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Study of the Biological Activity of Humine Substances for the Creation of Preparations against Desertification

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Abstract

Native and modified humic acids (HA) isolated from brown coals of Russia and Mongolia were studied. Their composition was characterized using technical and elemental analyses, and ^{13}C NMR (CPMAS) spectroscopy. A destructive alkylation of humic acids with butanol followed by debitumination, which changes the structural group composition of HA has been held. The biological activity of humic preparations in the form of sodium and potassium humates is investigated depending on the structural group parameters: the degree of aromaticity f_a, hydrophilic-hydrophobic parameter $f_{h/h}$ and parameter reflecting the ratio of aromatic and aliphatic fragments of organic mass of humic acids $f_{ar/al}$. It is shown that an increase in the degree of aromaticity HA leads to an increase in their biological activity.

Key words: desertification, humic acids; structural parameters; biological activity

INTRODUCTION

Desertification is the process of the irreversible change of soils and vegetation which may lead to complete destruction of the biospheric potential and to the transformation of a territory into a desert. At the territory prone to desertification, the physical properties of soils worsen, vegetation vanishes, ground waters become salty, biological productivity drops sharply, and the ability of ecosystems to recover is undermined.

The total area of territories prone to desertification exceeds 1 milliard ha almost at all the continents. Vast territories in the south of Russia, in Central Asia, in particular in Kazakhstan and Mongolia, are under the threat of desertification. In Russia, this process involves the territory of 50 mln ha, including the State Natural Biosphere Reserve "Chernye Zemly" in Kalmykia [1]. At present, among 182 mln ha of pasture lands in Kazakhstan, 14 mln ha have been completely disabled, and the total degradation area exceeded 50 mln ha [2]. In Mongolia, the area of non-desertified lands accounts for 22 %, weakly desertified territories occupy 35 %, medium desertification accounts for 26 %, strong desertification – 7 %, and very strong desertification – 10 % of the country territory [3]. For these and neighbouring countries, desertification may become a threat to the successful social and economic development and comprises a global ecological problem: 46 % of the area of all arable lands are prone to erosion. Counteraction to desertification includes a number of measures: recultivation of technogeneously disturbed lands, erosion control, development and introduction of land tenure systems providing high and stable productivity, improvement of the structure of sowing areas. At present, the most important task is to develop methods and preparations for this purpose.

The application of special humic preparations providing recultivation of the soil cover and stimulation of the productivity of agricultural and grazing cultures is a promising method to abate desertification. Humic substances (HS) attract special attention due to their biological activity to plants and soil organisms, as well as due to a number of specific properties improving the sate of soil.

Substantial amounts of HS are present in solid combustible fossils (SCF) with a low degree of coalification. Along with many functions such as accumulative, transport and protective, HS play also regulator and physiological functions [4]. The regulatory function involves the formation of the structure and water-physical properties of soil, such as the formation of agronomically valuable lumpy-granular structure, improvement of porosity and water permeability of heavy soils, prevention of the formation of cracks, crusts, regulation of ion exchange reactions between the soil and aqueous solutions; effect on the buffer capacity and the thermal regime of soil. Treatment with humates (GumNa, GumK, $GumNH_4$) causes an increase in the water-retaining capacity of soil by a factor of more than 10. This phenomenon is especially important for sandy ground. Attention is also attracted to the ability of HS to enhance the stability of plants against unfavourable environmental factors: excess doses of mineral fertilizers, high or low temperatures, chemical means of plant protection, radiation, *etc*. [5]. It was stressed [5–9] that small HS doses have a stimulating action on the development of plants, the consumption of nitrogen from mineral fertilizers by plants. Large doses of humates (above 0.1 %) inhibit the development of plants.

The physiological function of HS involves the action of HS on various organisms including soil microorganisms. The use of humates in agriculture causes an increase in the crop capacity of cereals, fodder crops, vegetables by 10–30 % as average. In addition, the seed germinating capacity and emergence of seedlings increase, plant metabolism improves, the absorption of mineral substances increases, and the root formation capacity enhances.

The most mobile and reactive part of HS is humic acids (HA). In the water-soluble forms, they take an active part in redox processes in cells, being the sources of activated oxygen on the one hand and hydrogen acceptor on the other hand [10].

