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AGROCHEMISTRY. PEDOLOGY

Elemental Composition of Humic Acids of Sod-Podzolic Clay Loam Soil of Cisuralia during Long-Term Use of Fertilizer Systems

N. E. Zav'yalova

Perm Agricultural Research Institute, Perm krai, 614532 Russia

e-mail: pniish@rambler.ru

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Abstract—The effect of various fertilizer systems on the elemental composition of humic acids of sod-podzolic soil has been studied in a long-term field experiment. The mineral fertilizer system promoted an increase in carbon content in the peripheral part of humic acid molecules and the organic system some increase in the aromatic part of humic acid molecules, their oxidation, and enrichment with nitrogen. With the organomineral fertilizer system, transformation of humic acids occurred toward an increase in the proportion of aromatic structures against the background of a high content of unsaturated aliphatic radicals.

Keywords: sod-podzolic soil, humic acids, elemental composition, fertilizer system

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It is known that the elemental composition—one of the most important characteristics of humic acids as a special class of organic compounds—is used in genetic soil investigations. Characteristics of soil types, subtypes, and varieties (including arable variants) are evaluated with its aid. The correspondence of the composition of humic acids to pedogenic conditions serves as the initial and a priori base for such evaluations. The average elemental composition of humic acids of various soil types is rather close: the content of carbon varies from 36.2 to 42.5, hydrogen from 32.0 to 43.5, oxygen from 16.7 to 22.3, and nitrogen from 1.7 to 3.2 at % [1–11].

The expression of the results of an elemental analysis in atomic percent allows revealing the role of individual elements in constructing humic acids (HAs) and gives information about those changes which occur with humic substances during pedogenesis. The ratios H : C, O : C, and C : N characterize the direction of processes of transformation of HAs during anthropogenic impact on soil: H : C determines the degree of benzoidness of HA molecules; O : C, the degree of their oxidation; and C : N, the value of nitrogen-containing components in constructing the molecular structures of HAs [2, 6, 7].

The purpose of the present work was to determine the effect of the long-term use of various fertilizer systems on the elemental composition of humic acids of sod-podzolic clay loam soil.

METHOD

The investigations were conducted on preparations of HAs isolated from soil of a long-term permanent experiment established in 1971 on the experiment field of the Perm Agricultural Research Institute. Soil samples of the plow layer (0–20 cm) taken at the end of the fourth cycle of the crop rotation in two nonadjacent replications of the following variants were used: (I) without fertilizers (control), (II) 10 t/ha manure per year, (III) NPK equivalent to 10 t/ha manure, and (IV) 10 t/ha manure + NPK equivalent to 10 t/ha manure. From 1971 through 2001, the soil received in mineral and organic fertilizers NPK (kg primary nutrients/ha) depending on the variants respectively $N_0P_0K_0$, $N_{1108}P_{830}K_{1543}$, $N_{1214}P_{734}K_{1550}$, and $N_{2422}P_{1464}K_{3086}$. The crop rotation was eight-course, including clean fallow, winter rye, wheat with clover undersowing, first-year clover, second-year clover, barley, potato, and oats.

The agrochemical properties, biological activity, and thermographic characteristics of soil HAs during the long-term use of fertilizers were given earlier [12–14]. Preparative isolation of HAs was accomplished by threefold extraction with a 0.1 N NaOH solution from decalcified soil. For cleaning out the clay fraction, we used the coagulator Na_2SO_4 and centrifugation. Humic acids were precipitated from the solution of humic substances cleaned of mineral admixtures by acidfication to pH 2–3 at 50–60°C. For further purification of the preparations, they were reprecipitated twice. The preparations were dried at 40°C. The elemental composition of humic acids was determined on a PerkinElmer CHN analyzer. The oxygen content was calculated from the difference.

Elemental composition of humic acids of sod-podzolic clay loam soil (upper row—mass fraction; lower row—atomic fraction); calculations are given for Ash-free preparations

Variant	Content, %				Atomic ratio			Degree of oxidation	Simplest formula
	C	H	O	N	H/C	O/C	C/N		
I	45.41	3.80	49.29	1.50	1.00	0.81	34.51	0.65	$C_{35}H_{34}N_1O_{28}$
	35.20	35.10	28.68	1.02					
II	50.02	4.30	42.84	2.84	1.03	0.64	20.55	0.26	$C_{21}H_{21}N_1O_{13}$
	36.78	37.75	23.69	1.79					
III	50.69	4.93	42.13	2.24	1.16	0.62	26.46	0.09	$C_{27}H_{31}N_1O_{17}$
	35.46	41.09	22.10	1.34					
IV	51.02	4.68	41.29	3.01	1.09	0.61	19.77	0.12	$C_{20}H_{22}N_1O_{12}$
	36.37	39.71	22.08	1.84					

RESULTS AND DISCUSSION

In the long-term permanent experiments, different fertilizer systems had a different effect on the elemental composition of HAs of the investigated soil. The HAs of soil of the control variant were the most oxidized ($W = 0.65$), weakly carbonized, and characterized by a minimum content of hydrogen and nitrogen (table). Such elemental composition is apparently due to the more severe conditions of humification of organic matter in long-unfertilized soil, under which conditions gradual breakdown and increase of the proportion of aromatic fragments in the structure of HAs occur. In this case, the soil is characterized by weak biological activity and low effective fertility [13].

