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HUMIC ACIDS COMPOSITION OF ARABLE SOD-PODZOLIC SOIL AFTER LONG-TERM APPLICATION OF TRADITIONAL AND UNCONVENTIONAL ORGANIC FERTILIZERS

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ABSTRACT

The elemental composition and structure of humic acids (HA) of arable sod-podzolic soil (Eutric Albic Retisols (Abruptic, Loamic, Cutanic) was studied in Perm Agricultural Research Institute – division of PFRC. Application of traditional and unconventional organic fertilizers was fulfilled in long-term stationary experiment. The carbon content in HA of sod-podzolic soil varied from 30.7 to 34.6; hydrogen – 28.9-35.5, oxygen – 21.1-27.9, nitrogen – 1.9-2.2%. The H/C ratio for all treatments was >1, the structure of the supramolecular associations of humic acids is predominantly aliphatic. Long-term use of manure, sewage sludge (SS) and their combination with mineral fertilizers led to the enrichment of humic acids with nitrogen. The maximum degree of HA oxidation was observed with the use of cattle manure. The FTIR spectra of humic acids had absorption bands of carboxyl, hydroxyl, methyl, methylene, methoxyl and other groups in a wide wavelength range. At 1720 cm^{-1}, an absorption band was recorded, which had a high intensity in the control variant and was due to oscillations of the >C=O group of carboxylic acids. With an increase in the load of the anthropogenic factor on the soil (application of organic and mineral fertilizers), a decrease in its intensity is observed. The structure of supramolecular HA aggregates of the control variant, with the introduction of NPK and unconventional organic fertilizer – SS, is characterized by a higher content of aromatic fragments, as evidenced by a clear existence of the absorption band at 1628 cm^{-1}. Cattle manure application promoted the formation of humic acids with a branched aliphatic structure.

Keywords: *element analysis, atomic ratios, humic acids oxidation degree, IR spectroscopy, fertilizers.*

INTRODUCTION

Soil organic matter undergoes continuous destruction, creating a continuum of more or less decomposed materials of varying size, composition, and structure (Lehmann, 2015; Mohinuzzaman, 2020). According to the International Humic Substances Society (IHSS) and the American Soil Science Society, the main criterion for determining humus substances today is still alkali solubility (Kleber, 2019). The different solubility of humus substances in acid-base media is the basis for their division into humic acids, fulvic acids, and non-extractable residue (humin).

The study of the transformation processes of humic acids (HAs) as the most important fraction of organic matter under long-term anthropogenic impact on the soil is of great scientific interest, since HAs exhibit high functional activity and determine the specificity of the water, physical, chemical and thermal properties of the soil. Their composition and structure depend on the conditions of soil formation and change under anthropogenic impact on the soil (Orlov, 1990; Stepanov, 2008; Kholodov, 2011; Hasanova, 2018).

Modern methods of spectroscopic analysis, in particular, the method of nuclear magnetic resonance, made it possible to characterize in more detail the chemical composition of humus substances in soils. Scientists concluded that humus substances and humic acids in particular are not heteropolymers, but are "supramolecular associations of self-assembled heterogeneous and relatively small molecules formed as a result of degradation and decomposition of dead biological material." The formation of supramolecular aggregates is provided by non-valent interactions (aromatic π-π and hydrophobic interactions, van der Waals forces, electrostatic and hydrogen bonds) (Piccolo, 2002; Semenov, 2013; Ivanov, 2017; Baveye, 2019; Olk, 2019; Kholodov, 2020).

The aim of the research is to reveal the effect of long-term use of traditional and non-traditional fertilizers on the elemental composition and structure of humic acids in arable soil.

MATERIAL AND METHODS

The object of the study was sod-podzolic heavy loamy soil (Eutric Albic Retisols (Abruptic, Loamic, Cutanic)) of a stationary field experiment founded in 1976 on the experimental field of Perm Agricultural Research Institute – division of Perm Federal Research Center Ural Brunch Russian Academy of Sciences. In a stationary experiment, the following treatments were studied: control (without fertilizers); manure 40 t/ha, sewage sludge (SS) 40 t/ha, NPK – background, background + manure 40 t/ha, background + SS 40 t/ha.