The direct dependence of the biological activity of HA on the content of carboxylic and phenol hydroxyls was not detected in previous experiments [11]. It is assumed [12] that their biological activity depends on the concentration of free radicals and the content of quinoid groups and phenol hydroxyls, and is determined by the ability to participate in redox reactions in a plant cell and the enhancement of these processes according to the theory of Bach–Paladin–Szent–Gyorgyi. Humic acids with the lower content of quinoid groups exhibit lower biological activity. For the HA of brown and oxidized coal, the content of carboxylic groups is 1.8–5.5, phenol hydroxyls – 0–6.0, quinoid groups – 0.6–4.0 mg-equiv/g [12]. The results of the tests of humic preparations with respect to cereals point to a directly proportional dependence of the biological activity not only on the degree of aromaticity f_a but also on other structural groups parameters, such as the hydrophilic-hydrophobic parameter $f_{h/h}$ and the parameter $f_{ar/al}$, depicting the relations between the aromatic and aliphatic fragments of the organic mass of HA [13].

The biological activity was also tested with a number of natural and modified HS obtained from various sources [14]. For the purpose of modification, some processes were carried out: hydrolysis, reduction, alkylation with methyl, detachment of alkyl fragments. It was discovered that the most efficient HS are those oxidized with potassium permanganate and alkylated with methanol.

So, the use of GS allows one to improve soil structure, recover and enhance its fertility, crop capacity, plant germination, plant stability against negative factors, and is one of the methods to solve the problem of soil desertification. At present, there is no united opinion on the active factor and the mechanism of the biological stimulation of plants and soil microorganisms by HS and the connection of this factor with HS structure. Because of this, it is necessary to carry out fundamental systematic research aimed at obtaining the structure – property dependences between the elemental and structural group composition of HS and the presence of biological activity.

The goal of the present work was to study the biological activity of HA isolated from some brown coals and peat, and substantiation of the choice of raw material sources of HA to obtain precursor preparations for the abatement of desertification.

EXPERIMENTAL

The substances chosen for investigation were humic brown coals from the Baga-nuur (BAG) and Shivee-Ovoon (ShO) deposits (Mongolia), Tisul deposit of the Kansk-Achinsk basin (BUTS), its naturally oxidized form (BUTSO); Tyulganskoe (BUT) and Mayachnoe (BUM) deposits in the Southern Urals (Russia); peat from the Krapivinskoe deposit in the Kemerovo Region (PK). Humic acids in the solid form were obtained from sodium or potassium humates (HumNa and HumK, respectively) through sedimentation by hydrochloric acid [15]. A series of modified humic acids (HAA) were isolated from the alkylated samples of coal and peat using the procedures described in [16, 17].

Initial coal samples, peat and HA samples were characterized by means of elemental technical and functional analysis (Tables 1 and 2), and ^{13}C NMR spectroscopy (Table 3).

The high-resolution ^{13}C NMR spectra in the solid phase were recorded with a Bruker AVANCE III 300 WB instrument at the frequency of 75 MHz using a standard procedure of cross-polarization and magic angle spinning (CPMAS).

To determine the total content of acid groups (carboxylic and hydroxyl), barite method was used. The content of carboxylic groups was determined using the acetate method [18], and hydroxyl groups were determined as a difference between the total contents of acid and carboxyl groups. The

TABLE 1

Results of technical and elemental analysis of the samples under investigation, mass %

Samples	W^a	A^d	V^{daf}	C^{daf}	H^{daf}	$(O + N + S)^{daf}$ from difference	$(HA)_t^{daf}$
BAG	–	26.3	52.6	67.5	4.4	28.1	31.2
HumNa BAG	6.9	17.9	–	60.5	3.8	35.7	52.8
ShO	–	31.6	52.2	70.5	4.4	25.1	34.0
HumNa ShO	16.2	24.8	–	66.8	4.5	28.7	58.9
BUTS	8.3	10.3	48.3	61.4	5.0	33.5	22.1
HA HumK BUTS	5.0	4.0	–	60.8	4.2	35.0	–
HA HumNa BUTS	3.8	1.9	–	59.8	3.5	36.7	–
BUTSO	10.0	43.5	80.3	69.3	6.0	24.7	60.9
HA HumK BUTSO	4.6	17.0	–	46.2	3.2	50.6	–
HA HumNa BUTSO	10.6	10.9	–	59.7	6.2	34.0	–
BUT	6.5	23.5	67.3	66.2	7.0	26.8	39.1
HA HumNa BUT	3.63	7.57	–	62.9	5.8	31.3	–
BUM	5.3	20.0	63.6	58.6	6.8	34.6	73.5
HA HumNa BUM	–	–	–	57.3	7.4	35.3	–
PK	11.2	12.3	72.6	46.8	5.9	47.3	32.4
HA HumNa PK	–	–	–	45.1	5.5	49.4	–

Notes. 1. W^a – analytical humidity; A^d – ash content; V – yield of volatile components; C, H, O, S, N – element content; $(HA)_t^{daf}$ – yield of free humic acids; daf – dry ash-free coal mass. 2. Dash means that determinaiton was not carried out.

