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GENERAL  
BIOLOGY

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## Soil Gels and Their Research

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Received September 29, 2011

DOI: 10.1134/S0012496612030015

The colloidal component of soil is known to play the most important role in soil fertility. It provides a high water-retaining capacity of soils, accumulation of nutrients and is responsible for the existence of soil macrostructure. At present, it is assumed that soil colloids cover soil particles in the form of gels and bind them to each other and thereby ensure the existence of soil as a system with a certain set of properties [1–3].

The colloidal component of soils has long being the focus of research, which requires the separation of soil colloids from larger particles. Different methods have been used for this purpose [3–7], and the preservation of the composition of the extracted fractions was taken into account.

Due to the studies of the nanostructural organization of soil gels [8], the development of a procedure for the separation of the gels has become an urgent problem. In this case, it is necessary to preserve both the composition of the gels and their native structural organization, and the methods used for the investigation of the composition of the colloidal component of soils have appeared to be unsuitable for this reason.

At first glance, the study of the gels in the soils seems to be the most efficient way to obtain information on their nanostructural organization. However, there are a number of technical problems associated with the complexity of the topology of the soil samples that do not allow solving the problem in this manner. This applies to both probe [9] and scanning electron microscopy.

Focused-beam electron microscopes have large depth of field and allow the formation of images that are similar to the ones observed visually [10]. It is related to the fact that more distant parts of the object look darker. In soil samples, gels cover particles and repeat all the roughness of the sample. As a result, the foreground shows alteration of dark and light regions, which provide the perception of the 3D image of a part of the soil sample; usually, in such cases, the fluctua-

tion of height significantly exceeds the size of bulges of the nanostructures, which are indiscernible in this case. As a result, such studies provide a little information and provoke the search for procedures for the recovery of gels from the soils, enabling the preservation of their nanostructural organization.

Earlier, it was shown [11] that, when preliminarily dried and capillarily moistened aggregates were placed into water, a gel film appeared on its surface. These films could be easily isolated from soils and applied onto atomically smooth surfaces for the investigation of their nanostructural organization. However, it was unclear why such gel films floated up and, for this reason, their identity with the soil gels was questionable.

The aim of the present study was to reveal the nature and the reasons of separation of gel films from air-dry soil samples and their floatation to water surface.

The study was carried out using samples of zonal soils from the collection of the Department of Soil Science of Moscow State University: illuvial iron podzol, podzol, sod podzol, gray forest soils, chernozems of different types, light and dark chestnut soils, sierozem, and krasnozem soils.

When isolating the gels from the soils for microscopy studies, air-dry soil aggregates several millimeters in size were placed into Petri dishes and capillarily moistened, and then, the water level was raised. As a result, soil aggregates were isolated, and the gel films floated to water surface. Then, the gel films were placed onto atomically smooth surface of freshly split mica by creating the contact between mica surface and water surface containing the film; the sample was dried at 40°C.

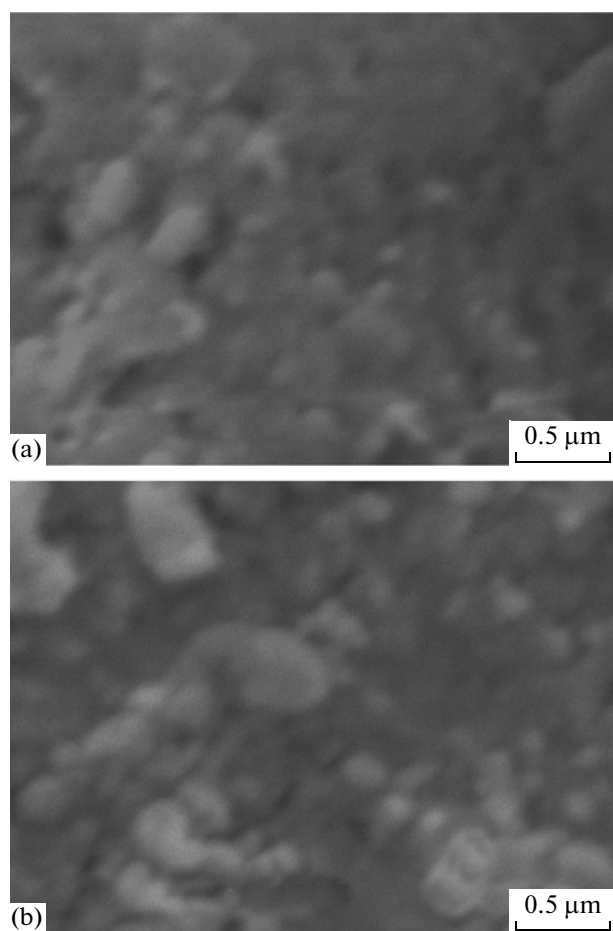
The microscopic studies were made using a JEOL 6060A scanning electron microscope (JEOL, Japan) with a tungsten cathode. Platinum was sprayed onto the samples before the study using a JFC-1600 device (JEOL, Japan).

