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ELEMENTAL ANALYSIS OF HUMIC ACIDS IN PEAT RESOURCES OF KHANTY-MANSIYSK AUTONOMOUS REGION - YGRA

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Abstract

This article describes an elemental composition of various humic acids and peats in one of Western Siberia regions. The differences in the content of elements, atomic ratios and benzenoid degree are revealed conditioned by specific terms of formation. A generalizing graphical statistical diagram is presented. The research results allowed to characterize some features of humic acids isolated from the peats of this area and to get the information about the principles of their structure.

It was shown that the elemental composition of peat humic acids in Khanty-Mansiysk Autonomous region - Yugra vary depending on a peat type and species. The lowest carbon content (47.73%) and the highest nitrogen (2.33%) and oxygen (45.33%) content is presented in humic acids of a peat litter, which are in the earliest stages of formation. In other compounds these figures are sufficiently uniform and vary lightly, namely: carbon in the range of 50-53%, hydrogen in the range of 5.5-6.5% and nitrogen in the range of 0.8-1.9%. Humic acids are most rich in nitrogen isolated from the peats of herbal botanical composition, especially the ones which contain Scheuchzéria.

Keywords: the elemental composition of humic acids, the botanical composition of peats, soil chemistry, Khanty-Mansiysk Autonomous region - Yugra.

1. Introduction

Currently, a considerable material describing the humic acids of peats is accumulated, however, many issues related to their formation, the dependence of their elemental composition of the botanical diversity of peat-forming plants, hydrothermal formation conditions are debated so far. There are different hypotheses about the causes of elemental composition changes [1,2].

The aim of this work was the use of elemental analysis data to characterize the composition peculiarities and the

principles of humic acid structure in various peats of Khanty-Mansiysk Autonomous region - Yugra. Thus, it proposed to compare the atomic ratios of elements and apply a graphic statistical analysis, which makes it possible to draw up simple formula and evaluate the direction of HA changes [3].

2. Objects of Research

Humic acids were studied in the work isolated from the peats of different botanical compositions of various provinces of Khanty-Mansiysk Autonomous region (Western Siberia). The territory, which was chosen for humic acid study of peat horizons is a unique one within the scale of waterlogging process by the region in the world. The area is located in a harsh continental climate. Winter lasts for 5 months, the average January temperature ranges from -18.6 to -22,2 °C. Minimum temperature during some days is reduced to -46 - 47 °C, while the maximum is increased up to + 33 °C. Thaw in winter is a rare and a short phenomenon. Spring is usually short (30-40 days) and cold, with an abrupt change of weather, with partial returns of cold and frost. An average duration of a frost-free period makes 84 - 96 days. The growing season lasts for 146-129 days. The sum of temperatures above 100 ° C makes 1960 - 1650. An average temperature of the warmest month makes 18 - 16,2 °C. Autumn is usually warm, but a short one (30-40 days) with a maximum volatility of a baric thermometer, an abrupt change in temperature and frequent frosts. The whole area is located in the zone of excessive moisture at low heat provision. An average annual rainfall is reduced from south to north from 520 to 460 mm. Summer rainfall is 2-2.5 times higher than the winter ones.

3. Methods of Research

The samples of peats delivered to the laboratory were brought to air dry condition, were ground on a disk mill and sieved through a sieve with the 1 mm holes. Lipids were preliminary removed from air dry peat samples by alcohol-benzene extraction (1:1) and decalcification was carried out with sulfuric acid for 12 hours until a negative reaction to calcium was demonstrated. The excess of sulfate ions was removed during the process of washing with distilled water. Humic acids were extracted by decimolar sodium hydroxide solution from decalcified soil.

The sedimentation of humic acids was carried out with 0.25 M of H_2SO_4 solution at pH = 1. The obtained humic acid gel was dried in vacuum at 60 C° for 6 hours, the purification of dried humic acids was carried out initially with water and then by sequential repeated treatments by tenfold amounts of 10% HCl and HF solutions in a boiling water bath. The precipitate was diluted with water and washed from F ions. After this humic acids were dried in vacuum at 60 C°.

The determination of carbon, hydrogen and nitrogen was carried out on the elemental analyzer of the company EURO, mod.EA3000 at the Collective use center of Organic Chemistry Institute at SB of RAS (Novosibirsk) according to a generalized method of long-term work on automatic CNH-analyzers [4].