TABLE 2

Content of active oxygen-containing groups in HA of coal samples from the deposits: Baganur (BAG) and Shivee-Ovoo (ShO), mg-equiv/g

Samples	Content of acid groups			Quinoid groups
	Carboxylic groups	Phenol hydroxyls	Sum	
HA HumNa BAG	4.33	3.42	7.75	2.75
HA HumNa ShO	5.13	3.52	8.65	3.17

TABLE 3

Integral intensities of special regions and structural parameters of the samples of coal and HA according to the data of ^{13}C NMR, %

Sample	Chemical shift, ppm							Structural parameters		
	220–187	187–165	165–145	145–108	108–90	90–48	48–5	f_a	$f_{h/h}$	$f_{ar/al}$
	C=O	COOH(R)	C_{Ar-OH}	C_{Ar}	$C_{O-Alk-O}$	C_{Alk-O}	C_{Alk}			
BUTS	4.4	4.7	4.2	19.1	3.5	7.5	55.6	23.3	0.3	0.3
HA HumK	4.4	6.1	5.0	15.1	4.2	8.0	55.2	20.1	0.4	0.3
HA HumNa	4.4	7.3	5.4	17.9	3.6	10.8	50.7	23.3	0.5	0.4
BUTSO	2.6	6.0	8.9	31.9	5.4	12.7	30.3	40.8	0.6	0.8
HA HumK	3.8	6.7	9.5	33.1	6.3	14.0	25.4	42.6	0.7	0.9
HA HumNa	3.5	7.4	8.2	32.7	6.3	14.8	26.8	39.9	0.7	0.8
BUT	4.2	5.8	3.6	25.1	19.6	19.6	41.6	28.7	0.5	0.5
HA HumNa	4.3	7.9	6.8	22.5	4.9	16.3	36.5	29.3	0.7	0.5
BUM	4.3	4.1	4.5	28.3	6.1	12.5	40.2	32.8	0.5	0.6
HA HumNa	4.7	4.9	3.7	26.1	5.9	13.7	41.1	29.8	0.5	0.5
PK	2.7	8.2	4.8	11.4	55.7	55.7	17.2	16.2	2.5	0.2
HA HumNa	3.4	8.0	7.0	15.8	9.2	38.5	18.1	22.6	1.95	0.3

content of quinoid groups was determined by means of their reduction by tin (II) chloride in the alkaline medium, followed by the titration of its excess with the solution of potassium dichromate [19]. Calculation of the content of functional groups was carried out taking into account the results of blank experiments.

To establish the 'structure – property' dependence, we carried out tests (phytotesting) to determine the biological activity of HA in the form of water-soluble potassium and sodium humates (concentration 0.02 %), obtained both from the initial coal and peat samples and those modified by alkylation, under the field and laboratory conditions. The seeds used in the experiments were varietal wheat "Novosibirskaya 89", garden radish of "Smak" variety; experiments were carried out according to the procedures described in [20, 21] and according to GOST (State Standard) 12038–84 and GOST 54221–2010 [22, 23]. The biological activity of HA and HAA was also determined from an increase in the length of wheat roots Δ (excess over the reference, %) and from the index of phytoactivity (IP) (% with respect to the reference) taking into account the energy of seed germination (GE), root length (RL) and seedling height (SH). For this purpose, the seeds were germinated at a constant temperature of 20 °C in the dark in special germinator troughs. The IP is a generalized index depicting the deviations from the reference and is calculated as an average value of the sum of GE, RL and SH expressed in the fractions of the unit:

$$IP = \frac{(GE + RL + SH)}{3 \times 100}$$

where GE, RL and SH are average values over three troughs, measured at the fifth day from the start of the experiment.

Distilled water was used for the reference test. The relative error in all experiments was 3–5 % for the significance level $\alpha = 0.05$.

