PALEOGEOGRAPHY

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*RESEARCH OF GROUP AND FRACTION COMPOSITION OF HUMUS IN HOLOCENE HIGH PEATLAND**

SUMMARY. This paper presents the results of stratigraphic and geochemical study of peat bog Toporkovsky riam located in the Omsk region. According to radiocarbon dating of peat samples at different depths the age of formation of peat deposits is estimated — it is about 5200 years, the rate of accumulation of peat in different time intervals is calculated. On the basis of layered distribution of geochemical parameters (pH, Eh, Loss on ignition), with the stratigraphic data, two basic types of peat are determined in the peat bog. At the bottom of the cut there is a lowland peat bog (4200-5155 years), which higher in the section gives way to upland (4200 years ago to the present day) and very poorly defined transition layer of peat, which indicates a dramatic change in terms of the transition period. Determination of group composition of organic matter (I.V. Tyurin method modified by V.V. Ponomareva and T.A. Plotnikova) showed that fulvic acids predominate in the humus at all depths of occurrence of peat. Distribution of groups and factions of humic and fulvic acids on the depth of cut has a number of areas that can be used for paleoclimatic reconstructions conditions of their formation.

KEY WORDS. Organic matter, humic acid, fulvic acid, peat.

The research of upland peat bogs is topical nowadays from the point of view of obtaining paleoclimatic and paleoecological information. A unique source of the organic substance is a peat bog. Possessing a high lag effect of properties, it stores in itself information on biochemical structure of plants and isotope structure of the atmosphere, types of photosynthesis, temperature and hydrological conditions [1-2]. The organic substance represents the main part of peat (80-95%). In upland bogs it is presented mainly by cellulose, hemicellulose, a lignin, wax rosin. Peats of such bogs are lightly humificated; humic substances make 10-15% from the general content of carbon, fulvic acids prevail in their structure. Peat of lowland bogs are humificated

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in much higher degree, it contains up to 40-50% of humic substances in which humic acids prevail.

Humic substances aren't individual chemical compounds, and represent the heterogeneous system of organic substances of complex composition and structure [3-5]. They can be found in peat bogs, both in a free condition, and in the form of various combinations with cations of metals, in the form of the adsorptive complexes. Distribution of groups of humic substances in forms of connections with mineral part of humus is characterized by fractional structure of humus. Among methods of investigation of organic substance methods studying the contents, structure, properties and a structure of organic substance of soils are distinguished [6-10].

The aim of this research was to determine the features of group and fractional structure of humus of peat, and also to obtain data for specification of paleoclimatic information.

Objects and methods. The samples which have been selected from an upland peat bog Toporkovsky riam (moor with regrowth), located in the Krutinsky region of the Omsk region (fig. 1) were taken for the research.

Figure 1. Location of Toporkovsky riam

Sampling was made by a method of an open pitting with layer-by-layer sampling with a step of 3 cm. At the same time the samples for radio-carbon dating were selected. Determination of residual activity of carbon is executed in laboratory of geology and a paleoclimatology of the Cenozoic of Institute of geology of the Siberian

Branch of the Russian Academy of Science on two-channel installation on benzene-scintillational option. For calculation of age the half-life period 14C equal of 5570 years is used, the age is calculated from 1950.

Samples for the geochemical analysis in vitro were transformed into an air and dry condition they, were crushed and sifted through a sieve (d = 2 mm). Assessment of the general geochemical characteristics was carried out in a water extract from peat (1 g of peat to 25 cm3 of water). PH, Eh were determined by an electrometric method, an ash-content and the general content of organic substance of peat (loss when calcinating — Lwc) — by a gravimetric method. Measurement of optical density of humic acids in visible area with lengths of waves of 465 and 650 nanometers were carried out with the help of UV-Vis Agilent 8453 spectrophotometer.