Organic fertilizers (SS, cattle manure) at 40 t/ha of natural moisture were applicated in the fallow one time per crop rotation. SS was applied in rotations I – VI, manure in III – VI rotations of the crop. Mineral fertilizers (rotation I – $N_{120}P_{120}K_{120}$, rotation II – $N_{90}P_{90}K_{90}$, III-VI rotation – $N_{60}P_{60}K_{60}$) were applied to all grain crops of the crop rotation before pre-sowing cultivation in the form of ammonium nitrate or urea, simple superphosphate and potassium chloride. The aftereffect of mineral fertilizers application was studied on red clover.

The soil of The experimental plots were located on sod-podzolic heavy loamy soil. Agrochemical characteristics of the soil at the time of the experiment: Corg – 1.28%, pHKCl – 4.8, Ng – 3.7 and S – 18.1 cmol (equiv) / kg, mobile P_2O_5 and exchange K_2O (according to Kirsanov) – 154 and 170 mg/kg, the content of physical clay according to the Kachinsky method (particles with a size of <0.01

mm) was more than 40%. The observations were carried out in a seven-course field crop rotation with following rotation scheme: bare (full) fallow – winter rye – spring wheat as cover crop for red clover – first year clover – second year clover – spring barley – oat. Treatment placing is systematic, each treatment has three replications on field area. Total area of each plot – 47.5 m^2, the accounting area is 24.0 m^2. m². SS and manure agrochemical characteristics are presented in the Table 1.

Table 1. Agrochemical characteristics of SS and manure (averaged data)

Fertilizer	Humidity, %	pH_{KCl}	Composition, % for absolutely dry matter			
			Organic matter	N_{total}	P_{total}	K_{total}
SS	68	6.5	66	1.5	3.1	0.5
Manure	75	7.3	75	1.7	2.1	1.0

Wastewater sludge from biological treatment facilities in the city of Perm were used in given experiment The SS used in the experiment in the V-VI rotations of the crop, in terms of agrochemical indicators and heavy metals content (HM) corresponded to the requirements of national standard GOST R. 17.4.3.07-2001. SS samples were used after holding on sludge sites for at least three years according to SanPiN 2.1.7.573-96; as a result, they are disinfected and they correspond to the required microbiological and parasitological indicators.

The soil samples were taken at the end of the sixth rotation in the 0-20 cm layer from two non-adjacent replication at five points on each plot. Preparations of humic acids were extracted according to the classical method of the Russian School of Soil Science, which differs from the recommendations of the International Humic Society (IHSS) (Swift, 1996): specifically, the soil was extracted with alkali at least three times in ordinary air medium, then combined extract was analyzed. The elemental composition of humic acids was determined on a CHN – elemental analyzer from Perkin – Elmer (USA), the amount of oxygen was calculated by difference (all calculations are given for ash free preparations); IR absorption spectra were recorded on a VERTEX-80v Fourier spectrometer (Bruker, Germany) in the range 4000–400 cm^{-1} at a spectral resolution of 2 cm^{-1}. The spectra were processed using the OPUS software package. Data processing included analysis of variance.

The studies were carried out in IV agroclimatic district of Perm Region. Regarding the physical and geographical conditions, the region is located in the subzone of the southern taiga and coniferous-deciduous forests. Perm Region belongs to the Vyatka-Kama soil province according with soil-ecological zoning (Eremchenko, 2016). The climate is temperate continental with cold, long, snowy winters and warm short summers. The sum of the average daily temperatures above 10°C is 1700-1900. The duration of the active growing season with temperatures above 10°C is 115 days average, with temperatures above – 15°C -60 days. The region belongs to the zone of sufficient moisture: annual precipitation is 470-500 mm, during the growing period is about 320 mm, evaporation from the soil surface is about 340 mm, hydrothermal coefficient 1,4. The number of days with snow cover averages 176 (Korotaev, 1962; Agroclimatic resources, 1979).

RESULTS AND DISCUSSION

The analysis of humic acids elemental composition in sod-podzolic soil showed that the carbon (C) content varied from 28.9 to 35.5 at. %, hydrogen (H) – from 38.5 to 43.2 at. %, oxygen (O) – from 21.1 to 27.9 at. %, nitrogen (N) – from 1.9 to 2.2 at. % depending on the experiment treatments (table 2). The H/C ratio for all treatments was >1, the structure of the supramolecular aggregates of humic acids was predominantly aliphatic. Long-term use of manure, SS and their combination with mineral fertilizers led to the enrichment of humic acids with nitrogen, the C/N ratio was 14.96-15.64 versus 16.18 in the control variant. The use of fertilizers increased the degree of oxidation (from 0.03 in the control variant to 0.28-0.52). When SS was applied on mineral fertilizers background, the degree of oxidation remained at the control level. The maximum degree of oxidation and the enrichment of humic acids with nitrogen was observed after cattle manure application - traditional organic fertilizer.

