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SOIL CHEMISTRY

Water Stability and Labile Humic Substances of Typical Chernozems under Different Land Uses

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Abstract—The water stability of typical chernozems was studied, as well as the content and composition of the labile humic substances (LHSs) in the structural units of perennial experiment treatments: C_{org} was 4.68% on an unmown steppe (fallow), 3.55% under continuous winter wheat without fertilizers, and 2.92 and 2.78% in two treatments of permanent black fallow. It was shown that the water stability of the chernozem's structure depended on the land use; it deteriorated in the following series: fallow > winter wheat > permanent fallow. No clear relationship was found between the content of C_{org} in the aggregates obtained by dry sieving and the size of these aggregates. At the same time, the content of C_{org} in the water-stable aggregates was shown to increase with their size. A positive correlation between the size of the water-stable aggregates and their content of LHSs was found for the unmown steppe and continuous winter wheat treatments.

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INTRODUCTION

Chernozems form the main pool of arable soils in Russia. The rational use of their fertility and the reduction of the carbon dioxide emission during the intensification of agricultural production are trends of priority in the sustenance of the agroecological safety of the country.

Degradation of arable chernozems is largely related to the loss of organic matter and the deterioration of the soil structure. The latter process is accelerated when natural chernozems are involved in agriculture and is usually accompanied by a decrease in the content of organic matter. At the same time, the mechanisms of the anthropogenic degradation of chernozems remain open to question.

One of the methods for revealing the relationships of the content and composition of the organic matter with the degree of aggregation of the soil material includes the comparison of the soil aggregate parameters under different land-use systems.

When the content of fallows and row crops in the rotation and the frequency of mechanical tillage increase, i.e., when the anthropogenic load on the arable soils increases, the content of agronomically valuable water-stable aggregates decreases and the relative content of particles and microaggregates <0.25 mm increases [15, 21, 22].

According to the conceptual model of the aggregate hierarchy [14, 16–18], the original mineral elementary soil particles (ESPs) are bound to the organic matter of bacterial or fungal origin and to plant residues, which results in the formation of microaggregates. The latter, in turn, interact to form macroaggregates. The binding agents are soil adhesives: mainly polysaccharides of plant and microbial origin, plant roots, and fungal hyphae.

The development of the conceptual model of the aggregate hierarchy revealed some relationships between the soil structure and the organic matter's quality and content [22]:

—The degradation of soil proceeds gradually: macroaggregates are decomposed to microaggregates, which in turn are decomposed to ESPs, and the entire process can be considered as an increase in the dispersing energy applied to the soil [17].

—The content of organic carbon in the aggregates increases with the increasing of their size (class): macroaggregates contain microaggregates plus binding organic matter [14].

—Larger amounts of recently formed labile organic matter are in macroaggregates compared to microaggregates [14, 16, 18].

The general regularities revealed previously for chernozem structural units largely agree with the conceptual model of the aggregate hierarchy. A general tendency toward an increase in the content of organic carbon in the agronomically valuable water-stable chernozem aggregates with the increasing their size was revealed [12].

However, the conceptual model of the soil aggregate hierarchy is not universally valid. For soils with a predominance of 2 : 1 clay minerals, the above-mentioned tendencies were confirmed. However, no significant differences in the content of organic carbon in the aggregates of different sizes were found for the soils containing similar amounts of 2 : 1 and 1 : 1 minerals.

Table 1. Structural composition of a typical chernozem under different land-use systems (%)

Experimental treatment	Air-dry aggregate size, mm					
	>5	5–3	3–1	1–0.5	0.5–0.25	<0.25
Fallow	17	21	39	5	7	11
Permanent fallow since 1947	26	12	36	7	10	8
Winter wheat	26	12	27	9	13	12
Permanent fallow since 1964	42	11	25	8	9	5

The increase in the anthropogenic load on the soil increases the content of organic carbon in all the size classes of aggregates and microaggregates in all soils regardless of their mineralogy [21, 22].