Group and fractional structure of humus was defined for 22 samples of the peat which have been selected at various depths. Fractionation of organic substance was carried out by I.V.Tyurin's technique in V. V. Ponomareva and T.A.Plotnikova's modifications [6], [11], [12]. The scheme of this technique gives the chance to subdivide humus into three fractions of humic acids (HA1, HA2, HA3) and four fractions of fulvic acids (FA1, FA1a, FA2, FA3). The course of fractionation of humus of the soil can be presented by the following scheme [6]:

1st sample of soil

↓

direct extraction
0,1 *н* NaOH
(HA1 + FA1)

2nd sample of soil

↓

decalcinating 0,1 *н* H_2SO_4
extraction *(FA1a)*

↓

0,1 *н* NaOH extraction after decalcinating
(HA1 + HA2 + FA1 + FA2)

↓

extraction (hydrolytic)
(HA3 + FA3)

The general content of organic carbon in the received extracts, and also the content of carbon of humic acids were determined by a titrimetric method. The concentration of carbon of fulvic acids was determined by a difference of the general content of carbon and carbon of humic acids in the corresponding extracts [6], [12].

Results and their review. Stratigraphy of a section has the following structure (from top to bottom): at the top, in the range of 0-10 cm three is amoss "pillow", then in the range of 10-40 cm there is a peat sod, 40-433 cm — peat upland of brownish-brown color. There are about 3 layers of burning. Along the specified horizon there are remains of buried timber. In the lower and average part of a layer there are birches, on top — there are pines. In the range of 433-510 cm the horizon of lowland peat with the large macroremains of water vegetation is opened. In a peat bog section they

are opened in the form of strips of blackish-grey color. In the basis of this horizon, in the range of 510-530 cm lake loam of black color, with organic chemistry is found. Deeper than 530 cm the grey lake loams can be found.

Radio-carbon age and speed of peat accumulation. According to the radio-carbon analysis the age of the basis of a peat bog is estimated in 5155±50 years. Dependence of radio-carbon age on a sample depth (fig. 2, a) has linear character of y = 9,7534 x (R2 = 0,98 at P = 0,95) according to which the average speed of accumulation of peat on a section makes 0,98 mm/year. However calculation of speed of accumulation of peat between radio-carbon datings shows that the speed of accumulation of peat during the different periods has been significantly changing (fig. 2, b). The maximum speed of accumulation was observed 3700-3900 (3,64 mm/year). High speed of accumulation (is approximately twice lower than maximum) was also observed three times — 2100-2700; 1200-1600 and during the previous 500 years. The minimum speed of accumulation of peat was observed respectively in the period of 500-1200 and 2700-3770 and also at the beginning of peat bog formation — 5000-5100. Such nature of speed distribution of peat accumulation testifies probably to periodic change of climatic conditions.

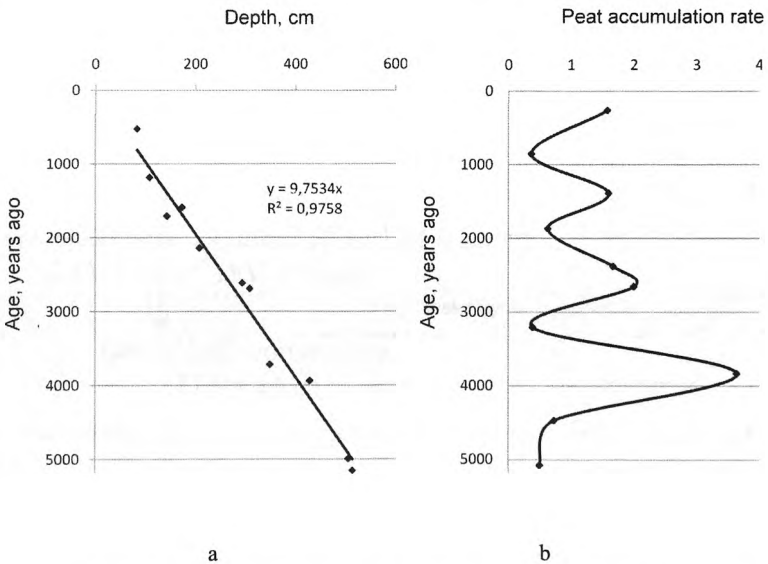


Figure 2. Dependence of radio-carbon datings on a depth of samples and distribution of speed of peat accumulation in Toporkovsky riam peat bog section

