Biogeotransformation of bog ecosystems organic substance of Northern Eurasia

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1. Introduction
Humification of organic residues is a complex biogeochemical process in which various groups of enzymes of microorganisms as well as extracellular enzymes accumulated in soil participate. According to the majority of researchers [1], peat formation occurs mainly in the upper (up to 0.5 m) layer where the vital activity of microorganisms is provided by the penetration of air oxygen and solar energy. The lower boundary of the aerated layer has seasonal variations which are synchronous with fluctuations of the bog water level. These factors determine the peat layer thickness. It is believed [2] that lower (anaerobic) layers of the peat deposit are characterized by the conservation of organic substances; thus, the component composition of peat is practically invariant with respect to time. The opinion about the attenuation of microbiological processes under anaerobic conditions is widespread. At the same time, by analogy with aquatic ecosystems for which these issues are considered in sufficient detail [3-5], one can expect that with incomplete assimilation of bioavailable organic substances in the aeration zone and in deeper anaerobic layers their decomposition takes place. This process occurs at the expense of anaerobic microorganisms: methanogens and sulfate reducers [6-8]. The metabolism of the former is possible only under conditions of almost complete absence of oxygen and is accompanied by the release of swamp gas (methane). The latter are capable of assimilating organic low-molecular compounds in transitional regions.

It should be noted that the simultaneous occurrence of individual stages of the peatogenesis process does not allow them to be isolated and sufficiently clearly described. Understanding of the
peculiarities of transformation of organic substances during peatogenesis was obtained as a result of research in regions with a relatively warm climate where the decomposition of plant remains is much faster than in cold climate conditions. At the same time, in the bog ecosystems of Northern Eurasia below the permafrost latitudes biogeotransformation of the peat organic mass takes place at a lower rate [9-10]. This allows us to hope that experimental sites located in such regions are suitable for a detailed study of the peat formation mechanisms.

In this study, the structural features and component composition of upland peat samples with gradation along the horizons of occurrence are shown using the Illassky wetland of Primorsky district, Arkhangelsk region as an example. In support of the proposed assumption, the performed studies have revealed some features of the structure formation process, the composition and properties of peat deposits under the conditions of Northern European Russia.

2. Methods and materials
A section of a bog located in Primorsky district (64 ° 19 'N, 40 ° 36' E) of Arkhangelsk region was used as a test site. The microlandscape in the selected area is a system of oligotrophic ridge-pool swamp complexes (with 50-60% of the area occupied by ridges) with lake-moss central parts (with numerous small lakes) [11]. Sphagnum (Sphagnum magellanicum, S. fuscum, S. angustifolium) prevails in the vegetation cover, with shrubs (cranberry, heather, Labrador tea), cotton grass, sundew, dwarf birch, and rare oppressed pines. The underlying rocks are loam. The peat deposit thickness at the sampling site was 3.5 m.

Peat sampling was carried out with the help of a manual peat borer TB-5 on visually distinct reservoir horizons of the peat deposit [9].

The group component composition of the peat organic substance was evaluated using a weight method by sequential separation of the components by various solvents according to [12]. The determination of the ORP (oxidation-reduction potential) and pH was carried out during peat sampling by the method of direct potentiometry [13-14] on a universal analyzer of liquids ANION 4100 (Infraspak-Analit, Russia) using an electrode pair from a silver-chloride electrode EVL-1M3.1 and a platinum electrode EVP-1SR to measure the ORP and a combined electrode ESK-10603 to measure the pH.

Meat-and-peptone agar (MPA) was used to count the total number of ammonifying bacteria utilizing the organic forms of nitrogen. The bacteria assimilating the mineral forms of nitrogen were taken into account on starch-ammonia agar (SAA). The fungi were calculated on a Saburo dextrose-peptone agar (DPA). Sowing was carried out in 3-5 fold replicates. The number of microorganisms grown on nutrient media was recalculated to 1 g of absolutely dry peat (a.d.p.) [15].

The effect of peat biodegradation on the hydrodynamic characteristics of humic substances was evaluated in solutions of peat humates isolated with 0.1 N NaOH from previously debituminized peat samples using petroleum ether. Solutions of peat humates were purified from excess alkali by dialysis on cellophane up to pH 7.5-8.0. The measurements of particles were carried out in solutions of humates immediately after dialysis (the concentration of humates varied from 1.5 g/l to 8 g/l). Then the solutions were adjusted to a concentration of 100 mg / l with distilled water and re-measured. The particle size distribution in the obtained humate samples was estimated by dynamic light scattering using a laser particle size analyzer Horiba LB550 [11].

3. Results and discussion
The results of measurements of the group chemical composition of peat are shown in Table 1. During the peat accumulation the share of easy hydrolysable substances (EHS) is most significantly reduced. Concomitantly the formation of new thermodynamically stable components, humic substances (Hum) occurred. The greater the depth of a peat deposit, the lower the content of hydrolysable substances and the higher the content of poorly-hydrolysable substances (PHSs) and lignin. This indicates that the processes of destruction and condensation occur simultaneously.
The content of bitumens also varies significantly. In the top aeration peat deposit layer, the initial stage of peat formation takes place, and the bitumen content decreases from 2.5 to 1.5%. Previous studies [9] showed that in these peat layers the least stable part of the original plants - pigments and vitamins - are oxidized readily. At a depth below 5-10 cm only their trace amounts are detected.

The transformation of other bitumen compounds proceeds much more slowly. Hydrolysis of esters, partial assimilation of the hydrolysis products by microbiota, and oxidation of the components with the formation of hydroxy acids and neutral compounds occurs [9]. Thus, with the depth of occurrence, the bitumen content increases by 5.5 - 6.0% due to the transformation processes.

