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DEGRADATION, REHABILITATION, AND CONSERVATION OF SOILS

Restoration of Soils and Vegetation on Reclamation Sites of the Kingisepp Phosphorite Field

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Abstract—Processes of initial soil formation were studied on long-term monitoring plots on dump rocks of quarry no. 3 of the Phosphorite production company in Kingisepp district of Leningrad oblast. Observations were performed in 1998, 2004, and 2014. It was shown that vegetation succession on the plots proceeds relatively quickly, and that the species composition of phytocenoses formed is typical of the areas with soddy-calcareous soils. Soil development proved to be correlated with the development of vegetation. Maximum changes in soil characteristics were observed with an increase in the density of forest vegetation and a decrease in the role of herbs. The molecular composition of humic acids in the studied soils remained stable; in particular, the ratio of aliphatic to alkyl aromatic fragments was virtually constant. This phenomenon could be due to the great amount of aliphatic components in the falloff of coniferous species subjected to humification.

Keywords: pedogenesis, succession, soil organic matter, quarries

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INTRODUCTION

The increase of intensity of open pit extraction of mineral resources results in the increase of the rate of land degradation. This process is common in the northwestern Russia; 22900 ha were damaged in the territory of Leningrad oblast as reported for January 1, 2010. [10]. The processes of ecosystem restoration on disturbed lands were impeded for a diverse reasons. Great amount of overburden rock was placed on the surface in the course of opencast mining; this rock was often very specific by properties, composition, suitability for plant cover restoration, and differed drastically from parent rocks of natural landscapes, to which zonal plant communities were adapted. Low concentrations of nutrients in overburden rock were often the factor, limiting restoration of technogenic ecosystems [38, 42]. Application of mineral fertilizers and organic ameliorants do not often enhance the processes of colonization by vegetation. This was connected with the fact that easily soluble substances were quickly lost by initial soils, and organic fertilizers were intensely mineralized in the absence of developed soil adsorption complex [1, 2].

Quarries of constructional and nonmetallic materials were suitable objects for studying some elementary soil-forming processes. Technogenic and especially post-technogenic ecotopes were good model to study the regularities of colonization by plants the sites without soil and plant cover and to estimate the rates of processes developing at initial stage of ecosystem formation in the course of primary succession.

As a rule, the succession of phytocenoses in the territory of rock-disposal complexes occurs gradually, beginning with the appearance of algocenoses. Then, separate plant communities are formed; meadow communities usually dominate at initial stages, and forest communities replace them with time. Regular changes begin in spatially heterogeneous soil layer, as edaphic influence of plants increases. Transformation of biogenic (soil) layer occurs along with the phytocenosis change; first, the sod of young soils is destructed in the course of displacement of meadow vegetation by the forest one, and a thin eluvial horizon can be formed under phytogenic fields of coniferous species. It was noted that microbial cenoses in young ecosystems had no pronounced dominants, and this was typical for early stages of ecosystem development unlike the stable ecosystems [10]. Some researchers considered that planting of seedlings was an optimal method of reclamation, because soil development was closely connected with the plant cover formation and accumulation of critical mass of dead organic matter. One can enhance the rate of pedogenetic processes by promoting the appearance of closed tree stand [6]. Plant community, which determines the appearance and development of all other components of ecosystem via starting the biological turnover of the matter and the main soil- forming processes [6]. Biogenic horizon plays a leading role in the processes of soil formation, because most roots and microorganisms are accumulated in this horizon. Plant rhizosphere is commonly believed to be the focus of soil formation; this is the place, where microorganisms, abiotic components of the substrate, and plant roots interact. Many researchers studied this phenomenon because of its strategic importance for soil formation [5, 30, 35, 43]. Formation of closed herbaceous cover is one of the most important moments in intense stage of plant and soil cover restoration. Development of herbaceous community results in active accumulation of great amount of biomass on the surface of substrate, therefore, in humification acceleration. Accumulation of organic carbon compounds, which rate of accumulation depends on the activity of microbial component, is activated simultaneously [10, 20]. Development of rhizosphere microorganisms is associated with the succession of plant cover [15].