Losses at calcinating (LAC). Figure 3 presents distribution of the main geochemical characteristics on a section of a peat deposit. Distribution of the general content of organic substance (lac) from peat age shows that on the most part of a section (600–

4200) the content of organic substance changes slightly. Average value of this indicator on this site 98,2 ± 1,2% (at an average on % coal mine 96,9±3,5). During this period it is possible to note three minima, when the content of organic substance considerably decreased (by 2%) — 970, 1540 and 3260. In the top layers of a peat bog (the last 550 years) sharp reduction (almost for 10%) contents of organic substance in comparison with average value in the main part of a section is observed. The most considerable fluctuations in the content of organic substance are observed in the lower part of a section. During the period 4800-5000. Lwc makes about 94%, then the content of organic substance increases for 2% and in the period of 4400-4700 makes about 96%. 3300 the content of organic substance sharply falls (to 94%) then there is sharp growth of the content of organic substance and its stabilization for the long period.

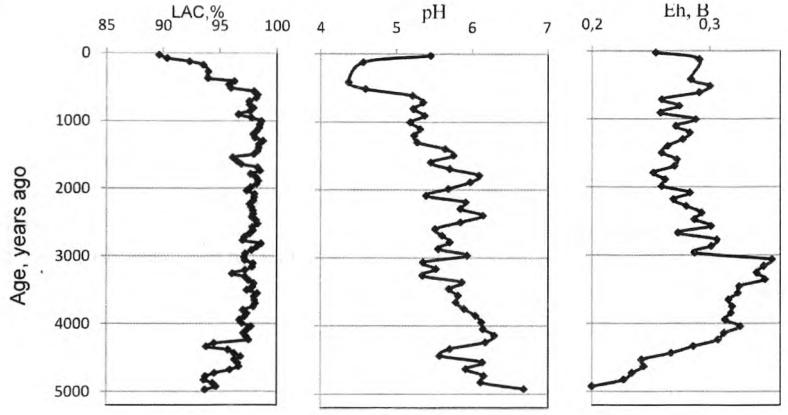


Figure 3. Distribution of the main geochemical characteristics on Toporkovsky riam peat bog profile

PH and Eh. In the lower part of a section (about 5000) the maximum value pH and the minimum Eh value on a section is observed. This horizon characterizes the period preceding formation of a peat deposit and can serve as the confirmation of the fact of formation of a peat bog on a place of the paleolake whose degree of an eutrophication reached the maximum sizes (Lwc — 94%). Section stratification according to which the eutrophication of the lake began much earlier (datings leads to such conclusion also are absent) and by this period there was almost full occlusion of a paleolake, in connection with sharp reduction of a water level and possible temperature increase. Within the next 200 years some increase in the content of the organic substance, being accompanied by sharp decrease pH and increase of OV of potential is observed. Such change of characteristics of deposits can testify to increase in amount of oxygen, defiant increase in growth and speed of decomposition of the

organic substance, conducting to acidulation of waters and soils. Later, within the next 300 years the geochemical situation changes slightly: potential is still displaced in positive area and acidulation of deposits proceeds. This period is accompanied by significant increase in the content of organic substance and its stabilization. According to morphology of a section at these depths lowland peat lies. Speed of accumulation of deposits is insignificant and makes 0,5-0,7 mm/year.

Since 4500 within 200 years the geochemical situation changes considerably: considerable shift of oxidation-reduction potential in positive area is observed, pH is thus displaced in sour area on 0,5 units, there is a sharp reduction of the content of organic substance in deposits. The next 100 years potential continues to be displaced in positive area, but size pH starts growing that leads to growth of the content of organic substance. It is possible to assume that this period was accompanied by fall of level of ground waters (humidity reduction) that led to formation of an upland peat bog on a place of the lowland. The transitional layer in this peat deposit is insignificant, change of conditions happened during rather short period (about 100 years). This «revolutionary» period was replaced by the millennium of relative stability of geochemical conditions: pH was a little acidified, potential was slightly displaced in positive area, the content of organic substance changed slightly. In spite of the fact that all other part of a peat deposit is identified as upland peat, nevertheless, one more quantum leap in change of geochemical indicators is observed about 3000; there is a small shift of pH in neutral area and considerable shift of potential in recovery area. Probably, it is connected with peat bog flood (increase in an amount of precipitation) that led to delay of decomposition of organic substance of peat. However this period was short.