An increase in aromatic fragments in the supramolecular associations composition of humic acids (H/C = 1.13) was noted in the variants "NPK – background" and "SS 40 t/ha". The use of traditional organic fertilizers (cattle manure) led to an increase in aliphatic groups in the HA structure, as evidenced by a wider H/C ratio of 1.44 (Figure 1). When organomineral fertilization system was used, the HA structure was formed, apparently consisting of a wide variety of aliphatic and aromatic fragments with various functional abilities. This structure is optimal from an agronomic point of view.

According to FTIR spectroscopy, humic acids of all variants have a wide absorption band at 3466-3423 cm^{-1}, caused by stretching vibrations of OH groups linked by intermolecular hydrogen bonds (Figure 2). In the range of C-H valence oscillations of methyl and methylene groups, the HA spectra show up to two absorption bands at 2927-2925 and 2863-2862 cm^{-1}. The absorption bands at 2925 and 2862 cm^{-1} (valence oscillations of C-H methylene groups) are most intensive in the control and NPK variants, which indicates the presence of branched aliphatic chains with terminal methyl groups in these HAs (absorption band at 2925 cm^{-1}). In other cases, the intensity of these absorption bands decreases.

Table 2. Elemental composition of humic acids in long-term experiment with traditional and non-traditional fertilizers.

Variant	Composition, %				Atomic ratios			Oxidation degree (*W*)
	C	H	O	N	H/C	O/C	C/N	
Control	38.16 35.5	3.67 40.9	30.21 21.1	2.75 2.2	1.15	0.59	16.18	0.03
Manure 40 t/ha	26.30 28.9	3.09 40.9	33.85 27.9	2.05 1.9	1.41	0.97	14.96	0.52
SS 40 t/ha	37.95 34.2	3.56 38.5	36.75 24.8	2.83 2.2	1.13	0.73	15.64	0.33
$N_{60}P_{60}K_{60}$ – background	34.05 34.4	3.21 38.9	32.03 24.8	2.44 2.1	1.13	0.71	16.27	0.28
Background + manure 40 t/ha	32.54 31.8	3.49 40.9	33.96 24.9	2.48 2.1	1.29	0.78	15.30	0.28
Background + SS 40 t/ha	31.04 31.8	3.51 43.2	29.39 22.6	2.41 2.1	1.36	0.71	15.02	0.06
LSD_{05}	2.01	0.1	1.1	0.3	-	-	-	-

Note: above the line — mass fraction, below the line – atomic fraction (all calculations are given for ash-free preparations). HCP_{05} is presented for mass fraction.

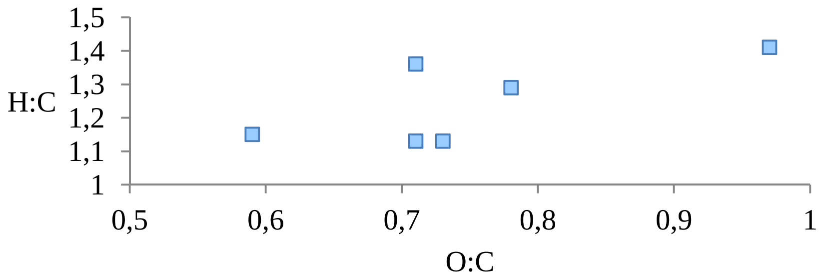

Figure 1. Diagram of atomic ratios of HA in sod-podzolic soil in long-term experiment:
1 – without fertilizers, 2 – manure 40 t/ha, 3 – SS 40 t/ha, 4 – NPK (background), 5 – background + manure 40 t/ha, 6 – background + SS 40 t/ha.

In the range of wavenumbers 1800-1300 cm^{-1} in the HA spectrum of the control variant, the absorption band at 1720 cm^{-1} of high intensity was recorded, which was caused by oscillations of the >C=O group of carboxylic acids. The increase of the anthropogenic impact on the soil (application of organic and mineral fertilizers) led to decrease in its intensity.

