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Elemental Composition Of The Humic Acids In The High-Moor Peats Of The Western Siberia Taiga Zone.

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ABSTRACT

The article presents the results of a study concerning the elemental composition of the humic acids extracted from the peats of stratigraphic column in Mukhrino bog located in the Middle Taiga of Western Siberia. Description of the botanical composition and a degree of decomposition of the original peats are presented herein. The carbon, hydrogen, nitrogen, oxygen and sulfur in humic acids are recalculated with reference to the anhydrous and ashless substance. The common borders are presented, in which the mass fractions of carbon (50.30 - 59.30%), oxygen (29.58 - 38.10%), hydrogen (4.68 - 6.13%), nitrogen (2.69 - 5.95%), and sulfur (0.10 - 1.87%) change. The elemental analysis data of the humic acids were grouped according to the original peat's botanical composition, and the average mass fractions were found. The humic acids extracted from the sphagnum peats have the highest carbon content of about 58%, however, the species differences do not make a significant difference. The carbon mass fraction of scheuchzeria peat is lower and amounts to about 56%. Grass-hypnum sapropel - 54%. Sapropel - 52%. The atomic ratios H/C, $(H/C)_{cor.}$ and O/C were calculated for the groups extracted on the basis of their botanical composition. The diagram of atomic ratios was constructed in coordinates $(H/C)_{cor.}$ – O/C. Based on the diagram, five groups of the humic acids that differ in original peat depth were identified.

Keywords: humic acids, elemental analysis, stratigraphy of peat deposit, Mukhrino, Middle Taiga, Western Siberia.

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INTRODUCTION

The transformation of plant residues and bacterial metabolites in the humic acids – humification - is one of the most important natural processes, as it maintains a balance between the mineralization and preservation of an organic substance. The humic acids have a number of biosphere functions; they are also used in medicine, agriculture and various industries. The best raw material for creating humic substances is peat, since the content of humic acids therein is very high, and the peat is a renewable natural resource, which reserves are enormous [4].

The humic acids are an extremely complex object to study. The best way to study them is a comprehensive approach, which uses a set of physical and chemical methods of study. The elemental analysis is one of the main methods. It is used to identify the humic acids and to solve some issues connected with the general principles of molecular structure and properties [7].

It can be concluded from the various published data that the elemental composition of the humic acids varies within certain relatively narrow limits: C - from 52 to 62%, O - from 31 to 39%, N - from 1.7 to 5%, H - from 2.8 to 5.8%. It also includes sulfur ranging from 0.7 to 1.2 and phosphorus – up to 0.5% The heterogeneity of the elemental composition is a fundamental property of the humic acids [1] [5] [11].

The main reason for varying the elemental composition is the variability of humification conditions, which implies the heterogeneity of the humic acids themselves [9]. Other reasons include different humic acid extraction techniques, errors in preparing samples for an analysis and during such analysis [8].

The errors mean inaccuracies, rather than humic acid extraction or analysis stages performed in an incorrect way. When analyzing differences in the humic acids depending on the climatic or other formation conditions on the basis of their elemental composition, it is necessary to reveal how significant errors are caused by differences in the extraction and analysis process. Thus, when using a standard humic acid extraction method, the confidence interval of the average mass fraction of carbon at $P = 0.95$ amounted to ± 1.4% for five measurements [10].

From the works on the elemental composition of the humic acids extracted from peats in the Middle Taiga of Western Siberia, the M.P. Sartakov's studies can be distinguished.He carried out a comprehensive study of the physico-chemical properties of the humic acids in various landscape provinces of the area. The following limits were obtained, within which the mass fractions of the humic acid elements change: carbon from 39 to 58%, hydrogen from 3.6 to 5%, nitrogen from 1 to 2.5% and oxygen from 35 to 55%. When comparing the humic acids by their location in the landscape provinces, no differences have been found [12] [13].

OBJECTS AND METHODS USED TO STUDY

The stratigraphic column was selected 30 kilometers to the south-west of the city of Khanty-Mansiysk around the field of Mukhrino educational and experimental station of the Yugra State University. This stationary is located on the left-bank terrace of the Irtysh River on a typical peatland (Mukhrino bog). The sampling point coordinates for the stratigraphic peat column: 60.89535N68.639033E.