The botanical composition and the degree of peat decomposition was determined using modern microscopic devices Zeiss Axiostar plus, Stemi DV4 with the ability of connection to a computer, which allows you to perform qualitative measurements.

4. Research Results

The results of performed elemental analysis allow to characterize some features of different peat humic acids in Khanty-Mansiysk Autonomous region - Yugra, and provide information about the principles of their structure.

For a more detailed analysis the studied humic acids are divided into 7 groups, depending on an original peat type and species: sphagnum peats, sedge peats, grass peats, wood peats, wood-grass peats, grass-sphagnum peats, moss peats. The botanical composition of studied peats grouped by type are presented in Table 1.

Table 1– Botanical composition of studied peats.

Main peat composing vegetation	%	R, %	Peat type
1	2	3	4
Sphagnum peats			
Sphagnum fuscum	100	5	Sphagnum fuscum peat
Magellan sphagnum	85	10	Sphagnum Magellan peat
Sphagnum brown	95	10	Sphagnum fuscum peat
Sphagnum fuscum	100	15	Sphagnum fuscum peat
Sphagnum brown	75	20	Sphagnum fuscum peat
Sphagnum angustifoliate	45	30	Sphagnum angustifoliate peat
Sphagnum angustifoliate	70	35	Sphagnum angustifoliate peat
Sphagnum brown	85	40	Sphagnum fuscum peat
Sphagnum brown	85	55	Sphagnum fuscum peat
Sedge peats			
Tufted sedge	100	10	Sedge
Uncertain sedges	80	15	Sedge
Slender sedge	40	25	Sedge
Perennial sedge	55	30	Sedge
Tussock sedges	55	35	Sedge
Tussock sedges	60	40	Sedge

Tussock sedges	90	45	Sedge
Tussock sedges	90	50	Sedge
Beaked sedge	45	55	Sedge
Grass peats			
Buck-bean Perennial sedge	20 20	15	Grass
Cotton grass	70	15	Grass
Cotton grass	80	25	Grass
Tussock sedges Buck-bean	50 35	25	Grass
Scheuchzéria	80	30	Grass
Buck-bean	45	40	Grass
Beaked sedge Buck-bean	45 40	45	Grass
Cotton grass	85	55	Grass
Buck-bean	100	60	Grass
Grass-sphagnum			
Sphagnum	30	10	Grass-sphagnum
Mud sedge Eriophorum vaginatum Magellan sphagnum	20 15 25	35	Grass-sphagnum
Cotton-grass Sphagnum brown	30 50	65	Grass-sphagnum
Woody peats			
Wood and birch bark	60	10	Woody
Semifrutex Pine	45 15	15	Woody
Pine	70	25	Woody
Downy birch and coals Shrubs	65 20	25	Woody
Downy birch Dwarf birch	65 10	45	Woody
Pine	45	50	Woody
Wood grass peats			
Downy birch Buck-bean	45 45	30	Wood grass

Downy birch Buck-bean	35 50	35	Wood grass
Downy birch Vilyui, tufted sedge	25 50	65	Wood grass
Moss peats			
Green hypnum moss (Politrihum ordinary Aulakomnium swampy Politrihum compressed Gelodium Blandova, etc.)	90	10	Peat layer

Notes: % – vegetation prevailing in peats, R – peat decompression grade

As we know the atomic ratios H/C, O/C, N/C show the number of hydrogen, nitrogen and oxygen atoms in the molecule (particle) of substance humic acids per one carbon atom. The smaller these ratios are, the greater the role of carbon atoms in the molecular structure development. Atomic ratio decrease indicates an increasing proportion of benzenoid fragments and the decrease of aliphatic side chain portion in the molecules of humic acids. According to the ratio in each of specified pairs they revealed a relative branching of the side chains, the role of nitrogen containing compounds in humic acid development.

The chemical composition of regional peat humic acids based on an ash-free substance is not a uniform one and varies depending on the kinds of original peats and their decomposition degree [5]. The carbon content in humic acids varies from 39 to 58%, the hydrogen content varies from 3.6 to 5%, the nitrogen varies from 1 to 2.5% and oxygen content varies from 35 to 55%. Ash content makes ± 1%.

For the conditions of Khanty-Mansiysk Autonomous region - Yugra the samples of peat humic acids did not show the dependence of their elemental composition on the types of original peats, on the peculiarities of their species conditioned by location.