The directions of soil changes under different plant communities are ambivalent. It was shown that simultaneous replantation of tree species had strong effect on the changes in soil structure, which could be obviously seen by the end of growing season [41]. Spatial heterogeneity of soil under herbaceous vegetation is less pronounced than under the arboreal vegetation [36, 48]. Invasion of plants and increase of plant cover density can result in the increase of either heterogeneity, or homogeneity of the soil. For example, roots in grass communities penetrated through the whole upper soil layer; maximal density of roots was observed in most fertile sites, quick consumption of nutrients resulted in quick exhaustion of these sites and increase of homogeneity [48]. The study of interactions in the soil—vegetation system is actual from the viewpoint of modern soil science, and this also allows giving scientific credibility to technologies of land reclamation. The sites of different age of reclamation and overgrowth of rock-disposal sites are suitable model to study pedogenesis.

This work was aimed at the study of restoration of soil and plant cover depending on the composition of lithological basis and type of phytocenosis of particular site. To achieve this goal, the following tasks were set: to describe the plant cover; to analyze and compare primary soils' properties; to evaluate qualitative and quantitative composition of soil organic matter.

OBJECTS AND METHODS

The study was carried out in the Kingisepp phosphorite field situated in western part of Leningrad oblast, in Kingisepp district between Kingisepp and Ivangorod cities. Monitoring plots established by Abakumov and Gagarina in 1998 [1] are situated on rock-disposal sites of different age deposited from the quarry no. 3 of Phosphorite production company. The quarry was intended to mine phosphorite associated with the Early Ordovician sandstone overlain by sandstone and dolomites, which were, in turn, is overlain by the Middle Devonian clays, marls, sands, and argillites. Glaciolacustrine sands and sandy loams, moraine loams and peats represented the Upper Quaternary deposits [2]. All these rocks composed the rock-disposal sites of quarry.

The phosphorite field was open-worked from 1960s. This territory is one of the largest by the area of disturbance and the scale of reclamation work in the northwestern part of Russia. In this result, rock-disposal sites of different age were formed, on which after several years of overgrowth and spontaneous rock subsidence the mining-engineering reclamation measures were carried out.

The study of initial (recent) soil formation was carried out in three monitoring plots 20 × 40 m, in 1998, 2004, and 2014. Peat-mineral mixture (Quaternary loamy-sandy rocks with peat admixture, 20–30%) was placed on blocky material on the first plot at the stage of mining-engineering reclamation after subgrading, then biological reclamation was carried out, it was spruce planting. The age of plantation was 19 years by the moment of observation in 1998. Mineral substrate composed of "loose" rock without peat admixture was placed on rock-disposal sites on the second and third plots after mining-engineering reclamation, which was surface leveling. Larch was planted on the second plot and pine was planted on the third plot. The age of these plantations was 15 and 10 years in 1998.

Botanical descriptions were performed and soil pits were established (3 pits per each plot) on every plot. Soil profiles were described and samples were taken from every horizon for subsequent laboratory analyses performed in triplicate for every sample.

Information about life form of plants and their ecological features was presented according to the recommendations of Sekretareva [13], and addressing to monographs on flora of Leningrad oblast [17–20]. Cenotic groups were given according to [22]. Coefficient of floristic similarity (Soerensen—Czekanowski) was calculated according to the formula: $k = 2c/(a + b)$, where c is the number of common species, a is the number of species on the first plot, b is the number of species on the second plot.

Content of organic carbon was measured with Tyurin's method by dichromate oxidizability. Carbon content in litter was determined by Anstett's method [12] (Tyurin's method modified for litter and peat). Particle-size composition was determined with Kachinskii pipette method with pyrophosphate peptization of microaggregates.

Levels of substrate-induced respiration (SIR) and basal respiration (BR) were measured according to Anan'eva method [4]. Substrate-induced respiration is based on recording of additional response of CO_2 to the introduction of additional substrate—glucose, BS was determined by the same method, but in native (not enriched) soil. Carbon of microbial biomass

(Cmic) in soil was calculated by formula suggested by Anderson [26]:

Cmic (μg C/g of soil) = SIR (μL CO_2/g of soil per hour) × 40.04 + 0.37, according the work by Anan'eva [4].

Microbial metabolic quotient (specific respiration of microbial biomass) was found as the ratio of basal respiration to carbon of microbial biomass: $q$$CO_2$(μg CO_2 C/mg Cmic/h) = BR/Cmic.

