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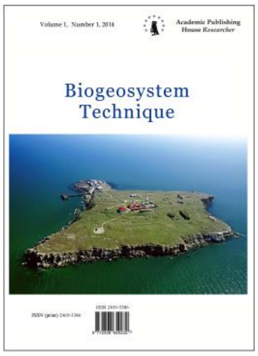

UDC 630

Aggregation of Natural Disperse Formations: Value of Organic Matter, Soluble Salts And Diatoms

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Abstract

Microaggregates in natural dispersed bodies – sustainable formations sizes less than 250 microns, in which the interparticle bonds are formed by organic matter, clay salts, diatomaceous spillways and some other substances. Organic matter in the microaggregates exist in inaccessible state in sustainable forms, and is not subjected to dehumification. But organic matter controls also the ability of soil to retain the structure in water; and the stability of the wet soil under external mechanical action. Dominant interactive forces between organic substances and the surface of mineral particles typically have sorption nature, hydrophobic interaction, ionic (or electrostatic nature) compound and van der Waals interactions. In saline soils and rocks microaggregates are presented in clay-salt formations. One of the possible types aggregate formation in saline soils may be the formation of quasicrystals. Packaging particle size and shape depend on the content of microaggregates and salts properties involved in their formation. The carbonates (calcite, dolomite) and ferruginous form clay-salt microaggregates. In many ways the formation of microaggregates in soils and other natural systems caused by bio-organic macromolecules produced by algae, particularly diatoms which uses a special strategy for connection with other particles (spines). A very promising direction is to study the formation of microaggregates under the influence of diatoms, which dominate in hydromorphic soils, moist habitats, river valleys. Numerous literature and own experimental data are discussed.

Keywords: aggregates, organic matter, saline soils, quasicrystals, carbon sequestration and water quality.

Introduction

Since the second half of the last century, the main attention of environmentalists was focused on processes related to global changes of the environment and climate in which the leading role belongs to the carbon cycle. Carbon cycle in terrestrial ecosystems is determined by the balance between carbon uptake by vegetation to create organic matter and the release of various levels of ecosystem in the process of respiration and as a result of man-made phenomena. A so-called "greenhouse effect" is the result of violation in the balance in the direction of increasing carbon dioxide in the atmosphere. The soil, disperse natural sea, river and lake sediments, also serve also serve, in turn, tanks accumulating carbon. The carbon and organic matter accumulates in soil organic matter (SOM), humus, for a long period of time, serves as a natural carbon sink. Consequently, the ratio in the soil ecosystem processes and soil organic mater dehumification influences the carbon balance in the atmosphere.

If we consider the number of citations of articles that examined the phenomenon of isolation and increasing the concentration of greenhouse gases, and especially CO2, in the atmosphere, revealed a picture of this kind of exponential growth of citations in recent years. In fact, the main work has been devoted to the emission of CO2 by different soils and ecosystems, and not so much the study of mechanisms of formation and emission of carbon dioxide (Fig. 1).