Table-2 breakdown is made by peat types as compared with humic acids by location there were no differences in landscape provinces, thus an entire material is considered depending on original peat type and its degree of decomposition.

A similar pattern may be traced in all physical and chemical methods of humic acid study concerning Khanty-Mansiysk Autonomous region - Ugra peats [6,7,8].

Table 2 Average values of humic acid elemental composition for Middle Ob region and atomic ratios.

Peat species	R, %	Humic acids							
		Ash content, %	Mass share per ash-free sample, %				H/C	O/C	N/C
			C	H	N	O			
Sphagnum	5	0,63	45,81	4,15	2,43	47,62	1,08	0,81	0,05
	10	1,11	53,46	4,64	2,51	39,40	1,03	0,55	0,04
	15	0,84	49,03	3,93	1,34	45,69	0,96	0,71	0,02
	20	1,03	54,78	4,59	1,94	38,69	0,99	0,53	0,03
	30	1,08	53,31	4,38	1,62	40,69	0,98	0,57	0,03
	35	0,99	55,9	4,48	1,82	37,81	0,95	0,51	0,03
	40	0,92	57,77	4,94	2,10	35,19	0,98	0,50	0,03
	55	0,93	58,13	4,49	1,35	36,03	1,02	0,46	0,03
Sedge	10	0,88	59,46	4,94	2,17	33,43	0,98	0,42	0,03
	15	0,96	55,48	4,46	2,29	37,77	0,95	0,51	0,03
	25	0,78	39,95	3,42	2,58	54,05	1,01	1,01	0,05
	30	0,88	56,27	4,64	1,80	37,29	0,92	0,47	0,02
	35	1,24	52,59	4,59	2,01	40.82	1,04	0,60	0,04
	40	1,25	56,62	4,25	1,98	37,15	0,89	0,49	0,02
	45	1,20	55,96	4,36	2,26	37,42	0,93	0,50	0,03
	50	1,00	57,91	4,90	2,10	35,09	1,01	0,46	0,03
	55	0,76	57,43	4,32	2,20	36,05	0,89	0,47	0,03
Grass	15	0,94	46,05	4,15	2,53	47,27	1,07	0,82	0,05
	25	1,14	57,55	4,78	2,03	35,64	0,99	0,47	0,03
	30	0,99	58,25	4,62	1,71	35,43	0,94	0,46	0,03
	40	1,01	57,43	4,36	1,66	36,55	0,90	0,48	0,03
	45	0,98	55,68	4,63	1,55	38,14	0,99	0,51	0,02
	55	1,06	57,31	4,35	1,67	36,67	0,90	0,48	0,02
	60	1,35	56,22	4,04	2,12	37,62	0,85	0,50	0,03
Grass-sphagnum	10	1,27	53,50	4,43	2,40	39,67	0,98	0,55	0,03
	35	1,17	40,02	3,23	1,85	54,90	0,95	1,02	0,03
	65	0,85	54,98	4,24	1,17	39,61	0,91	0,54	0,01
Woody	10	1,26	50,03	4,17	1,99	43,81	0,99	0,65	0,03
	15	0,88	48,58	4,90	2,55	43,97	1,19	0,67	0,04
	25	1,00	53,78	4,37	1,80	40,07	0,97	0,56	0,03
	45	1,16	55,52	5,40	2,93	36,15	1,16	0,49	0,05

	50	1,02	54,84	5,02	1,64	38,50	1,09	0,53	0,03
Wood-grass	30	1,15	58,56	4,96	1,68	34,80	1,01	0,45	0,02
	35	0,84	55,62	4,92	1,98	37,48	1,05	0,51	0,03
	65	0,85	57,74	4,40	1,77	36,09	0,90	0,47	0,03
Hypnum	10	0,98	53,13	4,46	2,04	40,18	1,05	0,57	0,03

Note: R – decomposition rate

This circumstance is taken into account in the drawing up of the subsequent tables for their greater visibility i.e. more detailed results. The increase of the hydrogen content takes place under the influence of excess peat moistening, i.e. the elemental composition corresponds to peat formation conditions.

This can be explained assuming the intensity of microbiological activity, as the defining factor of organic matter humification process development. Waterlogged peats develop recovery processes, which reduce biological activity. Under these conditions, humic acids are enriched with hydrogen and -CH2- groups, the degree of oxidation decreases.