Preparations of humic acids were extracted according to commonly adopted procedure [1]. The ratio soil/extractant was 1 : 10. Soil samples were decalcified by sulfuric acid before alkali application. Ash content determined with gravimetric method did not exceed 5%. Solid-state nuclear magnetic resonance spectra of 13C from preparations of HA from replantozems were recorded in pulsed NMR Brucker Ultra_Shield_500. There spectra were transformed into quantitative form via Fourier transform. Atoms in molecule resonate under the influence of magnetic field at different frequencies depending on chemical composition of the substance. The shift of atom resonation frequency is converted into the value of chemical shift, and this value is estimated in parts per million (ppm) because it is extremely small [23]. Structural fragments were identified by the ranges of chemical shift according to literature sources [10, 27, 31]. It should be noted that the approaches to interpretation of the ranges of chemical shift in NMR spectra are somewhat different, but are similar in general terms. We do not present in this work strong identification of individual chemical compounds by narrow groups of organic chemical classification. We determined the ratios between carbon concentrations in different structural components. Aromaticity was calculated as the ratio AR/AL (%), where the signals of aromatic structures were summed up by the ranges 105–164 and 183–190 ppm, and the signals of aliphatic structures were summed up by the ranges 0–105 and 164–183 ppm.

The post-hoc test was performed to evaluate the significance of dynamics of soil properties from 1998 to 2014. The difference between the samples was considered as significant in the cases, when significance level was less than 0.05 ($p < 0.05$). We analyzed such parameters as concentrations of C, N and several particle-size fractions; unfortunately, it was not always possible to form the sample. Statistical analysis was carried out with the help of Statistica 7 program.

RESULTS AND DISCUSSION

Self-organized growth on rock surface was observed just after mining-engineering reclamation stage by typical explerent species (*Tussilago farfara* L., *Chamaenerion angustifolium* (L.) Scop., and *Calamagrostis epigeios* (L.) Roth). Horizontal distribution of plant groups was mosaic in the first years. According to the field observations, small groups were associated with the less consolidated sites of substrate. It should be noted that there are several different hypotheses about the formation of mosaic structure of plant communities [9]. Effect of herbaceous species was high up to 6–8 years after tree planting; the decrease of diversity and projective cover first of all of explerent species was observed after thickening of the tree stand. The increase of the part of boreal and nemoral species was observed in the period of 1989–2014. In the whole, we can note that the plant cover formed was typical for the areas of soddy-calcareous soils (Rendzinas) [2].

Spruce forest without any litter layer was formed in the first plot by 2014, with 11 species of higher vascular plants (2 tree and 9 herbaceous species) from 8 families. The representatives of rootstock herbs were abundant in this plot: 4 short-rootstock (*Orobus vernus* L., *Pulmonaria obscura* Dumort., *Geum urbanium* L., and *Fragaria vesca* L.) and 2 long-rootstock (*Aegopodium podagraria* L. and *Stachys sylvatica* L.) species. As for cenotic groups of herbs, the forest-edge group was presented the best (*Aegopodium podagraria* L., *Stachys sylvatica* L., *Fragaria vesca* L., *Angelica sylvestris* L., and *Geum urbanium* L.), forest group included 3 species (*Hepatica nobilis* Mill., *Orobus vernus* L., and *Pulmonaria obscura* Dumort.), and one species (*Deschampsia cespitosa* (L.) *Beauv*) belonged to bog-forest meadow group. Relative to water regime, mesophytes (7 species) dominated, and two species belonged to mesohygrophytes. By demands to soil fertility, there were equal numbers of mesotrophs and mesoeutrophs (4 species in each group) and one eutroph.

Projective cover of herbaceous vegetation reached 25% on the second plot, where larch was planted. Sum total 14 species of higher plants from 10 families (4 tree and 10 herbaceous species) were found on this plot. Approximately similar number of species fell on different life forms: long- and short-rootstock, taproot, taproot-fibrous, and cespitosa perennial herbs. Herbs were dominated by the representatives of forest-edge group (*Fragaria vesca* L., *Aegopodium podagraria* L., *Viola mirabils* L., and *Vicia sepium* L.), and by two representatives in forest-edge meadow (*Hypericum perforatum* L. and *Calamagrostis epigeios* (L.)) and forest (*Orobus vernus* L., *Pulmonaria obscura* Dumort.) groups; one species fell on ruderal-riparian (*Tussilago farfara* L.) and bog-forest meadow (*Deschampsia cespitosa* (L.) Beauv) groups. The majority of herbs were mesophytes (8 of 10); xeromesophyte (*Hypericum perforatum* L.) and mesohygrophyte (*Deschampsia cespitosa* (L.) Beauv.) were also found. By demands to soil fertility, mesotrophs dominated (6 species), though all groups from eutrophs to oligotrophs were presented.

