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Spectral characteristics of water-soluble and alkaline-soluble organic substance of fallow light-gray forest soils

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Abstract. The content of organic matter (OM) and its individual fractions were studied in different ages (7 and 75-80 years-old) fallow soils. The qualitative composition of labile OM fractions was evaluated by the criteria of $SUVA_{254}$ and Sr , which were calculated from the absorption spectra in the UV range. It was shown that as deposits age, there is a significant increase in the content of total organic carbon (TOC) in soils and a change in the qualitative composition of its labile fractions. From the nature of changes in the degree of aromaticity and molecular masses of labile fractions with the age of deposits, a conclusion can be drawn that the factor of selective preservation of compounds resistant to degradation is relevant only to stabilize the water-soluble OM. The stability of alkaline-soluble OM fractions is most likely provided by the formation of organic and organic-mineral associations.

1. Introduction

Recently, the idea of humic substances (HS) in soils as supramolecular aggregates (ensembles) of low molecular weight [1, 2], low and high molecular weight [3], heteropolar [4] compounds, branched polyelectrolytes with a disordered molecular structure, has become increasingly popular. [5], which are interconnected into a single whole by non-valent intermolecular interactions. In the aspect of this concept of spatial organization of humic substances in the composition of the soil organomineral complex, the division of the total pool of soil organic matter (SOM) into its constituent parts, differing in lability and resistance to destruction by active heterotrophic microflora, becomes especially relevant. Traditionally, SOM is divided into three main pools: labile, stable, and inert; to identify them, a wide range of analytical methods based on physical, chemical, and biochemical principles are used [6]. Despite their diversity, to date, there are no reliable methods for unambiguous separation of SOMs into groups according to functional criteria, which is primarily due to the fact that carbon compounds in the soil form a complex continuum on genesis, composition and properties [7]. It seems relevant to study the qualitative diversity of humic substances falling into fractions extracted by solutions with different extracting abilities, which fall into one pool for lability and stability in soils. An interesting object for such studies is the material of the old arable horizons of fallow soils, which, because of postagrogenic transformation, is strongly differentiated in terms of quantitative content, qualitative composition and stability of SOM [8]. The purpose of this work: Assessment of the content of water and alkaline soluble OM in uneven-aged fallow light gray forest soils and the direction of the qualitative change in their composition.



2. Materials and methods

The objects of the study were the conjugate areas of uneven-aged fallows (7 and 75-80 years-old), located in the Pre-Volga region of The Republic of Tatarstan (Russia), confined to one relief element - the weak, ecological slope of the south-east exposure. Soils - light gray forest (Luvisols). Fallow vegetation is represented by stable forb-grass-meadow coenoses of different stages of succession. Samples from the old plow horizon were selected layer-by-layer (after 5 cm) to a depth of 20 cm by a special drill from 7 sampling points timed to 7 nodes of hexagonal systematic grids laid separately at each site. Samples to characterize the vertical heterogeneity of the plowing horizon were obtained by mixing separately in layers of 0–5 cm, 5–10 cm, 10–15 cm, and 15–20 cm of individual samples taken from 7 sampling points. After careful selection of the roots, the soil was ground and passed through a 0.1 mm sieve. In mixed samples, the total TOC content was determined by the Tyurin method. Labile fractions of SOM were extracted with hot water according to the Korschens method [9] and a mixture of Na₄P₂O₇-NaOH using the Kononova and Beľčikova methods [10]. All analyses were performed in 3 replicates. The absorption spectra of water-soluble and alkaline-soluble fractions were measured on a Lambda 35 two-beam spectrophotometer (PerkinElmer, United States) in the wavelength range of 450-250 nm and a cell length of 0.01 m.

3. Results

The results of determining the content of TOC in the layered soil samples from the old plow horizon of multi-aged fallow soils, as well as the content of organic carbon water soluble (OCW) and alkaline soluble (OCP) fraction are presented in table 1.

Table 1. Average value and error of the average content of TOC and carbon labile fractions.

