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A Comparative Study of Elemental Composition of Water-Soluble Humic Substances, Humic Acids, and Fulvic Acids Extracted from Sod–Podzolic Soils

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Abstract—Elemental analysis of water-soluble humic substances extracted from three sod–podzolic soils was carried out. Data on elemental composition were compared to those of humic and fulvic acids extracted from the same soils.

Keywords: water-soluble humic substances, elemental composition.

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Humic substances (HSs) of the soil solution represent the most soluble part of humus; this determines their high mobility and activity with respect to biota [12]. In a series of works, the effects of dissolved organic substances were demonstrated on the interactions of contaminating substances with soil components; this resulted in the change in their condition and, as a consequence, an increase [6–8, 13] or decrease [9, 10] in their mobility and a change in their bioavailability [5]. Thus, the study of the HS of the soil solution is a topical problem that has interest for both practical and theoretical agrology.

The purpose of this work is to compare the elemental composition of water-soluble humic substances (WHSs) of sod–podzolic soils of various states of cultivation and the humic and fulvic acids that were isolated from these soils.

MATERIALS AND METHODS

In order to isolate the preparations of HSs, three soils were used from the areas of various state of cultivation: virgin sod–podzolic weakly soddy deep–podzolic medium loamy on the limon under the forest (S^SV), cultivated sod–podzolic medium-tillable medium loamy weakly eroded on the limon (S^SC), and arable sod–podzolic deep-tillable medium loamy (S^SA). Individual samples (each was about 20 kg) were taken from a section with an area of ~10 m^2 from the upper humous horizon at a depth of 0–5 cm. In the virgin version, the layer was preliminarily removed. Selected samples were dried to an air-dry state and passed through a sieve with a cell diameter 1 mm. From the prepared soil an average sample was made, which was used for chemical analyses and isolation of HS preparations. The properties of soils determined by the known procedures [1] and the names of the preparations isolated from them are given in Table 1.

Humic acids were separated using the standard procedure by extraction with 0.1 M NaOH with further acidification to a pH of 1–2 by 0.1 M HCl [4]. The preparations were purified with electrodialysis. Fulvic acids were separated by the method used for natural waters [11]: the solution that remained after

Table 1. Chemical properties of soils and conventional signs of the preparations of humic substances isolated from them

pH_{H_2O}	pH_{KCl}	OC, %	C_{HA}/C_{FA}	Sum of exchange bases	H_H	WHS	HA	FA
				mg eq./100 g				
Virgin sod–podzolic weakly soddy deep-podzolic medium loamy soil on the limon								
5.0	4.5	4.3	0.2	7.2	5.5	WHS–S^SV	HA–S^SV	FA–S^SV
Cultivated sod–podzolic medium-tillable medium loamy weakly eroded soil on the limon								
7.8	–	1.5	0.7	17.1	2.0	WHS–S^SC	HA–S^SC	FA–S^SC
Arable sod–podzolic deep-tillable medium loamy soil								
7.3	–	3.8	0.3	37.1	1.3	WHS–S^SA	HA–S^SA	FA–S^SA

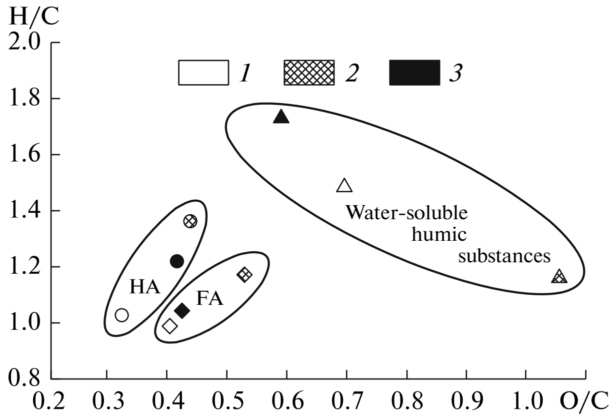
Table 2. Elemental composition of isolated preparations of WHS, HA, and FA

Preparation	Elemental composition (wt % on ash-free anhydrous sample)			Atomic ratios			Ash content, %
	C	H	N	H/C	O/C	C/N	
	Water-soluble humic substances						
WHS–S^{S}V	45.6	5.6	*	1.48	0.70	0	60.4
WHS–S^{S}C	37.5	3.6	*	1.16	1.05	0	46.7
WHS–S^{S}A	48.2	6.9	0.3	1.74	0.59	172	30.8
	Fulvic acids						
FA–S^{S}V	56.4	4.7	2.2	0.99	0.41	30	8.4
FA–S^{S}C	50.2	4.9	3.2	1.17	0.53	19	2.4
FA–S^{S}A	55.1	4.8	2.8	1.04	0.42	23	6.9
	Humic acids						
HA–S^{S}V	59.0	5.0	4.4	1.02	0.32	16	9.4
HA–S^{S}C	52.1	5.9	5.3	1.36	0.44	11	2.2
HA–S^{S}A	54.6	5.6	3.3	1.22	0.42	20	1.2

Note: * less than the detection limit.

the precipitation of HA was put through a column filled with Amberlite XAD-2 resin with further washing of chloride ions and desorption of FA from the resin by 0.1 M NaOH. The preparations that were obtained were purified using electrodialysis.

Preparations of water-soluble humic substances. A sample (1 kg) of air-dry soil passed through a sieve with a mesh size of 1 mm was filled with two liters of distilled water, thoroughly shaken, and left for a night. The aqueous extract was filtered through a Blue Ribbon paper filter and a membrane filter with a pore diameter of 0.45 μm for the separation of true dissolved organic substance from the colloidal. The procedure was carried out with 10 kg of each soil used. Filtered extracts were combined, acidified to pH 1–2 with 0.1 M HCl and put through a glass column filled with Amberlite XAD-2 resin for the separation of WHSs. Elution of the WHS preparation from the column and further desalination were analogous to those described for the separation of FA.