Twelve species of higher plants (3 tree and 9 herbaceous species) were found on the third plot, where pine was planted. Total projective cover of herbs was 25%, there were 4 short-rootstock (*Fragaria vesca* L., *Orobus vernus* L., *Pulmonaria obscura* Dumort., and *Solidago virgaurea* L.) and 4 long-rootstock (*Vicia sepium* L., *Tussilago farfara* L., *Calamagrostis epigeios* (L.) Roth, *Equisetum arvense* L.) species, and 1 (*Hypericum perforatum* L.) taproot species. It was difficult to separate a dominating ecological-cenotic group here. Forest, forest-edge, forest-edge meadow, meadow-riparian, and ruderal-riparian groups were presented by almost similar numbers of species. Relative to moisture demands, mesophytes dominated, and one species was xeromesophyte. Relative to nutrient demands, most species were mesotrophs (6 species), 2 species were oligotrophs, and 1 species was mesoeutroph.

Maximal floristic similarity was observed between phytocenoses of the second and third plots (Soerensen–Czekanowski index was 76%), there were about 50% of common species between spruce and pine and larch forests. It should be noted that the portion of forest-edge and forest species increased in the first plot in comparison with the second and third plots; herbs more demanding of soil fertility were grown in this plot. There were few explerent species typical for disturbed ecotopes on all the plots by 2014.

The restoration of the soil cover was closely connected with vegetation development and dominating type of life forms. Abiogenic transformation preceded biogenic transformation of the substrate. It was expressed by the redistribution of particle-size fractions among components of microrelief of reclaimed soil surface. Accumulation of fine earth was confined to microdepressions, where first plants settled mostly at a later time, soil shrinkage was also observed there. Seasonal cryogenic physical processes resulted in annual vertical and lateral displacement of large blocks, which caused the damage to root systems, which produced an adverse effect on the state of separate trees.

Primary sites of soil formation were associated at initial stages with separate parcels of vegetation, first of all of herbaceous species with relatively great aboveground biomass. This caused activation of humus accumulation process and appearance of incipient humus horizon. As the plant cover became more continuous, active structure formation and decrease of density began in the upper horizons. Tree crowns closed by 2004, importance of herbaceous vegetation in the processes of soil formation decreased, litter layer appeared, and the incipient humus horizon got transformed into a humus horizon. Species composition of herbaceous–dwarf-shrub layer changed by 2014, the portion of explerent species and their participation in the pedogenesis decreased. Gray-humus horizon is formed by now; gley process was observed in the lower horizons of the third plot. Thickness of embryozems changed rather quickly at the first stages of development in the case of second and third plots. Organic matter in the form of peat admixture was introduced in the first plot at reclamation stage; thickness of humus horizon practically did not change in the first years of observation; however, formation of phytocenosis and increase of the depth of root penetration promoted similar to another plots structure formation and decrease of soil density. Let us consider in detail chemical and particle-size composition of replantozems.

We determined the content of total carbon and total nitrogen in soil, and we considered that their origin was mostly biogenic; however, their mineral forms might be present as well. The latter suggestion was confirmed by relatively high contents of carbon and nitrogen in mineral horizons (Table 1). The problem of determination the content of rock-inherited carbon is far from solution [37], this can be not only the carbon of peat admixed to the rock, but also carbon of kerogenic type. Content of organic carbon and humus, respectively, was maximal in upper layers and decreased down the soil profile. The litter of 35-year-old replantozem on peat-mineral mixture under spruce had maximal content of organic matter, and this was apparently explained by longer time of plant growth and better destruction of organic matter. When comparing the results of 2014 with earlier observations, the decrease was observed of the portion of organic carbon in the lower layers in this plot in the period 1998–2014 owing to mineralization processes. It should be noted that the difference in carbon contents in 1998 and 2014 in the first plot was not significant according to the results of post-hoc test (Table 2). Carbon content in upper organic layers significantly decreased in the second and third plots in mineral substrate without peat admixture over this time, as distinct from the lower mineral horizons. This was probably connected with the decrease of importance of herbaceous vegetation and increase of the portion of needle falloff in litter, destruction of which proceeds more slowly. In general, the content of organic carbon under pine and larch differed insignificantly.

