Dependence of aggregates water stability from the contents of hydrophilic and hydrophobic components in the organic matter of chernozems

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Abstract

Soil humus substances are considered as a multicomponent system of amphiphilic (exhibiting both hydrophilic and hydrophobic properties) substances. Hydrophilic components of humus substances ensure the eluvial and eluvial—illuvial differentiation of the soil profile; hydrophobic components are responsible for the accumulative type of humus profile and the water stability of soil aggregates. Possible mechanisms for the formation of hydrophobic-hydrophilic properties of humus substances and its role in stable aggregates formation are discussed. The suitability of mathematical equations has been considered for the description of the decomposition dynamics of the soil aggregates in time, the selection of the best model, and the statistical analysis of the parameters of the corresponding models. The quantitative analysis of the interrelations between the parameters characterizing the water stability and the characteristics of the soil organic matter has revealed a unimodal relationship between the parameter responsible for the water stability of the aggregates and the content of the hydrophobic and hydrophilic components for the studied typical chenozem (Voronic Chernozems Pachic, WRB, 2006 or Haplic Chernozems, FAO, 1988) (Orenburg oblast). The optimal relation between hydrophobic and hydrophilic components for high aggregates water stability of typucal chernozem is about 60% of hydrophilic and 40% of hydrophobic components in the composition of soil organic matter.

Article Info

Introduction

The results of studies of performed up to now allow humus substances to be considered as a multicomponent system. The strategy of studying such objects involves simplification by the partition of components and their separate study. This approach implies the examination of the initial multicomponent system as a mixture of some discrete states, the number of which is determined and limited by the available experimental data. The crucial problem is the choice of the discriminative criterion. Since the middle of the last century, the separation of humus substances has been based on their solubility in acids and alkalis. Although this property is never realized in natural conditions, the solubility index is accepted in soil science as a genetic characteristic of humus and soils in the whole. In spite of the wide use of the acid-alkali separation of humus substances into components, this characteristic cannot reveal the formation mechanisms of the soil humus profile and explain the reasons behind differences among the humus components in soils of different genesis.

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The uncertain, conditional, and limited character of data on humus composition is more and more often noted in the course of their interpretation (Shein and Karpachevskii, 2007; Milanovskiy, 2009). Although the participation of humus substances in soil structurization is logically evident, the physicochemical nature of this process is far from clear. Analysis of an additional property of humus substances, which qualitatively differs in composition and genesis from the characteristic used and is somehow manifested in natural conditions, is apparently necessary. The capacity of humus substances to enter into hydrophobic interactions can serve as a more natural property of humus substances and criterion for their fractionation. The presence of humus components differing in capacity for hydrophobic interactions is confirmed by the results of salting out (Shein and Karpachevskii, 2007; Milanovskiy, 2009) and the fractionation of humus substances by hydrophobic interaction chromatography (HIC) (Milanovskiy, 2009). Really, the majority, if not the totality, of soil-forming processes proceed with the participation of water. The nature of interaction between a substance and water depends on the hydrophilic or hydrophobic properties of the former. All organic substances that are sources of humus substances (through humification or other processes) are of biological origin. Most biological macromolecules are amphiphilic compounds; i.e., they are capable of exhibiting both hydrophilic and hydrophobic properties (Shein and Karpachevskii, 2007; Milanovskiy, 2009). Their amphiphility is explained by the presence of both hydrophilic (polar) groups and hydrophobic (nonpolar) zones in their structure. The ratio between the hydrophilic and hydrophobic fragments in a molecule determines its solubility, spatial organization, and diversity of functional properties. Apparently, the more pronounced the hydrophilic properties of humus substances, the more mobile these substances in the soil profile and the more active they are as agents of acid hydrolysis of minerals. Hydrophobic humus substances, on the contrary, are immobilized on the site of their formation and are responsible for the accumulative characteristics of the profile. This circumstance apparently determines the significance and role of amphiphility in the formation of the humus soil profile. Apparently, amphiphility largely determines differences in the elemental composition and physicochemical properties of humus acid preparations from soils of different genesis.

