Вестник Томского государственного университета. Биология. 2019. № 48. С. 6–31

АГРОХИМИЯ И ПОЧВОВЕДЕНИЕ

UDC 631.41
doi: 10.17223/19988591/48/1

Evgeny V. Abakumov, Vyacheslav I. Polyakov, Ksenia S. Orlova

St. Petersburg State University, St. Petersburg, Russian Federation

Podzol development on different aged coastal bars of Lake Ladoga

This paper presents the result of the studies of soil formation on different aged coastal bars in the transgression zone of Lake Ladoga in the Nizhnesvirsky Nature Reserve (Leningrad region, North-West of the Russian Federation). The investigation presents the data on soil chronoseries, located on four Ladoga coastal bars of different ages from 70±25 to 1590±25 years BP. We estimated the trends of accumulation and transformation of organic matter, elemental composition of humic acids (HAs), development of plant communities and the influence of soil formation factors on the formation rate of soil horizons. We assessed the degree of soil organic matter stabilization using modern instrumental methods (spectroscopy of nuclear magnetic resonance CP/MAS ^{13}C-NMR). An integral indicator of the hydrophobicity of HAs, which represents the total fraction of unoxidized carbon atoms, is proposed. The Ladoga Holocene transgression is one of the most informative and applicable models for pedogenesis; successional processes occurring in young and mature areas can be traced here. We identified local processes of soil formation such as podzolization, gleyfication, peat formation and humus accumulation. Physical, physical-chemical and biological soil properties with a detailed description of the morphology of soil of different aged coastal bars are presented.

The paper contains 6 Figures, 7 Tables and 71 References.

Keywords: Humic substances; ^{13}C-NMR; soil genesis; soil formations; Podzols.

Funding: This work was supported by the grant of the Russian Scientific Foundation (Project No 17-16-01030).

The authors declare no conflict of interest.

Introduction

The study of soils of chronoseries of the coastal bars of Lake Ladoga transgression provides the most representative model of soil formation, unlike the chronoseries in post-mining dumps, dunes and under mounds. This model describes the formation of Podzols from 0 to about 3500 years, which allows to fully evaluate the formation of embryonic Podzols on the first coastal bars and fully formed Podzols in areas over 2000 years old, since it is generally accepted that the stage of quasiequilibrium occurs 1500-2000 years ago [1-3]. While the soil formation models in quarries can assess the rapid processes of soil formation, long-term soil formation processes can be evaluated.

Soil formation is a biolithogenic or biocosmic process that connects biological and geological cycles in time and space. The temporal cycles of pedogenesis reflect the rates of bio-nutrient interactions and can be investigated by the goal of parametrization of soil-biological processes in anthropogenic disturbances. In the modern ecology of soils, the issue of assessing the efficiency of soil implementation of the main ecological functions and parametrization of the efficiency of soil implementation of the most important ecosystem services is acute [4-5]. Soil formation as a modern process is becoming increasingly relevant in new regenerative models on uncovered land surfaces, dumps of quarries, territories of perspective development (brownfields) and reclamation areas. In these models, taking into account temporal development, variants of diversity of different aged stages of pedogenesis in space are realized, which is described by the property of ergodicity of soils i.e. the possibility of having an analogue of the temporal stages of ontogenesis in space [1, 6-8].

The evolution of soils is the result of their constant movement toward equilibrium with the environment. Periodic changes of external environmental factors determine the variability of soils in time. The study of uneven-aged coastal bars on sandy soil-forming rocks has long been considered a classic object of evolutionary soil science. Historically, it was the soils of different ages on the sands that became the main research object of the soil formation in the taiga zone [1, 5, 9-11]. Chronoseries of soil restoration and recovering by vegetation are more often found there. Chronoseries include continental coastal dunes, uneven-aged surfaces exposed as a result of the transgression of lakes, as well as dumps of quarries and substratum of military constructions [1, 4-5, 7, 12-17].

Soil evolution has been considered as a complicated process related, for the first time, to combination of soil forming factor or soil-formation potential as a cumulative result of soil forming factor interrelation [5]. A number of investigations [2, 14] showed that the rate (speed) of soil formation varies sufficiently and depends on natural zones, parent materials and type of vegetation community [13, 18]. Many studies were devoted to interpretation of soil morphological data in chronoseries [12, 17, 19-20], assessment of diversity of cultivated forms of microorganisms, their biomass and metabolical activity in soils, alteration of soil organic matter quality and mineral part transformation [20]. The obtained data were used to simulate modeling experiments in order to analyze temporal soil development dynamics and to develop methods and criteria for prognostic scenarios of soil/ecosystem development [21].

Mechanisms of Podzol formation, weathering agents and migration processes of organo-mineral compounds [22-23], have been poorly investigated in the study area. The Podzol formation process can be defined as a set of weathering phenomena in the surface layers of the weathering crust and continuously developing in time phenomena of transformation (decomposition and synthesis) and movement of substances, phenomena that are in close functional interdependence and which are based on bilateral exchange of substances between soil and vegetation. Even less studied are functional options between vegetative cover development and soil formation in the study area. The study of the carbon content of different aged soils is of a current interest from the standpoint of genetic and evolutionary soil science, since it provides information on the organic content in the soil profile.

The territory of the research area was affected by the retreat of the Valdai glacier and a series of transgressions of Lake Ladoga, which took place 8000-3000 years ago. About 2000 (1500) years ago, the level of transgression equaled the height of the watershed, and the Ladoga water flowed through it. The Neva was formed and the level of the lake dropped to the modern level in a few decades.

The southeastern part includes up to 20 sand bars oriented along the shore of Lake Ladoga. The strips of pine ridges are replaced in depressions mainly by mesotrophic bogs. The slopes oriented to the rivers and a richer vegetation related to an oxalis type characterize streams in the zone of diluvial drift.

Changes in the shoreline of Lake Ladoga during the Holocene have been actively studied in recent decades. The main sources of data for studying the fluctuations in the level of Ladoga Lake were the bottom sediments of lakes, marshes and peatlands of the Ladoga surrounding areas [24]. The main stages of the history of Ladoga Lake in the post-glacial period have been recreated. Nevertheless, the dating of the transgressive-regressive phases of the lake in the investigation of various authors is contradictory, as are the data on the altitude marks of the water level of the southern region in these periods. The change in the Ladoga shorelines is mainly associated with two factors: oscillations in the level of the Baltic Sea and isostatic uplift of Fennoscandia in the postglacial period [24].

The most controversial stage in the history of the Ladoga is the period of the Ladoga transgression, which followed a significant increase in the water balance of the reservoir, which led to an increase in the water level in the lake [25-27]. The Ladoga transgression is fixed in time (about 5000-2000 BP according to the scale of absolute age) and altitude (from 6 to 18 m) intervals [28].

The causes of the Ladoga transgression are uncertainly interpreted by many researchers. Obviously, the main reason was the lopsided glacio-isostatic uplift of the northern and southern parts of the Ladoga basin, as a result of which the flow from the lake in the northern part of the Karelian Isthmus decreased, and the territories of the southern Ladoga area were flooded [28]. The development of the Ladoga transgression is most often associated with a change in the direction of the water flow from Lake Saimaa system (south-eastern Finland) [27].

During the isostatic uplift of the given territory, the flow from the Saimaa system to the Gulf of Bothnia, and, later, to the Gulf of Finland, changed its direction towards the Ladoga basin, forming the Vuoksa River that sharply increased the water level of Lake Ladoga. However, AV Snitnikov (1957), according to MV Sheetov et al. (2010), believed that the development of the Ladoga transgression was due to the centuries-old rhythm of the fluctuation of the total moisture content in the Holocene, which resulted in a breakthrough of the water from Saimaa Lake and a significant increase in the flow to the Ladoga from the drainage basin. Several factors, endogenous and exogenous, contributed to changes in the hydrographic network of the drainage basin and the water balance of Ladoga Lake [25, 29].

The breakthrough of Saimaa Lake water through the Salpausselkä ridge system and the formation of the Vuoksa River, which is currently one of the main tributaries of the Ladoga, dates within 5000-3000 years ago (radiocarbon age). The difference in the uplifts of Ladoga Lake basin caused water overflow from the deep northern to the shallow southern part and the flooding of significant areas in the Southern Ladoga [30, 24]. Then the water level in the Ladoga began to rise and reached a maximum about 3200 years ago [24].

During this period, a breakthrough of the Ladoga water through the Mginsky-Tosnensky watershed occured, and the Neva River was formed [24-25]. DA Subetto (2007), referring to DD Kvasova, notes that the Neva Channel between Lake Ladoga and the Baltic Gulf was formed as a result of the glacier isostatic uplift of the northern Ladoga and the skewing of the Ladoga Basin, in consequence of which the southern part was flooded with the waters of Lake Ladoga; its water flowed into the valley of the Mga River, which flowed into the Ladoga. The Mginsky-Tosnensky watershed (about 18 m high), represented by moraine loams, was washed out, and the waters of the Ladoga fell into the valley of the Tosno River, which had previously flowed into the Gulf of Finland [25]. However, NN Versilin and GI Kleimenova (2012) in their research indicate that there is no reliable data to believe that over the past 6000 years Lake Ladoga level has risen above the absolute 15m mark, the formation of the Neva should be referred to the earlier dates [31]. Aleksandrovsky AA et al. (2009) note a sharp decrease in the level of Lake Ladoga during the period of 2800-2500 years, which caused the water level drop in the entire hydrological system, and links it to the formation of the river [32].