In the case of soil formation on peat-mineral mixture under spruce, humus enrichment with nitrogen gradually decreased in organomineral AY and C horizons and increased in the litter. In all appearance, organic matter introduced with peat at the first stage of reclamation was subject to mineralization. We consider that the processes were equilibrated in litter and humification began to dominate over mineralization; organic matter continued to be mineralized actively in organomineral horizons, which contained initially admixed organic matter [23]. Nitrogen content was stable or slightly increased in the second and third plots, where reclamation was carried out with piling up the rock without peat admixture. However, this trend was not significant. The C/N ratio decreased down the soil profile in the first plot, and was minimal in transitional AY horizon in the second and third plots. The increase of this ratio was caused by high carbon content in the upper layers and by minimal nitrogen content in the lower horizons.

Table 1. Concentrations of carbon, nitrogen, physical clay and clay, and pH of fine earth in studied soils

Horizon	Depth, cm	C_{tot}	N_{tot}	C/N	pH_{H_2O}	Content of particles, %	
		%				<0.001 mm	<0.01 mm
1998, 19-year-old replantozem on peat-mineral mixture, plot1							
Arz	0–6	7.18	0.69	12.2	6.4	18.5	23.0
AY	6–19	7.36	0.55	15.6	6.4	22.4	30.2
AC	19–52	6.93	0.54	15.0	6.3	27.0	41.1
1998, 15-year-old replantozem on mineral rock, plot 2							
Arz	0–4	4.28	0.30	16.7	7.3	16.9	35.4
AY	4–11	2.01	0.28	8.4	7.6	16.9	41.0
AC	11–26	1.36	0.22	7.2	7.7	22.4	56.3
C	26–33	1.27	0.20	7.4	7.8	24.0	63.2
1998, 10-year-old replantozem on mineral rock, plot 3							
Arz	0–3	2.67	0.21	14.9	7.3	21.9	40.9
AY	3–10	1.10	0.20	6.4	7.7	26.6	50.1
AC	10–26	0.36	0.08	5.2	8.0	19.9	48.7
C	26–33	0.22	0.02	12.9	8.1	19.9	42.8
2004, 25-year-old replantozem on peat-mineral mixture, plot1							
L	0–1.5	34.71	1.05	38.7	6.5	Not determined	
F	1.5–2.0	26.30	0.75	41.0	6.2	″	
Arz	0–2	7.33	0.50	17.1	6.3	16.2	34.0
AY	2–16	5.10	0.70	8.5	6.5	21.3	40.2
AC	16–28	3.75	0.52	7.2	6.9	20.2	39.8
2004, 20-year-old replantozem on mineral rock, plot 2							
L	0–1.5	25.70	0.70	42.9	Not determined		
F	1.5–2.0	13.02	0.63	24.2	″		
Arz	0–2	–	–	–	7.2	Not determined	
AY	2–14	2.69	0.35	9.0	7.5	19.0	38.2
AC	14–26	0.60	0.09	7.8	7.7	18.3	35.6
C	26–33	0.71	0.10	8.3	7.8	20.3	37.6
2004, 16-year-old replantozem on mineral rock, plot 3							
L	0–1	28.95	1.52	22.3	Not determined		
F	1–2	30.90	1.30	27.8	″		
Arz	0–3	3.02	0.50	7.1	7.2	22.5	37.8
AY	3–13	1.67	0.18	10.9	6.9	23.2	39.0
AC	13–26	0.92	0.11	9.8	7.7	25.6	40.5
C	26–35	0.60	0.07	10	7.8	27.5	39.9
2014, 35-year-old replantozem on peat-mineral mixture, plot1							
O	0–3	21.00	1.16	21	6.5	Not determined	
AY	3–18	2.00	0.20	11.6	6.5	15.0	33.2
AC	18–35	0.60	0.16	4.3	7	20.0	40.0
2014, 30-year-old replantozem on mineral rock, plot 2							
O	0–1	7.40	0.48	17.8	7.4	Not determined	
AY	1–18	2.40	0.31	8.9	7.6	22.0	36.0
AC	18–35	1.98	0.16	14.3	7.7	26.0	41.2
2014, 26-year-old replantozem on mineral rock, plot 3							
O	0–1	6.60	0.49	15.6	7	Not determined	
AY	1–10	1.90	0.46	4.8	7.2	24.3	36.0
ACg	10–30	1.56	0.10	18.1	7.2	26.0	40.3

Table 2. Results of statistical analysis (*post-hoc* test). The values $p <$ of each parameter are presented