The depth of sample selection	Fallows of 7 years-old					Fallows of 75-80 years-old				
	TOC, mg g ⁻¹	OCW		OCP		TOC, mg g ⁻¹	OCW		OCP	
		mg g ⁻¹	% TOC	mg g ⁻¹	% TOC		mg g ⁻¹	% TOC	mg g ⁻¹	% TOC
0-5 cm	10,3±0,3	0,51±0,01	5,0	4,7±0,1	45,7	28,0±1,4	1,55±0,14	5,5	11,7±0,2	42,0
5-10 cm	8,4±0,2	0,35±0,01	4,2	4,0±0,3	47,0	11,1±0,4	0,59±0,06	5,4	5,2±0,4	47,0
10-15 cm	7,1±0,3	0,30±0,02	4,2	3,3±0,2	46,4	8,2±0,6	0,33±0,03	4,0	4,2±0,1	51,8
15-20 cm	6,6±0,1	0,25±0,02	3,8	3,1±0,2	47,2	6,7±0,3	0,24±0,02	3,6	3,7±0,2	55,4

From the analysis of the data, it can be concluded that a significant accumulation of both TOC and carbon of the labile fractions occurs primarily in the upper layers of the old tillage horizon (within the 0-5 cm layer and to a lesser extent in the 5-10 cm layer). The process of accumulation of organic carbon naturally depends on the age of the fallow. Under the fallow vegetation of 75-80 years-old of age, the level of accumulation of all forms of carbon in the upper layers is significantly higher than under the 7 years-old deposits. However, the change in the share of labile fractions in the total SOM pool is not uniform. The proportion of water-soluble chemical agents in the upper layers of the old plow horizon is higher in the general pool of biological agents than in its lower part. Apparently, the accumulation of the water-soluble fraction is primarily in the upper layers and is slightly higher than the accumulation of TOC. The proportion of alkaline soluble OM, on the contrary, is in the upper part of the old arable horizon below. This can occur due to a significant accumulation of detrital humus in the upper part of old-cultivated horizons of fallow soils [11] with a low proportion of alkaline-soluble organic matter. Figure 1 shows the absorption spectra in the range of 450-250 nm of water-and alkaline-soluble OM fractions isolated from layer-by-layer samples of the old plow horizon.