The current studies are focused on determination of elemental composition of HAs, the degree of its decomposition and determination of soil organic matter stabilization degree. One of the methods for studying the molecular composition of organic matter is nuclear magnetic resonance (NMR), which enables to study the qualitative and quantitative characteristics of organic matter [33, 34, 35]. An application of this method give a possibility to identify the main trends of soil organic matter stabilization. It was shown that the accumulation of aliphatic compounds is associated with the processes of depositing fresh soil organic remnants, and the group of aromatic compounds indicates the processes of humification and stabilization of organic matter in the soil and accumulation of plant tissues [36].

In this work, we set the goal of the most complete characterization of the processes of Podzol formation, the accumulation of organic matter, analysis of microbiological activity in the chronoseries of Podzols. The research tasks include: 1) morphological characteristics of soil formation on sands, 2) determination of humus content, biological activity of soils of different ages, 3) molecular composition of the humic substances.

Materials and method

The study site

The Nizhnesvirsky Nature Reserve was established in 1980 in the southeastern Lake Ladoga region (Leningrad region). It is located in the Ladoga lowland and is bounded from the south and east by the Svir River, and from the west by the Gulf of Svir of Lake Ladoga, a part of which is a part of the reserve. The northern border is at the same time the border of Leningrad oblast and Karelia. The area of the reserve is 41000 hectares, of which 19000 hectares are occupied by forests, 14000 hectares by bogs, and 6000 hectares of the water area of the Gulf of Svir (strip 1-3.2 km from the coast), rivers and lakes. The study site is presented in Fig. 1.

Fig. 1. Study area. The Nizhnesvirsky Nature Reserve (60°34'58"N 33°00'24"E). Source: ESRI, GeoEye

The reserve is characterized by a temperate continental climate, the average annual air temperature is + 3.64°C, the annual precipitation is 737 mm, the average thickness of the snow cover is 76 cm [27]. The maximum height above sea level is 22-24 m. The coastal bars of Lake Ladoga, whose height is up to 40 m, cover a strip up to 4 km wide along the Gulf of Svir. The height of the rolls is 0.5-4 m, the width is 10-200 m. The depressions between bars have a width of 20-200 m. In general, the Ladoga lowland can be described as a sandy, lacustrine terraced plain. The largest water area is the Gulf of Svir Bay, which is rather shallow and, therefore, warms up well. In the north of the reserve, Segezha Lake (18 km^2) is located in the center of the Segezha bog. To the basin of the Svir River belongs the Lakhtinsky Bay, a part of the old river bed, 6 km long and 200-300 m wide. Several small rivers with a source in the Segezhsky bog flow into the Svir River. Into Lake Ladoga flow such small rivers as the Zubets, the Gumbarka and others. The location of soil pits is shown in Fig. 2.

Fig. 2. Location of soil pits. 1 - First coastal bar, 2 - Second coastal bar, 3 - Third coastal bar, 4 - Fourth coastal bar. Source: ESRI, GeoEye

The flat territory and the presence of depressions along geomorphological terraces with poor drainage cause a high percentage of swampy areas. Forests are located on hills, mostly composed of sands, so pine forests prevail here. They are severely damaged by waterlogging and fires, as well as by the military actions of 1941-1943. Therefore, nowadays, young plantations with lichen-green moss cover predominate. Pine sphagnum forests are widespread. Minor areas are occupied by oxalis and bilberry-sphagnum types of spruce forests. In the reserve, typical are secondary birch forests of bilberry, eagle fern and reed grass types growing on the sites of pine forests.

Factors of soil formation in the investigated region

On the territory of the drainage basin of Lake Ladoga the following processes of soil formation are widespread: podzolization, humus formation, gleyfication and peat accumulation.

The podzolization process develops in soils of an automorphic location under cover of coniferous and mixed-coniferous forests. When decomposing plant litter, which is poor with elements and coming mainly to the surface of the soil, aggressive organic acids are formed. Under their influence, intensive acid weathering of the soil-forming rock takes place and the moisture content of the decomposition products of minerals drifts downward to the lower horizons of the soil profile. The main role during the decomposition of primary and secondary minerals is played by fulvic acids. Illuvial-ferruginous Podzols form on sandy parent rocks; as the humidity of the terrain increases illuvial-humus-ferruginous Podzols and illuvial-humus (spodic) Podzols form. On loamy and clayey parent rocks form Podzols and podzolic soils without pronounced illuvial-humus horizon. They are the dominant type of soil in the study area [27].

The process of humus accumulation is associated with a high content of alkaline bases in the parent rock, which entails their high content in plant litter, and also with the entry of organic substances into the soil not only on its surface, but also deep in the soil profile due to decomposition of the remains of grass vegetation root systems. The sod process is developed under coniferous-deciduous forests with grass vegetation [27]. Humus formation can be considered as a biogeochemical mechanism of adaptation of plant communities to terrestrial living conditions in case of poor acids sandy textured parent materials in the boreal climate [37].

The process of gleyfication occurs under anoxic conditions when the water stagnates on the soil surface or the soil-groundwater is wedged out into the soil. Because of anaerobic decomposition of organic matter in the soil, reduction processes develop increasing the mobility of iron, manganese, nitrogen and phosphorus [27].

The process of peat accumulation takes place under conditions of constant excessive moistening. In this case, the mineralization of plant remains is difficult, the process of their conservation dominates. The formation of bog soils can proceed under conditions of excessive atmospheric moistening (upland bog soils) or due to groundwater feeding (lowland marsh soils). Combination of podzolization and gleying processes is common in such conditions. Histic Albic Podzol develop on loamy parent rocks, whereas peaty-podzolic soils with an illuvial humus horizon form on rocks of fine texture [27].

Chemical and physical-chemical methods of soil determination

To study the soils of the Ladoga transgression formed on the shoreline, we used chemical and physical-chemical methods. Classification of soils was carried out according to the WRB system [38].

Soil samples were air-dried (24 hours, 20°C), grounded, and passed through a 2 mm sieve. Soil samples were selected for each horizon to analyze physical and chemical properties. Analyses were conducted in the certified laboratory at the Department of Applied Ecology (St. Petersburg State University, St. Petersburg, Russia).

Soils were analyzed according to the following methods: determination of actual acidity (pH_{H2O}), potential acidity with $CaCl_2$, by a stationary pH meter in aqueous solution and 1M $CaCL_2$ solution, respectively [39].

The microbiological activity of soils, the basal respiration, using incubation chambers and substrate-induced basal respiration was determined [39].

The carbon and nitrogen content was conducted by “dry combustion” method by CHN Analyzer (Euro EA3028-HT, Italy). Data were corrected for water and ash content. Oxygen content was calculated by difference of whole samples mass and gravimetric concentration of C, N, H and ash.

The texture class was made by the Kachinsky method based on sedimentation of particles of various sizes [40-41].

The carbon content of the microbial biomass (Cmic) was determined in field moist samples with the chloroform fumigation-extraction method. A metabolical quotient was calculated as the ratio of respiration $C–CO_2$ to Cmic per day of incubation [42-43]. We determined the soil microbiological characteristics on all soil horizons, where the soil amount was enough. While the soil respiration and microbial biomass were measured in the described laboratory conditions, data obtained in this experiment cannot be interpolated directly to field conditions, but can only be used for a comparison of soil microbiological activity in the same experimental conditions (temperature 20 ºC, moisture 60% to initial soil weight) [44].

The exchange acidity was also investigated, it is caused by the hydrogen and aluminum ions present in the exchange state in the soil absorptive complex, which are extracted from the soil by a neutral salt solution. Usually $CaCl_2$ solution is used to determine the exchange acidity of soils. The exchange acidity is measured by the pH of the salt extract (pH_{CaCl_2}).

Hydrolytic acidity is caused by the amount of hydrogen and aluminum ions present in the exchange (partially non-exchangeable) state in the soil absorptive complex, which are extracted by a solution of the hydrolytically alkaline salt of a strong base and a weak acid (usually a 1M solution of sodium acetate CH_3COONa is used). The hydrolytic acidity is total of exchange and actual acidity [45].

The method of radiocarbon dating of ^{14}C was used to determine the age of coastal bars, it was carried out at the Laboratory of Radiocarbon dating and electron microscopy (Institute of Geography of the RAS, Moscow, Russia) and Center of Isotopic Research University of Georgia (Institute of Georgia, Athens, USA) [45].