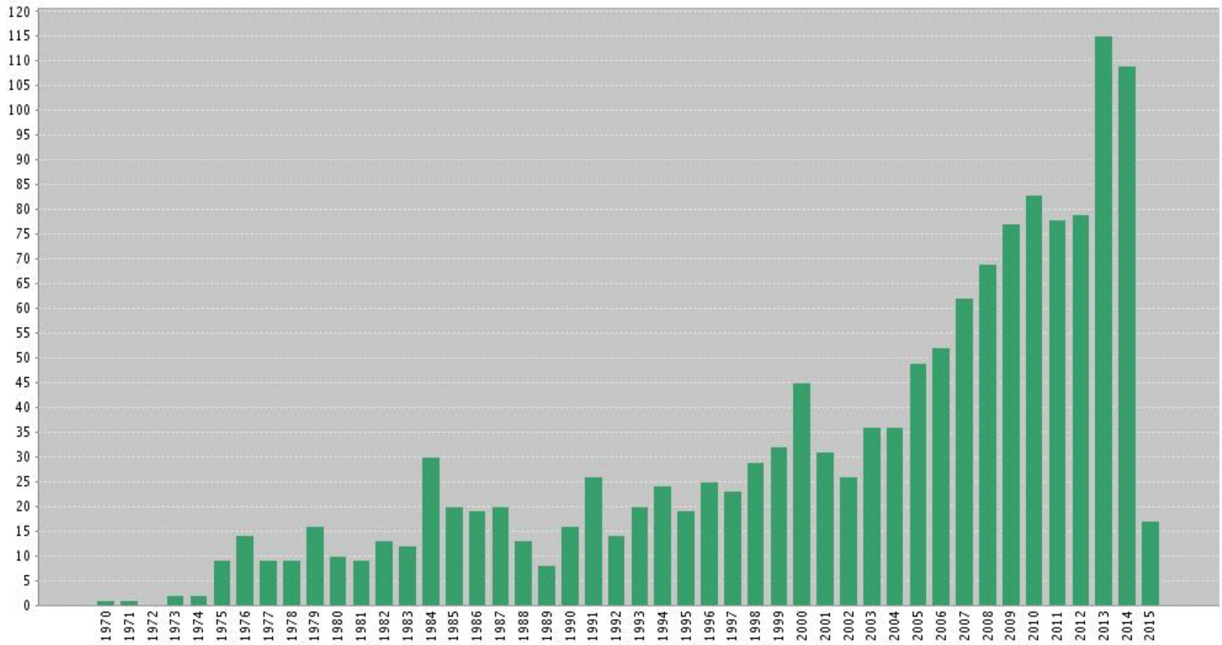

Figure 1. The number of citations of articles devoted to the study of the problem of allocation of CO_2 by soils and soil cover 1970 to 2014 (a search on Web of Science, on the «climate global change» in the titles of the articles)

This exponential growth of manuscripts on the phenomenon under consideration is certainly linked to the conservation challenges of maintaining health and prognosis. Human induced changes in the ecology of widespread among all ecosystems. They occur as a result of plowing land, accumulation of waste, industrial pollution, mining, urban expansion, etc. (Keil, Mayer, 2014; Hannah et al., 1995). Recently, most attention is paid to the processes of sustainable conservation (sequestration) of carbon in the natural disperse systems: soils, marine and river sediments, natural disperse systems, where this element becomes inaccessible for a long time and is part of the stable microaggregates.

Preservation carbon in soil aggregates. Aggregate formation in soils with soil organic matter.

However, in recent years more and more attention of researchers directed not so much on the study of soil CO2 emissions as the CO2 in soil conservation in the form of sustainable forms of soil organic matter (SOM) or soil humus. Such a stable (or inaccessible) form of SOM acquires while in a soil aggregates (soil, in natural waters, sediments and other natural dispersed bodies). The soil unit – a natural soil formation of three-dimensional., consisting of soil micro-aggregates as a result of their connection strong ties and connections of different nature. They are the main volume of the pore space of the soil that contains nutrients, water, air and soil microorganisms. Often indicate that the organic matter in the soil is resistant to degradation, particularly in aggregates (John, Yamashita, et al., 2005; Kaizer, Guggenberger, Haumaier, 2004; Kandeler, Tscherko et al., 2001; De Gryze, Jassogne et al., 2006; McCarthy, Ilavsky et al., 2008; Grosbellet, Vidal-Beaudet et al., 2011), presumably due to the particular conditions of oxidation (Chen, Wagenet, 1992; D'Acqui, Churchman et al., 1999). It is well-known over 100 years ago (Wollny, 1898, see Horn et al., 1989) that positive soil structure effects the root growth, the availability of water and air, the soil strength and as a rusult, soil fertility. Positive and negative (with soil compaction) the role of soil structure yields have repeatedly noted (Dexter, 1988; Peth, Horn et al., 2008; Piccolo, Joe, Mbagwu, 1999; Bachmann., Guggenberger et,al., 1992; Six, Elliott, Paustian, 2000). For agriculture, the soil should be not just a good structure, a structure that is long retains its stability and quality (Dexter, 1988) This author classifies the stability of the two grounds of the structure: (1) the ability of soil to retain the structure when exposed to water; and (2) the stability of the structure of the wet soil under external mechanical action (Palma, Arrigo, 1984; Perfect, Sukop , 2001; Peth, Horn et al., 2008). The first type is the stability of the structure is estimated by wet sieving; the structure stability under external stresses can be determined in compression tests and shear strength in a well-aggregated soil pore size distribution varies widely (Markgraf, Horn , Pet, 2006; Six, Elliott, Paustian, 2000; Sullivan, 1990. Large pore (> 30 microns) include cracks and extra-aggregate pores and biopores. The pore space, the size and number can influence by SOM content and its turnover. Conversely, SOM composition, agents and texture of the soil can have a significant effect on the porosity. According to limnology, geochemists, number geologists this two factors (size distribution and organic matter quality and quantity) play a role in most aggregate formation processes and the formation pore space (Keil, Mayer, 2014).