Samples for the elemental analysis were taken from the surface up to a depth of 510 cm in increments of 10 cm. Samples were obtained using an Eijkelkamp Peat Sampler (produced in the Netherlands). The sample of 0-10 cm was not examined because of a low yield of the humic acids; the samples of 60-70, 100-110, 170-190 and 200-210 cm corresponding to buried water layers were not examined either.

The peat deposit stretching from the surface to a depth of 220 cm consists of the layers of strongly watered bog-depression sphagnum peat and the remains of swampland sphagnum mosses (Sphagnum papillosum (Lindb.), Sphagnum Jensenii (Lindb.), Sphagnum Lindbergii (Schimp.), Sphagnum balticum (Russow) with negligible concentrations of scheuchzeria (5-15%) and cotton grass (5%) alternating with interlayers of scheuchzeria-sphagnum and scheuchzeria peats, in which the content of scheuchzeria residues increases up to 20-35% and 75%, respectively. The botanical composition of the studied peats is shown in Figure 1.

At a depth of 220-330 cm, the upper horizon of swamp peats is replaced by a layer of sphagnum fuscum peat combined with the complex sphagnum peat, which deposited in less watered conditions of pine-shrub-sphagnum communities dominated by Sphagnum fuscum (Schimp.) Klinggr. on hills and ridges and in more humid spaces between hummocks and hollows between them. 65-95% of sphagnum fuscum peat is composed of remains of the eponymous sphagnum moss with an admixture of shrubs (5-10%). Furthermore, the complex sphagnum peat includes some remains of swampland sphagnum mosses and scheuchzeria.