According to the current concepts based on the study of soil organic matter by physical methods, the readily decomposable organic matter plays an essential role in the formation and transformation of aggregates [13, 16, 20, 22].

The content of relatively young humic substances in chernozems can be assessed by determining the content of labile (according to Tyurin, mobile) humic substances extractable by 0.1 M NaOH from undecalcified soil [9, 11]. The undoubted advantages of this method are its relative simplicity and good reproducibility [6].

However, along with recently formed humic substances, those formed during the destruction of stable humus acids can also get into the labile fraction [4, 5, 11]. This fact significantly complicates the interpretation of the results and imposes some restrictions on the use of the method for assessing the role of LHSs in the formation of the soil structure.

The aim of this work was to assess the changes in the water-stable structure of a typical chernozem under different land-use systems and to study the role of the LHSs extractable by 0.1 M NaOH from undecalcified soil in the formation of the water-stable chernozem structure.

OBJECTS AND METHODS OF STUDY

Changes in the humus and structural statuses of chernozems occur with the increasing intensity of the anthropogenic impact on the soils. Therefore, experimental treatments with strongly different land-use systems were selected for studying.

Samples were taken from the upper (0- to 25-cm) horizons of typical chernozems under conditions of long-term ecological experiments in the Central Chernozemic State Biosphere Reserve (CCSBR) and the Petrinskii experimental station (PES) of the Dokuchaev Institute of Soil Science (Kursk oblast). The following experimental treatments were used:

—permanent fallow since 1947 (CCSBR);

—fallow, unmown steppe (CCSBR);

—permanent fallow since 1964 (PES);

—continuous winter wheat since 1964 (PES).

In each treatment, 4 undisturbed soil monoliths ($25 \times 25 \times 25$ cm in size) were sampled. Air-dry structural units were selected from the undisturbed samples by the Savvinov procedure; then, water-stable aggregates were selected from aggregates 3–1 mm in size using the Savvinov procedure modified by Khan [10, 12].

The LHSs were extracted with a 0.1 M NaOH solution from the soil samples and aggregates without decalcification using the Tyurin method [11] modified by Kogut and Bulkina [6].

The content of organic carbon in the selected soil samples, aggregates, structural units <0.25 mm, and extracts was determined by wet digestion with dichromate and spectrophotometric detection (microversion of the Tyurin method) [2].

The results of the studies were processed using mathematical statistics methods [1].

RESULTS AND DISCUSSION

The sieve analysis of the dry soil samples (Table 1) showed that the content of aggregates 3–1 mm in size was maximum in most cases. An exception was provided by the permanent fallow since 1964, for which the maximum content of structural units >5 mm was observed. The minimum content of particles <0.25 mm was noted in three out of four treatments.

It was found that the content of aggregates 5–3 and 3–1 mm in size in the soils under plants (the fallow and continuous winter wheat) was higher than that in the soils of the permanent fallows. It was also noted that a reliable decrease ($P = 0.95$) in the content of particles <0.25 mm was observed in the typical chernozem under permanent fallow compared to the fallow and continuous winter wheat. No significant differences in the aggregates of the other sizes were found between the chernozems under the different land-use systems.

In the aggregates separated by dry sieving, the content of organic carbon in the structural units was determined. Along with the revelation of the relationships between the aggregate size and the content of carbon,