Post-hoc test	C_{tot}	N_{tot}	Content of particles, %	
			<0.001 mm	<0.01 mm
1998-1 -2004-1	0.02	0.03	0.06	0.5
1998-2 -2004-2	0.03	0.06	0.06	0.5
1998-3 -2004-3	0.04	0.07	0.06	0.6
2004-1-2014-1	0.03	0.05	–	–
2004-2-2014-2	0.05	0.05	–	–
2004-3-2014-3	0.06	0.06	–	–
1998-1-2014-1	0.06	0.05	–	–
1998-2-2014-2	0.03	0.003	–	–
1998-3-2014-3	0.03	0.04	–	–

The pH of water suspension in all plots gradually increased down the soil profile or remained constant. It is highly likely that it was connected with acidifying organic matter, which was accumulated in upper soil horizons, and carbonates in the lower layers. The samples in the first plot under spruce had weakly acid reaction maybe because the rock initially contained organic matter. Also there is widespread belief that the spruce falloff acidifies the soil stronger than the falloff of other species in this region [8, 15]. It is interesting that pH of water suspension decreased as well as increased in the same plots in 1998–2014. The reason of this phenomenon may be two simultaneous processes: accumulation of organic matter (acid products of humus substances could additionally leach carbonates) on one hand, and weathering of coarse fractions and enrichment of fine earth with carbonates on the other hand. It was shown earlier that the processes of organic matter accumulation and decalcification as the result of weathering were dominating in calcareous rocks [24].

Replantozems were medium loams by particle-size composition. It was difficult to determine the trends in profile concentrations of fractions depending on a year. It was apparently the result of substrate turbation (churning) and heterogeneity. The changes in physical clay and silt contents from year to year were insignificant according to the results of post-hoc test.

This work considers the main biotic factors of soil formation process: plant cover and soil microbiome. The state of the latter determines soil fertility, maintenance of ecosystem functions of soil, and adaptation of plants to stress conditions. The data on the state of soil microbial community are presented in Table 3. The BR, SIR and Cmic values were always maximal in litter and most often decreased down the soil profile. The difference between the values of basal respiration in litter horizons and parent rocks reached five times. Producing of CO_2 by soils in response to substrate (glucose) introduction almost always increased, the difference between SIR in litter and lower layers reached ten times. Concentration of Cmic in the upper layer was almost 8 times greater than in the rock, but soils of natural ecosystems were characterized by values, which orders of magnitude were greater than those obtained by us [14]. Specific respiration of microbial biomass had relatively low values irrespectively of horizon (from 0.01–0.02 μg CO_2 C/mg Cmic/h). So, it can be said that litter was the most active in terms of biology, but generally replantozems were characterized by low microbiological activity. Significant difference was not found, when comparing these characteristics in soils under different phytocenoses. At the same time, it should be noted that the content of Cmic as well as SIR level were slightly greater in larch forest, pine forest was the second, and minimal values were observed in litter of spruce forest. It should be noted that such trend did not have reliable confirmation, but it can be assumed that species composition of microbial community in litter of spruce forest was different and was presented mostly by slowly growing acidophilic species. Litter under spruce indeed had a more acid reaction in comparison with other plots.

The data of ^{13}C NMR spectroscopy obtained for six preparations of humic acids from organomineral horizons (AY) of soil of different age allowed judging about the stability of carbon skeleton of macromolecules in time and evaluating the similarity of structural composition of HA under studied forest communities (Table 4). The ratio between aromatic and aliphatic fragments was in 2004 and 2014 (%): 36/64 and 33/67 in plot 1, 28/72 and 33/67 in plot 2, and 35/65 and 34/66 in plot 3. Yield of humic acids comprised 0.2–1.0% of the mass of initial dry fine earth.

Chemical shift in the range 0 to 50 ppm corresponds to resonances of carbon aliphatic structures [45]. Some researchers believe that presence of aliphatic structures can be the result of great contribution to humification processes of the substances of plant origin (wax, chitin, phospholipids, fatty acids) and products of life activity of microorganisms [33, 34].

