EFFECT OF THE SOIL TYPE ON THE MOLECULAR STRUCTURE, PROPERTIES AND CONDITIONS OF OCCURRENCE OF HUMOUS ACIDS

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A b s t r a c t. The study presented here concentrates on the characteristics of the humous compounds of humic and fulvic acid fractions of β-humus, originating from the typologically differentiated soils (podzolic soil and chernozem). The soils were chosen so as to emphasize differences between chemical structure and degree of aromatic nucleus condensation in the humous acids isolated from them.

It was found that the structure of the humous substances isolated from the podzolic soil is characterised by the lowest degree of condensation of the aromatic nucleus and the lowest polymerisation, while the humous acids from the chernozem are characterised by the highest degree of condensation of the aromatic nucleus and the strongest polymerisation.

K e y w o r d s: humous acids, molecular structure properties, soil types.

INTRODUCTION

Many papers point to significant modyfying role of soil forming processes on the properties of the humous acids [6,7,9,10].

It should be stressed that all and any research concerned with humous acids is aimed at the determination of their molecular structure and chemical composition which have not been satisfactorily explained yet as there is a variety of substrata that participate in their formation. The complexity of humous substance structures is related to the type and utilisation of soils [4,6,9,10].

Differences between the chemical structures of humous acids from the podzolic soil and the chernozem are confirmed by the tests on their elementary composition and the calculated ratios of C/H and C/N, as well as by the sorptive capacity which depends on the presence of carboxyl and hydroxyl functional groups of phenols, whose hydrogen takes part in exchange reactions. The reason for

the differentiated acid power of the functional groups is their location in the struc-
ture of the molecules, positioning within the aromatic ring or in the lateral ali-
phatic chains, the kind of substituents, and the degree of molecule polymerisation
[1,3,4].

One of the methods used to determine these properties is conductometric titra-
tion [2,7,12]. Application of this method yielded different courses of curves for the
relation between suspension pH and specific conductivity. In the case of humic
acid, specific conductivity of the suspension decreased with increasing pH, while
in the case of β-humus, specific conductivity increased with increasing pH [7].

MATERIALS AND METHODS

Humous fractions (humic acids and fulvic acid fraction of the β-humus) were
isolated from the humus-ferrous horizon (BHs) of a podzolic soil from a pine wood at
Hedwiżyn, and from the AH2 humus horizon of chernozem from Oszczów.

The soils differed from each other in order to emphasize differences in their
chemical nature and the degree of condensation of the aromatic nuclei of their hu-
mous acids [9,10].

The structure of the humous substances from the podzolic soil is characterised
by the lowest degree of condensation of aromatic nucleus, and by the weakest po-
lymerisation, while the humous acids from the chernozem are characterised by the
highest degree of condensation of aromatic nucleus and by the strongest polymeri-
sation. This strongly differentiated molecular structure of the humous acids from
the podzolic soil and the chernozem (further supported by tests presented below)
is, largely, the result of the character of soil formation processes, that are different
in the two types of soils [6].

Extraction of humous fractions from the soils was performed by means of the
Schnitzer's method [13], in the following way: a soil sample was flooded with
0.5M solution of NaOH at a ratio of 1 to 10, and then left for 24 hours in a nitro-
gen atmosphere, at room temperature, stired now and then. Conducting extraction
in the nitrogen atmosphere is necessary to avoid redox processes, to which qui-
none and phenol systems, as well as their derivatives present in the aromatic core
of humous acid particles, are highly sensitive. Humous acids extracted in this way,
were then separated from the non-soluble residue by centrifuging. Next, the solu-
tion was acidified to pH 2 using 6 M solution of HCl, and left for till the following
day. The sediment of humous acids was separated from the slution of fulvic acids by
centrifuging. Humic acid sediment obtained was purified by shaking with HCL-HF

mixture for 12 hours. The solution was separated from the sediment by centrifuging. The operation was repeated three times, and then the humic acid preparations were washed with distilled water until reaction to chlorides was eliminated.

