Chemodestructive fractionation of humus as an indicator of the functional state of soil organic matter

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Abstract. The content, composition, and properties of humus are the most important characteristics that reflect the features of modern soil formation, the genesis and evolution of soils, and their agrogenic transformation. The main criteria for assessing soil fertility are traditionally the content and reserves of organic matter in soils. At the same time, the decrease in soil fertility is associated not so much with a decrease in the total content of humus, but with the loss of its labile forms, which determine the life of the soil, its most important agronomic properties and crop yields. One of the integral indicators characterizing the state and functioning of soil organic matter (SOM) is the ratio of stable and labile forms of organic compounds obtained by chemodestructive analysis. The determination of the bichromate oxidizability of humus showed that the virgin soils of the Southern Cis-Baikal region contain an equal amount of stable and labile forms of organic compounds. Accordingly, the humus in them is a stable and balanced system in relation to external influences. Plowing led to a significant decrease in the easily and hardly hydrolysable humus fractions. In the fallow areas, the upper part of the humus horizon, in terms of the ratio of humus fractions, approaches virgin soils, and the lower part approaches the arable horizons of agricultural soils. The method of permanganate oxidizability of humus revealed a noticeable enrichment in easily oxidizable forms of virgin and, especially, fallow soils of the region. Compared to them, agricultural soils contained noticeably less labile humus, which indicates a sharp decrease in their fertility.

1 Introduction

For a long time, soil organic matter accumulates in soils as a result of soil and, above all, humus formation processes. Fallen leaves, litter and roots, entering the soil surface and into the soil, are the starting material for the formation of a complex heterogeneous, dynamic system of humic substances. Humic substances determine many genetic, ecological, biogeochemical, and agronomic properties of soils in various natural zones [1-6].

The content of humus is important for maintaining soil fertility and the productivity of agroecosystems. Its degradation is mainly associated with anthropogenic impact, and is due to the use of imperfect technologies or too intensive farming systems that are not adapted to...
2 Materials and methods
tops of the watersheds, on the northern and northeastern slopes, there are pine and larch forests and forb forests. The lower step of the vertical zonality, which occupies wide river terraces and gentle southern and southwestern slopes, is occupied by insular steppes. The soil cover contains soils of subtaiga, forest-steppe, steppe, and dry steppe landscapes: soddy-podzolic, gray forest, chernozems, and chestnut soils [4].

The objects of research were gray forest soils and ordinary chernozems. The first ones are widely developed in the coniferous-deciduous subzone of the taiga of the Southern Cis-Baikal region under light-coniferous (pine-birch) and sparse larch forests with a good grassy cover. Chernozems are located in patches on ancient river terraces, gentle southern slopes of bedrock banks under grass-wormwood associations and alternate with gray forest and meadow-chernozem soils. Soil samples were taken from the humus horizons of soil sections, on virgin soil and arable land from a depth of 0-20 cm, on fallows 0-8 and 8-20 cm in gray forest soil, 0-5 and 5-20 cm in ordinary chernozem, as well as in a radius of 5 m from the cut, using a special soil drill, in ten repetitions. The preparation of soil samples was performed in accordance with ISO 11464. For analytical studies, air-dry soil samples were dispersed (by grinding) so that the crushed mass passed through a 250 µm sieve.

The determination of the total carbon of organic compounds in the soil was carried out by the classical method of I.V. Tyurin with recalculation for humus [11]. To characterize the qualitative composition of soil organic material, which reflects the functioning of soil organic matter, the method of chemodestructive fractionation (CDF) proposed by A.I. Popov and V.P. Tsyplenkov [8] based on the method of bichromate oxidizability of humus was used. The use of a potassium dichromate solution in various proportions with sulfuric acid makes it possible to carry out fractional oxidative fractionation of the entire amount of humus and determine 11 SOM fractions. Its labile forms are oxidized by solutions with a low oxidizing ability, while relatively stable forms are oxidized by solutions with a higher one. The results obtained from the 1st to 4th fractions characterize an easily oxidizable (labile) pool of humus, which is obtained by exposing the soil to solutions with a low oxidizing ability (weak solutions of sulfuric acid in combination with potassium bichromate). Fractions 5 to 7 are represented by a moderately oxidizable pool, and fractions 8 to 11 are represented by a relatively hardly oxidizable (stable) pool of SOM. Each fraction (part of oxidized SOM) is expressed as a percentage of the total carbon content of organic compounds (C\text{tot}). To obtain results in differential form, the previous one was subtracted from each subsequent result (the amount of oxidized organic material) [9, 10].