Considerable change of a geochemical situation happened 600-700 to what sharp falling of pH from 5,50 units to 4,37 units to which there corresponds maximum peak on a curve of change of Eh, and then again increase to 5,45 units in pH to which there corresponds decrease in Eh values testifies. Thus the increase in a mineral component of peat can be explained or increase in speed of decomposition of organic substance (when process of decomposition of organic substance of peat happens quicker, than process of its formation), or increase of the input of mineral components, for example, at the expense of atmogenic processes.

On the basis of a stratigraphy and the analysis of geochemical characteristics of a peat deposit (fig. 3) it is possible to allocate two main types of peat: in the basis — lowland type (4200-5155) higher on a section being replaced upland (from 4200 to the present). Besides the layer-by-layer geochemical analysis of peat allows to allocate the short period of formation of transitional peat — 4200-4300 and also some periods of change of a geochemical situation during formation of upland peat. Most essential of them are 2900-3100, 1500-1700, 500-700. However these changes didn't cause basic changes in nature of formation of a peat deposit.

Organic substance of peat. According to the theory of humification [7-8] all organic components of soils can be divided into 2 groups: 1) labile, easily transformed, and 2) steady, collecting for a long time. Extent of decomposition of peat most are often defined visually or by a microscope, the following signs are thus considered:

plasticity, quantity and safety of fragments of plants, quantity and color of the wrung-out water. Usually extent of decomposition of lowland peat is much higher upland and makes from 10 to 60%, it has more dark color and a uniform consistence. Similar data can be obtained by determination of coefficient of the chromaticity, that Springer was characterized by the relation of optical density with lengths of waves of 465 and 650 nanometers. This relation expresses the steepness of falling of optical density at increase in length of a wave and characterizes relative degree of a condensation of humic substances. The sharper the curve falls, the highet is value of the relation of A465:A650, especially light coloring has solution of humic acids, especially the peripheral aliphatic component is developed at them. Small values of the relation emphasize big degree of a maturity of GC, their degree of humification and development of aromatic structures in nuclear part of molecules. Absolute values of the coefficients characterizing optical properties of humic substances (acids) depend on conditions of their formation. In dry and warm conditions the humic acids having well shaped aromatic part, making big share of macromolecules, and small aliphatic part, respectively small A465:A650 values are formed. In cold and damp conditions humic acids with a bigger share of peripheral part that is reflected in change of absolute sizes coefficients, characterizing optical properties of this component of soils [3], [6] towards their increase are formed.

According to the layer-by-layer analysis of tests of Toporkovsky riam peat the maximum value of the relation of A465:A650 is observed about 1500 (fig. 4), i.e. humic acids in these layers have the most branched structure that can correspond to cold and damp conditions [3], [6]. The maximum degree of humification of humic acids (the minimum value of the relation) is determined in the samples, the age of which is 2180, 3200 and 4800, probably it is caused by drier and warm conditions of a peat bog formation. In the range from 2200 to 3400 the average value of coefficient changes slightly and makes 8,4±2,2. Some decrease of A465:A650 begins with the depth dated 3400 that testifies to increase of degree of formation of humic acid, owing to accumulation and transformation of the organic plant material with the course of time, which leads to the formation of more complicated organic structures.

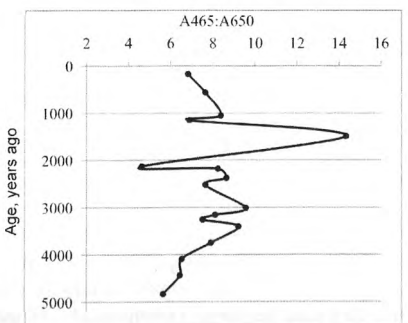


Figure 4. Distribution of coefficient of chromaticity of Springer (A465:A650) depending on age of a studied sample

Fractional structure of peat organic substance. During formation of the peat deposit, the vegetation forming it partially decays, and is partially settled in the form of the vegetable precipitation, little transforming during the period of bedding, owing to special geochemical conditions. According to group and fractional structure of humic components of organic substance of peat (fig. 5, a), humic acids prevail in its composition (not hydrolyzed residue which represents the inert part of humus being in strong connection with mineral part [7]), and from acids — fulvic acids. The average content of humic acids on a section makes 4,5 ± 1,4%, and fulvic acids — 14,4 ± 2,9% with the view of air-dry soil that is characteristic for upland peat bogs [3-5].