Statistical treatment of the experimental data was carried out by determining the Spearman coefficient of rank correlation with the help of the software package Microsoft Office Excel 2007 [24].

RESULTS AND DISCUSSION

On the basis of the analysis of literature data [12, 14, 25], three parameters were chosen for the detection of the correlation between the structural-phase composition of HA and their biological activity (see Table 3), calculated from the data of ^{13}C NMR (CPMAS) spectra of coal, peat and HA samples.:

1) the degree of aromaticity:
$f_a = C_{Ar-OH} + C_{Ar}$;
2) hydrophilic-hydrophobic parameter:
$f_{h/h} = (C{=}O + COOH(R) + C_{Ar-OH} + C_{O-Alk-O} + C_{Alk-O})/(C_{Ar} + C_{alk})$;
3) aromaticity/aliphaticity:
$f_{ar/al} = (C_{Ar-OH} + C_{Ar})/(C_{O-Alk-O} + C_{Alk-O} + C_{alk})$.

Results of laboratory experiments on the evaluation of the effect of HA on plant development show that the use of all preparations under in-

TABLE 4

Index of phytoactivity of humic preparations in the experiment with garden radish

Version	% to the reference			Phytoactivity index
	Germination energy	Root length	Seedling length	
HumNa BUT	100.8	135.8	113.6	1.17
HumNa BUTSO	112.0	183.4	137.3	1.44
HumK BUTSO	112.0	165.3	124.3	1.34
HumNa BUTS	112.0	185.5	120.9	1.39

vestigation has a positive effect on the energy of seed germination, the length of roots and seedlings (Tables 4 and 5). The effect of steeping the seeds of garden radish in HA solutions is most strongly expressed for the root length (see Table 4). As a result, the integral IP for HA is within the range 1.17–1.44 in comparison with the reference. The maximal value is peculiar to humates obtained from the naturally oxidized form of brown coal from the Tisul deposit (HumNa BUTSO). The statistical treatment of the data showed a reliable correlation of IP with parameters f_a and $f_{ar/al}$ of the structural-group composition of HA, which is determined by the intensity of NMR spectral regions C_{Ar} and C_{Alk}, as well as $C_{Ar\text{-}OH}$ and $C_{Alk\text{-}O}$. To a lower extent but at a rather high level, the length of radish roots is affected by the amount of carboxyl groups in HA detected from the chemical shift of the NMR spectrum in the region 165–187 ppm. However, the correlation coefficient of the linear function describing the dependence of IP HA on the content of carboxylic groups is equal to 0.66.

The highest efficiency of the effect of HA on the development of cereals by the example of wheat seeds is expressed for the length of seedlings (see Table 5). So, it is this parameter that, together with the integral IP, demonstrates the correlation with parameters f_a and $f_{ar/al}$ of the structural-group composition. Similarly to the version with garden radish, the correlation dependence of IP on the properties of HA is determined by the intensity of spectral regions depicting the content of carbon C_{Ar} and C_{Alk}. The index of HA phytoactivity is within the range of 0.94–1.38. The maximal value corresponds to humates obtained from brown coal of the Tisul deposit (HumNa BUTS).

Destructive O-alkylation of SCF by alcohols causes an increase in the yield of bitumoids on the one hand and leads to an increase in the aromaticity of debituminized sample [16, 26]. Humic acids isolated from the alkylated sample (HAA) correspondingly have a higher degree of aromaticity that HA isolated from initial SCF. So, prerequisites exist that these HAA should exhibit increased biological activity. The data on the structural-group composition of the samples of humic acids obtained from initial coal and peat (HA) and after destructive alkylation and debidumination (HAA) are presented in Table 6. The data shown in Table 3 and Table 6 illustrate an increase in the degree of HAA aromaticity in comparison with the corresponding HA for all studied SCF samples of humus nature. For instance, for HA isolated from the brown coal of the Tisul deposit, f_a is equal to 23.3. For HAA isolated from the same coal but alkylated with butanol preliminarily and then debituminized, f_a is equal to 31.9. At the same time, the minimal increase in the degree of aromaticity is observed for humic acids isolated from the peat of the Krapivino deposit: for HA f_a = 22.6; for HAA f_a = 22.8.