Soil structure is determined by the size, shape and arrangement of solids and voids, a continuous distribution functions, the ability to maintain and carry out solutions of organic and inorganic substances, maintain vigorous growth and development of the root system (Lal., 1991). It proposed several aggregation mechanisms. Forming unit occurs in stages with different particle dominant binding mechanism involving organic compounds, each next stage (Tisdall, Oades, 1982). Aggregate structure of the soil – the most important factor in the functioning of soil and its ability to support plants and animals, adjust the ecology of the environment, the ability of carbon sequestration and water quality). The complex aggregation dynamics – the result of the interaction of many factors, including the environment, land-use system, the plants influence and soil properties, such as the mineralogical composition, texture, the concentration of organic matter, the type of soil, microbial activity, exchangeable cations, stocks of nutrients and moisture availability (Kay, 1990; Six, Elliot, Paustian, 2000b;Pachepsky, Rawls, 2003). The microaggregates (<250 microns) are generated from organic molecules (of SOM) , connected with the clay (Cl) polyvalent cations (Ct), forming a fragment (Cl-Ct-OM), which is connected with other particles (Cl-Ct-SOM-), forming macroaggregates [(Cl-Ct-SOM) x] (Ensminger, Gieseking, 1939; Tisdall, 1996; Ellerbrock, Kersebaum,Kaiser, 2005; Golchin, Baldock, Oades,1997;Verchot, Dutaur, Shepherd, Albrecht, 2011). Macroaggregates may be formed around the particles of organic matter, forming a waterproof connection with cementing ties. In addition, the products formed by the decomposition of OM in microbial cenoses can serve structure formators. So, the decomposition of OM by microbial cenoses allocated microbial exudates that make macroaggregates more sustainable, lower C / N ratio and form microaggregates in macroaggregates. Thus, it is believed that the size analysis and aggregation density yields consistent trends in identification of SOM and other organic substance in its composition and content (Kaiser, Guggenberger, Haumaier, 2004; Knicker, 2004; Pichevin, Bertrand, Boussafir, Disnar, 2004; Six , Bossuyt, Degryze, Denef, 2004;Wagai, Mayer, 2007).

Currently several forming micro- and macroaggregates mechanisms are identified for micro-macroaggregation by natural dispersed organic substances of different nature. Dominant interactive forces between organic substances of protein origin and the surface of mineral particles typically have sorption nature, the compounds of hydrophobic interaction, ionic (or electrostatic nature) compound and van der Waals interactions (Asthagiri, Lenhoff, 1997; Baldock, Masiello , Gelinas, Hedges, 2004; Bennett, Ransom, Kastner, et al., 1999; De Cristofaro, Colombo, Gianfreda, Violante, 1999; Derenne, Largeau, 2001; Gu, Schmitt, Chen, Liang, McCarthy, 1994; Lutzow, Ko¨gel-Knabner, Ekschmitt, et al., 2006). It is generally believed that molecules of high molecular weight, with aromatic structures, often exhibit preferential adsorption from solution, and may also be 'irreversibly' adsorbed so that they can not be removed from the surface, thereby forming stable microaggregates. Microaggregates – the most resistant to various influences, well maintained by organic matter (Nguyen, Harvey, 2001; Ovesen, Nielsen, Hansen, 2011; Rabe, Verdes, Seeger, 2011; Ransom, Bennett, Baerwald, Hulbert, Burkett, 1999)