Humic acids (HAs) were extracted from each sample according to a published IHSS protocol [46]. The soil samples were treated with 0.1 M NaOH (soil/solution mass ratio of 1:10) under nitrogen gas. After 24 hours of shaking, the alkaline supernatant was separated from the soil residue by centrifugation at 1.516 × g for 20 minutes and then acidified to pH 1 with 6 M HCl to precipitate the HAs. The supernatant, which contained fulvic acids, was separated from the precipitate by centrifugation at 1.516 × g for 15 minutes. The HAs were then dissolved in 0.1 M NaOH and shaken for four hours under nitrogen gas before the suspended solids were removed by centrifugation. The resulting supernatant was acidified again with 6 M HCl to pH 1 and the HAs were again isolated by centrifugation and demineralized by shaking overnight in 0.1 M HCl/0.3 M HF (soil/solution ratio of 1:1). Next, the samples were repeatedly washed with deionized water until pH 3 was reached and then finally freeze-dried. HAs extraction yields were calculated as the percentage of carbon recovered from the original soil sample [47]. Solid-state CP/MAS ^{13}C-NMR spectra of HAs were measured with a Bruker Avance 500 NMR spectrometer in a 3.2-mm ZrO2 rotor. The magic angle spinning speed was 20 kHz in all cases and the nutation frequency for cross polarization was u1/2p 1/4 62.5 kHz. Repetition delay was 3 seconds. The number of scans is 6500-32000.

Results of the research

Morphology of soils

The soil description is presented in Table 1. The spatial soil distribution is clearly related to the age of the coastal bars. The observed soils are referred to a single group Podzols. Depending on the age, chemical, physical-chemical and morphological properties of soil change (thickness of horizons and texture), the vegetation cover also differs (Fig. 3).

Revegetation of coastal bars occurs gradually; firstly appear mosses and various shrubs and then trees. At the age of 70±25 years BP pine forests with a prevalence of bilberry and sphagnum were formed. High humidity and low degree of illumination are favorable conditions for mosses. The first coastal ridge is the youngest of the investigated region, the characteristic feature is the predominance of mosses. The soil cover is poorly developed, represented here by Entic Podzols. Due to the young age of the soil, the eluvial horizon, from which the mineral part of the soil is released under the action of organic acids and deposited in the illuvial horizon has not been formed. Soil formation proceeds according to the podzolic type and is associated with the destruction of the mineral part of the soil in the upper layers and transition of the soil particles down through the profile. The age of the coastal bars is presented in Table 2.

The next stage of revegetation is confined to the second coastal bar of 135±30 years BP, the moss and pines that occupy here 30% of the total cover replace shrubs.

A B

C D

Fig. 3. Morphological features of the studied soils. A - Fourth coastal bar; B - Third coastal bar, C - Second coastal bar, D - First coastal bar. Photo by EV Abakumov

The high content of mosses is also confirmed by waterlogging. The Podzol soil group forms here. With increasing age, the soil acquires the characteristics of the fully formed profile (climacteric condition), there is horizon E, where the mineral part of the soil is being destroyed. The underlying horizon accumulates mineral compounds, ferrous concretion is also noted, and coal particles are presented as the result of wildfires in the region.

The age of the third coastal bar is 455±30 years BP, the occurrence of pine and the crown density on the territory are increasing. A high level of groundwater leads to the formation of a gley horizon at a depth of 65 cm.

Here Podzols develop, the thickness of the podzolic horizon is 12 cm. It is connected with the active processes of weathering of soil particles. A high level of groundwater leads to the formation of ferrous conditions, in which the accumulation of ferrum compounds Fe^{2+} actively occurs.

The fourth coastal bar, 1590±25 years BP, was distinguished by the most developed soil profile. Well-drained conditions are formed here. This is a high degree of density and the prevalence of pines is up to 60%.

Table 1

The morphological description of the soils of the Ladoga transgression bars of different ages

Soil	Horizon	Depth	Soil horizon description	Location, vegetation description, Total vegetation cover (TVC) and individual cover of some plants, inclusions, coordinates, age
Folic Stagnic Podzol (a)	O	0-6	Forest floor, non-decomposed, 5YR 4/6	Fourth coastal bar *Pinus sylvestris* (L.) 60% *Vaccinium myrtillus* (L.) 20% *Sphagnum* sp. (L). 20% 60°38'44.7"N 32°57'53.9"E 1590±25 years BP
	E	6-11	Dry, grains of quartz, 5YR 7/1, Clay Loam	
	Bs (1)	11-45	Roots, moist, structureless, iron concretions, 5YR 6/6, Fine Sand	
	Bs (2)	45-70	Red spots of iron, GLEY 1 7/N, Fine Sand	
	Bg	70-90	Anoxic conditions, GLEY 1 6/N, Fine Sand	
Folic Stagnic Podzol (b)	O	0-11	Forest floor, non-decomposed, 5YR 4/6	Third coastal bar *P. sylvestris* 40% *V. myrtillus* 30% *Sphagnum* sp. 30% 60°38'47.4"N 32°57'51.3"E 455±25 years BP
	E	11-23	Dry, roots, 5YR 7/1, Loamy Fine Sand	
	Bs (1)	23-44	Pseudofiber, iron flow, wet, roots, 5YR 6/6, Sandy Loam	
	Bs (2)	44-65	Gray, pseudofiber, LEY 1 7/N, Fine Sand	
	Bg	65+	Wet, sand, GREY 1 6/N, Fine Sand	
Folic Podzol	O	0-10	Forest floor, non-decomposed, 5YR 4/6	Second coastal bar *P. sylvestris* 30% *V. myrtillus* 30% *Sphagnum* sp. 60% 60°38'44.4"N 32°57'46.6"E 135±30 years BP
	E	10-13	Dry, inclusions of stones, 5YR 7/1, Sandy Loam	
	Bs	13-75	Coal layer, ocher, rusty spots, 5YR 6/6, Fine Sand	
Entic Podzol	O	0-3	Forest floor, non-decomposed, 5YR 4/6	First coastal bar *P. sylvestris* 20% *V. myrtillus* 30% *Sphagnum* sp. 50% 60°38'43.4"N 32°57'42.3"E 70±25 years BP
	E	3-6	Sand, roots, 5YR 4/4, Clay Loam	
	Bs	6-40	Ocherous, moist, sandy, inclusions of coals, roots, red spots, 5YR 6/6, Sandy Loam	

In our opinion, high soil drainage prevents the development of a well-developed E horizon. In this soil, ferruginous pellicles were observed; an anaerobic environment and the development of gley processes occur at a depth of 70 cm. The thickness of the podzolic horizon is 5 cm with a high content of quartz. The underlying horizon is the horizon for the insertion of the mineral phase, which is divided into two parts, differing in colour and density of addition. The underlying horizon is denser and has a greater number of ferrous spots. This is due to the soil type which is close to the stage of quasiequilibrium (climacteric condition), or is already in this state.

Table 2

The age of the coastal bars in the transgression of Lake Ladoga

Soil	Depth, cm	Radiocarbon age, years BP±SD
Folic Stagnic Podzol (a)	11-45	1590±25
Folic Stagnic Podzol (b)	63-70	455±25
Folic Podzol	13-75	135±30
Entic Podzol	6-40	70±25

As a result of the analysis of spatial distribution of soils, it can be concluded that, as the age increases, the degree of weathering of the mineral part of the soil profile increases. That process of podzalization is closely related to the position in the landscape and the drainage of the territory. As the age increases, the occurrence of pines increases. The occurrence of mosses depends on the moisture content in the soil and the crown density. Soils develop according to the podzolic type, migration of ferrum elements and accumulation in gley horizons with the formation of ferruginous complexes occurs.

Physical-chemical characteristics of soils and biological activity

The main soil physical-chemical and biological analyses of soils were carried out. The results are shown in Table 3.

From the data obtained, pH of the soils is slightly acid (6.1-6.5), moderately acid (5.6-6.0), strongly acid (5.1-5.5) and very strongly acid 4.5-5.0. This is due to the presence of aggressive organic acids (fulvic acids) in the soil. The processes of Podzol formation are closely related to the acid reaction, due to the destruction of the mineral part of the soil by organic acids and the presence of ferrum and aluminum ions in the soil-absorbing complex. In the horizons, where there is active weathering of the mineral part, the lowest acidity is observed.

According to the data on the microbiological activity, the processes of biological transformation of a substance are actively undergoing in soils due to favorable conditions for the activity of microorganisms.

