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CHARACTERISTICS OF HUMIC ACIDS FROM UNDER CROP ROTATIONS WITH DIFFERENTIATED CEREAL SHARE

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A b s t r a c t. This paper presents the results of studies carried out to estimate the influence of crop rotation, with diversified cereal shares on the humic acid characteristics. The tested range covered humic acids separated from the following soil types: degraded chernozem developed from loess, Orthic Luvisol developed from boulder clay, Orthic Luvisol developed from loess. Samples were taken from the soil arable layer being under many-year crop rotation with a differentiated share of cereals (50 and 100%).

The results obtained show that soil use affected quality indices of humic acids. In the lessive soils under cereal monocultures, an increase of the atomic H:C ratio was observed in humic acids. This allows for a conclusion that the monoculture system causes an increase in the content of aliphatic structures in humic acid molecules or a decrease in the condensation degree of their nuclei. Moreover, a decrease in the optic density of humin solutions given in A_{465} values was found in the humic acids under cereal monocultures which proves a marked direction of changes.

In the case of humic acids extracted from chernozem, an analysis of elemental composition did not show any clear differentiation in the crop rotation with a 50% cereal share and a monoculture of cereal plants. The analysis of optic properties indicates a growth of the optic density (value of the E_4:E_6 ratio decreases) in the variant with a cereal plant monoculture which may suggest growth in the humification of individual humic acids.

K e y w o r d s: crop rotations, cereal share, humic acids, elemental composition, spectral properties.

INTRODUCTION

In the research on soil humus, there is a constant search for physico-chemical methods and indices that would enable a more precise evaluation of humus properties and structure. Elemental composition, as well as spectrophotometric properties of humic acids are characteristic for the soils with clear genetic differences.

These indices are sometimes used for the evaluation of the influence of agrotechnical factors on the structure of soil humus [1,2,5,8].

In the present research, evaluation of the effect of crop rotations with differentiated cereal share on the properties of humic acids was made using the indices mentioned above. Few investigations have been previously carried out on the trends of the humic acids quality indices related to crop rotation type [2,3,8,9].

The present paper gives results of research on humic acids from the soils of different origins, used in the Norfolk crop rotation and under a monoculture of cereal plants.

MATERIALS AND METHODS

The research included humic acids isolated from the following types of soil (Table 1): degraded chernozem derived from loess (A); soil lessive derived from boulder clay (B); soil lessive formed on loess (C).

Table 1. Mechanical composition and some properties of the soils investigated

Experimental field	Horizon	Grain size distribution in % (mm)			pH_{KCl}	Humus (%)	$CaCO_3$ (%)	Available forms (mg 100 g^{-1} soil)		
		1-0.1	0.1-0.02	<0.02				P_2O_5	K_2O	Mg
A	A_p	8	50	42	5.0	2.46	0.0	2.1	5.4	12.8
B	A_p	7	59	34	5.8	1.63	0.0	12.3	11.0	9.4
C	A_p	56	25	19	5.3	1.52	0.0	5.8	5.8	2.6

Samples taken for humic acid investigations came from the arable layer, from underneath many-year crop rotations with a differentiated cereal share (50% and 100%). An average mineral fertilization per crop rotation was 360 kg NPK ha^{-1} on the chernozem and soil lessive derived from boulder clay, whereas on the soil lessive formed on loess, it was 240 kg NPK ha^{-1}.

Humic acids were extracted with a mixture of 0.1 M $Na_4P_2O_7$ + 0.1 M NaOH using the Kononowa-Bielczikova's method [7]. The following features were determined in the humic acid preparations: ashness, elemental composition - CHN, with the Perkin-Elmer analyser - type 2700, oxygen (in fact O+S) was calculated from the difference. The following spectrophotometric investigations were made:

- optic properties within the visible light range for of humic acid solutions with the concentration of 0.02% in 0.05 M $NaHCO_3$;
- ratio of the extinction values at a wave length of 465 nm and 665 nm (E_4:E_6) was calculated;

- values for E_{465} extinction in a 1 cm layer of 0.001% solution in 0.05 M Na-HCO_3 were given.

Adsorption spectra of humic acids solutions were investigated using a spectrophotometer Hitachi UV-VIS.

Spectrophotometric analyses together with the values of atomic ratios of H:C and O:C, calculated on the basis of elemental analysis, were treated as the parameters that describe properties of the investigated humic acids.

RESULTS AND DISCUSSION

The results on the elemental composition of the analysed humic acids indicate their clear typological distinction (Table 2). Humic acids from chernozem, as compared to humic acids extracted from lessive soils, are different, and especially their carbon content is higher and hydrogen and nitrogen content is lower. It proves differentiation in the composition of soil humic acids from different taxonomic units. Humic acids separated from chernozem also have a higher internal oxidation. Moreover, they have greater molecular mass than the humic acids from lessive soils.

