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Carbon Sequestration by Soils of Ash Dump Forest Areas in the Middle Urals (Russia)

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Abstract: The purpose of this article was to assess the participation of young soils of ash dump forest communities in carbon sequestration by soils of southern taiga forests, considering the physico-chemical properties of the ash substrate and forest litter (pH, TOC, TN, content of P and K mobile compounds, and exchangeable Ca and Mg ions). It was revealed that on three Middle Ural ash dumps (composed of fly ash from various brown coals) over 50–60 years, forest communities spontaneously formed according to the zonal type (with the dominance of *Betula pendula* Roth and *Populus tremula* L.) with poorly differentiated young soils—technosols. For the first time, as a result of using an integrated approach to assess the direction of forest ecosystem formation on fly ash dumps, a tendency to increase carbon stocks in technogenic soils that have not reached the level of zonal soils was revealed, as well as the dependence of C accumulation on some physico-chemical characteristics of ash was established. Carbon stocks in Technosols are on average equal to 44 t/ha but vary significantly. It was shown that there is a medium negative relationship between the content and stocks of organic carbon in soils formed on a technogenic substrate and the content of mobile phosphorus compounds in them (the correlation coefficient is −0.58 and −0.53, respectively). The average carbon stocks in the litter of technosols, which is the main source of organic carbon in forest soils, are 3.2 t/ha. It was revealed that the carbon stocks in the litter are most influenced by the content of exchangeable calcium cations and magnesium in it (the correlation coefficients are −0.68 and −0.69, respectively). Any correlation between the studied litter parameters and carbon accumulation in the soils of ash dumps was found. The study revealed that the carbon stocks in the technosols of ash dump forest communities are two times less than the carbon stocks in the zonal forest soils of the Middle Ural southern taiga. The stocks of this element in the litter of young soils are equal to 1/3 of the litter of zonal soils. The composition of the humus substance system formed in the soils of forest areas of ash dumps and zonal soils is similar. The results of this study can serve to fill gaps in the knowledge about carbon sequestration by soils and aim to draw attention to forest communities of technogenic ecosystems to consider the contribution of their components to carbon sequestration.

Keywords: *Betula pendula* Roth; *Populus tremula* L.; forest community; fly ash; natural colonization; southern taiga; technosols; carbon sequestration; carbon stock

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1. Introduction

Anthropogenic activities associated with the combustion of fossil fuels are one of the main reasons for the increase in the concentration of greenhouse gases, of which carbon dioxide is the main one. According to various weather stations, the concentration of CO_2 in the atmosphere in 2022 set a record and exceeded 420 ppm [1]. The forests of the Earth make a significant contribution to the global carbon cycle; for instance, the forest fund lands make up 65.6% of the territory of Russia [2]. However, forest communities can also form spontaneously or thanks to the recultivation of various technogenic formations belonging to industrial lands, while they are not considered in the carbon balance, although they also contribute to climate regulation by sequestering greenhouse gas—CO_2—and depositing carbon in biomass and soil. For example, forest communities form on overburden rocks (generally close to natural formations) from the mining industry [3–8]. A significantly more human-modified substrate is that of tailing dumps formed during the enrichment of minerals, on which tree communities also develop [9–12]. Another variant of a specific substrate that is absent in nature is the ash formed during the combustion of coal, mainly stored in ash dumps that occupy large areas in some countries. The properties of ash, which in this case serves as a soil-forming substrate, can differ significantly, primarily due to the characteristics of the burned coals and technological factors, as well as the natural and climatic conditions of the location of ash dumps [13–15]. In addition, forest communities and soils in recultivated and non-recultivated areas of ash dumps are more likely to differ in carbon accumulation. The materials available in the literature characterize certain types of woody plants, mainly artificially planted on coal ash dumps, and the formation of young soils in reclaimed areas [16–21]. It should be noted that practically no work is devoted to carbon stocks in forest soils from ash dumps.

In connection with the above, data on carbon accumulation by soils of spontaneously formed forest communities of different ash dumps under certain climatic conditions are of high scientific and practical significance and are associated with a possible impact on the rate of this process in technogenic ecosystems. To solve the problems related to the features of the carbon cycle, in addition to the actual accumulation of carbon in technogenic soils, it is necessary to search for factors influencing this process. Since forest litter is the main source of carbon and nitrogen for the synthesis of soil organic matter in forest communities, the influence of litter quantity [22–26] and quality [27,28] on soil properties is actively investigated. At the same time, soil properties, in turn, determine the composition of the phytocenosis through the processes of assimilation and dissimilation of individual plant species. The influence of soil properties on forest communities should ultimately affect the quality and quantity of forest litter and, accordingly, the formation of soil organic matter, but this aspect is practically not given much attention.