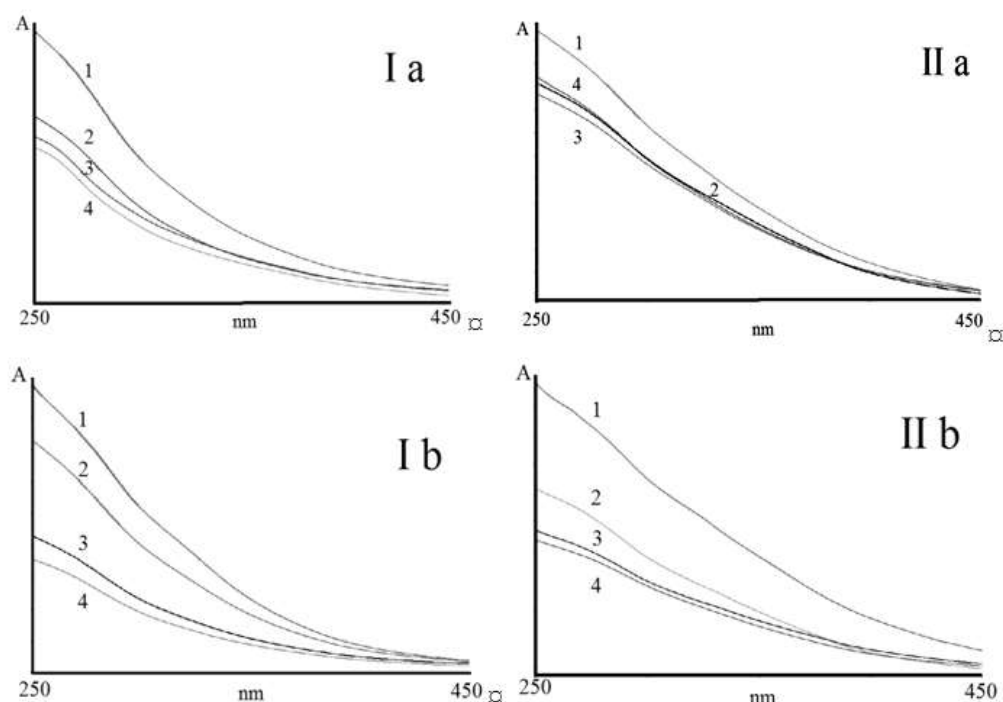


Figure 1. Absorption spectra of water-soluble (I) and alkaline-soluble (II) OM fractions of fallows 7 years-old (I a and II a) and 75-80 years old (I b and II b), 1- layer 0-5 cm, 2 - layer 5-10 cm, 3 - layer 10-15 cm, 4 - layer 15-20 cm).

For the qualitative characteristics of the selected OM fractions, the $SUVA_{254}$ criterion and the Sr criterion were calculated from the absorption spectra, which have recently been widely used to quickly evaluate the qualitative indicators in the chemistry of the humus substances of soil and natural waters. The $SUVA_{254}$ criterion is the ratio of the absorption coefficient ($a_{CDOM}(\lambda)$ (m^{-1})) of the colored solution of OM at $\lambda = 254$ nm to the content of organic carbon expressed in $mg\ L^{-1}$. The $SUVA_{254}$ criterion is considered a reliable indicator that has a close direct correlation with the degree of aromaticity of natural-colored organic compounds [12]. The Sr criterion is calculated as the ratio of the slope of the absorption spectrum in the range of 275-295 nm to the slope of the spectrum in the range of 350-400 nm, which are found by empirical modeling of the spectra. For empirical modeling, the units of optical density are also converted into absorption coefficients ($a_{CDOM}(\lambda)$ (m^{-1})) for each wavelength λ by the equation:

$$a_{CDOM(\lambda)} = 2,303A_{\lambda}L^{-1} \quad (1)$$

where:

A_{λ} – the absorption intensity at a wavelength of λ ,

L - the length of the optical cell in meters (in our case - 0.01 m.).

The slope value (S) is obtained either from the absorption spectra of the dissolved colored OM by fitting the fewest square data according to the exponential equation (2) or by linear modeling after logarithmic ($\ln a$) conversion of the absorption coefficient value [13].

$$a_{CDOM(\lambda)} = a_{CDOM(\lambda_0)} \exp[S(\lambda_0 - \lambda)] \quad (2)$$

where:

$a_{CDOM(\lambda)}$ – the absorption coefficient (m^{-1}) at a certain wavelength,

$a_{CDOM(\lambda_0)}$ – the absorption coefficient (m^{-1}) at a standard wave ($\lambda_0 = 412$ nm),

λ – the wavelength (nm),

S – the spectrum slope

In both cases, to determine the Sr index, the slope values are preliminarily calculated for the two spectral ranges of 275-295 nm ($S_{275-295}$) and 350-400 nm ($S_{350-400}$). The value of Sr is taken to be $S_{275-295} / S_{350-400}$. It is believed that Sr has a close inverse correlation with the molecular masses of the colored natural dissolved organic compounds [13]. The results of the calculations are presented in table 2.

Table 2. The values of the criteria $SUVA_{254}$ and Sr absorption spectra of labile OM fractions.

The depth of sample selection	Fallows of 7 years-old			Fallows of 75-80 years-old		
	SUVA ₂₅₄	Sr		SUVA ₂₅₄	Sr	
		exponential modeling	linear modeling		exponential modeling	linear modeling
Hot water soluble fraction						
0-5 cm	5,8	0,98	1,00	6,5	0,92	0,72
5-10 cm	5,8	0,99	1,04	6,8	0,96	0,83
10-15 cm	6,0	1,04	0,99	7,3	1,08	1,07
15-20 cm	6,7	1,06	1,01	8,4	1,08	1,1
Sodium pyrophosphate soluble fraction						
0-5 cm	30,7	0,94	0,86	29,8	0,87	0,73
5-10 cm	34,8	0,95	0,81	36,9	0,90	0,77
10-15 cm	40,1	1,04	0,95	37,9	0,97	0,95
15-20 cm	41,7	1,04	0,92	40,6	0,99	0,92