Table 3. Microbiological characteristics of replantozems

Horizon	BR (μg CO_2/g per hour)	SIR (μg CO_2/g per hour)	Cmic (μg C/g of soil)	qCO_2(μg CO_2 C/mg Cmic/h)
35-year-old replantozem on peat-mineral mixture, plot1				
O	0.1	0.21	8.93	0.011
AY	0.05	0.05	2.45	0.019
AC	0.02	0.03	1.59	0.010
30-year-old replantozem on mineral rock, plot 2				
O	0.09	0.31	12.6	0.007
AY	0.02	0.04	2.08	0.009
C	0.03	0.03	1.59	0.018
26-year-old replantozem on mineral rock, plot 3				
O	0.09	0.28	11.4	0.007
AY	0.03	0.03	1.59	0.016
ACg	0.01	0.03	1.47	0.009

Table 4. Structural composition of humic acids in organomineral horizons of replantozems, % of total intensity

Type of structural fragments	Chemical shift, ppm	Plot 1		Plot 2		Plot 3	
		2004	2014	2004	2014	2004	2014
H-, C-substituted aliphatic fragments	10–27	11.10	1.04	12.00	12.40	11.60	11.90
CH_2-alkyl structures	27–50	16.79	19.39	16.01	16.84	17.22	15.01
Methoxyl fragments, amino-acid and ester groups	50–70	14.90	1.52	17.80	15.80	15.20	14.80
O- and N-substituted aliphatic fragments	70–100	12.50	15.00	14.00	14.30	13.70	13.70
Anomeric aliphatic fragments	100–108	2.97	3.89	3.89	3.77	3.780	3.65
Protonated aromatic carbon	108–135	20.40	15.50	15.60	15.90	17.40	14.70
alkylaromatic groups	135–150	6.02	6.43	5.83	6.96	7.20	9.65
Aromatic carbon of phenols and esters	150–170	9.32	9.50	8.46	8.63	8.47	10.20
Carboxyl and carbonyl groups	170–190	6.18	4.71	6.41	5.40	5.43	6.39
Post-hoc test	One plot – different dates	$p < 0.06$		$p < 0.07$		$p < 0.07$	

The main resonance peaks fell on this range in all plots in both 2004 and 2014 (Fig. 1). This area could be subdivided into two parts: 10–32 ppm (H-, C-substituted aliphatic fragments, which belonged to most active and mobile compounds of alkyl nature) and 32–50 ppm (the most stable among alkyl compounds CH_2-alkyl structures).

Pronounced peaks, which could been observed in all spectra in the range 20–30 ppm, corresponded to the resonance of alkyl carbon; 23, 26 and 29 ppm corresponded to linear chains of hydrocarbons; 30 ppm corresponded to long-drawn-out aliphatic structures contained polymethylene groups [35, 39, 40, 45, 47]. Long linear chains of hydrocarbons were most developed in all plots in 2004, but some peaks of this range lost their intensity by 2014. According to some researches, genesis of humic acids was caused by accumulation of plant derivates, but not the products of microbial metabolism in the case of forest soils demonstrated peaks in the range of alkyl structures [45, 49]. No one significant peak fell on the second area of the range (32–50 ppm), this area corresponded to carbon protons and short branched aliphatic chains with CH_3 end groups [45].

The peaks in the range 50–60 ppm were observed in the second and third plots in both years of observation (more pronounced in the first of these plots in 2014). Some authors considered that this range corresponded to aliphatic parts of lignin molecules, products of degradation of coumaric, sinapic, and coniferyl alcohols [10, 11]. According to earlier works, this was the area of resonance of amino acid carbon [28].