Aggregate formation in saline soils

Of course, when the microaggregate formation process is marked in saline soils and geological deposits much attention is paid to the formation of stable cutans (surface organic films or in situ modifications of the solid plasma (Glossary of Soil Science Terms, 1996)). But on the effect of the clay cutans on physical properties of soils in soil literature data are very rare, cutans considered primarily as markers of soil processes such as illuviation. The industry has long used the ability of bentonite clays in the form of cutans on the sand particles to increase plasticity of molding sands (Fredlund, Venepalli, 2002;Snyder, Pietrioms, Miro, Lugo, 1993; Spielvogel, Prietzel, Kogel-Knabner ,2006; Strong, de Wever, Merckx, Recous, 2004, et al.). Apparently, and cutans and clay-salt formation play a significant role in aggregate formation, and in the formation of the physical properties of clay saline soils.

Soil geological depressions in arid conditions is always to some extent saline (carbonates and evaporites). To carry evaporites salt solubility greater than or equal to the solubility of gypsum. Of these, readily soluble evaporites, despite the ephemeral character (in the sense of localization and mineralogical forms) have a great influence on the chemical and physical properties of soil. If the issues of formations of carbonates and evaporites are widely discussed in the literature, the question of the role of soluble salts (their interaction with clay minerals) in the processes aggregate formation still remains debatable.

Interest in saline soils is associated with long marked characteristics of their microaggregate composition, due to the presence in their structure of the original "clay" sand (aggregates of clay particles of sand dimension). According to one hypothesis, their formation is the result of coagulation of silty sediment under salinity in arid climates. However, it is still unclear what mechanisms in this process occur, what types microaggregates formations (salt units, cutans and others) are preferable. One of the possible types aggregate formation in saline soils may be the formation of quasicrystals.

By electron microscopy and energy dispersive analysis for soil landscapes mounds Baer (Astrakhan region, Russia) clay-salt formations – microaggregates, cutans, salt units and quasicrystals – were discovered in the composition of the aggregates of sandy soil landscapes fraction Baer mounds. Type of clay-salt formations (cutans and/or microaggregates) depends on the content in the silt soil of clay part (mainly smectite). Packaging particle size and shape depend on the content of microaggregates and salts properties involved in their formation. The carbonate (calcite, dolomite and ferruginous) clay-salt microaggregates were found in all the studied soils. The first quasicrystal formation were detected in soils, in the solonchaks of the Baer mounds foothills, – pentagonal NaCl crystals up to 3 mkm with clay minerals, sodium and magnesium sulfates (Shein, Kharitonova, Milanovskii et al.,. 2013). This is a relatively newly opened special (intermediate between crystalline and amorphous) type of structural state of solids (Shechtman D. et al., 1984; Abe, Yan, Pennycook, 2004;Mikhael, Schmiedeber, Rausch et al., 2010; Shainberg I., Sumner M.E., Miller W.P. et al.,1989; Shechtman, Baronnet D. et al. 1992; Bind, Steinhardt, Yao, Lu. 2009; Fischer et al., 2011 et al). In addition to "forbidden" symmetry quasicrystals have special properties, of which the main – in addition to the sharp increase in the strength of the original matrix in the implementation of quasicrystals particles – are less wettability and density. For clay saline soils also noted an increase in mechanical strength, wettability and lower density for areas (horizons) increased salinity. Earlier in soils quasicrystals were not found. Our model experiments (Shein, Kharitonova, Milanovskii et al., 2013) also showed the possibility of the formation of quasicrystals at a salt interaction with clay minerals. It is shown that the severity of the formation of clay-salt aggregates, particle packing, size, and shape depend on the content and salt properties involved in their formation, and the hydrological regime of soils, which in turn depends on the soil situation in the mesorelief and its agricultural use.