It is convenient to try to identify the control of soil characteristics over the litter parameters and carbon accumulation in the soil at ash dumps because it is possible to select among them a single-factor series—several objects that differ in only one factor of soil formation (and, accordingly, accumulation of organic matter), for example, only in the chemical composition of the substrate. There are brown coal ash dumps in the Middle Urals located in similar geomorphological and climatic conditions, on which spontaneous overgrowth of vegetation started in the 1970s in the XX century and is currently represented by forest communities. The fly ash of these ash dumps is relatively homogeneous in physical properties [13,29,30], but our studies have shown significant differences in its chemical properties [31,32].

Thus, the aim of this work was to assess the participation of young soils of ash dump forest communities in carbon sequestration by soils of southern taiga forests, considering the chemical properties of the ash substrate and forest litter. Our hypothesis was that changes in carbon stocks in the young soil of ash dumps during the formation of forest communities tend to approach zonal soil variants; however, for half a century, C stocks in technosols did not reach the level of soils in natural forest ecosystems, and differences in the physico-chemical characteristics of the ash substrate had a significant impact on the accumulation of carbon in technogenic soils.

2. Materials and Methods

2.1. Site Description

The problem of carbon accumulation by soils of ash dumps in forest areas in connection with the properties of the ash substrate is considered in the example of three ash dumps if the Middle Urals—ash dumps of the Sredneuralskaya, Verkhnetagilskaya, and Nizhneturinskaya state district power plants (SUPP, VTPP, and NTPP) (Figure 1). They are located on an elongated line in the meridional direction, have an area of 60 to 124 hectares, a level surface, and are formed by coal ash from various deposits (Table 1). The studied ash dumps are composed of fly ash since they are derived from low-caking coals, which excludes the formation of slags [13,33].

Figure 1. The locations of the objects: 1—ash dump of the Sredneuralskaya power plant (SUPP); 2—ash dump of the Verkhnetagilskaya power plant (VTPP); 3—ash dump of the Nizhneturinskaya power plant (NTPP).

Table 1. Characteristics of ash dumps.

Ash Dump Number	Power Plant	Coordinates	Coal Deposit	Ash Dump Area, ha
1	Sredneuralskaya (SUPP)	57°00′ N, 60°27′ E	Ekibastuzskoe	104
2	Verkhnetagilskaya (VTPP)	57°20′ N, 59°56′ E	Chelyabinsk and Bogoslovskoe	125
3	Nizhneturinskaya (NTPP)	58°37′ N, 59°52′ E	Volchanskoe	60

All study objects are located on the eastern slope of the Middle Urals and have absolute elevations from 190 to 270 m above sea level. They are located in the temperate continental boreal climate zone with an average annual air temperature of +1.7 . . . +2.2 °C and an average annual precipitation of 600–670 mm [34]. The area of the ash dump location is typically forest, with indigenous vegetation represented by southern taiga pine and pine-spruce forests, as well as secondary birch and mixed birch-pine forests [35]. After the end of the operation, part of the surface of the ash dumps of SUPP, VTPP, and NTPP was not recultivated, and because of natural overgrowth, forest communities were formed in these areas by the time of the study.

Thus, the soils of the ash dumps under study constitute a single-factor series and are characterized by similarity in bioclimatic conditions (southern taiga), age (about 50–60 years), position in relief, and formation on a leveled surface, but differ in the properties of the soil-forming rock (ash substrate).

Background (control) sites were laid in mixed zonal southern taiga forests at 5–10 km from ash dumps.

2.2. Sampling and Analysis of Plant Communities

A geobotanical description was carried out on ash dump sites and background (control) sites in zonal forests in the same area. Crown density, height, diameter, and age of trees were determined for the stand. The test sites were laid in accordance with the generally accepted methods of geobotanical description. The description area of each site had the shape of a square and amounted to 250–300 m^2. When describing the tree tier, the species composition was considered, and a continuous enumeration of trees was carried out. The height was determined using a Suunto Precision Instruments (Finland), altimeter, and the diameter was determined at a height of 130 cm using a measuring fork for every fifth tree. The age of the stand is indicated in accordance with previous studies conducted at the sites [36].