The acid filtrate of fulvic acids was used to precipitate β-humus using the Stevensen's method [14]. For this purpose, the solution was alkalized to pH 4.8 using 5 M NaOH and 0.1 M NaOH. The resulting sediment of β-humus was centrifuged from the residue and washed twice with distilled water.

Preparations of humous acids, in the form of a sediment after purification and filtration, to avoid oxidation effect, as follows: they were placed on crystallizers and, under vacuum (12 mm Hg), their moisture content was lowered to the level corresponding to a pressure of $P/Po = 0.5$. Samples were initially dried, and then placed in an exsiccator, over concentrated sulphuric acid for further gradual drying.

The humous acid preparations obtained as described above, were then used for the following analyses:
-   ash content was determined by burning the preparations in a muffle furnace at a temperature of 800 °C;
-   elementary composition (C, H, O, N) was determined using the dry burning method;
-   C/H and C/N ratios were calculated;
-   content of carboxyl and phenol groups, i.e. the total capacity, was determined using the Kucharenko and Dragunova's method [4].
-   exchange capacity was determined by the same method as above;
-   conductometric titration was performed, using a TTT 80 Titrator with a Type GK 240 1 C compound electrode, in nitrogen atmosphere and at a constant temperature to prevent oxidation. A Polish-made CC-311 conductometer was used (made by Elmetron), to determine changes in electrolytic conductivity in the course of titration. That way the relation between the suspension pH and the specific conductivity was determined. Samples of 0.1 g were used for the determinations; 10 ml of 0.01 M NaOH with 0.01 M NaCl was added when titration was performed by means of 0.1 M HCl with 0.1 M NaCl. NaCl was added to the solutions tested, as well as to the titrate, in the quantities that kept its concentration at 0.01 M/litre [11]. The purpose of this was to make sure that during titration, electrolyte activity did not change, while it was diluted with pure titrate.

RESULTS AND DISCUSSION

Analyzing the degree of contamination, elementary composition, C/H and C/N ratios, sorptive capacity and conductometric titration curve shapes, one observes

differences between humic acids and the β-humus fraction. The β-humus preparations are characterized by a high degree of contamination despite their careful purification. Content of contaminants in humic acids is from 3.98 to 5.25%, while in the β-humus preparations the contaminant content values varies from 22.17% to 35.13%. β-humus from the podzolic soil had a much higher ash content than the corresponding sample from chernozem, which resulted from a higher content of iron, aluminum, and other contaminants in the test horizon of that soil profile [6]. One can assume that the β-humus fraction is a permanent, organic-mineral combination occurring in soils. Humic acids have a much higher carbon content (from 55.9 to 56.5%), compared to the β-humus fraction which contains from 32.9 to 45.4% of C. In the case of hydrogen, on the other hand, the opposite relation was observed, as the β-humus fraction contained somewhat more H – from 5.7% to 5.8%, compared to the humic with the H content from 4.6% to 6.4%

Nitrogen content in humic acids varied from 2.8% to 3%, while that of oxygen varied from 35.0% to 35.9%. A differentiated and at the same time opposite nitrogen content was observed in the β-humus preparations. The preparation from the podzolic soil contained 1.5% of N, and from the chernozem - 4.2% of N.

Differentiated elementary composition brings about various values of quantitative ratios, which are used to characterise variability of humic acid [3-5,8]. Humic acids have a higher C/H ratio – falling within a range from 8.8 to 12.3 compared to the β-humus preparations in which C/H ratio varies from 5.7 to 7.9. This indicates a weaker aromatization of the β-humus preparations due to the lower C content and somewhat higher H content than in the humic acids. Although the β-humus preparations contain basic particles with a structure similar to that of the humic acids, they have less strongly formed aromatic nucleus.

The C/N ratio in the humic acids varies from 10 to 20.2. A considerably different, and at the same time greatly varied C/N ratio was observed in the β-humus preparations, where its value was 29.5 for the podzolic soil and 7.8 for the chernozem. The broad C/N ratio for the β-humus fraction from the podzolic soil (29.5) indicates slow humification and mineralisation of organic substance, producing slight amounts of mineral nitrogen (1.5%). The β-humus fraction from the chernozem showed a lower C/N ratio (7.8), which indicates intensive humification and mineralisation, leading to the production of greater nitrogen amount (4.2%), (Table 1).