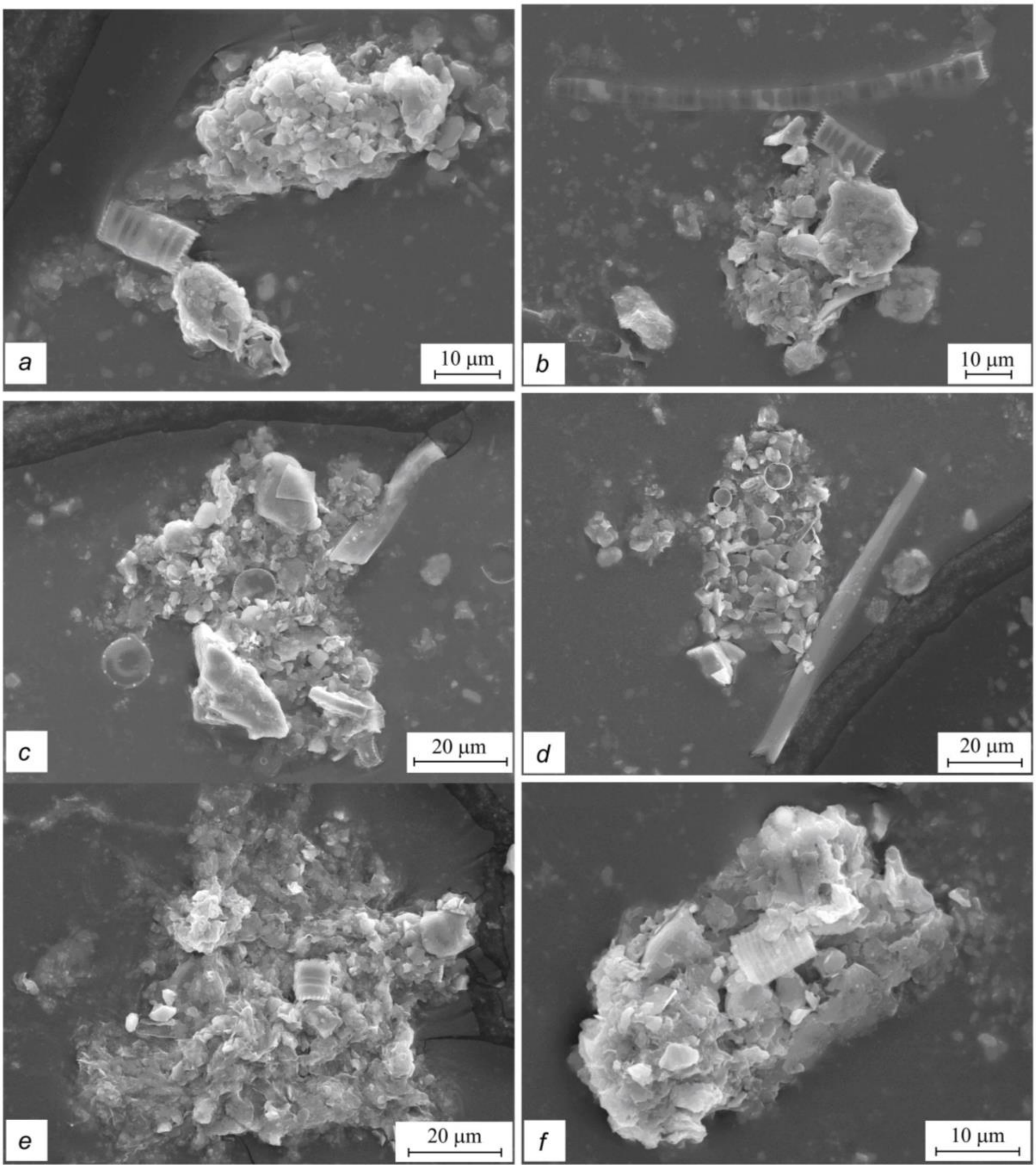

Fig. 2. The micrographs suspensions r. Amur and the surrounding lands: a, b – microaggregates from the surrounding land , c, d – aggregation of diatoms; e-h – microaggregates with diatoms.