The coverage of the shrub (undergrowth) layer was determined by eye at 10 sites with a size of 2 $\times$ 2 m. To determine the projective cover of individual species of the herb-shrub and moss-lichen layers, 25 square sites (each equal to 0.25 m^2) were laid on each test area. An ecological-phytocenotic approach was used to identify the vegetation of the test sites and the main features of the structure of the community [37]. To combine them into one syntax, the species composition was used, taking into account the abundance of species and predominant life forms. Thus, the lowest classification (associations) includes communities with the dominance of the same species in all the main layers.

The stock of aboveground phytomass in the soil cover of communities (the herb-shrub layer) was calculated to determine the floristic composition and abundance of herb-shrub layer plants. It is essentially the weight of dry organic matter contained within the living plants of a community. The stock was determined on 13 plots of 25 $\times$ 25 cm, laid out within each main test site. The plants were cut at the soil level, arranged by species, and weighed in an air-dry state.

Based on the occurrence of species on plots of 0.25 m^2, species saturation was determined, and the Shannon–Wiener diversity index was calculated using the formula $H = -\Sigma pi \ln(pi)$ [38]. The dominant species were identified based on the assessment of the projective cover and the phytomass stock.

2.3. Sampling and Analysis of Soils

Soil sections and their morphological descriptions were performed on each ash dump site in the range of 3 to 8, depending on the ash homogeneity (in total, 15 sections) in the summer period of 2019–2021. Samples for analytical studies were taken from the upper strata of ash dumps in detail, layer by layer, considering the visible boundaries of the horizons, and prepared for analysis by conventional methods [39,40]. Special sampling was performed for bulk density determination.

Particle size distribution was determined by the pipette method, and bulk density was determined by the volumetric cylinder method [41]. pH values were measured in the soil by water suspension (1:2.5) using a pH meter (Anion 4100 ("Infraspak-Analyte", Novosibirsk, Russia). The content of total organic carbon (TOC) was analyzed using the Tjurin wet-combustion method (with $K_2Cr_2O_7$) and total nitrogen content (TN) by the Kjeldahl wet combustion method (using a Heating Digestor DK 20 Velp and Distillation Unit UDK 12 Velp, (Velp Scientifica, Usmate, Italy) with titrimetric termination. Exchangeable Ca^{2+} and Mg^{2+} were detected by titration with Trilon B after KCl extraction; available phosphorus content (P_2O_5) was determined by ammonium molybdate method spectrophotometrically (using UV Probe-1650 spectrophotometer, Japan); available potassium (K_2O)—in the same extract by flame emission (using photometer PFA- 378, (Unico-sis", Saint-Petersburg, Russia) [39]. The composition of humus was determined by the modified method of Tyurin [42]. The weighted average values of the studied indicators were calculated to establish the physico-chemical characteristics of a particular layer of the ash substrate (0–20 cm or 20–40 cm). The thickness of the horizons that make up each layer was considered. Organic carbon stocks were calculated using the data on the thickness, bulk density, and element content of each soil horizon.

Statistical processing was carried out using the Mann–Whitney criterion [43]. The STATISTICA 8. package (StatSoft Inc., Tulsa, OK, USA, 1984–2007) and Microsoft Excel (2016) were used to calculate correlations, average values, and present the data graphically.

3. Results

3.1. Plant Community Parameters

As a result of geobotanical studies at the ash dumps of SUPP, VTPP, and NTPP and background (control) sites, it was found that forest phytocenoses with a predominance of small-leaved tree species and a small admixture of coniferous trees are formed during 50–60 years in the process of self-growing on non-recultivated ash (Table 2).

Table 2. Geobotanical characteristics of forest phytocenoses.