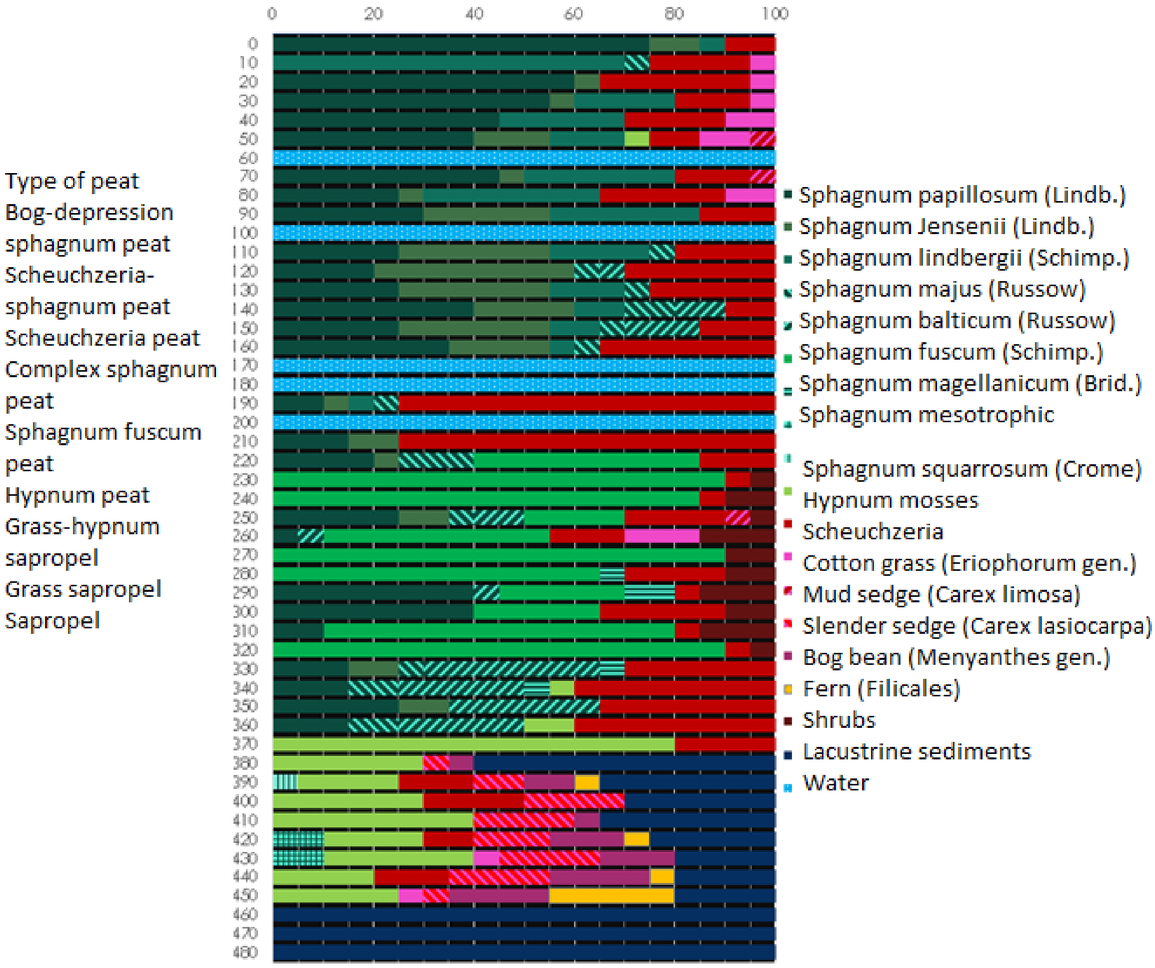

Figure 1. Botanical composition of the studied peats from the surface up to 480 cm

A layer of scheuchzeria-sphagnum peat presents again the lower horizon of the high-moor peat (330-370 cm) in the peat column. A thin hypnum peat interlayer (370-380 cm) separates it from the meter layer of lacustrine sediments with remains of aquatic macrophytes lying at the bottom of peat deposits. Starting with 470 cm, the samples consist entirely of lacustrine sediments. Degree of decomposition of the studied peats is shown in Figure 2.

The humic acids were extracted according to standard Instorf procedures modified at the Department of General Chemistry of the Tyumen State Agricultural Academy [4], but without the hydrochloric acid demineralization, which leads to a partial removal of aliphatic periphery and averaging of results.

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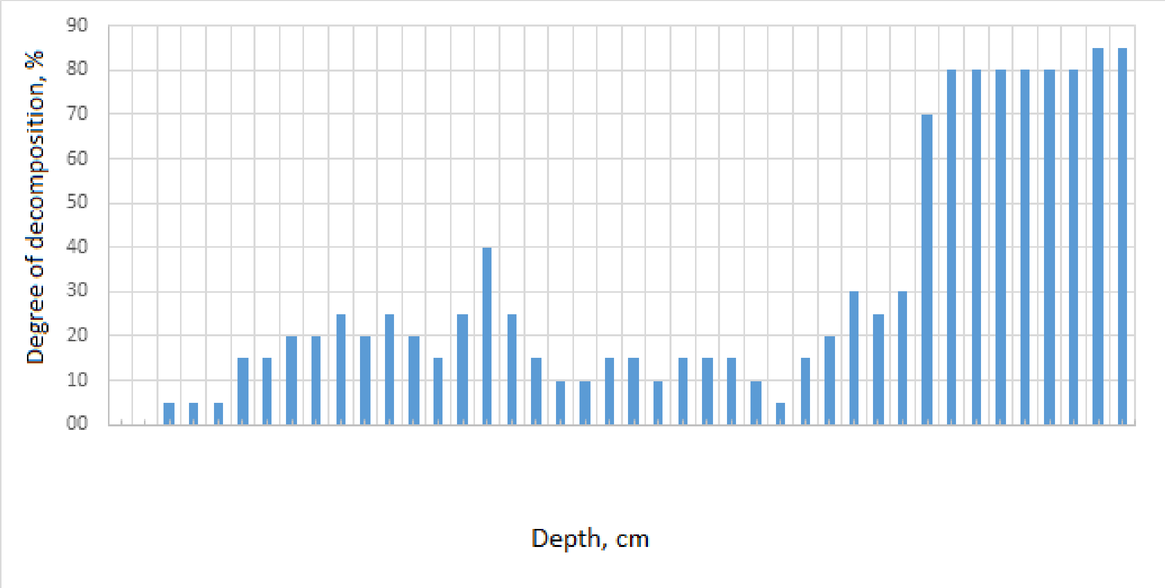

Figure 2. Degree of decomposition of the studied peats

Elemental analysis of the humic acid samples was conducted at the Novosibirsk Institute of Organic Chemistry (Siberian Branch, Russian Academy of Sciences) using EA3000 Elemental Analyzer (produced by EuroVector). Each sample was measured twice.

RESULTS AND DISCUSSION

Due to the absent deashing with hydrochloric acid, the humic acids extracted from the peat column have a rather high ash content averaging about 8% of the studied sample's weight. The mass fractions of the humic acid elements obtained on the elemental analyzer were recalculated for an ash-free, anhydrous substance. The mass fraction of oxygen was calculated by subtracting the mass fractions of carbon, nitrogen, hydrogen, and sulfur. Figure 3 shows the elemental analysis results. For greater clarity, the mass fractions of H, N and S were transferred onto the auxiliary ordinate axis, and the mass fractions of C and O remained on the major axis.