Microscopic examination of samples from different depths in the initial state and after step-by-step removal of soluble components showed that the destruction of capillary-porous plant material structure begins with some delay. This process starts after the oxidation of the accompanying and inlaying substances. This is because of the cellular structure of the plant residues and the screening effect of bitumens [10].

The nonmonotonicity of change in the content of the main components of the peat organic matter with the depth of occurrence under biogeo-transformation is, apparently, explained by various destructive and condensation oxidative processes: humification and mineralization.

| Table 1. Influence of occurrence depth on group component composition of peat. |
|---------------------------------|--------|--------|--------|--------|--------|
| Depth, cm | Bitumens | Hum | EHS | PHS | Lignin |
|----------|---------|-----|-----|-----|-------|
| 0-5      | 2.40    | 17.30 | 40.46 | 20.74 | 19.10 |
| 5-15     | 1.72    | 9.88 | 50.11 | 18.78 | 19.51 |
| 15-75    | 2.28    | 10.03 | 50.14 | 17.83 | 19.72 |
| 75-100   | 3.77    | 14.27 | 39.34 | 22.95 | 19.67 |
| 100-150  | 3.99    | 14.22 | 35.45 | 21.64 | 24.70 |
| 200-250  | 5.97    | 17.02 | 27.77 | 32.07 | 17.17 |
| 300-350  | 5.66    | 22.78 | 27.23 | 23.27 | 21.06 |

The change in the oxidation-reduction potential with increasing depth of the deposit (Figure 1) indicates less intensive processes below the groundwater. Probably, in the peat deposit lower layers the transformation processes occur with the participation of anaerobic biota under the influence of exoenzymes or an acidic medium (pH = 3.7-4.9).

The ORP data presented indicate that as the surface moves weakly deeper into the deposit, the oxidative conditions (400-500 mV [14]) are gradually replaced by intensively reduction ones (<200 mV [14]). In this case the gradual deoxidation of peat is observed, which is evidenced by an increase in the pH.

In order to clarify the mechanisms of organic matter anaerobic transformation, the microbiological activity was studied (Figure 2).

The maximum number of ammonifiers was fixed in the peat bog upper layer (0-20 cm). This seems logical taking into account the maximum amount of bioavailable organic compounds, organic nitrogen, and the most favorable temperature and water-air conditions. The depth from 60 to 100 cm is characterized by a reduction of the total number of microorganisms with the predominance of ammonifiers. In the 130-170 cm layer the number of bacteria that assimilate organic and mineral nitrogen is practically of the same order. At a depth of 230-270 cm the number of bacteria absorbing mineral nitrogen was 18 times as large as that of ammonifiers. It proves that intensification of the
transformation processes of mineral nitrogen forms takes place with depth. The number of yeast-like fungi is not high (6-22 cells/g). However, in the layer of about 60-100 cm their content sharply increased up to 14.7 * 10^3 CFU/ a.d.p. and reached the number of the ammonifiers. At a depth of 130-170 cm they were not detected. Further studies are required to interpret these facts.

![Figure 1](image1.png)  ![Figure 2](image2.png)

**Figure 1.** Influence of occurrence depth on ORP in peat deposit.  **Figure 2.** Influence of depth on structure and abundance of microbial communities.

It is logical to expect that the physico-chemical properties of the humic acids formed as a result of biogeotransformation of the organic mass essentially depend on the humification conditions. Experimental data presented in Figure 3 clearly demonstrate the influence of the deposition depth occurrence and the associated degree of decomposition (R) on the hydrodynamic characteristics of humic substances.

The dimensions of the molecularly dispersed particles of humic and fulvic acids are within the range of 4-12 nm. In this case the humic acids isolated from slightly decomposed ones (peat from the deposit surface) are prone to the formation of supramolecular formations (d = 800-4000 nm) even in the low concentration area (100 mg/l). This is most probably because of greater saturation of their molecules by polar functional groups. In biogeotransformation some of the HA functional groups are oxidized. Accordingly, humates from the peat with a higher degree of decomposition are less likely to form intermolecular aggregates in the crossover area.

It should be noted that in the area of high concentrations (> 1 g/l) the macromolecules of humic substances are exclusively in the form of aggregates, d = 800-6000 nm (Figure 3b). Their polydispersity increases markedly with the occurrence depth of peat. This also indicates significant changes in the structure of humic substances in the anaerobic zone of the peat deposit.

The regularities revealed, beyond doubt, affect the peat moisture-holding capacity, the sorption and other properties important for the functioning of ecosystems. With immobilization of the incoming compounds, both physical adsorption by the capillary-porous peat matrix and hemosorption by its components are possible [16-17]. The distribution of the substances along the section in these cases will be significantly different. In the former case the incoming compounds due to the movement of
water streams during periods of floods and low water are transported to layers below the level of the groundwater fluctuations. In this case they accumulate being sorbed by the capillary-porous peat matrix. In the second case the elements of external action bind more firmly to individual components of the natural matrix (for example, with humic substances), and the distribution into the lower layers occurs after the saturation of the upper horizons.
Figure 3. Hydrodynamic characteristics of humates isolated from peat from various occurrence depths.

4. Conclusions
Thus, the processes of deep biogeotransformation of organic matter under the Northern Eurasia climate conditions occur both in the aerated (peat-forming) layer of the peat deposit and in the relatively anaerobic conditions of the conservation zone. This is proved by the stratigraphic variability of the oxidation-reduction potential, the chemical composition of the organic matter, and the structure of the microbiological peat communities.

The biodegradation of the peat organic matter is largely due to hydrolysis and assimilation by the microorganisms of readily hydrolyzable compounds, as well as of some bitumen components.

5. References
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