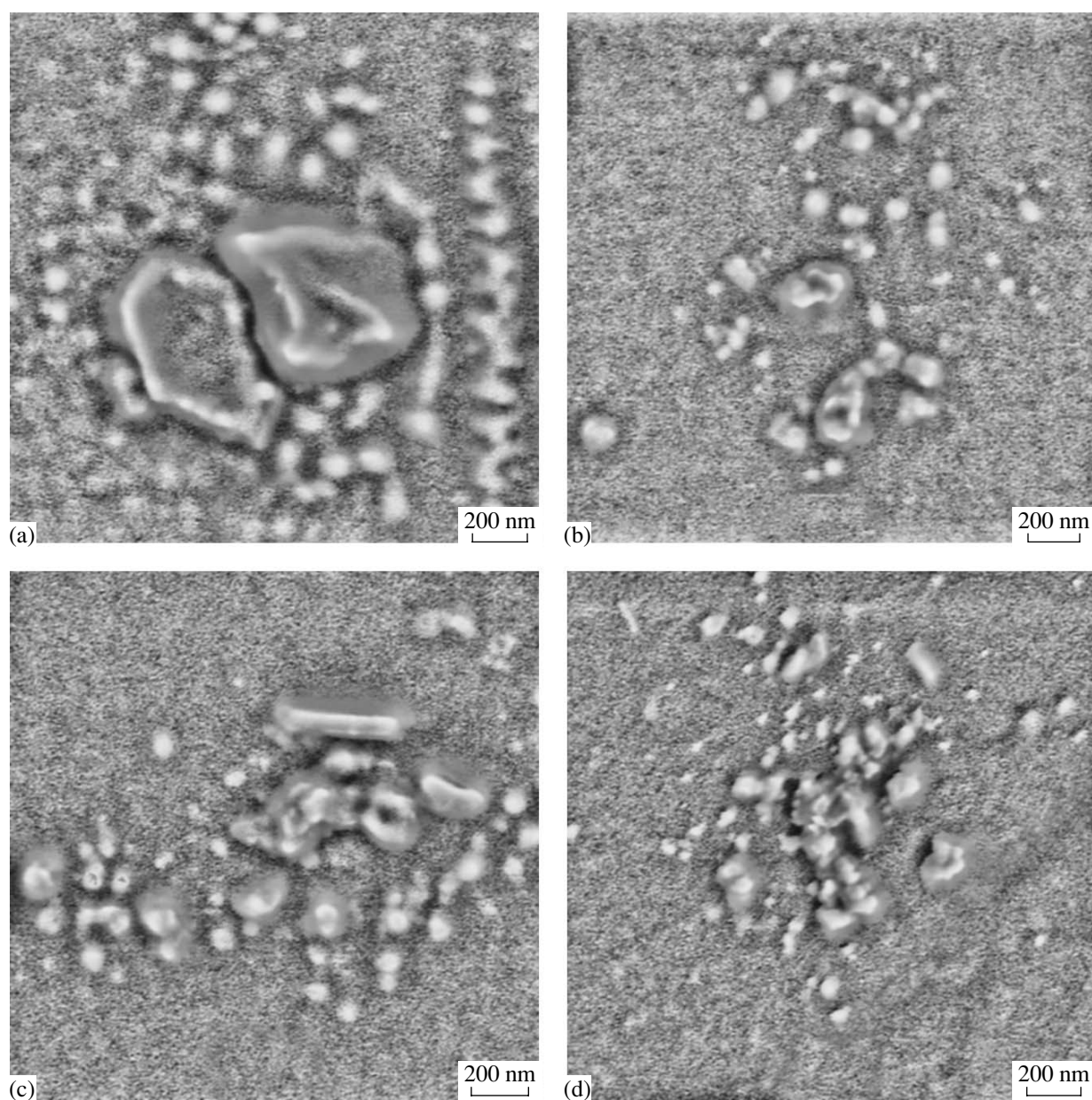


Fig. 3. Electron micrographs of soil solutions isolated by pressing from soils wetted to the field capacity on a mica support: (a) soddy-podzolic soil; (b) chernozem; (c) krasnozem; (d) greenhouse substrate.

Thus, the fractal organization in soil colloids apparently develops via the following mechanism. The micron-size particles are fixed in the humus gel. Their surface is covered by a layer of colloidal particles being the products of reactions of the transformation of minerals diffusing in the gel. The humus gel contains a large number of polar groups; therefore, particles pass some distance and are then fixed on humus macromolecules. The greater the distance from the primary particle in the center of a cluster, the smaller the number of colloidal particles capable of traversing it. As a result, the concentration of colloidal particles decreases when going from the cluster center to its periphery. Some

micron-size particles are completely decomposed, and clusters consisting of colloidal particles without micron-size nuclei are observed in electron micrographs.

The agreement between the results of electron-microscopic studies of films and soil solutions indicates that soil solutions isolated from soils by pressing contain fragments of gel structures representing the humus gel reinforced by colloidal particles. It can be suggested that soil solution also contains fragments of humus gel containing no inorganic colloidal particles, but they cannot be detected because of their small thickness and transparency for the electron beam.