The elemental composition of the humic acids extracted from peats in the stratigraphic column is heterogeneous, and it varies subject to a type and degree of decomposition of original peats. The carbon content in the humic acids is in the range from 50.30 to 59.30%. The oxygen content varies in the range from 29.58% to 38.10% and repeats distortedly the reverse graph of carbon content. In increasing the mass fraction of carbon, the mass fraction of oxygen falls, which is characteristic for the humic acids. The hydrogen content ranges from 4.68 to 6.13%, nitrogen content - from 2.69 to 5.95%, sulfur content – from 0.10 to 1.87%. Figure 3 shows the elemental analysis results.

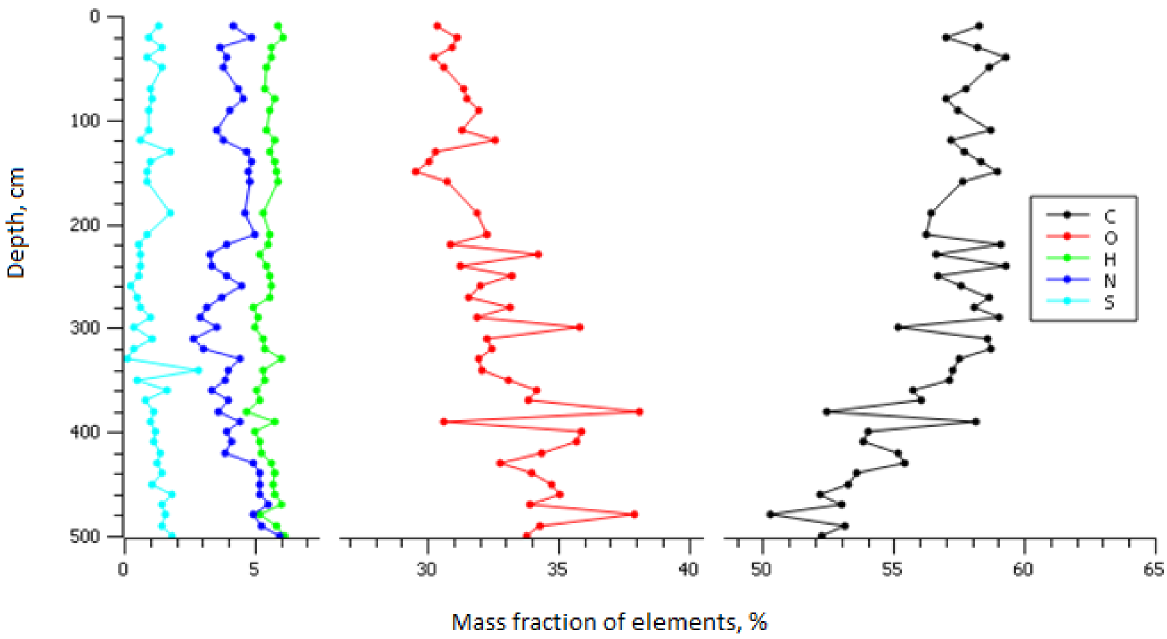

Figure 3. Results of humic acid elemental analysis

In order to establish statistically significant differences, the elemental composition data of the humic acids were grouped by a peat type and depth. The groups represented by one sample – hypnum peat (370 – 380 cm) and grass sapropel (460 – 470 cm) were not examined due to a small number of measurements, and the results of their elemental analysis were included in other groups similar in their botanical composition and peat depth.

It resulted in 8 groups, 6 of which were different in a type of peat: bog-depression sphagnum peat (6 samples), scheuchzeria (2 samples), complex sphagnum peat (4 samples), sphagnum fuscum peat (6 samples), grass-hypnum sapropel (8 samples), sapropel (5 samples) and two groups of scheuchzeria-sphagnum peats differing in the peat depth: 10 – 170 cm (8 samples), 300 – 380 cm (6 samples). Two measurements correspond to each sample. The group-specific average values of the mass fraction of carbon and confidence intervals thereto were calculated. Figure 4 represents corresponding results.