This is linked with the high humidity of the sites under investigation and the availability of organic material in the soil. It is also possible to note the high microbial biomass in the investigated areas. Forest ecosystems are characterized by high activity of microbial biomass in the upper horizons, referring to our data, microbial biomass is concentrated in horizon O, where microorganisms transform vegetative forest litter. Down through the soil profile, this indicator drops. In the

Table 3

Physical-chemical characteristics of soils of the Ladoga transgression bars

Soil horizon	pH_{H_2O}	pH_{CaCl_2}	Exchange acidity	Hydrolytic acidity	Basal respiration, mg_{CO_2}/g/hour	Substrate-induced basal respiration, mg/g/hour	Cmic, mg*g^{-1}	Metabolic quotient	Texture class		
									sand	silt	clay
Folic Stagnic Podzol (a)											
O	6.01	5.04	0.5	1.5	0.17	0.18	7.72	0.02	n/d	n/d	n/d
E	4.44	3.85	0.6	0.6	0.02	0.03	1.71	0.01	43	30	27
Bs (1)	5.35	4.69	0.1	0.6	0.03	0.03	1.56	0.02	98	2	1
Bs (2)	5.66	5.01	0.1	0.2	0.04	0.04	1.94	0.02	90	9	1
G	5.99	5.21	0.4	0.5	0.02	0.03	1.50	0.02	87	12	1
Folic Stagnic Podzol (b)											
O	5.98	4.99	0.6	1.0	0.18	0.26	10.86	0.02	n/d	n/d	n/d
E	4.58	4.15	0.9	0.9	0.03	0.04	1.94	0.02	78	21	1
Bs (1)	5.41	4.86	0.3	0.6	0.04	0.04	1.94	0.02	81	7	12
Bs (2)	5.63	4.97	0.2	0.6	0.02	0.03	1.70	0.01	90	9	1
G	5.01	4.13	0.1	0.6	0.04	0.04	2.10	0.02	98	1	1
Folic Podzol											
O	6.23	5.46	1.0	1.5	0.1	0.2	8.24	0.01	n/d	n/d	n/d
E	4.92	4.17	0.5	0.6	0.01	0.01	0.57	0.01	75	20	5
Bs	5.67	4.92	0.2	0.4	0.04	0.04	1.86	0.02	93	7	1
Entic Podzol											
O	6.2	5.74	1.0	1.3	0.09	0.16	6.66	0.01	n/d	n/d	n/d
E	5.42	4.17	0.5	1.5	0.05	0.13	5.61	0.01	32	35	34
Bs	5.73	4.83	0.4	0.9	0.03	0.04	1.96	0.02	78	14	8

soil of the coastal bars of Lake Ladoga, there is a trend towards an increase in biological activity with age. More developed soils have a high index of microbial activity and microbial biomass. The metabolic quotient is an indicator of the stability of the microbial community, the higher it is the less stable the community is. The microbial communities of the studied region are stable in the ecosystem. There were no significant differences between young and old age coastal ridges. On the first and second bars, the microbiological activity and biomass are slightly higher. Climax forest communities are characterized by a high level of energy conservation.

Data on the content of organic carbon and nitrogen in the soil were also obtained, and the C/N index was calculated, the data are presented in Table 4.

Table 4

The content of organic carbon, nitrogen and C/N index of the soils of the Ladoga transgression bars (m±SD)

Soil horizon	C, g*kg^{-1}	N, g*kg^{-1}	C/N
Folic Stagnic Podzol (a)			
O	223.1±11.15	11.2±0.5	20
E	3.2±0.16	0.2±0.01	16.0
Bs (1)	1.6±0.08	0.3±0.01	5.3
Bs (2)	1.1±0.05	0.2±0.01	5.5
G	0.9±0.05	0.2±0.01	4.5
Folic Stagnic Podzol (b)			
O	345.0±17.25	23.0±1.1	15
E	4.3±0.21	0.3±0.01	14.3
Bs (1)	2.7±0.13	0.3±0.01	9.0
Bs (2)	1.9±0.09	0.3±0.01	6.3
G	1.5±0.08	0.2±0.01	7.5
Folic Podzol			
O	364.0±18.2	23.4±1.1	12
E	2.3±0.11	0.3±0.01	7.7
Bs	1.1±0.05	0.2±0.01	5.5
Entic Podzol			
O	365.0±18.2	29.8±1.4	12
E	19.7±0.98	0.9±0.05	21.9
Bs	2.3±0.11	0.3±0.01	7.7

The content of carbon and nitrogen in soils is not high, which indicates a high activity of microorganisms in this region. The carbon content can present an inverse of the microbiological activity; the higher the carbon content in the soil, the lower the microbiological activity index. The enrichment of humus with nitrogen is high in the lower horizons. In podzolic horizons it is low, this is due to active weathering processes. The carbon content in the soil decreases with the depth, the same dependence is also noted for the nitrogen content. Most of the organic residues accumulate in the upper horizon and are represented by plant litter; due to the activity of microorganisms this material is transformed and re-absorbed by plants, the part that is not absorbed by plants goes into organomineral compounds and migrates down the profile. Depending on the age of the ecosystems, the content of organic matter in the soil decreases, as does the nitrogen. This is due to the involvement of carbon and nitrogen pools in the biological cycle of substances.

We analyzed the soil texture; the results are shown in Table 3. According to the data obtained, we can identify some patterns in the formation of the mineral part of the soil profile. With increasing age of soils, the destruction of soil aggregates and the migration of soil particles down the profile are clearly pronounced. First, this is due to the high level of moistening in the region, as well as to the active processes of Podzol formation and, as a consequence, the destruction of the mineral part of the soil by aggressive organic acids. In the E horizons, active chemical weathering of minerals occurs, as well as their further accumulation in the underlying horizons of the soil profile.

Elemental Composition of HAs

The obtained data on the HAs elemental composition, atomic ratios and degree of oxidation are presented in Table 5. From the distribution of organic carbon in HAs, it can be noted that they are divided into two groups, the first, up to 40% and more than 40%. In the fourth coastal bar, which is the oldest, in the elemental composition of HAs, the carbon content reaches 39%, this is due to the leaching of low-carbon molecules from organogenic horizons. In profiles of other coastal bars, the distribution varies from 42 to 49%. In the third coastal bar, the carbon percentage reaches 42%, which is also associated with the active leaching of low-carbon molecules. In the first coastal bar (youngest bar), the carbon content also reaches 42%, this is due to the low profile development and accumulation of organic matter in the upper horizon, the process of removal of mineral and organic particles is poorly developed here. The highest carbon content is observed in the profile of the second coastal bar. Also noted is the pattern of increasing the oxygen content with age, in the fourth coastal bar the oxygen content reaches 51%, in the second from 44 to 49%. An analysis of the elemental composition of humic acid preparations showed that soil HAs are the most humified, their low values of atomic ratio H/C mod and high O/C values indicate this.

An increase in the degree of hydromorphism in taiga soils is accompanied by an increase in H/C values. This is due to the lower microbiological activity of podzolic soils, which contributes to better preservation of carbohydrate and amino acid fragments in the structure of HAs. Assessment of the degree of hydromorphism was carried out based on signs of gley processes (color, peat accumulation and oxidation degree). Analysis of the elemental composition of HAs of the studied soils revealed a decrease in the profile values H/C mod in all soils, which indicates an increase in the share of aromatic fragments in the HAs structure of the mineral horizons (Fig. 4).

Table 5

Elemental composition of the studied humic acids from surface soil horizons (m±SD)

Sample No	Soil horizon	C, %	H, %	N, %	O, %	C/N	H/C	O/C	H/C mod*	W**
Folic Stagnic Podzol (a)										
1	O	39±1.95	6±0.3	4±0.2	46	11	1.89	0.97	3.19	0.05
Folic Stagnic Podzol (b)										
2	O	42±2.1	6±0.3	2±0.1	45	21	1.74	0.87	2.91	0
3	E	48±2.4	6±0.3	2±0.1	39	24	1.52	0.68	2.44	-0.15
4	Bs	49±2.4	6±0.3	2±0.1	38	25	1.35	0.67	2.24	-0.02
Folic Podzol										
5	E	49±2.1	6±0.3	3±0.15	37	17	1.39	0.64	2.25	-0.11
Entic Podzol										
6	O	42±2.1	6±0.3	3±0.15	44	19	1.80	0.89	3.00	-0.02
7	E	42±2.1	6±0.3	3±0.15	44	18	1.59	0.88	2.77	0.17
8	Bs	48±2.4	6±0.3	3±0.15	38	18	1.56	0.68	2.48	-0.20

Note: *H/C mod - The number of substituted hydrogen atoms in the humic acids; (H/C) mod = (H/C) + 2 (O/C) x 0.67; H/C and W indexes are calculated according to DS Orlov (1985). * H/C mod - The number of substituted hydrogen atoms in the HAs. (H/C)mod = (H/C) + 2(O/C) x 0.67. ** W - Oxidation coefficient. W = (2C–H)/O. C/N, H/C, O/C, H/Cmod and W was calculated from mole fraction of carbon, hydrogen, oxygen and nitrogen content.

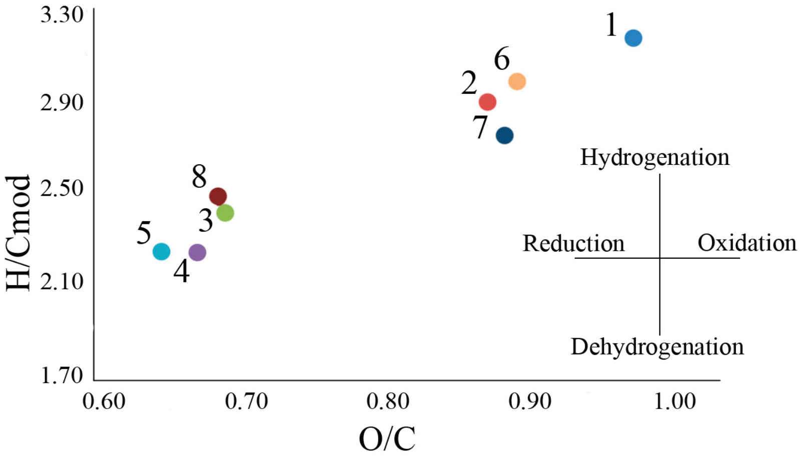

Fig. 4. H/Cmod and O/C atomic ratios of the elements in humic acids. H/C mod - The number of substituted hydrogen atoms in the humic acids, (H/C) mod = (H/C) + 2*(O/C) * 0.67. Sample numbers correspond to Table 5

The degree of oxidation showed that almost all studied HAs were weakly reduced (from –0.20 to 0.05). The exception was the HAs of the first coastal bar, the degree of oxidation reaches +0.17. Weak reduction of preparations of HAs of organogenic horizons is determined by the constant flow of fresh organic residues and their weak humification.