Results of the tests of biological activity for all the samples of humic acids (HA and HAA) are shown in Fig. 1. One can see that the biological

TABLE 5

Index of phytoactivity of humic preparations in the experiment with wheat

Version	% to the reference			Index of phytoactivity
	Germination energy	Root length	Seedling length	
HumNa BUT	100.0	71.5	111.3	0.94
HumNa BUTSO	100.0	125.7	133.8	1.20
HumK BUTSO	100.0	127.2	135.4	1.21
HumNa BUTS	100.0	146.7	168.5	1.38

TABLE 6

Integral intensities of the spectral regions of HAA sample according to the data of ^{13}C NMR, %

Sample	Chemical shift, ppm							Degree of aromaticity
	220–187 C=O	187–165 COOH(R)	165–145 C_{Ar-O}	145–108 C_{Ar}	108–90 $C_{O-Alk-O}$	90–48 C_{Alk-O}	48–5 C_{Alk}	f_a
Brown coal from the Tisul deposit месторождения								
HA	4.4	7.3	5.4	17.9	3.6	10.8	50.7	23.3
HAA	1.3	6.3	6.9	25.0	4.3	10.6	45.6	31.9
The same, naturally oxidized in coal bed								
HA	3.5	7.4	8.2	32.7	6.3	14.8	26.8	40.9
HAA	1.6	5.3	10.2	32.9	5.1	11.0	33.8	43.1
Brown coal from the Tyulgan deposit								
HA	4.3	7.9	6.8	22.5	4.9	16.3	36.5	29.3
HAA	3.8	8.6	8.5	28.2	5.8	16.9	27.9	36.7
The same, Mayachnoe deposit								
HA	4.7	4.9	3.7	26.1	5.9	13.7	41.1	29.8
HAA	4.1	8.2	7.4	34.8	7.5	16.5	20.9	42.2
Peat, Krapivino								
HA	3.4	7.9	6.7	15.9	8.6	35.4	22.2	22.6
HAA	3.4	8.0	7.0	15.8	9.2	38.5	18.1	22.8

activity of HA, evaluated from the crop capacity of wheat "Novosibirskaya 89", is directly proportional to the parameters $f_{ar/al}$ and $f_{h/h}$. So, an increase in the degree of aromaticity and hydrophily of HA leads to an increase in crop capacity.

Results of the experiments with the seeds of wheat and garden radish are presented in Fig. 2: the dependence of the excess length of wheat roots over the reference Δ and IP of radish seeds on the degree of aromaticity f_a of the used HA. The biological activity of HA and HAA evaluated on the basis of parameters Δ and IP, is also directly proportional to the structural parameter f_a. Humic acids HAA isolated from the coal alkylated and debituminized preliminarily are close in the degree of aromaticity to highly active natural HS of naturally oxidized coal (see Table 3 and Table 6) of the brown coal stage of maturity and exhibit increased biological activity in comparison with HA isolated from initial coal samples.

The field tests of the obtained HA were carried out under the conditions close to those existing in the natural arid regions. For this purpose, recultivation sites within the technogenic land-

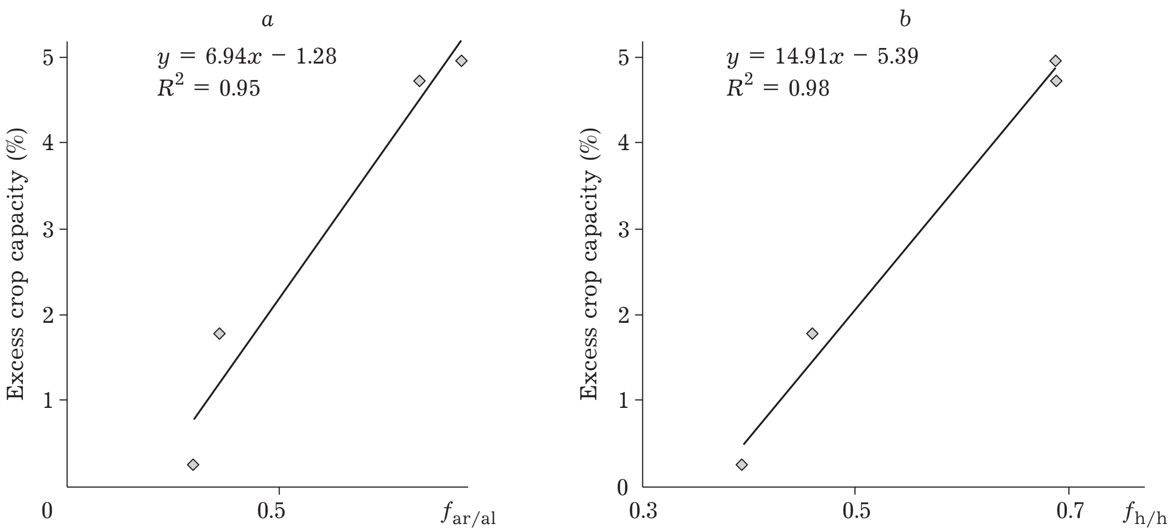

Fig. 1. Dependence of biological activity on structural parameters $f_{ar/al}$ (*a*) and $f_{h/h}$ (*b*) of HA samples.