To test the identity of the gels floating to water surface as result of soil moistening and the native soil gels, we performed a comparative electron microscopy study of the gels in soils and the gels recovered from soils. As noted above, such studies do not allow dis-

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**Fig. 1.** Electron microscopy images of (a) the soil gels in chernozem (Krasnodar krai), horizon B and (b) gels recovered from this soil.

cerning the nanostructures in gels and soil samples, but one can clearly observe the general morphology at a level of above 100 nm.

The analysis of electron microscopy images showed that in no sample studied did the morphology of the gels in soils significantly differ from the morphology of the gel films recovered from soils. As an example, Fig. 1 shows the microimages obtained for the samples from horizon B of south chernozem.

Therefore, the validity of identification of the floating gel films with the soil gels was doubtless.

To find the reason of the floatation of the gel films, we made several experiments that showed the following:

- When mechanically affected, the gel films that were isolated and floated up after the capillary moistening of the soil aggregates followed by raise of the water level behaved as solid systems.
- The protection of the external surface of the aggregates followed by their division into parts did not arrest the process of separation of the gel films.

- The gel films did not float in alcohol.
- The gel films floated in solutions of surfactants.
- When heptane was added into the system immediately after the floatation of the films to water surface, the films moved to the surface of heptane, which was on the surface of water.
- After 12–15 h of staying on water surface, the gel films swelled and were elastic when mechanically affected; i.e., they behaved as typical gel systems.
- When heptane was added into the system after the swelling of the gel films on the water surface 12–15 h after the floatation, the swelled gel films stayed on the water surface under the heptane layer.
- The gel films recovered from sod podzol soils and chernozem soils contained 94–95% of minerals, while the water concentration was nearly the same as the concentration of the organic substance.

These experiments demonstrated that water-floating gel films were separated from the surface of the soil particles that were not only in the external layer of the soil aggregates.

It could be also concluded that the observed gels were blocks of gel separated from the soil particles under the influence of water, rather than fragments of gels resulting from drying (since, in this case, they would have floated in alcohol as well). The study [12] reported cases of stability loss as a result of swelling, this effect being associated with the loss of the mechanical stability of the thin surface layer of the polymer after contact with the solvent that could cause its swelling. Obviously, the loss of the gel stability was associated with the interaction between the swelled external and non-swelled internal layers, leading to the separation of soil gel blocks.

The presented results evidence that the floatation of the separated blocks of soil gel is related to its low specific weight (as compared to heptane). The swelling of the soil gel on the water surface increases its specific weight, and it does not float in heptane any more and stays at the heptane–water interface. Comparison of the data on the concentration of humus substance, water, and minerals in the gels with their floatation due to the low specific weight allows estimating the porosity of the humus matrix in the gels of air-dry soils; this parameter appeared to be surprisingly large, namely, 97–98%

Therefore, the floatation of the gels onto the water surface is related to their low specific weight due to porosity of the humus matrix. Consequently, only those gel films separated from the soil particles whose total specific weight provides their floatation float to water surface. Hence, it cannot be assumed that the floating soil gels provide information about all soil gels.

This is confirmed by the results of the study on the concentration of heavy metals in the gel film floating to water surface and the soils themselves [13]. It has been demonstrated that the concentration of heavy metals in soils and gel films recovered from these soils are significantly different. The concentration of zinc in soils is about 40- to 400-fold higher than in gel films, while the concentrations of copper, cadmium, and lead are 10- to 150-, 50- to 1000-, and 5- to 10-fold lower, respectively. These results show that soils contain several kinds of gels. In addition to the water-floating gel films, which accumulate copper, cadmium, and, to a less degree, lead, there are other gels that are stronger bound to soils or have larger specific weights (humus matrix with a lower porosity) and accumulate zinc.