Long-term manuring of soil was accompanied by the formation of HAs with a higher hydrogen and carbon content than in the control. The increase in carbon content was possibly related to already "prepared" HAs introduced with manure. The share of oxygen in HAs of variant II was 5% lower than in the unfertilized soil, and the nitrogen-containing groups were more expressed in the structure of the molecules. The H : C ratio and degree of oxidation indicated substantial participation of aliphatic fragments in the structure of HAs of soil fertilized with manure for a long time. However, HAs of this soil were quite deeply humified, which was probably related to the high biological activity of manured soil characterized by maximum emission of CO_2.

The long-term use of mineral fertilizers in an amount equivalent to 10 t/ha manure promoted the formation of HAs with an increased hydrogen and decreased oxygen content. The value of H : C was considerably higher than for HAs of unfertilized soil and was equal to 1.16. Consequently, an increase in the content of carbon-containing aliphatic radicals occurs in HAs under the effect of mineral fertilizers; in this case, the molecule is depleted in stable nuclear structures, which agrees with the results of [14].

The degree of oxidation of HAs was minimum and amounted to 0.09. The nitrogen content with the mineral fertilizer system changed insignificantly and was 1.34 at%. It should be noted that the structure of HA molecules of this variant was characterized by less resistant to microbiological and anthropogenic effects, which can lead to degradation and reduction of potential soil fertility.

Humic acids enriched with carbon, hydrogen, and nitrogen formed under the effect of the organomineral fertilizer system. The degree of their oxidation was 0.12. On the whole, the use of mineral and organic fertilizers separately and jointly promoted nitrogen enrichment of HA molecules and reduction of the degree of their oxidation. The data of elemental analysis of HAs of variant IV indicated development of both the central (stable structure) and peripheral parts actively participating in the cycle of matter.

An assessment of the character of transformation of HAs under the effect of various fertilizer systems by means of graphical-statistical analysis showed that two regions corresponding to the elemental composition of HAs are distinguished on the diagram of atomic ratios (figure). An independent position is occupied by HAs of the control variant, the transformation of which was accompanied by demethylation, carboxylation, and oxidation processes. The van Krevelen graphical-statistical analysis [15] demonstrated a higher degree of oxidation and lower degree of carbonization of soil HAs of this variant compared with the fertilized. The change in the composition of HAs of sod-podzolic soil under the effect of organic fertilizers is due to demethylation, dehydration, and weakly expressed oxidation processes. According to the data of the diagram, a maximum carbon content of aliphatic chains is inherent to HAs of variant III. Their transformation is determined by methylation, reduction, and hydration processes. The HAs of variant IV occupy, with respect to all positions, an intermediate place between HAs of soil fertilized only with manure or only NPK.

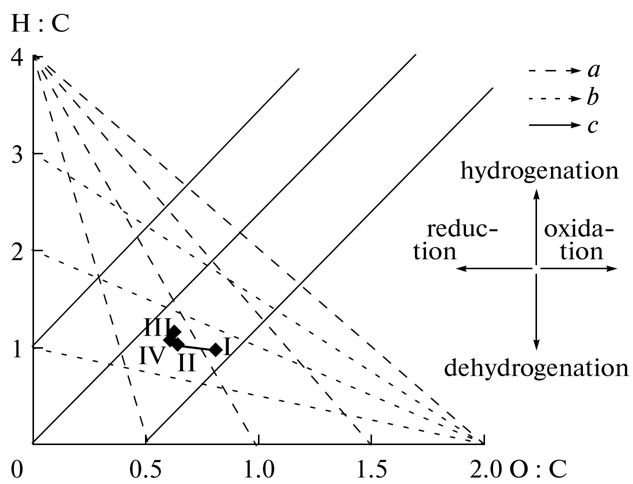

Diagram of atomic ratios H : C and O : C: (I–IV) experiment variants; (*a*) demethylation (CH_3 losses), (*b*) decarboxylation, (*c*) dehydration.

Thus, the method of elemental analysis made it possible to establish that HAs of sod-podzolic clay loam soils of Cisuralia keep the general principle of structure and delineated limits of the content of C, H, O, and N characteristic for sod-podzolic soils. However, they have particular zonal genetic features. The HAs of the investigated sod-podzolic soil are weakly carbonized and are characterized by an increased degree of oxidation and low nitrogen content in the composition of molecules.

The most probable causes explaining the special features of the composition and structure of HAs include the following:

the genetic characteristics of the soil (low degree of humification, fine texture, low provision with nitrogen, acid reaction, leaching water regime, etc.);

low level of soil biological activity, which leads to a decrease in the rate of mineralization of nonspecific organic matter and increase in the share of aliphatic side chains in the composition of molecules;

qualitative characteristics of organic matter entering the soil; this is mainly nitrogen-poor crop and root residues; the proportion of perennial leguminous grasses in crop rotations is mainly not higher than 25%, and in this case the stand is removed.

Thus, a tendency toward an increase of carbon content in HAs of fertilized soils was revealed. The mineral fertilizer system promoted an increase of the carbon content of the peripheral part of HA molecules, broadening of the H : C ratio, and decrease of the degree of their oxidation. Organic fertilizers (manure) provided some increase of the aromatic part in HA molecules, oxidation, and nitrogen enrichment. With the organomineral fertilizer system, transformation of HAs occurred toward an increase of the proportion of aromatic structures against the background of a high content of unsaturated aliphatic radicals. Such composition of HA molecules promotes their participation in biochemical processes and preservation of potential and increase of effective fertility of arable sod-podzolic clay loam soils.

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