Arrangement of the preparations of humic substances of sod–podzolic soils on a Van–Krevelen diagram: (*1*) S^{S}V, (*2*) S^{S}C, and (*3*) S^{S}A.

The elemental composition of the preparations of humic substances was determined on a Carlo Erba Strumentazione-1106 CHN-analyzer (Italy); ash content was determined by combustion in a quartz tube (850°C; 40 min). The content of oxygen was calculated by the difference between the mass of the sample and the total content of ash and CHN.

The composition of the ash of HSs was determined by atom-emission spectroscopy with atomization of the sample in induction-bonded plasma (AES IBP). The element composition (Al, B, Ca, Cu, Fe, K, Mg, Mn, Na, Si, Ti, and Zn) was determined in salt-free solutions used for solid preparations (WHS and FA) or in solutions prepared by the dissolution of the sample in 0.1 M KOH (HA preparations).

RESULTS AND DISCUSSION

Preparations substantially differed by their elemental composition (Table 2). Atomic ratios (H/C) varied in the range of 0.99–1.74; this agrees well with the data of other researchers [3]. An increase in this value was observed in the sequence FA < HA < WHS. This confirms that along the preparations under study water-soluble humic substances have maximum unsaturation. The maximum values of the O/C ratio characterize the oxidation of the macromolecules of humic acids were noted for WHS of the virgin sod–podzolic soil. For HA–FA pairs isolated from one soil, the higher O/C value was observed for FA preparations

Table 3. The content of the ash in the preparations of WHS, HA, and FA, calculated from the data of AES IBP

Preparation	Content of the ash form of the mineral element, mg/g of organic substance											
	Na_2CO_3	K_2CO_3	$CaCO_3$	$MgCO_3$	Al_2O_3	Fe_2O_3	SiO_2	TiO_2	MnO_2	ZnO_2	B_2O_3	CuO
Water-soluble humic substances												
WHS–S^SV	72.3	1.8	8.6	1.2	3.5	1.9	2328	0.4	1.37	0.39	2.7	0.13
WHS–S^SC	29.2	1.9	4.8	1.5	1.6	0.7	618	0.2	0.95	0.15	1.6	0.14
WHS–S^SA	30.4	1.6	7.1	1.0	3.9	1.6	921	0.3	2.12	0.28	3.2	0.22
Fulvic acids												
FA–S^SV	6.2	170.0	1.3	0.2	0.8	0.4	14	0.1	0.17	0.07	1.2	0.02
FA–S^SC	18.6	963.1	13.9	0.4	1.7	0.6	47	0.1	0.52	0.10	3.3	0.16
FA–S^SA	25.5	21.5	9.4	0.5	2.9	1.9	100	0.2	0.56	0.29	9.6	0.09
Humic acids												
HA–S^SV	39.0	–*	0.8	0.3	2.9	3.1	5	0.4	0.24	0.03	0.2	0.03
HA–S^SC	58.8	–	1.6	1.4	6.8	2.5	16	0.3	0.30	0.15	0.3	0.05
HA–S^SA	49.8	–	0.9	0.7	4.4	1.5	11	0.1	0.28	0.06	0.3	0.05

Note: * the determination of potassium in HA solutions was not carried out, because solutions prepared from 0.1 M KOH were used for AES IBP analysis.

enriched in oxygen-containing functional groups. On the whole, the O/C ratio was in the following order: HA < FA < WHS. It is noteworthy that nitrogen was practically not detected in WHS preparations. An exception was made for the preparation obtained from arable soil; this can probably be determined by the introduction of nitrogen fertilizers into the soil.

The Van-Krevelen diagram built on the basis of the data obtained (figure), vividly demonstrates the differences in the elemental composition of the preparations of humic acids. As follows from the figure, humic substances of the water extract are more hydrated with respect to fulvic acids and the latter, in turn, are enriched with carboxylic groups compared to humic acids.

Thus, on the basis of the data of the elemental analysis it can be concluded that in comparison with humic and fulvic acids water-soluble humic substances have elevated unsaturation levels and are enriched with oxygen-containing functional groups and depleted in nitrogen.

The data from Table 2 confirm the abnormally high ash content of the isolated preparations of humic substances of the water extract. Therefore, they were analyzed for their contents of mineral elements by AES IBP. Using the results thus obtained and knowing the concentration of HSs, the molar content of the element in the preparation was calculated. After this, on the basis of the chemical properties of the given element and the conditions of the determination of the ash content (combustion of the preparation in an oxygen flow at 850°C), the form was proposed that it contains in the ash [2]. So, due to the thermostability of the alkaline and alkaline-earth metal carbonates, we proposed that they form carbonates in the conditions of the experiment, and other metals form oxides.

On the basis of the obtained values the mass of the ash form was calculated for each element on the unity of the organic substance of humic substances. The results are given in Table 3.

As follows from Table 3, the main ash components are silicon, calcium, aluminum, iron, and potassium. The preparations can be arranged in the following order by an increase in the content of silicon: HA < FA < WHS. Assuming that the procedure of the isolation of the preparations of humic acids of the water extracts of the soils included filtration through 0.45 μm membrane filter, it can be concluded that silicic-acid fragments are strictly bonded to humic substances and these are not mechanical admixtures. This probably confirms that during the extraction of the isolated preparations the humic acids are mainly represented by organomineral compounds.

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