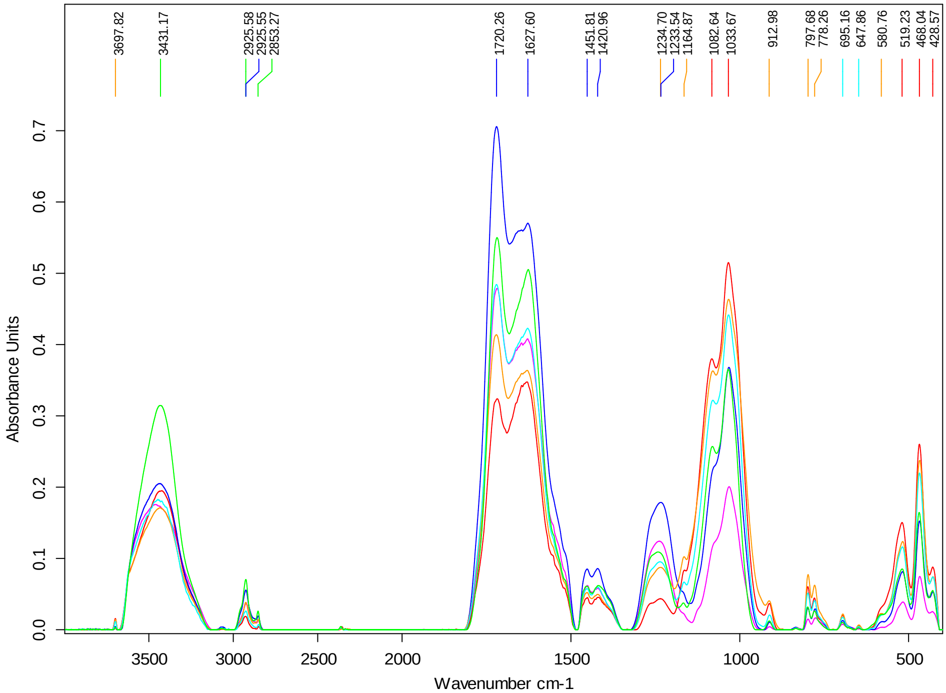

Figure 2. IR spectra of HA of sod-podzolic soil in long-term experiment: control (dark blue), manure 40 t/ha (red), SS 40 t/ha (pink), NPK – background (green), background + manure 40 t/ha (light blue), background + SS 40 t/ha (brown).

In the HA spectrum of the control treatment, a clear presence of the absorption band at 1628 cm^{-1} was observed. This absorption band was quite intense for the NPK variant. Absorption in this area indicates the presence of aromatic rings in the supramolecular associations of HA due to valence oscillations of double bonds of carbon atoms. The use of organic fertilizers (manure and SS) caused the least impact on the intensity of this absorption band.

The absorption bands (1440–1430 cm^{-1} and 1405–1400 cm^{-1}) can be caused by deformation vibrations of C–H methyl and methylene groups, carboxylic acids, carboxylate ion, and the intensity of these bands in the HA spectra of the control variant is significantly higher compared with other experiment variations.

Spectroscopic study of humic acids preparations made it possible to reveal some differences in the set of absorption bands and in the magnitude of their intensity, as well as the generality of their structure. That was especially true for the IR spectra of humic acids in the soil of the control variant: clear absorption bands in the range of 1720 cm^{-1} (C=O carbonyl group) and at 1628 cm^{-1} (C=C aromatic rings) characterize a greater number of aromatic structures in the composition of HAs than in other experiments. Mineral fertilization system ($N_{60}P_{60}K_{60}$ – background) also contributed to the enrichment of supramolecular aggregates with aromatic fragments. The application of cattle manure and SS together with NPK led to increase of aliphatic groups in humic acids composition.

CONCLUSION

The humic acids preparations extacted from sod-podzolic heavy loamy soil in long-term experiment correspond to humic acids of natural sod-podzolic soils according to the data of elemental analysis and IR spectroscopy. They have a common structural composition, but are characterized by an individual set of absorption bands and their different intensities depending on the degree of anthropogenic load on the soil. Extensive (without fertilizers) cultivation of agricultural crops and the use of only mineral fertilizers led to an increase in aromatic functional groups in the structure of HA. Such composition of supramolecular aggregates is resistant to microbiological and thermal decay. The increase in the number of functional groups in humic acids composition was observed after long-term use of organic fertilizers (manure, sewage sludge), separately and together with NPK. The process of transformation of their structure is moving towards the strengthening the aliphatic nature of HA. Humic acids with such structure are characterized by high functional activity.

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