Characterization of HAs by ^{13}C-NMR spectroscopy

Spectra's of the CP/MAS ^{13}C-NMR are given in Figure 5. Various molecular fragments were identified by CP/MAS ^{13}C-NMR spectroscopy (Table 6): carboxyl (–COOR); carbonyl (–C=O); CH_3–, CH_2–, CH–aliphatic; –C–OR alcohols, esters and carbohydrates; phenolic (Ar–OH); quinone (Ar=O); aromatic (Ar–), which indicates the great complexity of the structure of HAs and the polyfunctional properties that cause their active participation in soil processes [48].

The presence of carboxyl, hydroxyl, and carbonyl groups in combination with aromatic structures ensures the ability of HAs to enter exchange and donor-acceptor interactions, formation of hydrogen bonds, and active participation in sorption processes.

Table 6

Chemical shifts of atoms of the ^{13}C molecular fragments of humic acids

Chemical shift, ppm	The type of molecular fragments
0-46	C, H-substituted aliphatic fragments
46-60	Methoxy and O, N-substituted aliphatic fragments
60-110	Aliphatic fragments doubly substituted by heteroatoms (including carbohydrate) and methine carbon of ethers and esters
110-160	C, H-substituted aromatic fragments; O, N-substituted aromatic fragments
160-185	Carboxyl groups, esters, amides and their derivatives
185-200	Quinone groups; Groups of aldehydes and ketones

The group's chemical shifts are given in Table 7. The aromatic group is calculated from the sum of the shifts of 110-185 ppm. Aliphatic fragments are calculated from the sum of the shifts of 0-110 ppm, 180-200 ppm. $AL_{h,r} + AR_{h,r}$ (total number of unoxidized carbon atoms) - the signals were summed over the regions 0-46 and 110-160 ppm. C, H–AL / O, N–AL. Signals from C, H–alkyls were summed in the range 0-47 ppm, O, N–alkyl at regions 46–60 and 60–110 ppm [48]. The presence of all peaks of the carbon species which are required for identification of the studied substances as humic acids was revealed. The most pronounced peaks were related to the aliphatic carbon groups. Also, the presence of evident peaks of aromatic and carboxylic areas was obvious as well. This indicates that the investigated powders could be identified as humic substances, namely, as humic acids.

From the obtained morphological data, we can conclude that the development of soils of the coastal bars proceeds through a podzolic type of soil formation with the accumulation of long aliphatic chains (fatty acids, phospholipids). They are dominated by oxygen-containing fragments, which can cause their high migration ability. They promote the mobilization of mineral compounds and their migration along the soil profiles. On different aged coastal bars, the accumulation of aromatic fragments of humic substances was discovered. On the fourth and first coastal bars, carboxyl groups accumulate (26-31%). Aliphatic groups accumulate on the second and third coastal bars, which is associated with excessive moisture and reduction of environmental conditions.

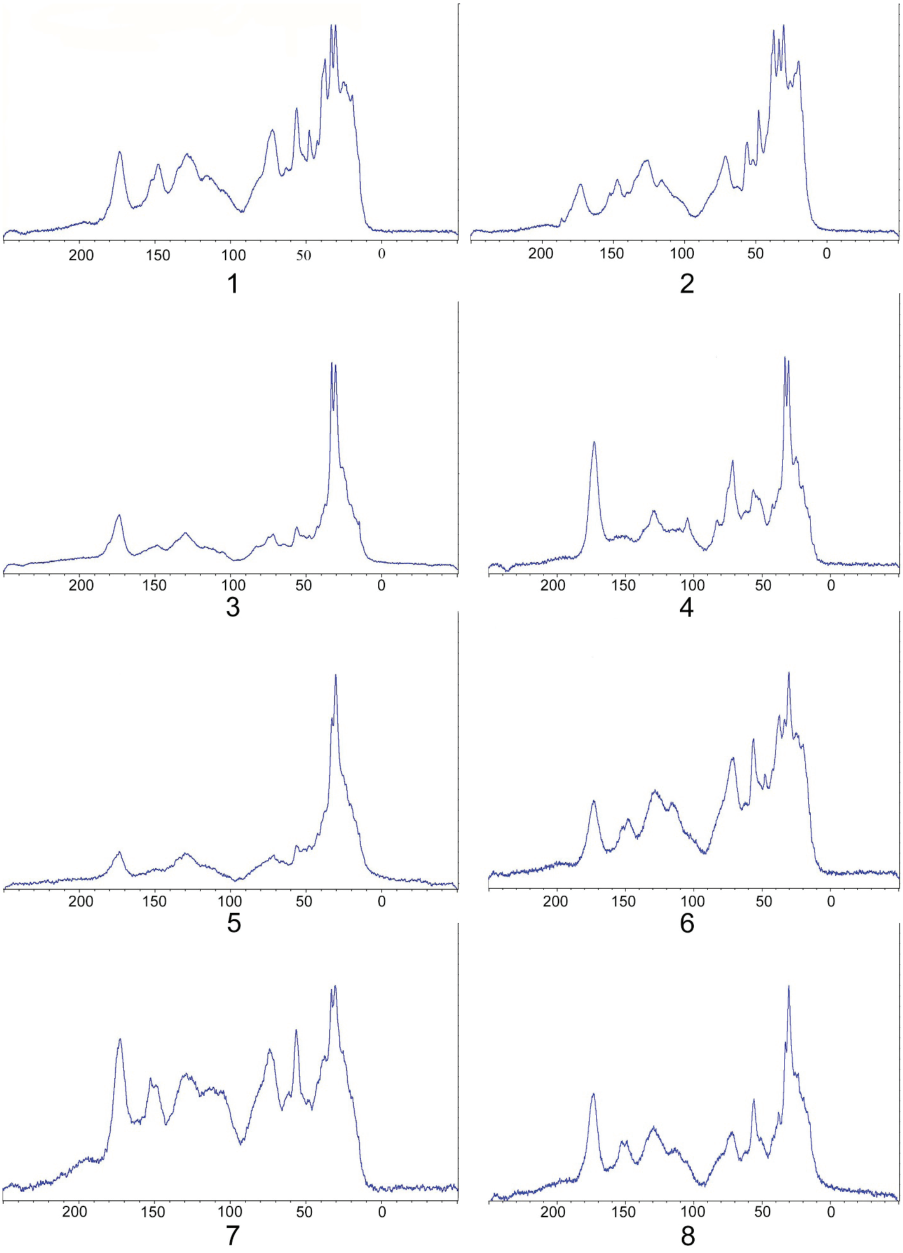

Fig. 5. CP/MAS ^{13}C-NMR spectra of soils from the coastal bars.
Number corresponds to Table 7;
Horizontal axis - Chemical shift, ppm,
Vertical axis - Relative intensity, dimensionless

Table 7

Percentage of carbon in the main structural fragments of humic acids from the studied surface soil horizons (according to CP/MAS ^{13}C-NMR data)

Sample No	Soil horizon	Chemical shifts, ppm						AR	AL	AR/AL	AL h,r + AR h,r	C,H-AL/O,N-AL
		0-47	47-60	60-110	110-160	160-185	185-200					
Folic Stagnic Podzol (a)												
1	O	40	9	23	19	7	2	26	74	0.35	59	1.23
Folic Stagnic Podzol (b)												
2	O	47	12	17	18	5	1	23	77	0.30	65	1.62
3	E	49	10	13	14	9	5	23	77	0.30	63	2.12
4	Bs	37	19	17	14	11	1	25	75	0.34	52	1.03
Folic Podzol												
5	E	59	6	14	13	6	3	19	81	0.23	71	2.96
Entic Podzol												
6	O	38	10	24	19	6	2	25	75	0.34	58	1.12
7	E	26	8	30	24	7	5	31	69	0.45	50	0.68
8	Bs	38	8	20	19	11	4	29	71	0.41	57	1.35

Note: *AR - Aromatic fraction; AL - Aliphatic fraction; AL $_{h,r}$ + AR $_{h,r}$ % - Hydrophobicity degree; C,H-AL/O, N-AL - The degree of decomposition of organic matter.