The elementary composition of the humic acids was correlated with the results of the total and exchange sorptive capacity [1,3-5]. Humic acid from the podzolic soil had a total capacity of 2.31 me/100 g, while the humic acid from the chernozem 1.45 me/100 g, and the β-humus fraction 3.95 me/100 g. The exchange

T a b l e 1. Elementary composition (%) of dry mass cinderless and ash (%) humic acids (humic acids and β-humus)

Sample	Ash	C	H	N	O	C/H	C/N
Humic acids Podzolic soil	5.25	56.5	4.6	3.0	35.9	12.3	19.0
Humic acids Chernozem	3.98	55.9	6.4	2.8	35.0	8.8	20.2
β-humus Podzolic soil	35.13	45.4	5.8	1.5	47.3	7.9	29.5
β-humus Chernozem	22.17	32.9	5.7	4.2	57.1	5.7	7.8

capacity of the humic acid from the podzolic soil was 1.15 me/100g, while that of the humic acid from the chernozem 1.05 me/100 g (Table 2).

Considerable differences were observed in the molecular structure between the humic acids and the β-humus fraction, and between the humic acids from the podzolic soil and chernozem. This was also supported by the results of the con-ductometric titration (Figs 1 and 2). In the course of the titration the ionic compo-sition of the solution changes, and since ions differ in their mobility, the titration curve assumes a characteristic shape [2,12]. In the case of humic acid, specific conductivity observed showed a decrease of (in mS) with increasing pH of the sus-pension, while in the case of β-humus, the relation was opposite – the specific conductivity increased [7]. This can probably be ascribed to the differences in the molecular structure of those fractions. In its molecular structure, the β-humus has more hydrophilic groups, more lateral chains, a larger amount of functional groups – COOH, OH and others (which is confirmed by the total capacity determinations).

T a b l e 2. Total and exchange sorptive capacity, carboxyl and phenol groups in me/100g

Sample	Total sorptive capacity	Exchange sorptive capacity	Carboxyl groups -COOH	Phenol groups -OH
Humic acids Podzolic soil	2.31	1.16	1.15	1.15
Humic acids Chernozem	1.45	0.40	1.05	1.05
β-humus	3.95	-	-	-

Conductometric graph
Beta-humusu (chernozem)
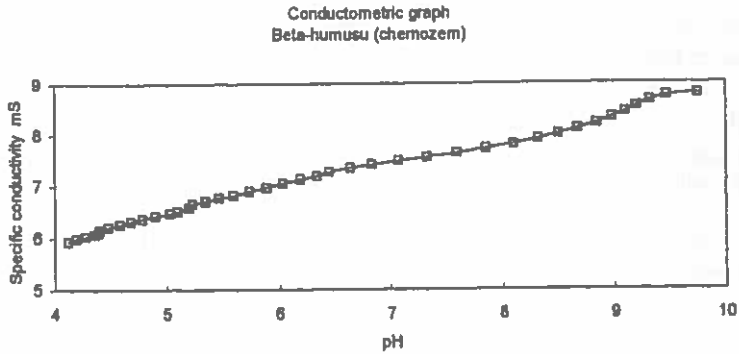

Fig. 1. Conductometric graph - β-humus.

Conductometric graph
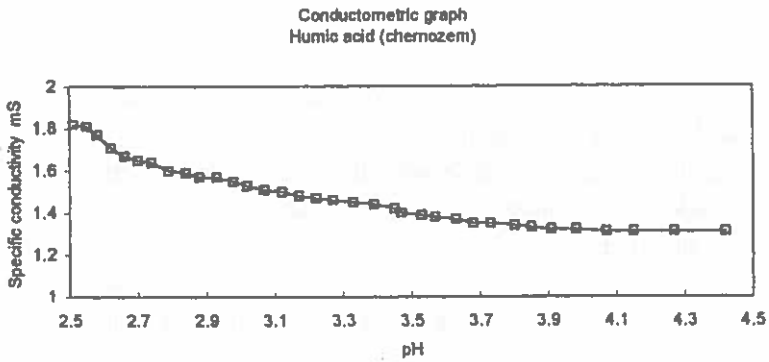**Humic acid (chernozem)**

Fig. 2. Conductometric graph - humic acids.