According to our hypotheses and experimental data obtained for soil (aggregates) and the sample as a whole, apparently readily soluble salts may form both individual crystals and isolating co-crystallization with each other and clay minerals, including quasicrystals clay-salt microaggregates and cutans. Recently, a lot of work (the highest level using the latest methods of analysis of the fine structure of minerals such as EXAFS-spectroscopy) dedicated to the study of the interaction of clay minerals with salts of heavy metals, but they are discussed mainly the issues of the external inner-surface complexes with heavy metals clay matrix formations, the formation of clay-salt aggregates and microaggregates (the next step in our view after the formation of complexes) are not considered (Rimmer , Greenland, 2001; Roth, Pavan, 1991; Shechtman D. et al., 1984, et al.).

Diatoms

A natural microbiota (bacteria and diatoms) also takes active part in the formation of micro- amd macroaggregates. It is in the microaggregates the organic-products formed by microbiota interactions with clay minerals substances are concentrated (Keil, Mayer, 2014; Kaiser, Ellerbrock, Sommer, 2009). The development of the microbiota is most clearly manifested in the aquatic environment and soil humid climate.

In many ways the formation of microaggregates in soils and other natural systems caused by bio-organic macromolecules produced by algae, particularly diatoms are discussed (Bennett, Ransom, Kastner, et al., 1999; Foster, et al., 1985). Most of the diatom uses a special strategy for communication with other particles: communication manual by thorns (spines) (Kiørboe, Hansen, 1993; Round et al., 1990) and bonding allocated mucopolysaccharides (Bernhardt et al., 1989; Decho, 1990; Decho, Lopez, 1993; Kiørboe, Hansen, 1993; Kies, 1995). Whereby diatoms (live and dead cells) are a substrate for the generation units of the number and size of the aggregates in aquatic systems (Uhlmann, 2001; Zimmermann-Timm, 2002; Wörner et al., 2000; Zimmermann et al., 1996, 1998) . In the river solid aggregates the organic content is low, but it is stable and up to 65% of it falls into the estuaries and marine ecosystems (Degens, Ittekot, 1984; Ittekot, 1988; Ittekot et al., 1992). Our study of river sediment (r.Amur, Russia) showed that microaggregates of the river contain not only from land environment (it was shown by Eisma, 1993; Kies, 1995;. Zimmermann-Timm et al., 1998), but also a large amounts of microaggregates with diatoms (Fig. 2.). Diatoms own form as separate aggregation (Fig. 2c,d), and microaggregates with clay minerals and primary minerals (Fig. 2e-f). The basis of the aggregations are predominantly centric diatoms. The greatest number of cells forming microaggregates, falls on the species of the genus Stephanodiscus (Coscinodiscophyceae class, family Stephanodiscaceae) due to the presence of thorns and allocated as a result of physiological processes polysaccharide exudates. With studs they are retained on particles of clay minerals (Fig. 2e), but capable of retaining microaggregates and a larger primary particle minerals (Fig. 2f). With the participation of both this mechanisms the diatoms become centers of microaggregates formation with mineral particles and form microaggregates in size from 20 to 100 m (Fig. 2c-e). Unfortunately, the study of aggregates in the river systems has received little attention, although high concentrations of suspended organic and inorganic substances are common to most river systems (Findlay, Pace, Lints, 1991) and takes part in aggregation of disperse natural systems.

Conclusion

The goal of this study was to discuss the problems concerning the formation, stability and functioning of microaggregates in natural soils, rocks, sediments. This issue is very complex and multi-faceted: in different natural formations aggregation may be due to the forces and substances of different nature and composition, such as the mineralogical composition, texture, the concentration of organic matter, the type of soil, microbial activity, exchangeable cations, stocks of nutrients and water availability. The microaggregates (<250 microns) are generated from organic molecules, connected with the clay, polyvalent cations, forming a fragment, which is connected with other particles and fragments, forming macroaggregates. Macroaggregates may be organized around the particles of organic matter, forming a waterproof connection with cementing ties. Clay-salt formations – microaggregates, cutans, salt units and quasicrystals – are discovered in the composition of the aggregates of sandy soil landscapes in arid zone of Russia. Type of clay-salt formations (cutans and/or microaggregates) depends on the content in the silt soil of clay part (mainly smectite). A very promising direction is to study the formation of microaggregates under the influence of diatoms, which dominate in hydromorphic soils, moist habitats, river valleys.

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