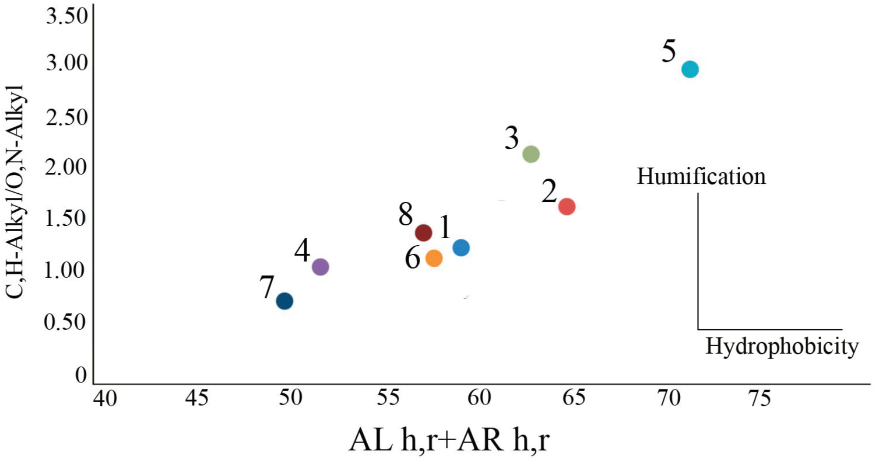

Fig. 6. The diagram of integrated indicators of the molecular composition of humic acids. Sample numbers correspond to Table 7; AL $_{h,r}$ + AR $_{h,r}$ indicates total number of unoxidized carbon atoms

For a numerical description of the structure of humic acids, we used the method of graphical representation of the data in the coordinates C,H-alkyl/O, N-alkyl – AL $_{h,r}$ + AR $_{h,r}$ (Fig. 6), which serves as a convenient technique to demonstrate the contribution of oxidation (humification) processes and hydrophobicity (sustainability).

HAs of the studied soils are represented by weakly oxidized compounds and are more resistant to environmental factors. Excessive moistening not only leads to accumulation of humic substances, but also causes accumulation of humic substances in the hydromorphic soils enriched with aliphatic structures.

Discussion of the research

The investigations of chronoseries allow analyzing the dynamics of ecosystems in time and determining the trends of accumulation and transformation of organic material [1, 3, 10]. Time and spatial distribution of soils are the most important factors of soil formation, which provides the appearing of material and energy factors that are a necessary condition for the evolution of soils [1-2, 14].

There are many studies of chronoseries of anthropogenic landscape (post-mining areas, dumps). The development of Podzols occurs according to the zonal types of soil formation, the accumulation of organic material, microbiological activity increase and the stable microbial communities in old-age areas form. According to our data, the same dependence is revealed, young sites are characterized by low biomass stability and low microbiological activity [49-52].

The content of nitrogen and carbon in young natural ecosystems is higher than that in anthropogenic ecosystems. The ratio of carbon and nitrogen in natural ecosystems is higher. These factors develop due to the involvement of carbon and nitrogen pools in the natural cycle. Young ecosystems are most similar to the ecosystems of the Arctic and Antarctic regions affected by the alluvial factors due to poor development of the soil cover. It is also worth noting that research of technogenic postchronoseries can begin at the first stage of soil formation, whereas natural ecosystems are usually old-age systems, this article describes a chronoseries of four transgression bars with an age of 70±25 to 1590±25 years BP. This allows to study the processes of soil formation considering the time of their activity. The main parameter by which developing soils of regenerative biogeocoenoses of new lithogenic surfaces can be referred to models is the determined time of the beginning of soil formation in certain bioclimatic and lithologic-geomorphological conditions [18, 53-57].

To determine the age of the coastal bars, we used the method of radiocarbon dating, which made it possible to determine the age of the investigated soils with high accuracy. To determine the age of the coastal bars, we used the method of radiocarbon dating, which made it possible to estimate the age of the investigated soils with high accuracy [58-63]. The evolution of the humus state is clearly distinguished in the ranks of chronoseries of anthropogenic and natural landscapes. For natural ecosystems with stable microbial communities, organic matter is involved in the cycle, whereas on technogenic ones, accumulation occurs under conditions of a low microbial biomass content. The formation of Podzols is associated with a change in the chemical characteristics of fine texture soils. This is due to the weathering of the mineral part in the soil profile, expressed primarily in the decarbonatization of fine particles, which leads to a decrease in the pH of the aqueous suspension [64].

In general, the elemental composition of the HAs is comparable with previous data for soils of the boreal zone [35-36, 47-48, 65-66]. Features of HAs formed in cold conditions and, especially, in hydromorphic soils are characterized by a relatively high H content and a reduced O content compared to sub-boreal and polar soils [67-69]. The elemental composition of HAs is the most important indicator determining the progress of humification, oxidation and degree of condensation of HAs [66, 70]. The term hydrogenation refers to a chemical reaction involving the addition of a hydrogen molecule to an organic substance [71]. An increase in the hydrogen content of the humification products indicates that long aliphatic chains are formed or can be inherited from parent material. Excessive moistening not only leads to the accumulation of humic substances, but also affects their molecular composition, and causes the accumulation of humic substances in the studied soils enriched with aliphatic structures.

The molecular composition of HAs is also similar to HAs isolated from the boreal zone, the prevalence of the alkyl zone is noted, which is associated with a low degree of humification of the organic material [35-36, 47-48, 65-66]. Depending on the age, the molecular composition of the HAs from Podzol changes; more mature soils contain more aromatic fragments. In younger soils, the content of aromatic fragments decreases, while in the youngest studied Podzol, the content of aromatic fragments increases again. Such dynamics can be associated with precursors of humification, composition of plant residues, and hydrophobicity degree.

Conclusions

As a result of the study of the soil chronoseries of transgression bars, it was determined that all soils are of the Podzol group with varying degrees of profile development. The youngest soils (70±25 years BP) are characterized by a thin profile with signs of podzolic horizon (Entic Podzols). As the thickness of the podzolic horizon increases, a powerful horizon with signs of Stagnic appears and anaerobic conditions near the entry of groundwater form. All investigated area is composed of sediments of Lake Ladoga and is well drained and aerated, the type of texture class is sandy, loamy sand and sandy loam. The formation of Podzols in waterlogged conditions leads to the leaching of organic carbon into Lake Ladoga, this is due to the light texture class and a high hydrogen content in HAs.

The content of carbon and nitrogen in the soil, the degree of enrichment of humus with nitrogen, and microbiological activity were determined. In chronoseries, the carbon content connects with the microbiological activity. Thus, as the age increases, carbon and nitrogen content decreases and microbiological activity increases. This is due to the high level of carbon involvement in the biological cycle of the ecosystem. The decrease in nitrogen content is associated with a change in vegetation on the coastal transgression. A high rate of stability of microbiological communities in the investigated areas was noted.

Analysis of the molecular composition of HAs showed that aliphatic groups accumulate in the soils. This is due to the precursors of humification. Because of the increased oxidation, HAs molecules have a high migration ability. Due to evolution of Podzols, aliphatic groups and the accumulation of humic substances in the soil increased, with an increase of -OCH compounds in molecular composition of HAs; it makes HAs more aggressive and leads to increased migration ability. The molecular composition of HAs of young soils is enriched with aromatic fragments and oxygen-containing functional groups, which ensures their high thermodynamic stability.

References

1. Abakumov EV. Accumulation and transformation of organic matter in different-aged dumps from sand quarries. *Eurasian Soil Science*. 2008;8:988-963. doi: 10.1134/S1064229308080061
2. Mokma DL, Yli-Halla M, Linfqvist K. Podzol formation in sandy soils of Finland. *Geoderma*. 2004;120:259-272. doi: 10.1016/j.geoderma.2003.09.008
3. Bronick CJ, Mokma DL. Podzolization in a sand pit in Northern Michigan. *Soil Science Society of America J*. 2005;69(6):1757-1760. doi: 10.2136/sssaj2004.0119
4. Abakumov EV, Lisitsyna OV, Gagarina EI. Samovosstanovleniye rastitel'nosti i nachal'nykh stadiy pochvoobrazovaniya v posttekhnogennykh mestorozhdeniyakh Maluksinskogo peschanogo kar'yera (Leningradskaya oblast') [Self-restoration of vegetation and initial stages of formation in the post-technogenic landscapes of the Maluka sand pit (Leningrad region)]. In: *Ekologiya i biologiya pochv* [Ecology and biology of soils]. Kazeev K and Kolesnikov S, editors. Rostov on Don: Tsentry valeologii vuzov Rossii Publications; 2004. pp. 3-7. In Russian
5. Aleksandrovsky AL, Alexandrovskaya EI. Evolyutsiya pochv i geograficheskaya sreda [Evolution of soils and geographic environment]. Moscow: Nauka Publ.; 2005. 223 p. In Russian
6. Paton TR, Mitchell PB, Adamson D, Buchanan RA, Fox MD, Bowman G. Speed of podzolisation. *Nature*. 1996;260(5552):601-602. doi: 10.1038/260601a0
7. Abakumov EV, Gagarina EI, Popov AI. Humus formation and development of Podzol soil during primary succession of plant on mining-quarries complex in taiga zone (Leningrad Region). *Ecology and Future-Bulgarian Journal of Ecological Science.* 2003;3(4):22-25.
8. Dymov AA, Gabov DN. Pyrogenic alterations of Podzols at the North-East European part of Russia: Morphology, carbon pools, PAH content. *Geoderma*. 2015;241-242:230-237. doi: 10.1016/j.geoderma.2014.11.021
9. Burges A, Drover DP. The rate of Podzol development in sands of the Woy Woy district, N.S.W. *Australian Journal of Botany.* 1953;1:83-94. doi: 10.1071/BT9530083
10. Barrett LR, Schaetzl RJ. An examination of podsolization near Lake Michigan using chronofunctions. *Canadian J Soil Science*. 1992;72:527-541. doi: 10.4141/cjss92-044
11. Alexander EB, Burt R. Soil development on moraines of Mendenhall Glacier, southeast Alaska: 1. The moraines and soil morphology. *Geoderma*. 1996;72:1-17. doi: 10.1016/0016-7061(96)00021-3
12. Dickson BA, Crocker RL. A chronosequence of soils and vegetation near Mount Shasta, California: III. Some properties of the mineral soils. *J Soil Science.* 1954;5:173-191. doi: 10.1111/j.1365-2389.1954.tb02186.x
13. Jauhiainen E. Age and degree of podzolization of sand soils on the coastal plain of northwest Finland. *Soc. Sci. Fenn. Commentat. Biol.* 1973;68:1-32.
14. Emmer IM. *Humus form and soil development during a primary succession of monoculture Pinus sylvestris forests on poor sandy substrates*. PhD Thesis. Amsterdam: Universiteit van Amsterdam; 1995. 135 p.