The generalized correlation dependence between the percentage content of C, H and O in the humic acids of Khanty-Mansiysk Autonomous region - Ugra peats, shows that the increase of carbon content percentage, increases the percentage of hydrogen and oxygen content, and the less the percentage component of oxygen in humic acids, the greater the percentage of hydrogen content there.

The value of atomic ratios differs greatly from percentage ratios during the comparison of element pairs with sharply different atomic weights (C-H, O-H). At close atomic weights the percentage and atomic ratios are almost identical sometimes.

It is useful to use "benzenoid degree" (α) indicator for conditional value of aromatic and aliphatic components.

$\alpha = C_{benz.} : (C_{benz.} + C_{aliph.})$, or $\alpha = C_{benz.} : C_{gen.} \cdot 100\%$, where

$C_{aliph.}$ – carbon content in aliphatic fragments,

$C_{benz.}$ – carbon content of benzenoid fragments in humic acids, $C_{gen.} = C_{aliph.} + C_{benz.}$

A more accurate calculation of "benzenoid degree" must take into account the number and nature of oxygen functions as a significant portion of hydrogen atoms is replaced by oxygen ones.

Based on the above stated principles, it was calculated by the way of limiting structure interpolation according to the modified Van Krevelen formula.

The "benzenoid degree" of humic acids is shown in Table 3.

Table 3: Atomic ratios and the "benzenoid degree" of various peat humic acids in the Middle Ob region.

Peats		Humic acids			
Types	R, %	H/C	O/C	$C_{aliph.}$	α, %
Sphagnum	5	1,08	0,81	0.74	27
	10	1,03	0,55	0.69	32
	15	0,96	0,71	0.70	30
	20	0,99	0,53	0.68	32
	30	0,98	0,57	0.69	31
	35	0,95	0,51	0.67	34
	40	0,98	0,50	0,66	34
	55	1,02	0,46	0,66	34
Sedge	10	0,98	0,42	0.65	35
	15	0,95	0,51	0.66	34
	25	1,01	1,01	0.76	24
	30	0,92	0,47	0,65	35
	35	1,04	0,60	0,70	31
	40	0,89	0,49	0.65	35
	45	0,93	0,50	0,66	34
	50	1,01	0,46	0,66	34
	55	0,89	0,47	0.64	36
Grass	15	1,07	0,82	0,73	27
	25	0,99	0,47	0,66	34
	30	0,94	0,46	0.65	35
	40	0,90	0,48	0,65	35
	45	0,99	0,51	0,67	33
	55	0,90	0,48	0,65	35
	60	0,85	0,50	0.64	36
Grass - sphagnum	10	0,98	0,55	0.68	32
	35	0,95	1,02	0.75	25
	65	0,91	0,54	0.66	34
Woody	10	0,99	0,65	0.70	30
	15	1,19	0,67	0.73	27
	25	0,97	0,56	0.68	32
	45	1,16	0,49	0,69	31
	50	1,09	0,53	0,69	31
Woody-grass	30	1,01	0,45	0,66	34

	35	1,05	0,51	0,68	32
	65	0,90	0,47	0,64	36
Hypnum	10	1,05	0,57	0,69	31

Note: R – peat decomposition degree, α – benzenoid degree level

At that it was assumed that H:C of the aromatic portion ($H:C_{arom.}$) is equal to 0,33 и К – an oxygen function consideration ration is equal to 0,67. The benzenoid degree determination of studied humic acids (α) varies from 23 to 36%.

$$(H:C)_{aliph.} = (H/C)_{ha}+2(O/C)_{ha}\cdot K-(H/C)_{arom.}$$

$$C_{aliph.} = (H/C)_{aliph} - (H/C)_{arom.}: ((H/C)_{aliph.}+(H/C)_{arom.})$$

It should be noted that the study results of peat humic acid aromaticity degree by alkaline oxidation method with potassium permanganate agree with the result of benzenoid degree (α) and elemental composition and are equal to 28-35%.

An important indicator according to Van Krevelen is the atomic ratio H:C, which clearly characterizes the class of hydrocarbons [3]. For the humic acids of peats this ratio makes usually 1.0 approximately, which formally refers the prevalence of aromatic structures. An accurate interpretation of GW composition by the method of graphic statistical analysis is complicated by the fact that there is no complete information about oxygen functions in a molecule and a number of carbon atoms per molecule.