The use of potassium permanganate KMnO\textsubscript{4} as an oxidizer of soil organic matter has a number of significant advantages over other common oxidizing agents (concentrated sulfuric acid, chlorates and perchlorates, hexavalent chromium, etc.) [1, 12–15]. These are, first of all, low toxicity for people, especially researchers, and "friendliness to the environment". An improved method for determining reactive carbon using 0.02 M KMnO\textsubscript{4} in 0.1 M CaCl\textsubscript{2} was applied to estimate the labile pool of soil organic matter. In order to assess the labile part of the soil organic matter, a neutral or slightly alkaline solution of potassium permanganate is used as an oxidizing agent of medium strength. This methodological approach makes it possible to isolate the chemically labile part of soil organic matter, which is widely used in modern natural sciences (soil science, ecology). Based on the ratio of easily and hardly oxidized by potassium permanganate forms of organic matter, it is possible to calculate the C management index (CMI), which is proposed to be used to assess the rate of changes in total organic carbon in arable agricultural soils in relation to virgin soils. In the formula for calculating CMI, its values for virgin soil are taken as 100% [12]:

\[
CMI = CPI \times LI \times 100
\]
3 Results

It has been established that the content of humus in virgin soils corresponds to its average content: in gray forest soil it was 4.88%, in ordinary chernozem – 4.34% (Figure 1). During plowing, the amount of humus sharply decreased: in agricultural gray soil by 2.75 times, in agricultural chernozem – by 1.85 times, which indicates a sharp decrease in potential fertility. In fallow soils, the values of humus increased markedly. In the gray forest soil, they have not yet reached its values in the virgin lands, and they even exceeded them in the chernozem. This indicates the process of restoration of soil fertility, moreover, in the chernozem – more intense than in the gray forest soil.

A study of the bichromate oxidizability of humus showed a certain predominance of the easily oxidizable fraction in the virgin gray forest soil (Figure 2) as compared to the arable land.

![Figure 1](https://example.com/figure1.png)

**Fig. 1.** Humus content (%) in gray forest soil (a) and ordinary chernozem (b) on virgin soil, arable land and fallows.

![Figure 2](https://example.com/figure2.png)

**Fig. 2.** Fractions of bichromate oxidizability of humus in gray forest soil (a) and ordinary chernozem (b) on virgin soil, arable land and fallows.
Moderately and hardly oxidizable forms in it are 25 and 30%, respectively, which indicates the presence of a balanced system of humic substances that is resistant to external influences [9, 10]. The ordinary chernozem on the virgin lands turned out to be more enriched in easily oxidized forms of SOM (54%) compared to the gray forest soil, 33% are hardly oxidizable forms. The smallest amount contains medium oxidizable humus 14%, which indicates the instability and imbalance of the system of humic substances. Any intensification of oxidative processes in such a system can lead to a sharp decrease in the content of labile compounds.

In the process of agricultural use, in the arable horizon of agricultural gray soil and agricultural chernozem, there was a decrease in the easily oxidized fraction of humus by 2 times (20% and 48%, respectively), compared with virgin soils. Perhaps this is due to its partial mineralization and the decomposition of the easily oxidizable fraction and with the transition to medium and, especially, hardly oxidizable forms, since their proportion has markedly increased. For the agricultural gray soil, the reduction in the amount of the easily oxidizable fraction led to a decrease in the nearest reserve of soil fertility. A decrease in the easily and moderately oxidizable fractions was also observed in the agricultural chernozem, while the number of hardly oxidizable humus forms noticeably increased.