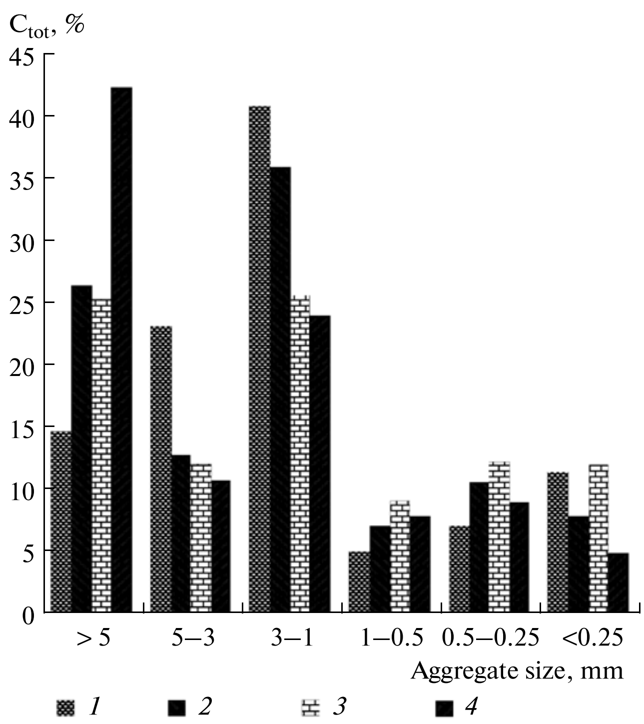
Table 2. Organic carbon (% of the fraction weight) in the structural units of a typical chernozem under different land-use systems

Experimental treatment	Air-dry aggregate size, mm					
	>5	5–3	3–1	1–0.5	0.5–0.25	<0.25
Fallow	4.00	4.97	4.75	4.72	4.76	4.84
Permanent fallow since 1947	2.97	3.00	2.94	2.84	3.04	2.73
Winter wheat	3.63	3.61	3.48	3.59	3.54	3.56
Permanent fallow since 1964	2.86	2.81	2.87	2.77	2.76	2.58

the procedure was used for determining the contribution of organic matter from the different structural units to the total organic matter in the top chernozem layer under different land-use systems (Table 2).

The content of C_{org} in all the structural units regularly decreased in the following series: fallow > continuous winter wheat > permanent fallows; i.e., it decreased in parallel with the content of the total C_{org}, which was 4.7, 3.6, and 2.9 and 2.8%, respectively.

The maximum content of organic carbon was found in the fallow aggregates 5–3 mm in size. The minimum content of organic carbon was observed in the particles <0.25 mm of the permanent fallow since 1964.



Contribution of the organic carbon from the size fractions of typical chernozems under different land-use systems separated after dry sieving to the total organic carbon of the soil. Experimental treatments: (*1*) fallow; (*2*) permanent fallow since 1947; (*3*) continuous winter wheat; (*4*) permanent fallow since 1964.

The statistical analysis of the data showed (P = 0.95) that almost no reliable differences in the content of organic carbon between the macroaggregates and the nonaggregated material (fraction <0.25 mm) were observed for all the treatments with grown plants (the fallow and continuous wheat).

However, in the treatments with permanent fallow, the content of organic carbon in the fraction <0.25 mm was reliably lower ($P = 0.95$) than that in the chernozem macroaggregates. This could be related to the absence of plant residues (which cause an error in the determination of C_{org}) in this fraction from the permanent fallow.

It is known that plant residues should be removed during the preparation of a soil sample for the analysis of the C_{org}. Our observations showed that, when the size of the structural units became smaller, the removal of the plant residues became more difficult and even impossible for the particles <0.25 mm. Hence, the error of the organic carbon determination in air-dry structural units increased with the decreasing of their size; therefore, the relationship between the size of these structural units and their content of C_{org} became more difficult to reveal.

Thus, for all the considered chernozems under the different land-use conditions, no clear relationship was found between the size of the air-dry aggregates and their content of organic carbon. Other authors also noted the absence of a correlation between these parameters [7, 8, 10, 12]. However, a reliably lower content of C_{org} in the particles <0.25 mm compared to the larger structural units was shown in the experimental treatments of permanent fallow.

On the basis of the structural analysis data and the contents of organic carbon in the structural units of different sizes, the contribution of each class of these units to the total organic carbon of the soil was calculated (figure).