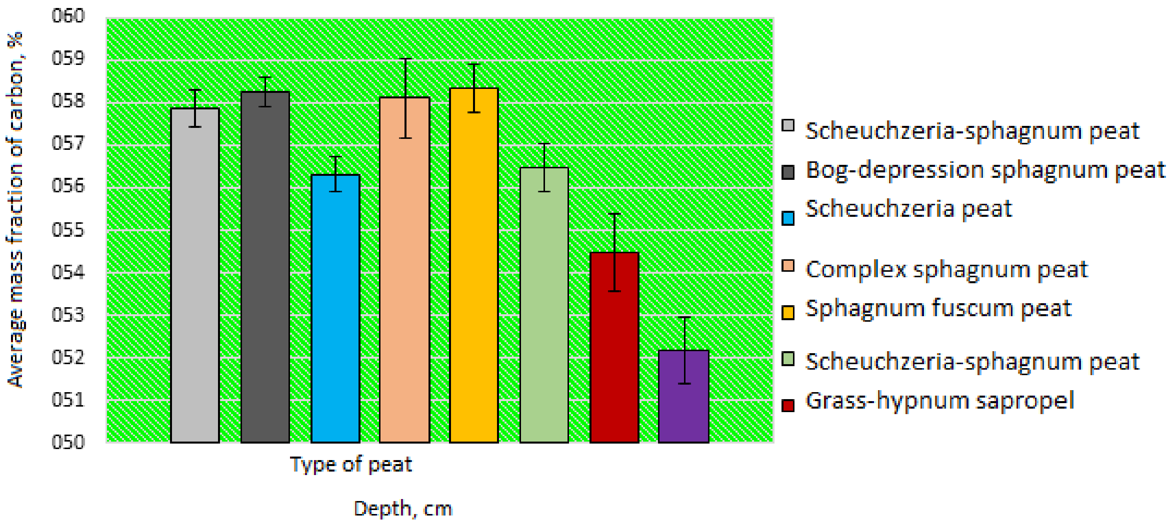

Figure 4. Group-specific average values of mass fraction of carbon in the humic acids

As can be seen from the diagram, the highest carbon content in the humic acids of the stratigraphic column is typical for sphagnum peats; in this case, the sphagnum species differences do not make any significant changes (scheuchzeria-sphagnum peat 57.85±0.44%, bog-depression sphagnum peat 58.25±0.34%, complex sphagnum peat 58.01±0.92%, sphagnum fuscum peat 58.33±0.56%). On the other hand, increase in the content of scheuchzeria results in a drop of the average mass fraction of carbon (scheuchzeria peat 56.32±0.43%, scheuchzeria-sphagnum peat 56.47±0.58%). The humic acids extracted from the sapropel from a depth of 460 cm have a minimum carbon content of 52.18±0.77%, while the grass-hypnum sapropel takes an intermediate place between the peat and sapropel and contains 54.49 ± 0.91.

Calculation of the atomic ratios allows estimating the principles of the humic acid structure, as well as the aromatic versus aliphatic structure ratio in a molecule. The resulting values for H/C are strongly underestimated, because they do not consider the substitution of some carbon and hydrogen atoms by oxygen and nitrogen. In order to obtain more accurate data, the atomic ratios of H/C were recalculated into corrected atomic ratios - $(H/C)_{cor.}$ according to the formula proposed by Orlov [6]. Table 1 presents the calculated groups-specific average atomic ratios of the humic acids.

Table 1. Average atomic ratios of H/C and O/C in the humic acids

Peat group	Depth, cm	H/C		$(H/C)_{cor.}$		O/C	
Scheuchzeria-sphagnum peat	10 - 170	1.18	±0.02	1.70	±0.03	0.39	±0.01
Bog-depression sphagnum peat		1.16	±0.03	1.66	±0.03	0.38	±0.01
Scheuchzeria peat	190 - 220	1.15	±0.06	1.70	±0.07	0.41	±0.03
Complex sphagnum peat	220 - 330	1.12	±0.04	1.66	±0.04	0.40	±0.02
Sphagnum fuscum peat		1.08	±0.03	1.63	±0.03	0.41	±0.01
Scheuchzeria-sphagnum peat	300 - 380	1.14	±0.05	1.72	±0.05	0.43	±0.01
Grass-hypnum sapropel	380 - 460	1.17	±0.05	1.78	±0.05	0.46	±0.02
Sapropel	460 - 510	1.32	±0.06	1.97	±0.06	0.48	±0.01

To detect structural differences in the humic acids, a diagram of atomic ratios has been constructed in the coordinates $(H/C)_{cor.}$ – O/C, see Figure 5. The scale on the ordinate axis is half as much as on the abscissa axis. This diagram permits expressing differences in the structure of the humic acids using summary chemical processes.