The evaluation of atomic relations allows to solve some of transformation mechanism issues in respect of plant residues and individual groups of humic substances. For this purpose, it is convenient to use the diagram of atomic ratios H/C - O/C (Fig. 1), which shows the results of HA elemental composition analysis in respect of studied peats.

H/C ratios vary from 0.85 (buck-bean lowland peat, R = 60%) to 1.19 (pine-shrub, upper, R = 15%). An average value of H/C HA peats of Khanty-Mansiysk autonomous region (48 samples) makes 1.05.

Three different areas may be specified on a diagram. The main HA weight (39 samples) is in the region I, wherein an average ratio of H:C = 0.97, O: C = 0.50, 5 samples form the area II (H:C = 1.09, O:C = 0.75) and 4 samples form region III (H:C = 1.02, O:C = 1.04).

During the transition from the region III to the region II and then to the region I decarboxylation takes place (more precisely, the loss of C and O atoms in the ratio of 1:2) and dehydration (the loss of H and O atoms in the ratio of 2: 1). The differences between these regions are more related to the difference in the number of oxygen atoms, and H:C ratios are more uniform in all three regions.

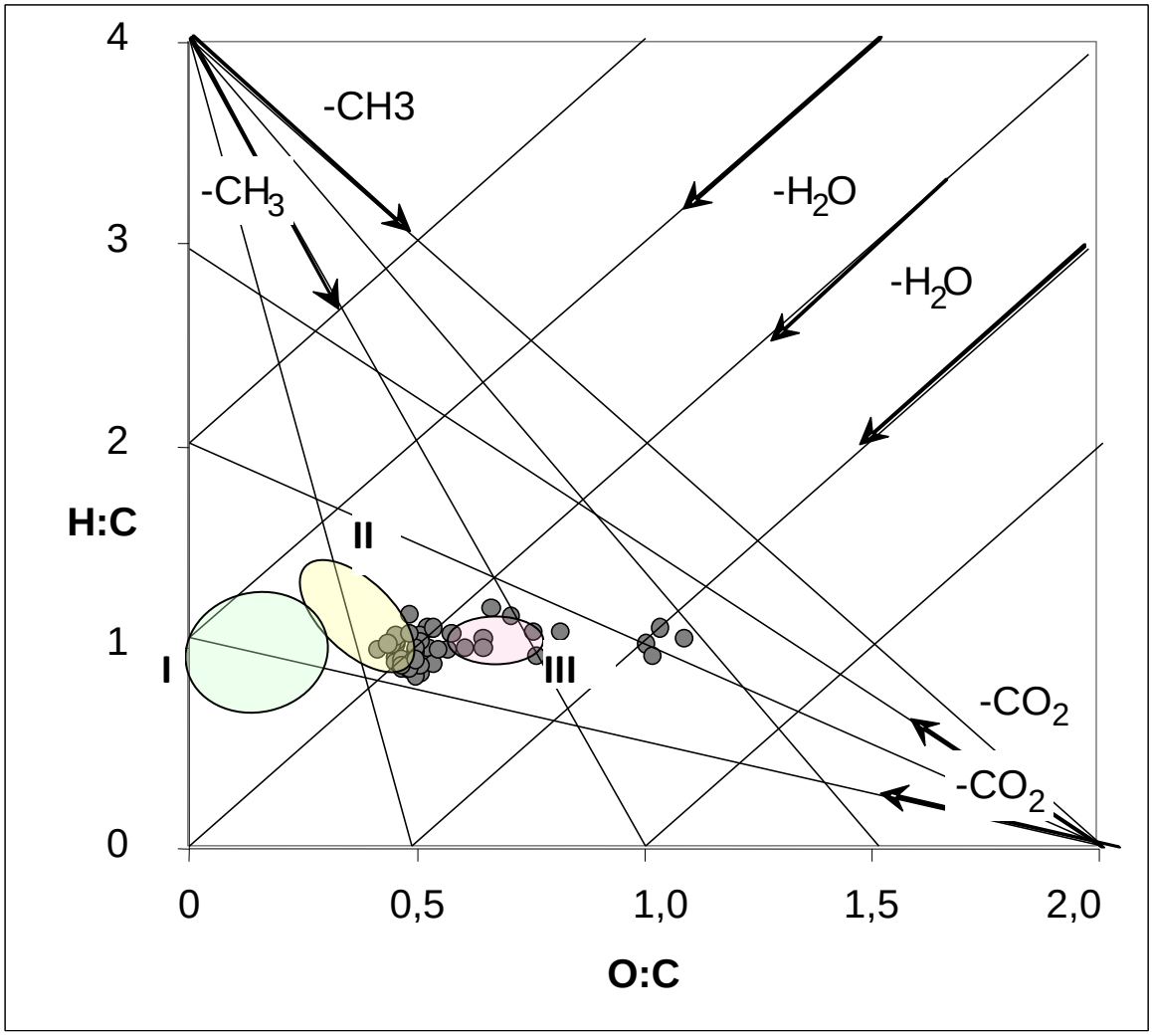

Figure 1 – General diagram of H:C-O:C atomic relations concerning the humic acids of peats.

The atomic ratios of humic acid elements in a general form on the obtained diagram are characterized by the presence of three distinct areas, which within the conditions of Khanty-Mansiysk Autonomous region - Ygra are not related with the provincial landscape in any way, and depend only on the botanical composition of original peats and the degree of their decomposition. However, not all groups of humic acids separated by botanical composition, can be unambiguously characterized by this way. It may be noted that sphagnum and sedge peats have three concentration areas of atomic indices, and wood, peat-sphagnum, grass and hypnum peats have two areas and woody grass peats have only one area.

5. Conclusions

An elemental composition of peat humic acids corresponds to the conditions of peat formation and humification and depends on the botanical composition and peat decomposition degree; humic acids developed from the peats with the decomposition degree up to 35%, with significant prevalence of sphagnum (95-100%), hypnum green moss, grass, grass and grass-sphagnum peats in the botanical composition, containing a multi-component mixture of peat-forming

elements, wood and wood-grass peats, 85% of which consists of woody vegetation, or of cranberry and rosemary bushes by 50%.

6. Summary