It can be seen that, in most of the cases considered (the fallow, permanent fallow since 1947, and continuous winter wheat), the carbon from the aggregates of 3–1 mm made the largest contribution to the total organic matter of the soil. The smallest contribution to the total organic carbon of the soil was made by the C_{org} from the aggregates of 1–0.5 mm in the same experimental treatments.

Thus, the aggregates of 3–1 mm are of greatest interest for revealing the relationships between the soil structure and the soil organic matter. Therefore, the further study of the water-stable structure of the chernozems and the revelation of the role of the LHSs in the formation of the water-stable structure were performed with air-dry aggregates of this size.

The water stability of the 3- to 1-mm aggregates was assessed by sieving in water. From the data obtained, the coefficient of vulnerability K_V characterizing the hazard of the soil structure degradation by water was calculated [19]. The coefficient was calculated from the equation

$$K_V = x/MWD,$$

where x is the mean diameter of the air-dry aggregates, mm (in our case, 2 mm), and MWD is the mean weighted diameter of the aggregates obtained after sieving in water (using sieves of 1.0, 0.5, and 0.25 mm), mm.

It is seen from the above equation that the higher the K_V, the less water-stable the structure, and the closer its value to 1, the higher the water stability of the soil.

The water-stability parameters of the chernozem structure obtained by wet sieving for the different land-use systems are given in Table 3.

The maximum water stability was observed for the fallow: only 20% of the air-dry aggregates were degraded during the wet sieving. The minimum content of water-stable air-dry aggregates of 3–1 mm was found in the permanent fallow since 1964. In all the experimental treatments, except for the fallow, the maximum content of particles after the wet sieving was found in the fraction <0.25 mm. A clear tendency of the increasing weight yield of the structural units and the reducing of their size should be noted. Thus, all the land-use systems, except for the fallow, significantly decreased the water stability of the chernozem structure.

The values of K_V varied from 1.2 for the fallow to 7.3 for the permanent fallow since 1964. The obtained values fell within the range typical for this parameter [19]. Using the K_V parameter, the experimental treatments were ranked according to the water stability of the chernozem: fallow > winter wheat > permanent fallow since 1947 > permanent fallow since 1964.

In the separated water-stable aggregates, the content of organic carbon was determined (Table 4). In all the separated fractions, a tendency of decreasing of the C_{org} content in the water-stable aggregates with reducing of their size was noted for all the land-use systems. The minimum content of organic carbon was found in the particles <0.25 mm. A similar tendency was noted by other authors for chernozems [12] and some other soils [17, 22]. This tendency is typical for the soils in which organic matter is the main binding agent for the formation of water-stable aggregates [14, 22]. Thus, the water stability of the chernozem structure is primarily determined by the content of organic matter.

Table 3. Water-stable aggregates (%) in air-dry particles 3–1 mm in size of a typical chernozem under different land-use systems

Experimental treatment	Air-dry aggregate size, mm				K_V
	3–1	1–0.5	0.5–0.25	<0.25	
Fallow	80	5	3	12	1.2
Permanent fallow since 1947	5	10	26	59	5.9
Winter wheat	9	17	27	47	4.3
Permanent fallow since 1964	1	8	29	62	7.3

Table 4. Organic carbon (% of the aggregate weight) in water-stable aggregates obtained from air-dry particles 3–1 mm in size of a typical chernozem under different land-use systems

Experimental treatment	Air-dry aggregate size, mm			
	3–1	1–0.5	0.5–0.25	<0.25
Fallow	4.99	4.49	4.39	3.76
Permanent fallow since 1947	3.10	3.29	3.12	2.79
Winter wheat	3.98	3.86	3.86	3.49
Permanent fallow since 1964	3.15	2.98	2.89	2.84

As was noted above, some recent works showed that the water-stable aggregates in many soils are formed from fresh organic matter [14, 16, 18]. To study the qualitative composition of the organic matter in the separated water-stable aggregates and particles <0.25 mm, their content of LHS carbon (C_{LHS}) was determined, and its contribution to the total organic carbon of the structural units was assessed (Table 5).