15. Melkerud P-A, Bain DC, Jongmans AG, Tarvainen T. Chemical, mineralogical and morphological characterization of three podzols developed on glacial deposits in northern Europe. *Geoderma.* 2000;94:125-148. doi: 10.1016/S0016-7061(99)00043-9
16. Gagarina EI, Shelemin AN. *Evolyutsionnyye aspekty pochvoobrazovaniya na zemlyanykh voyennykh ob"yektakh* [Evolutionary aspects of soil formation at land military sites]. In: *Problemy evolyutsii pochv* [Problems of the evolution of soils. Proceedings of the Russian Conf.]. Pushchino: Pushchino Scientific Center of the Russian Academy of Sciences Publ.; 2003. pp. 157-160. In Russian
17. Cerli C, Celi L, Johansson M-B, Kogel-Knabner I, Rosenqvist L, Zanini E. Soil organic matter changes in a spruce chronosequence I. Carbon and lignin dynamics. *Soil Science.* 2006;171:837-849. doi: 10.1097/01.ss.0000228061.23334.98
18. Abakumov EV, Frouz J. Evolution of the soil humus status on the calcareous neogene clay dumps of the Sokolov quarry complex in the Czech Republic. *Eurasian Soil Science*. 2009;7:773-779.
19. Cerli C, Celi L, Kaiser K, Guggenberger G, Johansson M-B, Cignetti A, Zanini E. Changes in humic substances along an age sequence of Norway spruce stands planted on former agricultural land. *Organic Geochemistry*. 2008;39:1269-1280. doi: 10.1016/j.orggeochem.2008.06.001
20. Abakumov EV, Trubetskoj O, Demin D, Celi L, Cerli C, Trubetskaya O. Humic acid characteristics in podzol soil chronosequence. *Chem Ecol*. 2010;26:59-66. doi: 10.1080/02757540.2010.497758
21. Nadporozhskaya MA, Mohren GMJ, Chertov OG, Komarov AS, Mikhailov AV. Soil organic matter dynamics at primary and secondary forest succession on sandy soils in the Netherlands: An application of soil organic matter model ROMUL. *Ecol. Model*. 2006;190 (3/4):399-418. doi: 10.1016/j.ecolmodel.2005.03.025
22. Schaetzl RJ, Isard SA. The distribution of Spodosol soils in southern Michigan: A climatic interpretation. *Annals of the American Association of Geographers.* 1991;81:425-442. doi: 10.1111/j.1467-8306.1991.tb01703.x
23. Valerio MW, McDaniel PA, Gessler PE. Distribution and properties of podzolized soils in the northern rocky mountains. *Soil Science Society of America Journal.* 2016;80(5):1308-1316. doi: 10.2136/sssaj2016.04.0109
24. Gerasimov DV, Subetto DA. History of lake Ladoga in the light of archaeological data. *Izvestia: Herzen University Journal of Humanities & Sciences.* 2009;106:37-49. In Russian
25. Subetto DA. The history of Ladoga lake forming and of it's connection to the Baltic sea. *Society. Environment. Development.* 2007;1:111-120. In Russian
26. Biske YS, Sumarev IV, Sheetov MV. Late Holocene paleoseismic event at southeastern coast of Lake Ladoga. I. Principles of research and deformation structures. *Vestnik Sankt-Peterburgskogo Universiteta. Seriya 7. Geologiya. Geografiya = Vestnik of Saint-Petersburg University. Earth Sciences*. 2009;7(1):3-25. In Russian
27. *Ladoga*. Rumyantseva VA and Kondratieva SA, editors. St. Petersburg: Nestor-History Publ.; 2013. 467 p. In Russian
28. Ludikova AV. Diatom evidences for the mid-Holocene Lake Ladoga transgression. *Izvestiya Russkogo Geograficheskogo Obshchestva.* 2015;147(4):38-51. In Russian
29. Sheetov MV, Biske YS, Sumarev IV. Late Holocene paleoseismic event at southeastern coast of Ladoga Lake. II. Parameters. *Vestnik Sankt-Peterburgskogo Universiteta. Seriya 7. Geologiya. Geografiya = Vestnik of Saint-Petersburg University. Earth Sciences*. 2010;7(3):18-28. In Russian
30. Sheetov MV, Biske YS, Pleshivtseva ES, Marakov AY. Late-Holocene water-level changes of the Volkhov river near Staraya Ladoga Late-Holocene water-level changes of the Volkhov River near Staraya Ladoga. *Vestnik Sankt-Peterburgskogo Universiteta. Seriya 7. Geologiya. Geografiya = Vestnik of Saint-Petersburg University. Earth Sciences*. 2005;7(4):3-16. In Russian

31. Versilin NN, Kleimenova GI. On the problem of comprehension of Ladoga transgression and origin of Neva River. *Izvestiya Russkogo Geograficheskogo Obshchestva*. 2012;144(4):33a-41. In Russian
32. Aleksandrovskii AL, Arslanov KA, Davydova NN, Doluchanov PM, Zaitseva GI, Kirpichnikov AN, Kuznetsov DD, Lavento M, Ludikova AV, Nosov EN, Savel'eva LA, Sapelko TV, Subetto DA. New data on the Ladoga transgression, the Neva River formation, and agricultural development of northwestern Russia. *Doklady Earth Sciences*. 2009;425:274-278. doi: 10.1134/S1028334X09020226
33. Lodygin ED, Beznosikov VA. The molecular structure and elemental composition of humic substances from Albeluvisols. *Chemistry and Ecology*. 2010;26:87-95. doi: 10.1080/02757540.2010.497759
34. Ejarque E, Abakumov E. Stability and biodegradability of organic matter from Arctic soils of Western Siberia: Insights from ^{13}C-NMR spectroscopy and elemental analysis. *Solid Earth*. 2016;7:153-165.
35. Lodygin E, Beznosikov V, Abakumov E. Humic substances elemental composition of selected taiga and tundra soils from Russian European North-East. *Polish Polar Research*. 2017;38:125-147.
36. Celi L, Schnitzer M, Nègre M. Analysis of carboxyl groups in soil humic acids by a wet chemical method, Fourier-transform infrared spectrophotometry, and solution state carbon-13 nuclear magnetic resonance. A comparative study. *Soil Science*. 1997;162:189-197. doi: 10.1097/00010694-199703000-00004
37. Ponomareva VV. Usloviya vodno-mineral'nogo pitaniya rasteniy kak glavnyy faktor fitotsenogeneza i pochvoobrazovaniya [Conditions of water-mineral nutrition of plants as the main factor of phytocoenogenesis and soil formation]. *Pochvovedenie = Eurasian Soil Science*. 1984;8:29-38. In Russian
38. *IUSS Working Group WRB*. World reference base for soil resources 2014. International soil classification system for naming and creating legends for soil maps World Soil Resources Reports 106. FAO. Rome; 2015. 203 p.
39. *Assessment methods for soil carbon*. Lal R, Kimble JM, Follet RF and Stewart BA, editors. USA: Lewis Publ.; 2001. 676 p.
40. Wentworth CK. A scale of grade and class terms for clastic sediments. *The Journal of Geology*. 1922;30(5):377-392.
41. Rozhkov VA, Bondarev AG, Kuznetsova IV, Rakhmatulloev KR. Fizicheskie i vodno-fizicheskie svoystva pochv: Uchebno-metodicheskoe posobie [Physical and hydrophysical properties of soils. Manual]. Moscow: MGUL Publ.; 2002. 75 p. In Russian
42. Jenkinson DS, Powlson DS. The effects of biocidal treatment on metabolism in soil. V. A method for measuring soil biomass. *Soil Biology and Biochemistry*. 1976;8:209-213. doi: 10.1016/0038-0717(76)90005-5
43. Vance ED, Brookes PC, Jenkinson DS. An extraction method for measuring soil microbial biomass. *Soil Biology and Biochemistry*. 1987;6:703-707. doi: 10.1016/0038-0717(87)90052-6
44. Abakumov EV, Mukhametova N. Microbial biomass and basal respiration of selected Sub-Antarctic and Antarctic soils in the areas of some Russian polar stations. *Solid Earth*. 2014;5:705-712. doi: 10.5194/se-5-705-2014
45. Orlov DS. Khimiya pochv [Chemistry of soils]. Moscow: MSU Publishing House; 1981. 376 p. In Russian
46. Swift RS. Organic matter characterization. In: *Methods of soil analysis. Part 3. Chemical methods*. Sparks DL, editor. Bigham JM, editor-in-chief. Madison, Wisconsin, USA: Soil Science Society of America, Inc. and American Society of Agronomy, Inc.; 1996;5:1018-1020.
47. Vasilevich RS, Lodygin ED, Beznosikov VA. Molecular-mass distribution of tundra soils humic substances from the European northeast of Russia. *Vestnik of Saint-Petersburg State University. Seriya 3. Biologiya*. 2015;4:103-111. In Russian