Table 2. Layer study of a solonetz by the small-angle neutron scattering method

Layer, cm	Air-dry soil		Soil paste	
	fractal dimension	scattering intensity, cm ⁻¹	fractal dimension	scattering intensity, cm ⁻¹
0–3	2.9 ± 0.02	242	2.73 ± 0.02	324
3–10	2.93 ± 0.02	251	2.74 ± 0.02	500
10–20	3.02 ± 0.02	256	2.73 ± 0.02	490
20–30	3.05 ± 0.02	301	2.76 ± 0.02	564

Unfortunately, it is difficult to pass from qualitative suppositions to quantitative calculations basing on the electron micrographs. This is related to the superposition of clusters, the problems of their separation in calculations, and the transition of three-dimensional clusters into two-dimensional clusters under drying.

Let us consider the results of the soil study by small-angle neutron scattering in terms of the proposed mechanism for the formation of colloidal structures with fractal properties.

The colloidal particles diffuse in humus gel to longer distances when the humus gel contains a lower amount of functional groups and the concentration of humus-forming molecules in the gel is lower. Soddy-podzolic soils contain significantly less humus than chernozems and krasnozems. In addition, their humus is of fulvate type, i.e., it contains more functional groups than the chernozem humus. Therefore, the rate of decrease in the concentration of colloidal particles in clusters of soddy-podzolic soil should be higher than in chernozem clusters. Consequently, the fractal dimension of the colloids in the soddy-podzolic soil should be higher than that in the chernozem. When the humus content is low, the colloidal particles can come in contact under the removal of water, and this can result in the transformation of mass fractals into surface fractals. It is also notable that the humus containing many functional groups should swell more strongly in the interaction with water, and the fractal dimension of colloids in soddy-podzolic and brown forest soils and the krasnozem should decrease in the interaction with water to a greater degree than in the chernozem, as was observed in the study of soils by the small-angle neutron scattering method.

Along with the content and type of humus, the solonetzicity (exchangeable sodium content) of soils affects their fractal dimension. In this case, the swelling capacity of the humus gel should increase, which apparently results in the observed changes in the fractal dimension for the light chestnut soil.

A change in the scattering intensity characterizing the concentration of colloidal particles in an object is notable (Table 1). The scattering intensity in the interaction of soil with water decreases in soddy-podzolic and brown forest soils, remains constant in chestnut soil, and increases in the other soils. This can be explained by the fact that two processes occur during

the interaction of water with soil result in opposite changes in the fractal dimension. First, a decrease in the concentration of organic colloidal humus particles is possible when they pass into the expanded molecular state. This process apparently prevails in soddy-podzolic and brown forest soils. Second, the transformation of aggregates from colloidal particles is possible in the interaction with water due to the swelling of humus gel in the aggregate and the distancing of colloidal particles.

Interesting results were obtained for solonetz (Table 2). The elevated content of sodium ions apparently resulted in a smaller number of bonds between macromolecules forming the humus gel and, hence, in the smaller strength of the humus matrix. The increase in exchangeable sodium with depth [6] clearly affected the fractal characteristics of the soil colloids in the solonetz. In the upper 0- to 10-cm horizon, the strength of the humus matrix was still sufficient to retain colloidal particles at a distance from one another under drying. However, at a high content of exchangeable sodium, a mass fractal was transformed into a surface fractal; i.e., the number of contacts between colloidal particles increased. The scattering intensity also increased with the depth, which correlated with the increasing concentration of colloidal particles along the solonetz profile.

Our experiments on the study of peat soil suspensions by the small-angle neutron scattering method provided additional evidence for the proposed mechanism of fractal organization in soil colloids. For the original peat soil, a linear relationship between the scattering intensity and the applied pulse with a “rock” parameter of 2.83 for paste was observed in logarithmic coordinates. After the soil paste was passed through a disintegrator, the linearity disappeared; i.e., the fractal properties of colloidal components of the peat soil disappeared. This could be related to the disturbance of the distribution of the cluster-forming colloidal particles in the humus matrix.

We could not create fractal colloidal structures of calcium carbonate in agar gel by the double diffusion method [4]. Different versions of this method were used for forming samples studied by the small-angle neutron scattering method, but no linear relationship between the scattering intensity and the pulse used was observed in logarithmic coordinates. This testifies that the fractal organization of soil colloids develops

through the diffusion of colloidal particles in the humus matrix rather than through the diffusion of ions capable of forming insoluble compounds.

The results obtained contribute to the understanding of the structural organization and the development of soil colloids and, hence, to the behavior of soil.

CONCLUSIONS

(1) In soils, colloidal particles are arranged in the matrix of humus gel.

(2) The fractal properties of soil colloids result from the transformation of minerals in the humus matrix with the formation of colloidal particles and the diffusion and fixation of these particles in the matrix.

The proposed approach explains the changes in the fractal dimension of soil colloids and the scattering intensity of neutron radiation in different soils during their interaction with water.

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