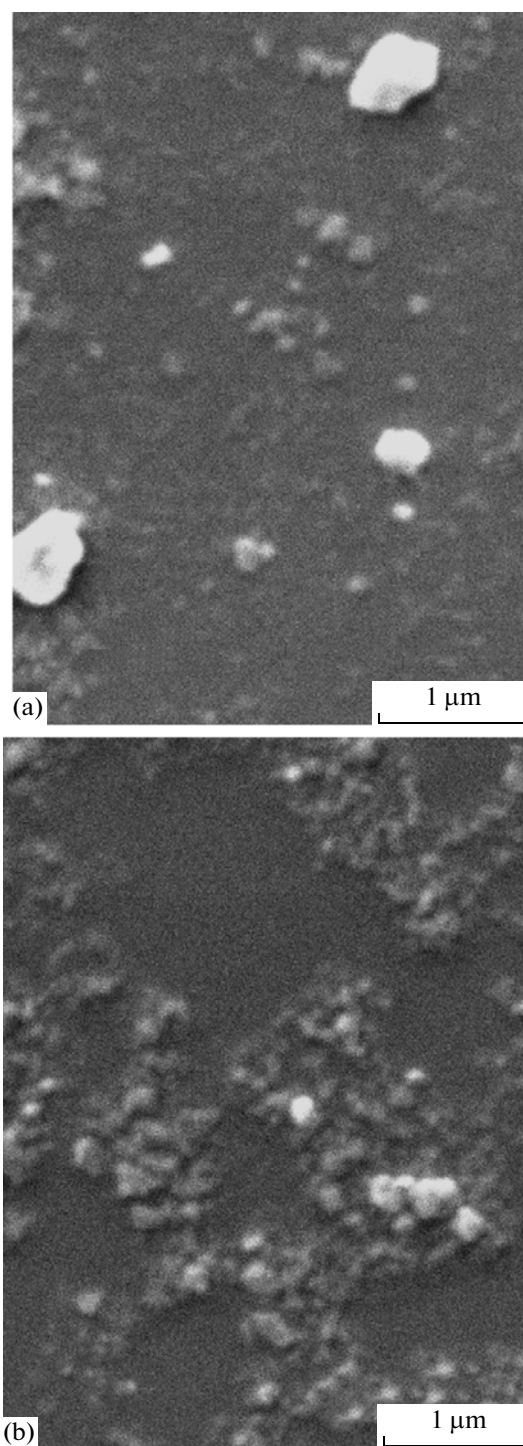
Many authors noted the existence of several kinds of colloidal structures [3, 4, 14]. Tyulin called them gels of groups 1 and 2 [3]. Some of them easily separated from soils under influence of water or weak solutions of sodium salts, the other were retained by the soils much stronger. They were recovered, and the compositions of these gels and humus in different kinds of gels were studied. Summarizing the information reported earlier, one can assume that stronger bound gels are enriched with sesquioxides, and their humus contains fewer polar groups.

To estimate whether it was correct to investigate the soil gels floating to water surface when dry soils samples are moistened as typical representatives of a certain type of soil gels, we used the method of fractional peptization proposed by A.F. Tyulin and removed the gels of group 1 from the soils by careful multiple washing of the soils from water-peptized gels. Then, the samples were dried, and the water-floating soil gels were recovered. We refer to the gels recovered from the samples of the initial soils as gels of type 1 and to the ones extracted after removal of water-peptized gels from the soil as gels of type 2.

The results of studying them indicate that the gel films of type 2 contain significantly fewer mineral particles, but the nanostructural organization is much stronger than in gels of type 1 due to the separation of a new phase. The data of electron microscopy studies of gels of type 1 and type 2 recovered from chernozem are shown in Fig. 2 as an example.

Visually observed reduction of the concentration of minerals on the surface of gels of type 2 suggests a lower porosity of their humus matrix, this assumption correlating with the increased concentration of sesquioxides in strongly bound gels [3]. The increase in the concentration of sesquioxides causes an increase in hydrophobization and compaction of humus substance [15].

Therefore, comparison of the data with the results of the investigation of the composition of soil gels [3]



**Fig. 2.** Electron microscopy images of gels of (a) type 1 and (b) type 2 recovered from the samples collected from humus-accumulating horizons of typical chernozem of Kursk oblast.

allow us to assume that the gels of type 1 are analogs of soil gels of group 1, which determine the water resistance of the soil structure and contain most nutrient elements, according to Tyulin [3]. For this reason, investigation of the structural and nanostructural organization is very important.

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