The peat humic acids from a depth of 0 to 330 cm have no significant differences in the atomic ratios of $(H/C)_{cor.}$ The further humic acids of the grass-hypnum sapropel have a higher value of $(H/C)_{cor.}$ than a majority of the peat humic acids. The maximum values of $(H/C)_{cor.}$ show the humic acids extracted from the sapropel.

The humic acids extracted from the peats at the surface (10 – 170 cm) have the minimal atomic ratios of O/C, which grow unevenly with increased sample depth. The maximum values of O/C also relate to the humic acids extracted from the sapropel (460 – 510 cm).

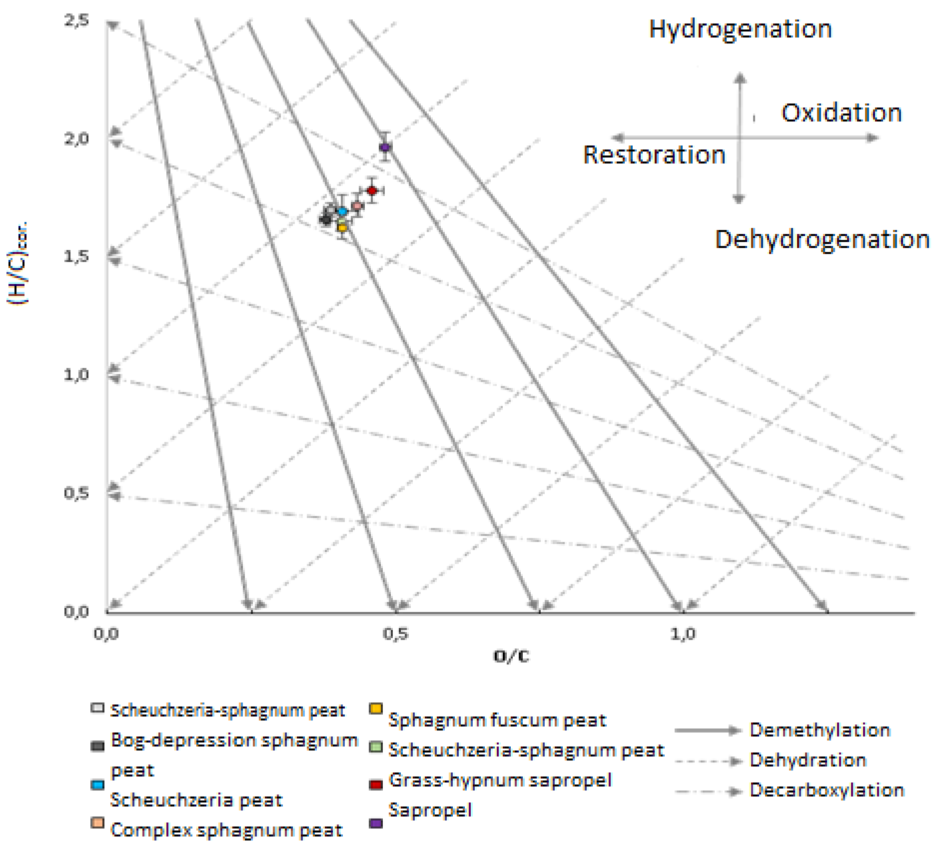

Figure 5. Diagram of average atomic ratios of $(H/C)_{cor.}$ – O/C in the humic acids

In order to simplify the scheme, the groups were combined according to close values of average ratios $(H/C)_{cor}$ and O/C.As a result, five groups were formed different in the peat depth: 10–220 cm (scheuchzeria-sphagnum, bog-depression sphagnum, scheuchzeria peat), 220–330 cm (complex sphagnum, sphagnum fuscum peat), 330–380 cm (scheuchzeria-sphagnum), 380–460 cm (grass-hypnum sapropel), 460–510 cm (sapropel). The results are given in Table 2.