The elemental composition of humic acids in Middle Ob peats is not the same and meets the conditions of peat formation. It was stated that according to H:C ratio and the graphic statistical analysis data of the elemental composition, the chemical nature and the physical-chemical properties of humic acids depend on the botanical composition of the original peat and its degree of decomposition.

In the first field of graphic and statistical diagram humic acids are presented. These acids are extracted from peat with varying decomposition degree from 10 to 65%, but according to our data only some of humic acids extracted from peats are located in the second and the third field with decomposition degree from 5 to 35%. Humic acids extracted from peats with the decomposition degree from 40 to 65% are located only in the 1st area of the diagram. They have a maximum development degree - the "maturity" of molecular structure, as well as all humic acids, located in the first field. The reason of an assumed lesser structure formation of humic acid 9 samples compared to other acids can be explained by the specificity of botanical composition, used peat and its decomposition degree. Why some humic acids extracted from the peat with the decomposition degree from 5 to 35% are located in the 2nd and the 3rd field? First of all, this fact indicates that they have a smaller proportion of aromatic structures in a molecule. On the contrary, humic acids of the 1-st field, indicate by its location the maximum share of aromatic structures in their composition. It was found that the humic acid structure depends on the botanical composition of peat and its decomposition degree [9]. With this regard the data on elemental composition were analyzed and relevant characteristics were obtained. According to elemental composition results all HA samples of the 2nd and the 3rd diagram have generally a low carbon content (up to 40%) and a high oxygen content (up to 55%), and a low percentage of benzenoid degree corresponds to them (α = 23-27 %).

The diagram area with the results of the minimum humic acid formation degree includes only a few of them. They were extracted from all peat groups with the decomposition degree from 5 to 35%: sphagnum, sedge, grass, grass-sphagnum, wood, wood-grass and hypnum peats. The influence of a particular botanical composition is traced probably for some samples of hydrothermal formation conditions.

According to elemental analysis data, humic acids with used peat decomposition degree from 0 to 35% have the minimum "maturity". They are extracted from sphagnum peats, with the significant prevalence of sphagnum (95-

100%), hypnum peats in the botanical composition with a great variety of hypnum green moss in peat composition, and herbal and grass-sphagnum peats containing large amounts of peat-forming plants (13-14 names). The decomposition degree among all these groups of peats does not exceed 35%.

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