In order to compare elemental composition of humic acids separated from the investigated soils and to evaluate the influence of the cultivation system on their structure, diagrams of atomic ratios of H:C and O:C were elaborated (Fig. 1).

Different character of humic acids isolated from chernozem to those from soil

T a b l e 2. Elemental composition of humic acids in atomic percentage (converted into ashless mass); degree of internal oxidation; mass of basic molecules of the analysed humic acids

Cereals share in crop rotation (%)	C	H	O	N	H:C	O:C	ω= (20-H):C	Formula	Mass of the basic molecule
Degraded chernozem derived from loess									
50	39.89	34.70	23.13	2.27	0.86	0.58	0.289	$C_{18}H_{15}O_{10}N$	405
100	40.09	35.38	22.35	2.17	0.88	0.56	0.232	$C_{18}H_{16}O_{10}N$	406
Soil lessive derived from boulder clay									
50	36.87	39.93	20.64	2.55	1.08	0.56	0.036	$C_{14}H_{16}O_8N$	326
100	36.39	41.07	20.03	2.50	1.13	0.55	-0.027	$C_{14}H_{17}O_8N$	327
Soil lessive derived from loess									
50	38.44	39.04	19.78	2.74	1.02	0.51	0.013	$C_{14}H_{12}O_7N$	306
100	36.34	39.43	21.56	2.66	1.09	0.59	0.101	$C_{14}H_{15}O_8N$	325

lessive is especially clear when the results of elementary analysis are presented graphically. In the van Krevelen's scheme, humic acids from chernozem cover a clearly separated area, which indicates their differentiated character as compared to the humic acids from the lessive soils.

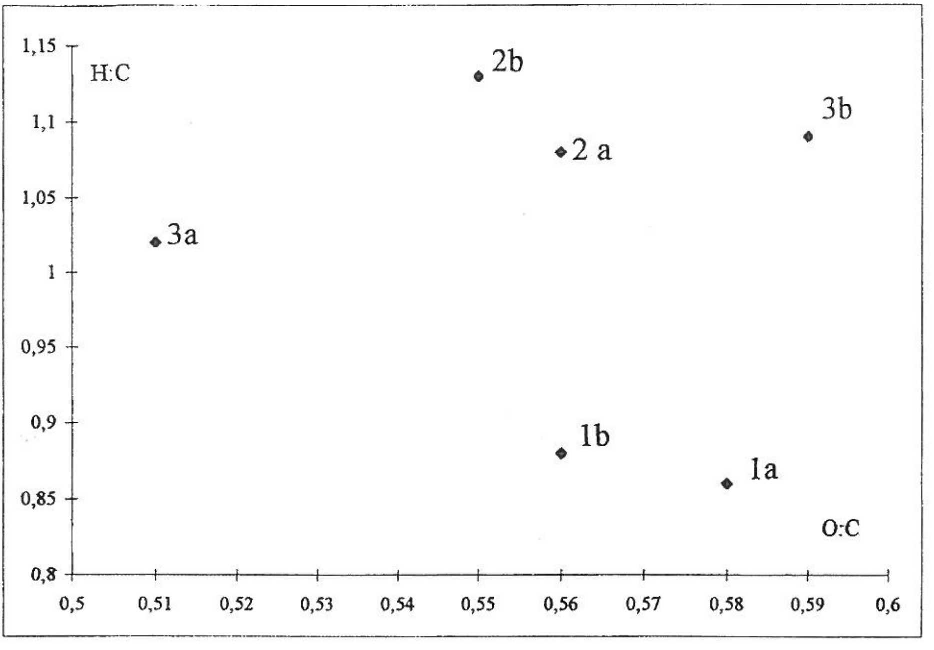

Fig. 1. Diagrams of H:C and O:C atomic ratios of the analysed humic acids. 1 - degraded chernozem derived from loess; 2 - soil lessive derived from boulder clay; 3 - soil lessive derived from loess; a - 50% share of cereals in crop rotation; b - 100% share of cereals in crop rotation.

In the described soils, the way of utilisation affected the nature of its basic units, i.e. humic acids (Table 2). In the lessive soil derived from boulder clay, an increase in the hydrogen content was observed in the humic acids from underneath a monoculture, as compared to the humic acids from under a Norfolk crop rotation. A decrease in the carbon content was observed underneath a monoculture in the humic acids of the lessive soil formed on loess. In the humic acids of both lessive soils, in the monoculture variant, the atomic ratio of H:C had higher values when compared to the crop rotations with a 50% share of cereals.

The smallest differences in the values of the atomic H:C ratio between a monoculture and a Norfolk crop rotation, were observed in the humic acids extracted from chernozem. Numerical values of the atomic H:C ratio allow us to evaluate the structure of humic acids; those values are inversely proportional to the aromatics of organic compounds. The values of the atomic H:C ratio presented above, and an increase of the humic acids from under the monocultures, allow us to conclude that cereal monocultures increase aliphatic structures in the molecules of humic acids or decrease condensation degree of their nuclei.