When soils enter the fallow regime, there is a rapid increase in the easily oxidized humus fraction in the upper part of the humus horizon: up to 60% in agricultural gray soil and up to 74% in agricultural chernozem. The content of LOM in its lower part drops sharply to approximately the same values as in the plow horizon of agro-soils. This clearly indicates that the humus horizon of the fallow lands consists of two parts: the upper one is soddy and the lower one is former arable, retaining signs of agrogenic impact. At the same time, the proportion of moderately oxidizable forms of humus increased significantly. Perhaps this is due to the fact that the newly formed fresh organic matter on the deposits does not have time to pass into hardly oxidized fractions. It is possible that the increased content of humus fractions of the easily oxidized pool in the virgin chernozem, as well as in its agro- and post-agrogenic variants, compared to the gray forest soil, is associated with their high carbonate content. A solution of potassium dichromate on sulfuric acid has the ability to oxidize carbonates and hydrocarbonates of soils, which may slightly overestimate the values of the LOM.

In order to more accurately assess the labile part of soil organic matter, a neutral or slightly alkaline solution of potassium permanganate is used as an oxidizing agent of medium strength. It is able to oxidize simple carbohydrates, amino acids, amines, amino sugars and other carbon-containing substances containing hydroxyl or carbonyl groups, aliphatic components. The application of this method makes it possible to isolate only the chemically labile part of soil organic matter [1, 12]. The study of the permanganate oxidizability of humus in the soils of Cis-Baikal showed that fallow soils containing the largest amount of plant residues, the composition of which differs from those contained in virgin soils, turned out to be more enriched in labile humus (Figure 3).
Fig. 3. LOM at permanganate oxidizability of humus (Сlab, mg/g) in gray forest soil (a) and ordinary chernozem (b) on virgin lands, arable land and fallow lands.

Arable soils contained the lowest values of the easily oxidized pool, which is associated with a sharp loss of total humus and its labile forms as a result of their intensive use. In terms of the number of easily oxidized forms, virgin soils occupied an intermediate position between fallow and arable land. At the same time, virgin chernozem and its agrovariants were somewhat more enriched in the easily oxidized humus fraction compared to gray forest soil.

Based on the ratio of forms of organic matter easily and hardly oxidized by potassium permanganate, the C management index is calculated, which is used to assess the rate of changes in total organic carbon in soils of agricultural and natural systems, as well as soil quality due to anthropogenic impact. The higher the index, the better the soil quality.

Calculation of CMI of agro-gray soil on arable land in relation to CMI of virgin soil, taken as 100%, showed its high values, reaching 95%. On the fallow lands in the soil layer of 0-8 cm, it amounted to 127% in relation to the virgin lands. The CMI values of agro-chernozem are also quite high (76%), but noticeably lower than in agro-gray soil. This indicates a more intense depletion of agro-chernozem by labile forms of humus compared to agro-gray soil. CMI in fallow soil were close to virgin soil and amounted to 1.05%.

4 Discussion

The data of bichromate and permanganate oxidizability of humus for the soils of the Southern Cis-Baikal are in good agreement with the previously obtained results for the chernozems of the Kansk forest steppe of the Krasnoyarsk Territory (55°–57° N and 94°–96° E) [14]. Thus, the maximum values of humus were recorded in the chernozem of the virgin area. In the arable agrochernozem, they were minimal and on the fallow land they occupied an intermediate position. The content of humus in the chernozems of the Kan forest-steppe turned out to be higher than in the Southern Cis-Baikal region: on virgin lands – 1.95, on arable land – 2.35, and on fallow land – 1.5 times. This is due to more favorable bioclimatic conditions for the formation of chernozems in the Kansk forest-steppe. The climate of the region is sharply continental, but it is less continental in comparison with the Southern Cis-Baikal region. The average annual precipitation is about 445 mm, the average annual temperature varies less (–0.5–1.3°C), the sum of active temperatures is 1561–1818°C. The Kansk forest-steppe is included in the zone of grassy light-coniferous forests and insular forest-steppes of Central Siberia. The soil-forming rocks are Paleozoic (Cambrian and Devonian), Mesozoic (Jurassic) deposits, often overlain by Quaternary o
cenes.
At the same time, the proportion of the moderately oxidizable part also decreased, and the proportion of hardly oxidizable fraction increased significantly. In fallow areas, a sharp increase in easily oxidized forms is again observed with a decrease in medium and difficultly oxidized humus fractions. The study of the permanganate oxidizability of humus in the chernozems of the Kansk forest-steppe, taking into account only the easily oxidizable fraction of humus, which is an indicator of their humus state, revealed the greatest enrichment of fallow soil with it (3.5 C lab., mg/g-1). It was the least contained in the arable soil (2.75 C lab., mg/g-1). Virgin chernozem occupied an intermediate position in this indicator (3.25 C lab., mg/g-1). The calculation of the CMI of the arable chernozem of the Kan forest-steppe showed that its values were 85% of the virgin soil, which is slightly higher than in the chernozem of the Southern Cis-Baikal region. This indicates a better quality of humus and a higher level of soil fertility in the Kansk forest-steppe. On the fallow soil, CMI turned out to be slightly higher than on virgin soil and amounted to 108%.