48. Lodygin ED, Beznosikov VA, Vasilevich RS. Molecular composition of humic substances in tundra soils (^{13}C-NMR spectroscopic study). *Eurasian Soil Science*. 2014;47:400-406. doi: 10.1134/S1064229314010074
49. Olsson M, Melkerud P-A. Chemical and mineralogical changes during genesis of a Podzol from till in Southern Sweden. *Geoderma.* 1989;45(3-4):267-287. doi: 10.1016/0016-7061(89)90011-6
50. Nierop KG, Buurman P, de Leeuw JW. Effect of vegetation on chemical composition of H horizons in incipient podzols as characterized by NMR and pyrolysis-GC/MS. *Geoderma*. 1999;90(1-2):111-129. doi: 10.1016/S0016-7061(98)00095-0
51. Frouz J, Keplin B, Pižl V, Tajovský K, Starý J, Lukešová A, Nováková A, Balík V, Háněl L, Materna J, Düker C, Chalupský J, Rusek J, Heinkele T. Soil biota and upper soil layer development in two contrasting post-mining chronosequences. *Ecolog. Engineer.* 2001;17:275-284. doi: 10.1016/S0925-8574(00)00144-0
52. Buurman P, Jongmans AG. Podzolisation and soil organic matter dynamics. *Geoderma*. 2005;125(1-2):71-83. doi: 10.1016/j.geoderma.2004.07.006
53. Emmer IM, Sevink J. Temporal and vertical changes in the humus form profile during a primary succession of *Pinus sylvestris*. *Plant and Soils*. 1994;167:281-295.
54. Dai KH, Johnson CE. Applicability of solid-state ^{13}C CP/MAS NMR analysis in Spodosols: chemical removal of magnetic materials. *Geoderma*. 1999;93:289-310. doi: 10.1016/S0016-7061(99)00072-5
55. Parfitt RL, Yuan G, Theng BKG. A ^{13}C-NMR study of the interactions of soil organic matter with aluminum and allophane in podzols. *European Journal of Soil Science*. 1999;50:695-700. doi: 10.1046/j.1365-2389.1999.00274.x
56. Frouz J, Novakova A. Interactions between soil development, vegetation, and soil fauna during spontaneous succession in post mining sites. *European Journal of Soil Biology*. 2004;44:109-121. doi: 10.1016/j.ejsobi.2007.09.002
57. Bardy M, Fritsch E, Derenne S, Allard T, Nascimento NR, Bueno GT. Micromorphology and spectroscopic characteristics of organic matter in waterlogged podzols of the upper Amazon basin. *Geoderma*. 2008;145(3-4):222-230. doi: 10.1016/j.geoderma.2008.03.008
58. Lentz H, Lademann HD, Ziechmann W. Proton resonance spectra of humic acids from the solum of a Podzol. *Geoderma*. 1973;18:325-328. doi: 10.1016/0016-7061(77)90040-4
59. Skjemstad JO, Waters AG, Hanna JV, Oades JM. Genesis of Podzols on coastal dunes in Southern Queensland. IV. Nature of the organic fraction as seen by ^{13}C nuclear magnetic resonance spectroscopy. *Australian Journal of Soil Research*. 1992;30:667–681. doi: 10.1071/SR9920667
60. Wilcken H, Sorge C, Schulten H-R. Molecular composition and chemometric differentiation and classification of soil organic matter in Podzol B-horizons. *Geoderma*. 1997;76:193-219. doi: 10.1016/S0016-7061(96)00107-3
61. Reintam L, Elmar K., Rooma I. Development of soil organic matter under pine on quarry detritus of open-cast oil-shale mining. *Forest Ecology and Management.* 2002;171:191-198. doi: 10.1016/S0378-1127(02)00472-3
62. Sauer D, Wagner S, Brukner H. Soil development on marine terraces near Metaponto (Gulf of Taranto, southern Italy). *Quaternary international*. 2010;222:48-63. doi: 10.1016/j.quaint.2009.09.030
63. Abakumov EV. Chronology of primary soil ontogenesis: A problem review. *Vestnik Sankt-Peterburgskogo Universiteta*. *Seriya 3. Biologiya*. 2011;3:114-119. In Russian
64. Kurach V, Frouz I, Kurach M, Mako A, Shustr J, Chepek D, Romanov OV, Abakumov EV. Changes of some physical properties of soils in the chronoserry of the sites of self-emergence of the farm-department Sokol complex, Czech Republic. *Eurasian Soil Science*. 2012;3:309-316.

65. Dutta K, Schuur AG, Neff JC, Zimov SA. Potential carbon release from permafrost soils of Northeastern Siberia. *Global Change Biology*. 2006;12:2336-2351. doi: 10.1111/j.1365-2486.2006.01259.x
66. Beznosikov VA, Lodygin ED. High-molecular organic substances in soils. *Proceedings of the Komi Science Centre of the Ural Division of the Russian Academy of Sciences*. 2010;1:24-30. In Russian
67. Baldock JA, Preston CM. Chemistry of carbon decomposition processes in forests as revealed by solid-state carbon-13 nuclear magnetic resonance. In: *Carbon Forms and Functions in Forest Soils*. Kelly JM and McFee WW, editors. Madison, Wisconsin, USA: Soil Science Society of America Inc.; 1995. 89-117 pp.
68. Panettieri M, Knicker H, Murillo JM, Madejón E, Hatcher PG. Soil organic matter degradation in an agricultural chronosequence under different tillage regimes evaluated by organic matter pools, enzymatic activities and CPMAS ^{13}C NMR. *Soil Biology and Biochemistry*. 2014;78:170-181. doi: 10.1016/j.soilbio.2014.07.021
69. Xu J, Zhao B, Chu W, Mao J and Zhang J. Chemical nature of humic substances in two typical Chinese soils (upland vs paddy soil): A comparative advanced solid state NMR study. *Science of The Total Environment*. 2017;576:444-452. doi: 10.1016/j.scitotenv.2016.10.118
70. Polyakov V, Abakumov E. Molecular composition of humic substances isolated from selected soils and cryconite of the Grønfjorden area, Spitsbergen. *Polish Polar Research*. 2019;40(2):105-120. doi: 10.24425/ppr.2019.128369
71. Orlov DS. Pochvennaya khimiya: Uchebnik [Soil Chemistry: A Textbook]. Moscow: Moscow State University Publ.; 1985. 376 p. In Russian

Received 16 August 2019; Revised 27 November 2019;
Accepted 05 December 2019; Published 27 December 2019

Author info:
Abakumov Evgeny V, Dr. Sci. (Biol.), Professor, Department of Applied Ecology, Saint Petersburg State University, 13B Universitetskaya Emb., St. Petersburg 199034, Russian Federation.
ORCID iD: http://orcid.org/0000-0002-5248-9018
E-mail: e_abakumov@mail.ru
Polyakov Vyacheslav I, Engineer, Department of Applied Ecology, Faculty of Biology, Saint Petersburg State University, 13B Universitetskaya Emb., St. Petersburg 199034, Russian Federation.
ORCID iD: http://orcid.org/0000-0001-6171-3221
E-mail: slavon6985@gmail.com
Orlova Ksenia S, Student, Department of Applied Ecology, Saint Petersburg State University, 13B Universitetskaya Emb., St. Petersburg 199034, Russian Federation.
ORCID iD: http://orcid.org/0000-0003-3063-0604
E-mail: Orlkse@yandex.ru

For citation: Abakumov EV, Polyakov VI, Orlova KS. Podzol development on different aged coastal bars of Lake Ladoga. *Vestnik Tomskogo gosudarstvennogo universiteta. Biologiya = Tomsk State University Journal of Biology*. 2019;48:6-31. doi: 10.17223/19988591/48/1