Table 2. Average atomic ratios of H/C and O/C in the humic acids

Depth, cm	$(H/C)_{cor.}$		O/C	
10 - 220	1.71	±0.02	0.40	±0.01
220 - 330	1.66	±0.02	0.42	±0.01
330 - 380	1.74	±0.05	0.45	±0.01
380 - 460	1.81	±0.05	0.48	±0.02
460 - 510	2.00	±0.06	0.50	±0.01

The diagram of atomic ratios allows drawing a conclusion only about the total result of the humic acid transformation process with the stages not being disclosed. Figure 6 shows a scheme of the depth-specific humic acid transformation. Based on the Middle Taiga peat deposits stratigraphy made by Liss [3], the peat depth, peat age and the climatic conditions of that period can be linked [2].

The sapropel represents the depth of 460-510 cm; that confirms the Mukhrino bog's lacustrine origin. Most likely, this group corresponds to the cooling period in Siberia in the early Holocene, and it might refer to the Preboreal period about 9,800 years ago. The humic acids were formed in the bottom sediments of macrophytes at constant overwetting, thereby they have the maximum atomic ratios of H/C and O/C.

The grass-hypnum sapropel presents the depth of 380-460 cm; this indicates that the reservoir began to dry out due to the climate warming. It is most likely that this group belongs to the Boreal period, which is characterized by warming and decreased precipitation. The recent bottom sediments are observed at a depth of 380-390 cm, which points to the complete drying of the lake. The processes of bog formation and peat accumulation began at this stage. The degree of decomposition indicates a still high moisturizing value. Hypnum mosses and scheuchzeria appeared in the peat-forming vegetation, which led to a significant drop in the ratio of H/C.The moisture content decline led to the decreased O/C value. Transition from a group with a depth of 460-510 cm can be expressed by dehydrogenation reaction and dehydration.