In general, according to the content of LHSs in all the fractions of water-stable aggregates and particles <0.25 mm, the treatments of the typical chernozem formed the following series: fallow > winter wheat > permanent fallow since 1964 ~ permanent fallow since 1947.

For the treatments with the input of plant residues to the soil, a tendency of increasing of the LHS content with the increasing size of the structural units was observed. The content of C_{LHS} was about 1.2% in the fallow water-stable aggregates 3 to 0.5 mm in size and about 0.9% in the soil units of 0.5 mm and smaller; the contributions of their LHSs to the total organic carbon of the structural units were similar (21–26%).

A clear increase in the content of C_{LHS} from 0.46 to 0.75% with the increasing particle size was noted for the treatment with winter wheat. An increase in the proportion of LHSs in the total organic carbon of the soil units from 13 to 19% was also observed. The increase of the LHS proportion in the total carbon of

Table 5. Organic carbon of labile humic substances in water-stable aggregates of a typical chernozem

Experimental treatment	Aggregate size, mm	C_{LHS}	
		% of the structural unit weight	% of C_{org} in the structural units
Fallow	3–1	1.16	23
	1–0.5	1.15	26
	0.5–0.25	0.92	21
	<0.25	0.93	25
Permanent fallow since 1947	3–1	0.41	13
	1–0.5	0.57	17
	0.5–0.25	0.50	16
	<0.25	0.55	20
Winter wheat	3–1	0.75	19
	1–0.5	0.70	18
	0.5–0.25	0.59	15
	<0.25	0.46	13
Permanent fallow since 1964	3–1	0.50	16
	1–0.5	0.47	16
	0.5–0.25	0.39	14
	<0.25	0.43	15

the water-stable aggregates with the increasing their size indicated that these substances significantly contributed to the formation of the water-stable chernozem structure under this land use system.

The observed tendencies can be explained in terms of the conceptual model of the aggregate hierarchy [14], according to which the products of plant decomposition recently arriving to the soil and their derivates were utilized for the formation of soil aggregates. Thus, the enrichment of the larger water-stable aggregates with the LHS fraction was observed. This supposition was also confirmed by the distribution of the LHSs among the structural units of the different land-use systems. No monotonous increase in the content of the LHSs with the increasing size of the water-stable aggregates was observed in the fallow. The distribution of LHSs in the water-stable aggregates of different sizes was of threshold character: the content of LHSs was relatively low (about 0.9%) in the particles <0.5 mm and higher by almost 25% (about 1.2% of the aggregate weight) in the aggregates >0.5 mm; when the size of the aggregates increased further, the content of LHSs remained almost unchanged. The observed tendency could be related to the yearly excessive input of plant residues to the soil, which resulted in the establishing of an equilibrium in the fallow; the excessive LHSs were utilized for the formation of aggregates, which explains the similar contents of C_{LHS} in the large aggregates of different sizes. It should be noted that the limit size of the aggregates corresponding to an abrupt change of their characteristics, which is usually taken equal to 0.25 mm, was slightly shifted in this treatment to 0.5 mm, after which value the content of LHSs abruptly increased. This could be related to the land-use system: the presence of excessive plant residues, including coarse particles from which humic substances could not be extracted by alkaline solutions. These particles had a diluting effect on the content of LHSs and explained the observed tendencies.

In the treatment with winter wheat, the input of organic residues to the soil was insufficient, and the water-stable aggregates were formed under a deficiency of LHSs, which explained the monotonous increase in the content of C_{LHS} in the structural units with increasing of their size.