Distribution of the content of the general carbon which has undergone humification is presented in fig. 5, b. The share of humificated carbon in a studied section averages to 34,3±6,2% from its general content (Lwc) and changes depending on the depth of samples from 23 to 55%.

In the figure the periods corresponding to the maximum humification of vegetation are accurately allocated: 4400-4800, 3200, 2100-2200. A relatively high degree of humification of organic substance is observed in the last 600 years. The minimum decomposition of vegetation is observed in a layer, formed 3800-4100 1100.

Calculation of the relation of the total content of humic acids to the general content of fulvic acids (Sgk:sfk) (fig. 5, c), also characterizing the extent of soil humification, allowed to establish that this indicator within a studied section changes from 0,11 to 0,69, at average value of 0,36±0,15. The curve has similar character with distribution of the general content of humic substances, at least practically all extrema on curves coincide. This result allows claiming that the increase in peat humification leads to the increase of humic acids in relation to fulvic acids.

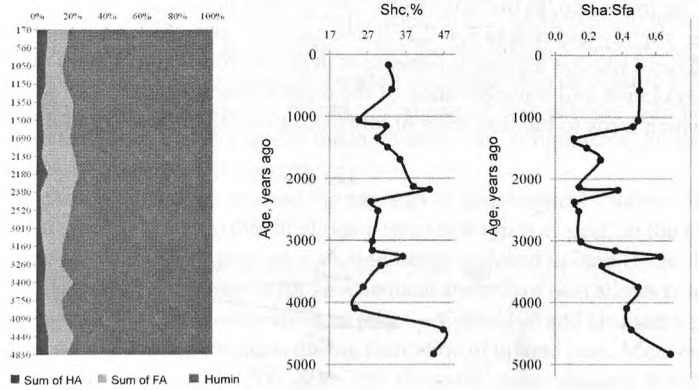
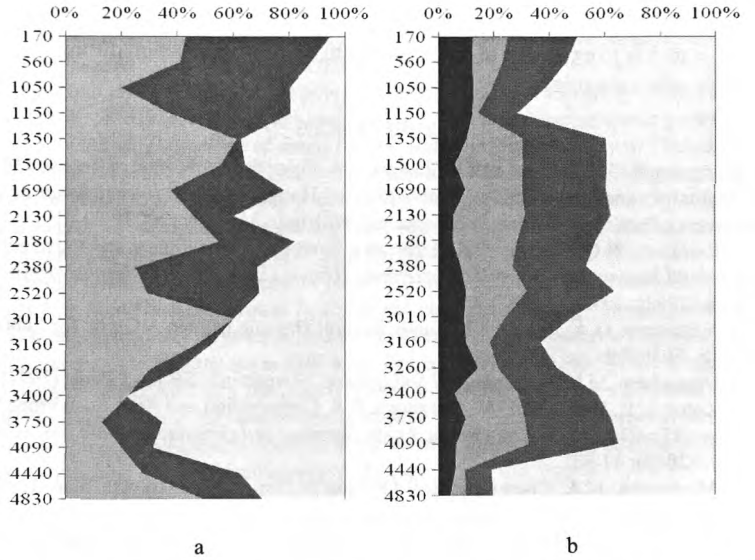


Figure 5. Distribution of humic substances components (a), general content of humic substances (b) and the relations of acids concentration Sha:Sfa (c) on a section of Toporkovsky riam upland peat bog