Of interest are the data on the permanganate oxidizability of humus obtained for the soddy-podzolic surface gleyed soil of the territory of Western Ukraine in the upper reaches of the Dniester River basin, (49° N, 23° E), characterized by a mild temperate continental climate, formed under the conditions of transboundary air transport under the influence of the barrier effect of the Carpathians [1]. The average annual precipitation is about 700 mm, the average annual temperature is 7.8°C, the sum of active temperatures is 2400–2600°C. Oak and oak-hornbeam forests predominate within the flat part of the Upper Dniester basin. Old-aged oak and oak-hornbeam stands can be 210–240 years old, and the age of individual trees of previous generations can exceed 300 years. The soils of Upper Transnistria are formed mainly on alluvial Upper Pleistocene and Holocene deposits. They differ in the degree of development of the podzolic process of soil formation and are represented by two genetic types—soddy-podzolic gleyed soils, as well as gray and light gray soils. In soddy-podzolic gleyed soils of undisturbed old-growth stands, the largest amount of humus is accumulated in the surface layer of 0–5 cm and is more than 10%. With depth, this figure decreases by 2 times. In the soil on the site after clear-cutting of the tree stand (hornbeam), the amount of humus decreased to 5%, and under the hayfield used as agricultural land for more than 20 years, the humus content was minimal and amounted to 3.45%.

As for the permanganate oxidizability, the values of the labile humus fraction in the 0–5 cm soil layer of the old-growth undisturbed forest stand turned out to be noticeably higher than in the gray forest soils of the Southern Cis-Baikal region and amounted to 2.89 mg/g-1, which is associated with the excellent bioclimatic conditions of Transnistria. Carrying out forestry activities (clear felling of the hornbeam sub-edificator) led to a significant decrease in the content of the labile pool to 1.98 mg/g-1. In the soil under the hayfield, the content of humus LM was also low and amounted to 2.00 mg/g-1. The CMI values for the felled and hayfield soils were 69%, which is noticeably lower than in the arable and fallow soils of Eastern Siberia.

5 Conclusions

The application of the method of bichromate oxidizability of humus showed that the soil organic matter of the studied virgin soils of Cis-Baikal turned out to be represented by equal values of easily, moderately, and hardly oxidizable forms. Plowing led to a significant decrease in the proportion of LOF and an increase in humus fractions that are difficult to oxidize, which indicates the destruction processes taking place in arable soils. In them, biochemical and physicochemical inactivation of humus occurs, which reduces soil
fertility. In fallow soils, the amount of L\textsubscript{OM} in the upper part of the humus horizon approaches virgin soils, and in its lower part, to the plow horizons of agrosoils.

2. The permanganate oxidation of humus made it possible to detect the greatest enrichment of fallow soils with its labile forms. Agrosoils contained the least amount of them, and virgin soils occupied an intermediate position in this indicator. In ordinary chernozem, the amount of L\textsubscript{OM} turned out to be slightly higher than in gray forest soil, which indicates a higher level of its fertility.

3. The method of bichromate oxidizability of humus can be the most informative diagnostic indicator for assessing the state of soil organic matter in terms of the ratio of easily, medium, and hardly oxidizable forms of humus in soils. The method of permanganate oxidizability of humus turned out to be a highly sensitive express method for determining its labile part, which makes it possible to determine the level of actual soil fertility, as well as the degree of their agrogenic transformation. Maintaining a high content of easily oxidized SOM fractions in soils due to various types of chemical, physical, and other protectors will allow a greater amount of organic matter to participate in humification processes, followed by humus formation and humus accumulation.

References


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