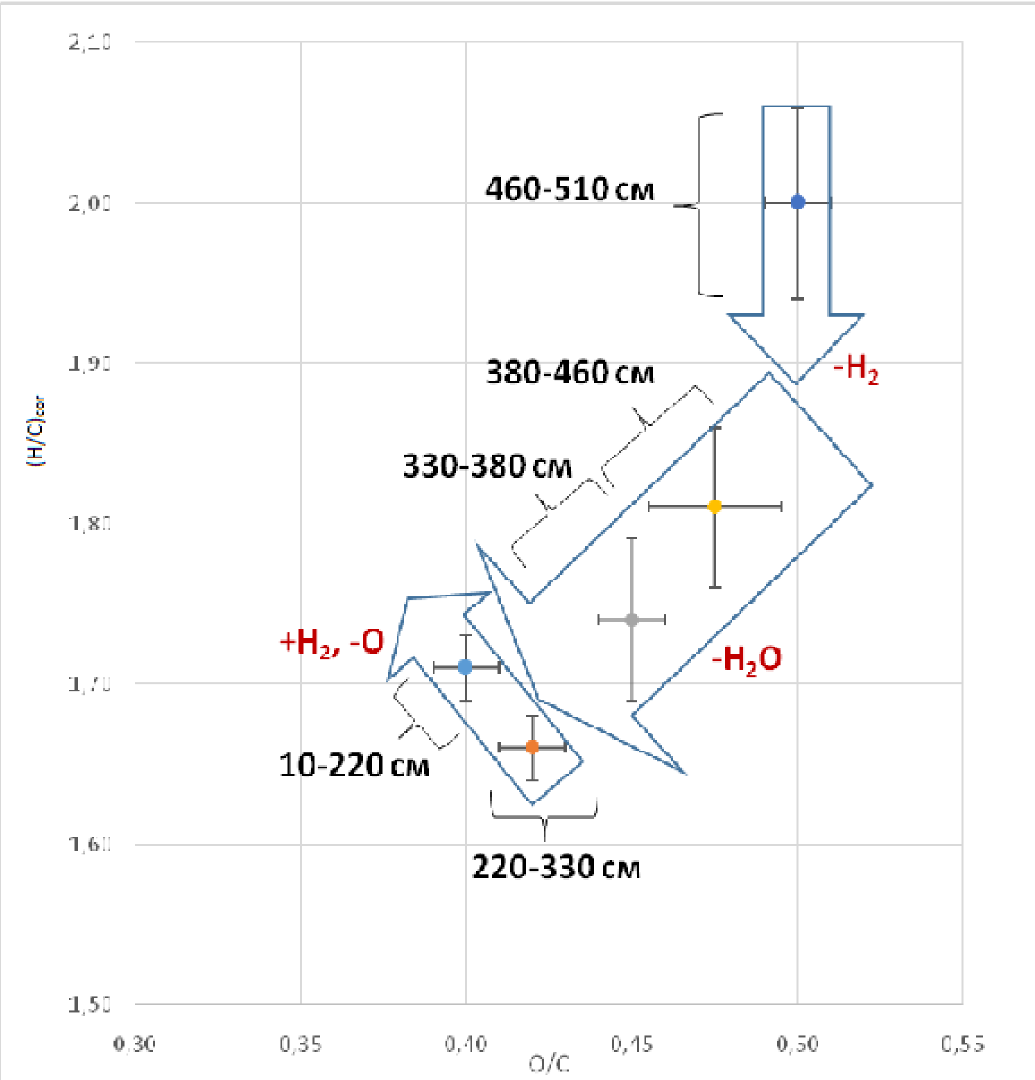

Figure 6. Scheme of the humic acid transformation

The depth of 330-380 cm is presented by scheuchzeria-sphagnum peat with an average degree of decomposition. Most likely, this group belongs to beginning of the Atlantic period, which is characterized by slight cooling and decreased precipitation. These climatic conditions saw active processes of bog formation and peat accumulation. The peat-forming vegetation: sphagnum moss and grass. The reduced amount of atmospheric precipitation resulted in the O/C ratio fall. Transition from the previous period can be expressed by dehydration reactions.

The successive areas of complex sphagnum and sphagnum fuscum peat with a low degree of decomposition represent the depth of 220-330 cm. This group allegedly belongs to the Atlantic period - the Holocene Climatic Optimum. The hypnum mosses are predominant, there is also grass and shrubs. The humic acid ratios of H/C and O/C continue to fall. Transition is expressed by the dehydration.

The depth of 10-220 cm is presented by successive areas of bog-depression sphagnum and scheuchzeria-sphagnum peat. This group belongs to the Subboreal and Subatlantic periods that are less warm and more humid compared to the Atlantic period. The bog formation and peat accumulation are activated. According to the degree of decomposition, this peat group is divided into two areas: lower at a depth of 110-220 cm with an average degree of decomposition and upper at a depth of 0-100 cm with a low degree of decomposition, but with still ongoing processes of microbial transformation of plant residues. Hypnum mosses are replaced by sphagnum. The amount of Scheuchzeria and cotton grass increases. It is a stage that the bog is completely transformed from the low-moor to the high-moor. The atomic ratios of H/C are rising, and the atomic ratios of O/C are reduced.Transition is described through restoration of carbonyl groups to methyl ones.

CONCLUSIONS

Common borders of the humic acids extracted from the Mukhrino bog's stratigraphic column, in which the mass fractions change, include: carbon from 50.30 to 59.30%, oxygen from 38.10 to 29.58%, hydrogen from 4.68 to 6.13%, nitrogen from 2.69 to 5.95%, sulfur from 0.10 to 1.87%.

The humic acids extracted from the sphagnum peats have the highest carbon content of about 58% (scheuchzeria-sphagnum peat - 57,85±0,44%, bog-depression sphagnum peat – 58.25±0.34%, complex sphagnum peat – 58.01±0.92%, sphagnum fuscum peat 58.33±0.56%), however, the species differences do not make a significant difference. For scheuchzeria peats, the carbon mass fraction is lower and totals about 56% (scheuchzeria peat – 56.32±0.43%, scheuchzeria-sphagnum peat - 56.47±0.58%). The grass-hypnum sapropel contains 54.49±0.91% of carbon. The sapropel is composed of 52.18±0.77%. The carbon content falls with the increased depth.

The diagram of the average atomic ratios of $(H/C)_{cor}$ – O/C for the humic acids extracted from the stratigraphic column in the Mukhrino bog's peats shows how the global climate change has affected the humic acid structure. Warming and reducing the amount of atmospheric precipitation resulted in a decrease of oxygen and hydrogen content, while cooling and increased precipitation led to the growth of the carbon and hydrogen content.

The humic acids of lacustrine sapropels aged about 9-10 thousand years have the most oxidized form. With subsequent warming and decreasing the atmospheric precipitation, the humic acids get into condition.

SUMMARY

The results of this work can be used to forecast changes in physical and chemical properties of the humic acids extracted from the Middle Taiga peats according to a peat depth.

In the future, confirmation of the alleged climatic periods is planned using the radiocarbon analysis.

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