In such groups, hydrogen can be replaced by a variety of cations. In a strongly acid medium, hydrogen is strongly bound and not easily replaced by other cations. Only with increasing pH hydrogen gets ionized and can be replaced by other cations, which means that the process of ionic exchange prevails. This results in fundamental changes in the humus properties, and hence an increase in the specific conductivity. In the case of the humic acid, as pH increases, the particles of the humic acid begin to dissolve, therefore the number of less mobile particles grows and that results in a decrease in their specific conductivity.

CONCLUSIONS

1. The type of soil has a primary effect on the molecular structure, chemical composition, and the sorptive capacity of humous acids.

2. The present study confirmed differences between humic and fulvic acids. The fulvic acid fraction of β-humus is characterized by a high degree of contamination

(22.17-35.13%), which leads to the assumption that it is an organic-mineral combination of the soils that enhances their sorptive properties.

3. Humic acids have a higher degree of aromatisation, a lower content of active functional groups capable of ionic exchange, and therefore a lower sorptive capacity.

4. The β-humus fraction has a lower degree of aromatisation, a higher content of active functional groups, and therefore higher sorptive properties.

5. The conductometric curves, representing the relation between the specific conductivity of suspensions of humous acid preparations and pH, indicate that as pH increases in the β-humus, the specific conductivity notably increases, while in the case of the humic acid, an increase in pH results in a notable decrease in the specific conductivity.

6. The opposite courses of the conductometric titration curves for the humous acids are due to the differences of their molecular structure and to the resultant differences in the ionic exchange of the fractions under study.

REFERENCES

1.**Bulter H.**: Functional groups of soil humic acids. Diss. Illinois Univ., U.S.A.,1967.
2.**Davis H., Mott C.J.B.**: Titrations of fulvic acid fractions:Interactions influencing the dissociation-reprotonation equilibria. J. Soil Sci.,32, 1981.
3.**Grisina L.A.**: Gumusoobrazovanije i gumusnoje sostajanie poczv. Iz. Moscovskovo Universiteta, Moskwa, 1986.
4.**Kononowa M.**: Substancje organiczne gleby, ich budowa, właściwości i metody badań. PWRiL, Warszawa, 1968.
5.**Ghosh K., Schnitzer M.**: Macromolecular structures of humic substances. Soil Sci., 129, 5, 266-276, 1980.
6.**Kuźnicki F., Sklodowski P.**: Wpływ procesów glebotwórczych na zawartość żelaza i glinu w kompleksach próchniczno-mineralnych. Roczn. Glebozn., 20, 1, 3-23, 1969.
7.**Księżopolska A.**: The role of humic acids fractions in formation surface phenomena of soil material. Ph.D., Institute of Agrophysics, Polish Academy of Sciences Lublin, 1996 (in Polish).
8.**Księżopolska A., Flis-Bujak M., Żukowska G., Stawiński J.**: Chemical composition and surface area of β-humus fraction extracted from soil fertilized with organic wastes. Polish J. Soil Sci., 32(2), 45-51, 1999.
9.**Turski R.**: Charakterystyka związków próchnicznych w glebach Polski. Roczn. Nauk Roln., S. D-Monografie, 212, 1987.
10.**Turski R.**: Związki próchniczne gleb Polski. Roczn. Glebozn., 37, 2-3, 1986.
11.**Podsiadło H.**: Ćwiczenia laboratoryjne z chemii fizycznej. Skrypt Akad. Ekon., 1990.
12.**Shigemitsu A., Kumada K.**: An interpretation of the conductometric titration curve of humic acid. Geoderma, 19, 1977.
13.**Schnitzer M., Schluppli P.**: Method for the sequential extraction of organic matter from soils and soil fractions. Soil Sci. Soc. Am. J., 53, 1989.
14.**Stevensen F.J.**: Humus Chemistry. Genesis, Composition, Reactions, J. Wiley, New York, 1982.