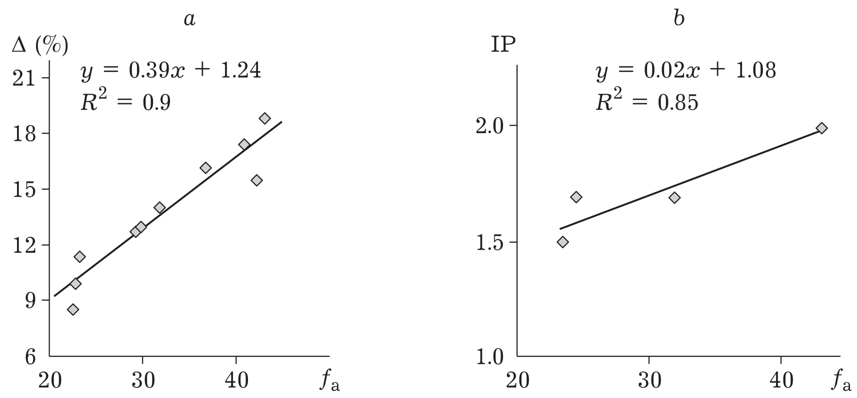

Fig. 2. Dependences of the wheat root length (excess over the reference Δ) (*a*) and the index of phytoactivity IP (*b*) of garden radish seeds on the degree of aromaticity f_a of HA samples.

scapes of the open-pit coal mine Zarechnyi (Kemerovo Region) were chosen. The versions of the field experiment included three kinds of substrates with different degree of xeromorphy depending on their physical and chemical properties (Table 7). Their combination promotes differentiation of the degree to which the xeromorphy of experimental sites was pronounced depending on moisture content. The larger deficit of moisture is observed at the site with technogenic eluvium of dense sedimentary rocks. The optimal conditions for plant development exist at a ground where the fertile soil layer was deposited. The site formed through peat filling serves as an analog of hydromorphic soil because of lower density and high water-retaining capacity.

The effect of HA on the growth and development of cereals under the field conditions was estimated from the height of the young growth of wheat (variety "Novosibirskaya 89"), the seeds of which were treated before sowing in a 0.02 % solution of sodium and potassium humates. As the reference version, seed treatment before sowing was carried out using distilled water for each kind of substrate. The height of plants was measured at the phase of the third leaf and tillering. Experiments showed (Fig. 3) that generally HA have a positive effect on the plants under the conditions of deficit and optimal moisture. At the site with peat filling (P) a small effect was observed only at a later phase, which is likely to be connected with the excess of the own HA of peat in the soil solution, which suppresses the growth of plants. At other sites, there was the differentiation of the efficiency of HA over phases. At the plots characterized by optimal moisture content and plant feeding conditions (FSL), the maximal effect of the application of humic preparations was detected at the first term of measurement (the phase of the third leaf). The excess of plant height above the reference (more than 60 %) in this phase was detected for the seeds treated with the solution of sodium humate obtained from the naturally oxidized brown coal (HumNa BUTSO), with high f_a. However, at the second term the delay in the development was detected.

Under the conditions of the lack of moisture (TE), the largest effect of HA was detected at the phase of tillering in the case when the seeds were treated with humates isolated from all the studied brown coal samples. The average height of the plants exceeded the reference by 21.4 %.