 Mineral soil components are hydrophilic; therefore, organic matter is responsible for the formation of more hydrophobic surfaces in the soil. The degree of surface hydrophobicity of organo-mineral particles determines their capacity for interacting due to hydrophobic binding and formation of water-stable aggregates or their susceptibility to peptization due to the formation of hydrogen bonds. We suppose that hydrophobic humus substances determine the formation of structural bonds and are responsible for the formation and stability (water resistance) of soil structure. The formation of aggregates due to the hydrophobic interaction between elementary soil particles covered by humus substances is related to the formation of the energetically more favorable surface of the aggregates formed (in an aqueous environment). Strong interactions among water molecules are disturbed during the "dissolution" of the substance in water. In the case of ionogenic (hydrophilic) compounds, these disturbances are balanced by the replacement of the water-water interaction by the ion-water interaction. The dissolution of nonpolar (hydrophobic) substances does not involve such a balancing, and no dissolution of substances in water takes place. The association of hydrophobic particles upon the least disturbance of interaction between water molecules is energetically more profitable in this case (Milanovskiy, 2009). On the whole, hydrophobic binding can be determined as an interaction between particles that is stronger than their interaction with water and which cannot be due to covalent or hydrogen bonds, electrostatic attraction, or charge transfer. On this basis, the degree of hydrophobicity of humus substances will determine the water stability of soil structure and probably its general resistance to external impacts. The confirmation of this statement was the first task of this work. Finally, the explanation of reasons and conditions for the formation of humus substances with different amphiphilic properties is of great importance. To find the reasons and explain the mechanisms of the interrelation between the soil mineral particles and soil organic matter with the use of mathematical models was the fourth task of this work.

Thus, the aim of this work was the theoretical and experimental substantiation of the analysis of functional role of amphiphilic properties of humus substances (manifested in both hydrophobic and hydrophilic interactions) during the soil-forming processes.

The objectives of the work were to reveal the interrelation between the amphilitic properties of humus substances and (1) investigation of water stability of aggregated of typical chernozem in different kinds of use (agricultural, natural steppe, forest), (2) determination of the hydrophilic and hydrophobic components contents in different kinds of chernozem , and (3) determination the relationship between water aggregate stability and contents of hydrophilic and hydrophobic components in soil organic matter.

Material and Methods

The physical properties of chernozems were studied in the forest_steppe region of the zone of leached and ordinary chernozems in Aksakovo raion of Orenburg oblast. For comparison, an ordinary chernozem was taken from plots under a plowland (in black fallow at the moment of the study), a dead_cover forest, and herbaceous plants (meadow) located 35 m from each other (at 53°3′50.6′′ N, 053°43′50.6′′ E). The objects and their properties were described in more detail previously (Shein et al., 2007). The aggregates 3-5 mm were used to investigate the water stability he analysis of the amount of degraded aggregates in water during the time by the modified Andrianov method.

Exponential equations such as $y = n1(1 – \exp(– n2t))$ (where y is the total amount of aggregates degraded by the moment t) are best suitable for describing the degradation of aggregates under the effect of water (in the analysis of the amount of degraded aggregates in time in water by the modified Andrianov method (Pachepsky, 1992; Shein et al., 2007, 2009). Figure 1 demonstrates the experimental plots of the process of aggregate destruction in time and exponential equation which was used to describe this process.
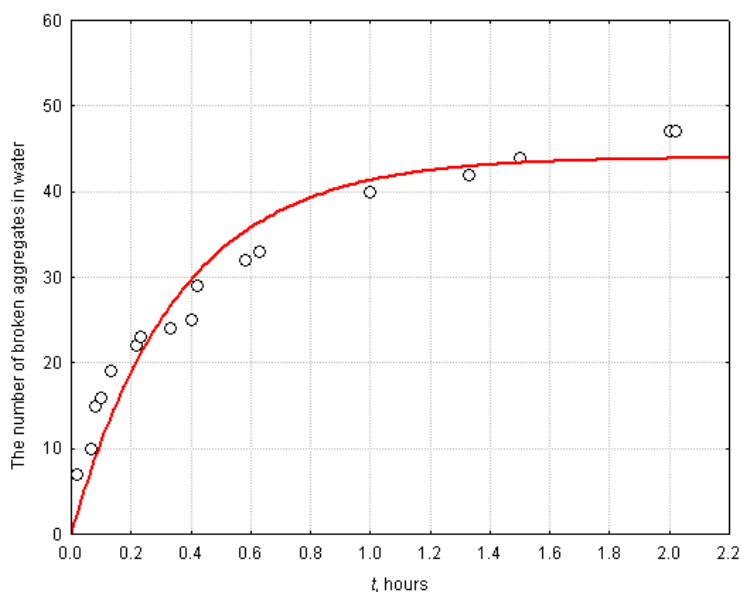