The presented H:C and O:C diagrams indicate that humic acids from under the cereal monocultures are better hydrated than humic acids from under a Norfolk crop rotation (the smallest difference was on the chernozem). Humic acids from under cereal monocultures of chernozem and lessive soil derived from clay are less oxidised, as compared to the humic acids from the Norfolk crop rotation. Humic acids from under the cereal monoculture of a lessive soil derived from loess are higher oxidised than the humic acids from under the rotation with a 50% share of cereals.

The presented results of the elemental composition indicate that it is conditioned not only by the habitat factors but it can also be modified, to a lesser degree, by the kind of crop rotation used.

Beside the above analysis that provided information on the mutual relations between the main elements included in humic acids, spectral analysis of humic acids was carried out (in fact the research on solutions of their salts - humins). Changes in the optical density of sodium humins were presented in values of E_{465} and E_4:E_6 and shown in Table 3.

The analysis of indices of the optical properties of the investigated humic acids proved a clear difference in the E_{465} value of the types, as well as a tendency of changes related to the type of soil usage. The highest E_{465} values were observed in the humins from chernozem (0.07). The above mentioned values of extinction are within the range that characterises humic acids of medium optic density [6]. The range of E_{465} extinction values for the solutions of humins from lessive soils (0.046-0.06) qualifies them as humic acids of low optic density [6]. E_{465} denotations proved that the optic density of humins is also conditioned by the kind of crop rotation. In the lessive soils, a monoculture usage system caused a decrease in the optic density of humic acids expressed as E_{465} values. It was especially clear in the humic acids extracted from the lessive soil derived from loess. In the humic acids from under a Norfolk crop rotation, the E_{465} value equals 0.066, and from under a monoculture, it equals 0.046 (Table 3). Absorption of radiation in the range of UV-VIS by humin solutions decreases with a decreasing aromatic carbon ratio in the nucleus to carbon in the aliphatic chains. In the case of the humin solutions from chernozem, the values of extinction - E_{465} were higher in the variant from under the cereal monoculture. Within the presented E_4:E_6, values the lowest

Table 3. Spectrophotometric properties of humic acids

Cereal share in crop rotation (%)	E_{465}	E_{665}	$E_4:E_6$	E_{465} (0.001%)
Degraded chernozem derived from loess				
50	1.420	0.320	4.44	0.071
100	1.525	0.400	3.81	0.076
Soil lessive derived from boulder clay				
50	1.000	0.200	5.00	0.050
100	0.900	0.180	5.00	0.045
Soil lessive derived from loess				
50	1.200	0.250	4.80	0.060
100	0.950	0.200	4.50	0.045

are those for the solutions of humic acids from chernozem. This correlates with a higher carbon content and greater molecular mass of humic acids separated from chernozem (Table 2). Colour coefficients of $E_4:E_6$ for the solutions of humic acids extracted from lessive soils have the values of 4.5-5.

In cases of both lessive soils, the usage system did not affect the value of the $E_4:E_6$ coefficient. For the solutions of humic acids from chernozem under a cereal monoculture, the values of the $E_4:E_6$ coefficient were lower (3.8) than from under crop rotation (4.4). Absorption measurements of humic acids solutions related to the data on the elemental composition allowed us to prove differences in the structure of humic acids separated from typologically different soils, as well as within the type between crop rotations with different cereal share.

Comparing the properties of humus substances extracted from soils of arable fields on which cereals were grown in monoculture and the Norfolk crop rotation, as well as drawing conclusions, require great caution.

The results obtained show that the usage method affected quality indices of humic acids especially in the lessive soils. In the lessive soils under cereal monocultures, an increase of the atomic ratio of H:C was observed in the humic acids. This allows us to conclude that a monoculture system causes an increase in the content of aliphatic structures in humic acid molecules or a decreases in the degree of their nuclei condensation. Moreover, a decrease in the optic density of humin solutions given in E_{465} values was noted in the humic acids under cereal plant monocultures which proved a marked direction of changes.

In the case of humic acids extracted from chernozem, analyses of elemental composition did not show any clear differentiation in the crop rotation with a 50% cereal share and a monoculture of cereal plants. An analysis of optic properties indicates an increase in optic density (value of the E_4:E_6 ratio decreases) in the variant of a cereal plant monoculture which may suggest an increasing humification of individual humic acids.

The present study on humic acids from under crop rotations with differentiated cereal share can be related to the evaluation of the effect of crop rotations and different kinds of monocultures on humic acid properties. Such evaluations were made by many authors [2-5,8].

CONCLUSIONS

Within the analysed typological units (chernozem, lessive soils), a monoculture system of usage affected humic acids properties mainly in lessive soils. Humic acids of the lessive soils from under cereal plant monocultures, as compared to humic acids from crop rotations with a 50% cereal share, have higher values of the H:C atomic ratio, as well as lower optic density given in indications of the E_{465} extinction.

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