Systematization of the obtained results and their correlations with the properties of humates allowed us to reveal several dependences. First of all, under the conditions of sufficient wetting (FSL), a close correlation of the phase parameters of wheat seedlings with the degree of aromaticity f_a and the parameter characterising the ratio $f_{ar/al}$ of the aromatic component to the aliphatic one is

TABLE 7

Major physical and chemical properties of the substrates

Substrate	Stoniness, %	Density, g/cm^3	Organic carbon content, %	pH_{aq}
Technogenouseluvium (TE)	61	1.6	2.7	7.5
Fertile soil layer (FSL)	0	1.2	3.1	7.2
Peat (P)	0	0.83	30.3	6.8

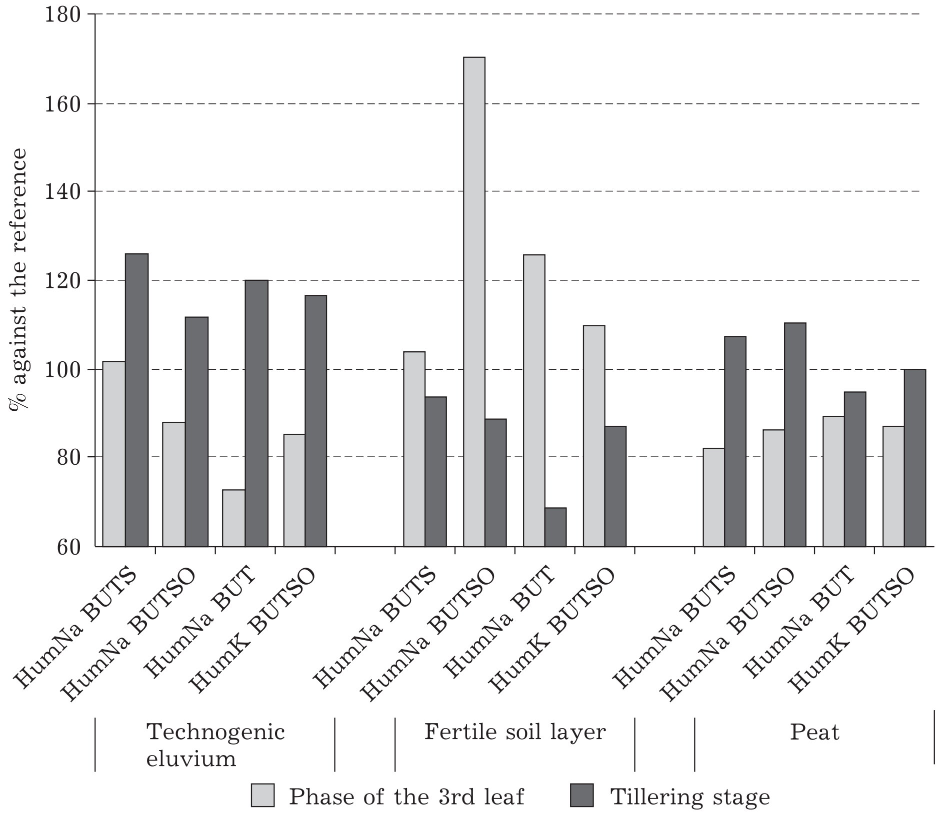

Fig. 3. Height of wheat seedlings over the phases of development on various substrates.

observed. One more dependence is exhibited most vividly after the statistical treatment of the results of tests with the technogenic eluvium: under the conditions of a sharp deficit of moisture, the determinative parameter becomes the hydrophobic-hydrophylic parameter $f_{h/h}$.

CONCLUSION

It is established that the biological activity is directly proportional to the following structural parameters of humic acids: the degree of aromaticity f_a, hydrophilic-hydrophobic parameter $f_{h/h}$ and parameter $f_{ar/al}$ depicting the ratio of aromatic and aliphatic fragments of the organic mass of HA.

It is demonstrated that sequential alkylation and debituminization of humic brown coal cause an increase in the content of aromatic structures in HA isolated from the modified sources. These HA are close in their composition to highly active natural HS of naturally oxidized coal of the brown-coal stage of maturity and exhibit increased biological activity. A promising direction is a purposeful change of the functional composition of humic preparations for the purpose of obtaining the substances with the high degree of aromaticity connected with the biological activity.

The investigation aimed at the revelation of the dependence between the composition of HA of brown coal and their biological activity showed that all the preparations under investigation have a positive effect on the growth and development of plants. In general, the highest efficiency was exhibited by HA isolated from the brown coal of the Tisul deposit in the Kansk-Achinsk basin, and especially sodium humates obtained from the naturally oxidized form of that coal (HumNa BUTSO). For the conditions of Mongolia, humic brown coal from the Baganur and Shivee-Ovoo deposits are promising sources of HA with the high content of phenol and quinoid functional groups.

Thus, the results obtained in the investigation may be used to choose the raw material basis as brown coal for the development of biologically active humic preparations.

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