Figure 1. Total amount of degraded aggregates (y) as a function of time (t) for the 3 to 5_mm aggregates of an ordinary chernozem under forest. The approximation equation $y = (44.0153)(1 – \exp(–(2.80306)t))$, $R = 0.969$, and $F = 0.61248$ at a significance level of <0.01.

Method of hydrophobic fractioning was used to separate hydrophobic and hydrophilic components of SOM. SOM was isolated from mineral soil horizons by the solution $0.1M\ Na_4P_2O_7 + 0.1N\ NaOH$ solution at the soil : solution ratio 1:10. The extract of humus substances was purified from mineral impurities by centrifugation (8000 rpm; 15 min) and filtration through a 0.45-µm membrane filter. Hydrophobic interaction chromatography was operated on Octyl_Sepharose CL-4b (Pharmacia). SOM preparations dissolved (5 mg/ml) in 0.05 M TRI-HCl buffer with pH 8.0 and humus substances directly extracted from soils were fractioned. The sample volume was 0.5 ml; the rate of filtration was 1 ml/min; eluate was monitored at 280 nm; a 1 x 10 cm column was used. The gradient elution was supplemented with the elution of the last fraction with a 0.1 N NaOH + 5 mM EDTA solution. The first two fractions (fractions 1 and 2) eluted from the column in the presence of ammonium sulfate had predominantly hydrophilic properties (we shall name them hydrophilic fractions), and the following fractions (fractions 3, 4, 5 and 6) were hydrophobic.

Results and Discussion

The obtained approximation parameters can be qualitatively and quantitatively interpreted. In the example with the approximation of the water stability of the aggregates, the numerical values of the parameters $n1$ and $n2$ for a specific object were also obtained. The parameter $n1$ reflects the total amount of degraded aggregates for the time tending to infinity. For example, the analysis of 50 aggregates by the Andrianov method gave the dynamics of the aggregate degradation, i.e., the total amount of degraded aggregates as a function of time. Then, the approximation with the equation $y = n1(1 – \exp(–n2t))$ determined $n1 = 45$,

which signified that 45 aggregates in our set were water unstable and 5 aggregates were stable in the infinitely long experiment. Thus, (50 – $n1$) is the indicator of the water stability for a set of 50 aggregates. The parameter $n2$ is the rate of degradation. For example, the same 50 aggregates could degrade within 10 min or within 10 h. Obviously, the larger $n2$, the more rapidly the aggregates decompose. Thus, $n2$ reflects the degradation rate of the aggregates. From the values given in Fig. 2, it can be seen that $n1 = 44$ and $n2 = 2.8$. These values indicate that 6 aggregates were long_term stable and the degradation rate was also relatively high. Thus, the object can be characterized and different objects can be compared in this way.

This is the qualitative analysis of the approximation parameters. The quantitative analysis is also possible, in which the characteristics of the analyzed objects can be statistically compared on the basis of the obtained approximation parameters for different objects at the use of the same equation for the description of the experimental data. Obviously, it is necessary to first analyze whether the approximation parameters themselves are reliable, which is automatically done in almost all statistical software packages.

Given the approximation parameters and their statistics (in particular, the average standard errors Sb), the studied objects can be use in soil properties assessment.

The presented example with chernozems aggregates destruction shows that the use of the approximation parameters of the soil characteristics allows one to perform an additional analysis of the studied phenomena, to statistically assess the effect of any factor, and to advance supplementary hypotheses for the occurring processes (Pachepsky, 1992).