Analysis of the data shows that the labile fractions isolated from different layers of the old plow horizon differ in their quality indicators. According to the Sr values, a slight increase in the molecular masses of the labile fractions is observed in the upper part of the old plowing horizon. The results of exponential modeling provide smoother and more regular values of this criterion than the results of linear modeling. According to the values of the $SUVA_{254}$ criterion, in the upper part of the topsoil horizon there is an accumulation of both water-soluble and alkaline-soluble OM with a lower degree of aromaticity, most likely due to the predominant accumulation of younger aliphatic HS. With age, the deposits of aromaticity of water-soluble OM increases, which may indicate the preferential selection of water-soluble molecules that are more resistant to degradation. In the case of alkaline-soluble OM, this tendency practically does not manifest itself, most likely since the factor of selective preservation of stable compounds for this fraction is not so relevant. The stability of alkaline-soluble organic matter in soil is most likely due to spatial unavailability for heterotrophic microorganisms due to the formation of supramolecular aggregates and interaction with minerals and metal ions. These factors are considered the most important mechanisms for creating a sustainable organic pool in virgin soils [14].

4. Conclusion

In general, it can be concluded from research that with the age of the deposits there is a significant change in the quantitative content and qualitative composition of OM in general and its individual labile fractions. From the change in the qualitative composition of OM labile fractions with age of deposits, it can be concluded that the factor of selective preservation of compounds resistant to degradation is relevant, most importantly, for the stability only of the most labile water-soluble fraction. The stability of alkaline-soluble OM fractions of fallow soils is most likely determined by their spatial inaccessibility to heterotrophic microorganisms due to the formation of organic and organic-mineral associations.

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References

- [1] Piccolo A 2001 *Soil Sci.* **166** 810-32
- [2] Simpson A J, Kingery W L and Hayes M H B 2002 *Naturwissenschaften* **89** 84-8
- [3] Baalousha M, Motelica-Heino M, Galaup S and Coustumer P L 2005 *Microsc. Res. Techniq.* **66** 299-306
- [4] Fisher T 2017 *Chemosphere* **183** 437-43
- [5] Perminova I V 2013 Humic Substances-Assisted Synthesis of Nanoparticles in the Nature and in the Lab, Functions of Natural Organic Matter in Changing Environment *Springer Dordrecht* 735-40
- [6] Strosser E 2010 *J. Agrobiology* **27** 49–60
- [7] Krasilnikov P V 2015 *Eurasian Soil Sci.* **48** 997-1008
- [8] Mueller C W and Koegel-Knabner I 2009 *Biol. Fertil. Soils* **45** 347-59
- [9] Korschens M, Schulz E and Behm R 1990 *Zentralbl. Mikrobiol.* **145** 305-11
- [10] Kononova M M and Belchikova N P 1961 *Sov. Soil Sci.* **10** 75-87
- [11] Giniyatullin K G, Shinkarev A A, Fazylova A G, Kuzmina K I, and Shinkarev A A (Jr.) 2012 *Uchenye Zapiski Kazanskogo Universiteta. Seriya Estestvennye Nauki* **154** 61–70
- [12] Weishaar J L, Aiken G R, Bergamaschi B A, Fram M S, Fugii R and Mopper K 2003 *Environ. Sci. Technol.* **37** 4702-8
- [13] Helms J R, Stubbins A, Ritchie J D, Minor E, Kieber D J and Mopper K 2008 *Limnol. Oceanogr.* **53** 955-69
- [14] Lützow M, Kögel-Knabner I, Ludwig B, Matzner E, Flessa H, Ekschmitt K, Guggenberger G, Marschner B and Kalbitz K 2008 *J. Plant Nutr. Soil Sci.* **171** 111–24