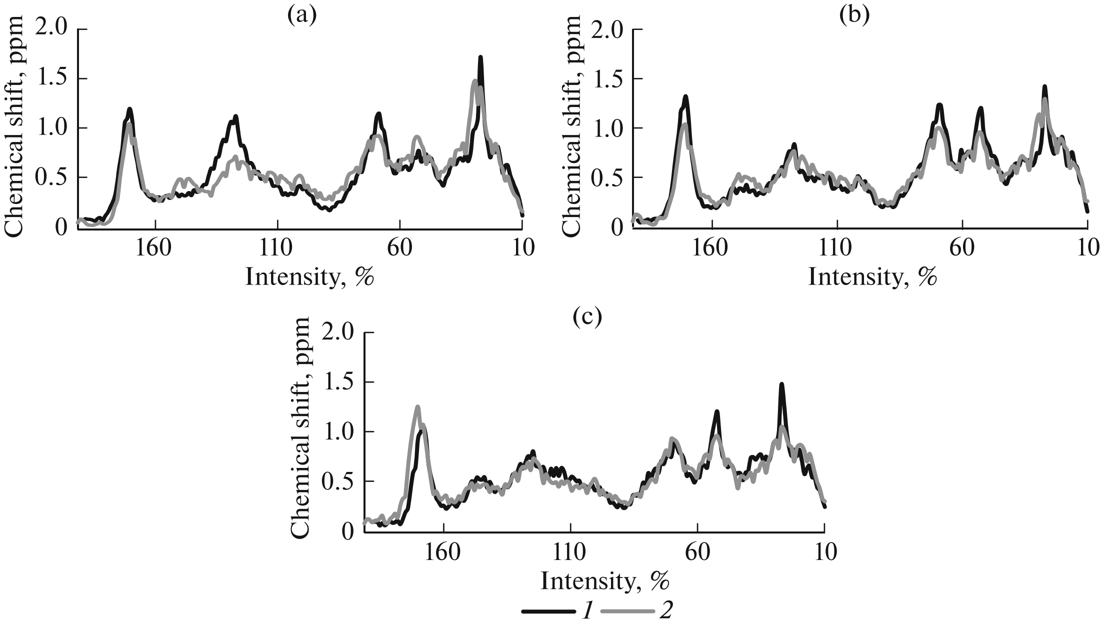

Fig. 1. ^{13}C NMR spectra of humic acids from organomineral horizon AY (depth of sampling 4 cm) under spruce (a, plot 1), larch (b, plot 2), and pine (c, plot 3) in 2004 (*1*) and 2014 (*2*).

The peaks in the range 64–73 ppm were observed in all studied samples and characterized O- and N-substituted aliphatic "carbohydrate" fragments.

Relatively wide range 108–170 ppm corresponded to typical aromatic structures. Maximal area of peaks among aromatic fragments fell on the range 108–135 ppm (protonated aromatic carbon). Pronounced peak in the first plot under spruce at 128 ppm in 2004 and less intense peaks in the other plot could characterize H- and C-substituted aromatic structures supposedly in the form of substituted phenyl propane. Chukov [23] considered that these were most probably single aromatic rings connected with the remaining part of molecule by aliphatic chains. He called them single, and noted their good mobility. Pronounced peaks in the area 167–170 ppm, clearly expressed in all samples, represented the range of resonance of aromatic carbon in phenols and esters.

Analysis of molecular structure of humic acids demonstrated that aliphatic groups predominated over the aromatic ones in all samples. The ratio between groups of structural fragments practically did not change over 10 years. It is commonly agreed that the development of humic acids is related to the increase of the portion of benzoid aromatic fragments and decrease of aliphatic fragments [1, 3, 10]. Some researchers noted that the portion of aliphatic fragments of humic acids increased in the course of soil and plant cover development and replacement of herbaceous communities by the forest ones [32]. Upper soil horizons in forest communities were also characterized by increasing content of alkyl carbon structures in comparison with herbaceous communities.

Webster et al. [46] suggested to calculated the ratio of the area of peaks in the range 0–52 (C_{Alk}) to the range 52–108 ($C_{Alk\text{-}O}$) in order to judge about the degree of organic matter destruction. The greater was this parameter, the greater was the degree of organic compounds decomposition and more intense was the microbiological activity. The $C_{Alk}/C_{Alk\text{-}O}$ ratio in studied plots comprised in 2004 and 2014: 101 and 0.97 in plot 1, 0.92 and 0.96 in plot 2, and 0.98 and 0.92 in plot 3, respectively. This parameter was practically similar in studied samples from all plots and almost did not change over 10 years.

CONCLUSIONS

Performed study attested to the dynamical restoration of phytocenoses and soils on calcareous loamy dump rocks from a quarry of the Phosphorite Production Company. Relatively intense development of vegetation resulted in the formation of forest communities that are most typical for taiga zone of European Russia. In general, we can note very favorable properties of substrate (pH and particle-size composition) for plant development, and this suggested relative efficiency of such method of reclamation. It was found that gradual mineralization of organic matter took place in the case, when substrate initially contained organic matter, and this resulted in the decrease of organic matter content in fine earth and increase of humus enrichment with nitrogen. Gradual increase of organic matter content was observed in the case of initially humusless substrates. It was determined that soil formation was connected with the initial characteristics of the plant cover, its further development, and its species composition. It was shown that maximal difference in morphogenetic characteristics of soil profiles was observed during the process of decrease of herbaceous vegetation participation and development of forest vegetation. Pedogenesis proceeded in a similar way under different forest phytocenoses. It has been proved that all studied plots had very low level of microbial community functioning. The results of qualitative and quantitative analyses of humic acids revealed low level of carbon skeleton changes in time and similarity of humic acids composition under different communities. It was determined that aliphatic groups contained in great amount in needles predominated appreciably over the aromatic ones, and this fact attested significant importance of forest falloff in soil humus formation.

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