Given the quantitative parameters of a soil characteristic, its relationship with conventional properties can be found. For example, one can attempt to reveal and analyze the relationships of the parameters of the water stability ($n1$ and $n2$) of the aggregates with such conventional properties as the contents of the organic substances and the hydrophobic and hydrophilic components in the soil organic matter, which are probably responsible for the formation of water_stable bonds. Given 30 to 60 data for the parameters $n1$, and $n2$, as well as data on the content of he hydrophobic–hydrophilic fractions. Note that the hydrophobic–hydrophilic fractions are usually combined into the group of (fractions 1–3 in hydrophobic chromatography) and hydrophobic fractions (fractions 4 and 5) (Milanovskiy, 2009).

Thus, the relationship between the content of the hydrophilic components and the parameter reflecting the instability of the aggregates in water ($n1$) is nonlinear with a maximum at the specific content of the hydrophilic components (Figure 2).
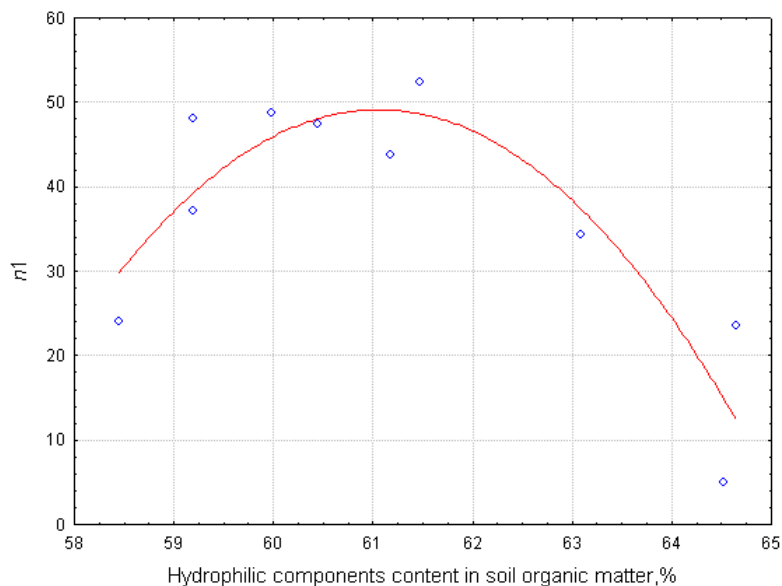

Figure 3. Parameter $n1$ reflecting the water stability of the aggregates as a function of the content of hydrophilic components in the soil organic matter for the aggregates of an ordinary chernozem.

An analogous relationship is also typical for the content of the hydrophobic components of the soil organic matter. This implies that the soil organic matter of the chernozems forms water_stable aggregates at specific proportions of the hydrophilic and hydrophobic components, which determines the specific formation mechanism of the water stable bonds.

Conclusion

(1) The quantitative estimation of the soil characteristics and distributions, their comparative analysis, and their use in physically based forecasting simulation models require the mathematical description of the soil characteristics (the dependences of the property on the affecting factor) and the property distributions (the size distribution of the particles: the grainsize, micro_, and macroaggregate compositions, etc.).

The assessment and comparative analysis are based on the approximation parameters of the specific data using the selected mathematical model, which can be statistically described and compared. (2) The exponential equations $y = n1(1 - \exp(-n2t))$ (where y is the total amount of aggregates degraded by the moment t) are best suitable for describing the degradation of the aggregates under the effect of water (in the analysis of the amount of degraded aggregates in time by the Andrianov method).

(3) The quantitative analysis of the relationships of the parameters characterizing the wedging resistance of the aggregates as a function of the water content and the aggregate degradation in still water (the water stability) with the conventional soil properties and the characteristics of the soil organic matter showed that an optimal dependence (with one maximum) of the parameter responsible for the water stability of the aggregates with the contents of the hydrophobic and hydrophilic components exists for the studied typical chernozem (Orenburg oblast).

Achknowledgement

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