Thus, the water-stable aggregates in the fallow were formed under an excess of organic matter and accumulated it in the maximum possible amounts, including LHSs in the aggregates; during the cultivation of the winter wheat, the formation of water-stable aggregates occurred under a deficiency of organic matter and was accompanied by its active decomposition; therefore, only the structures most resistant to physicochemical and biological impacts were formed, which affected the observed relationship between the size of the water-stable aggregates and their content of LHSs. From the data obtained, it can be concluded that LHSs significantly contributed to the formation of the water-stable chernozem structure at the regular input of plant residues.

Thus, the direct extraction with a 0.1 M NaOH solution is a good indicator of the LHS content in chernozems occupied by plants.

On the other hand, no similar tendencies were observed for the treatments with permanent fallow. Based on the definition of LHSs as freshly formed readily transformable humic substances [11], we concluded that these substances should be present in insignificant amounts, if any, in the treatments of permanent fallow, where there are no input of plant residues. However, the values of C_{LHS} in these treatments were relatively high: 0.39–0.57% of the aggregate weight and 14–20% of the total carbon. The changes in the content of LHSs among the water-stable particles of different sizes were insignificant: 0.16% for the fallow since 1947 and 0.11% for the fallow since 1964. No relationship between the size of the aggregates and their content of LHSs was noted. The observed situations can be explained by the fact that, along with the fresh humic substances, the 0.1 M NaOH solution extracted from the chernozems other presumably degraded humic substances that lost their bonding with calcium, sesquioxides, or the clay fraction and hence became accessible to the alkaline solution. This possibility was already indicated earlier [5, 11].

Another reason can be that 0.1 M NaOH always dissolves only a small part of the humic substances from the other fractions (bound to calcium, sesquioxides, clay, etc.) till the establishment of a chemical equilibrium.

Thus, the partial extraction of the conservative humic substances introduces an error into the determination of the LHSs. However, this method is quite suitable for a rapid analysis in ecosystems where the input of plant residues exceeds the degradation of humic substances.

At the same time, as was noted above, the content of organic carbon in the water-stable aggregates from the permanent fallows was reliably higher than that in the particles <0.25 mm. Consequently, other organic matter fractions besides LHSs are involved in the formation of the water-stable chernozem structure. It should be supposed that these are more biothermodynamically stable substances capable of sustaining water-stable structures, including calcium-bound humic substances. They could be present in small amounts in chernozems under other land-use systems, but they ensure the long-term stability of the chernozem structure. Another reason could be the capacity of aggregates to physically protect organic matter from decomposition. When aggregated around plant residues, soil material creates conditions hampering the decomposition of organic substances within the aggregates formed, which increases the content of carbon in the large aggregates. However, this problem requires further investigation.

CONCLUSIONS

The most significant contribution to the total content of organic carbon in typical chernozems is due to the aggregates of 3–1 mm, which makes them the determining component of the soil structure. The analysis of this size fraction revealed the structural features of chernozems depending on the land-use system and assessed the role of LHSs in the formation of the water-stable structure of these soils. On the basis of the studies performed, we drew the following conclusions:

—The water stability of the chernozem structure depends on the land-use system and decreases in the following series: fallow > winter wheat > permanent fallows.

—Similar series are formed according to the content of C_{org} for the entire soils and structural units obtained by dry or wet sieving.

—Organic matter plays a leading role in the formation of the water-stable chernozem structure.

—There is no relationship between the size of the aggregates obtained by dry sieving and their content of organic carbon.

—The size of the water-stable aggregates obtained from water-dry aggregates of 3–1 mm is related to their content of organic carbon: the content of organic carbon in an aggregate increases with its size.

—In plant ecosystems, LHSs play an appreciable role in the formation of the water-stable chernozem structure: their content is higher in the large aggregates and lower in the particles of <0.25 mm.

—The direct treatment with a 0.1 M NaOH solution from a chernozem extracts, along with the relatively young humic and prohumic substances formed from fresh plant residues, a small amount of other humic substances. This fact should be taken into consideration in the study of agroecosystems with a predominance of degradation processes, including permanent fallows.

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