In fig. 6 the division of each group of acids on fractions on different horizons of a peat deposit is presented. In middle part of a section (3000-1150), fractions 1 and 2 of humic and fulvic acids prevail in the composition of organic substance, i.e. compositions connected with sesquioxides and calcium. The chart characterizing the maintenance of fulvic acids (fig. 6, a) indicates that the concentration of the 3rd fraction, i.e. the fulvic acids connected with clay minerals is slightly reduced in the top horizons. But at the same time its contents increase in the lower part of a section. Among FC fractions only free forms and complexes with mobile R2O3 (fraction 1) possess independent value. Their content changes equally to the change of an ecological situation and is one of exponents of expressiveness of humus acid properties [8]. Results of research confirm [3], [12] that the fulvate structure of humus is characteristic for upland peat.



a b

Figure 6. Fractions distributions of humic (a) and fulvic acids (b) on depth of a section of Toporkovsky riam upland peat bog:

a) HA1 — free and connected with mobile sesquioxides
HA2 — connected with Ca
HA3 — connected with clay minerals and steady sesquioxides
b) FA1a — free and connected with mobile sesquioxides («aggressive» fraction)
FA1 — free and connected with mobile sesquioxides
FA2 — connected with Ca
FA3 — connected with clay minerals and steady sesquioxides

The peak observed at a depth dating 2180 is traced at determining all indicators, thus it should be noted that during this period the total of organic substance and amount of humic acids considerably increased.

Climate change leads to change of oxidation-reduction potential of the environment, and as a result fulvic acids prevail in the composition of organic substance under oxidizing conditions. Fulvic acids contain less carbon and more oxygen than humic acids whereas shift of value of oxidation-reduction potential in recovery area (3000-4000) corresponds to maxima in the content of humic acids.

Thus, as a result of the research of fractional and group structure of humus of an upland peat bog Toporkovsky riam, we can claim that information on structure of organic substance is an important part when carrying out paleoclimatic researches. Results of research confirm [3], [12] that the fulvate structure of humus is characteristic for upland peat. According to the analysis the maximum extent of humification of vegetation is observed during the following periods: 4400-4800, 3200, 2100-2200, 1150. A relatively high degree of humification of organic substance in the last 600 years can testify to existence of the tendency to humidity reduction during this period and to possible warming.

REFERENCES

1. Lapteva, E.M., Vanchikova, E.V., Popova, L.A. About the Application of Research Methods for Qualitative and Quantitative Composition of Humus. *Second International Scientific Conference «Humic Compounds in Biosphere»: Abstracts*. Moscow (2003): 80-81.

2. Kovaleva, N.O. Organic Soil Matter as a Source of Paleoclimate and Paleolandscape Data. *Second International Scientific Conference «Humic Compounds in Biosphere»: Abstracts.* Moscow (2003): 40-41.

3. Nekrasova, O.A. Research Methods for Soil Organic Matter. A Guide for Laboratory Research. Ekaterinburg (2008): 107.

4. Dergacheva, M.I. *Archaeological Soil Science*. Novosibirsk: SB RAS Publ., (1997): 228.

5. Kotov, V.V., Nenahov, D.V., Gasanova, E.S. Composition and Acid-Base Properties of Fractions of Leached Chernozem Fulvic Acids. *Sorption and chromatographic processes. Vol. 10. № 1.* (2010): 47-53.

6. Martynova, N.A. Chemistry: Soil Organic Matter. Irkutsk: Irkutsk State University Publishing (2011): 257.

7. Orlov, D.S. Soil Humic Acid and General Theory of Humification. Moscow: Moscow State University Publ. (1990): 332.

8. Orlov, D.S., Birjukova, O.N., Suhanova, N.I. Organic Matter of Russian Federation soil. Moscow: Nauka (1996): 256.

9. Schnitzer, M. Humus Substances: Chemistry and Reactions. *Soil Organic Matter* / ed. M. Schnitzer and S.U. Khan / Development of Soil Science (N 8). Ottawa (1978): 1-64.

10. Stevenson, F.J. Humus Chemistry: Genesis, Composition, Reactions. 2nd ed. N.Y.: John Wiley and Sons (1994): 496.

11. Ulankina, A.V. Comparative Characteristics of Fulvic Acids Separated from Soils by the Tyurin and Forsyth Methods (PhD thesis)]. Moscow (2002): 88.

12. Orlov, D.S., Grishina, L.A. Practical Tutorial on Humus Chemistry: Teaching aid. Moscow: Moscow State University Publ. (1981): 272.