Characteristics	Ash Dump			Background Forests
	SUPP	VTPP	NTPP	
Crown density	0.40–0.60	0.45–0.65	0.70	0.40–0.60
Tree height, m	17.5–18.5	14.5–16.0	7.0–16.0	18–25.0
Composition of the forest stand	8Pp2B	6B2PpSPn	6Pp3BPn	7B2PnS + Pc
Average diameter, cm	16.8	16.1	13.7	25–30
Age, years	45–50	38–40	50–55	80–100
Shrub layer cover, %	15–40	5–30	45–50	20–30
Coverage of the herb-shrub layer, %	75–90	30–35	30–65	85–90
Coverage of the moss-lichen layer, %	5–10	3–5	0.5	25–35
Shannon–Wiener index (H)	3.13–3.19	2.55–2.80	2.8	3.27–3.60
Species saturation, number of species per 0.25 m^2, (min–max)	9.1 (6–15)	5.4 (3–9)	7.8 (4–11)	11.19 (4–19)
Floristic richness in the accounting area, (min–max)	36.0 (31–42)	37.0 (35–38)	28.0 (30–24)	66.0 (60–72)

In general, forest phytocenoses formed on ash dumps have similar characteristics to background forests in terms of the density of the tree layer and the species composition of forest-forming species but differ in the morphometric indicators of the tree stand and the composition and formation of the undergrowth and lower layers. The herb-shrub layer of forest phytocenoses on ash dumps is characterized by lower indicators of projective cover and species richness in comparison with background forest communities. The species richness of the studied forest communities of ash dumps is represented by 63 species of vascular plants (18 families), which is 1.7 times lower than the background communities, where 108 species (25 families) were recorded. The Shannon–Wiener diversity index in forest phytocenoses on ash is 1.2 times lower than in background communities, except for the ash dump of the SUPP.

Having a similar species composition as the main forest-forming species, forest communities of ash dumps differ in the share of individual tree species and are characterized by a relatively complex spatial structure and the ratio of biomorphs (Table 3). The stand is dominated by *Betula pendula*, *B. pubescens*, and *Populus tremula*, as well as *Pinus sylvestris* and *Salix caprea* in lesser abundance.

Table 3. Structure of forest phytocenoses.

Biomorphs	Group Name	Species Number	Dominant and Codominant Species (Proportion of Herbaceous by Weight up to 4%)
		SUPP ash dump	
Woody	Trees	6	*Populus tremula, Betula pendula*
	Shrubs	7	*Sorbus aucuparia, Chamaecytisus ruthenicus, Padus avium, Viburnum opulus*
Herbs	Dwarf shrubs and semishrubs	3	*Rubus saxatilis*
	Cereals	5	*Agrostis tenuis, Festuca rubra,Deschampsia cespitosa*
	Legumes	4	*Vicia sylvatica, Lathyrus pratensis*
	Forbs	17	*Equisetum pratensis,Fragaria vesca*
		VTPP ash dump	
Woody	Trees	5	*Betula pendula, Populus tremula, Pinus sylvestris Salix caprea*
	Shrubs	5	*Sorbus aucuparia, Padus avium, Salix myrsinifolia, Chamaecytisus ruthenicus, Rosa acicularis,*
Herbs	Dwarf shrubs and semishrubs	3	*Pyrola rothundifolia, Orthilia secunda*
	Cereals	5	*Agrostis tenuis, Calamagrostis arundinacea, Poa pratensis, Festuca rubra, Deschampsia cespitosa*
	Legumes	6	*Amoria repens, Lathyrus pratensis; Trifolium medium, Trifolium pratense, Vicia cracca*
	Forbs	12	*Alchemilla vulgaris, Equisetum pratense, Plantago media, Fragaria vesca, Platanthera bifolia*
		NTPP ash dump	
Woody	Trees	4	*Betula pendula, Populus tremula*
	Shrubs	5	*Chamaecytisus ruthenicus, Rosa acicularis, Sorbus aucuparia*
Herbs	Dwarf shrubs and semishrubs	1	*Rubus saxatilis*
	Cereals	4	*Agrostis tenuis, Poa pratensis*
	Legumes	3	*Vicia sepium*
	Forbs	13	*Chamerion angustifolium, Fragaria vesca*
		Background sites	
Woody	Trees	5	*Betula pendula, Populus tremula, Pinus sylvestris*
	Shrubs	8	*Chamaecytisus ruthenicus, Rosa acicularis, Rosa majalis, Sorbus aucuparia, Padus avium, Viburnum opulus*
Herbs	Dwarf shrubs and semishrubs	4	*Rubus saxatilis, Orthilia secunda*
	Cereals	8	*Agrostis tenuis, Brachypodium pinnatu, Calamagrostis arundinace, Deschampsia cespitosa*
	Legumes	5	*Lathyrus vernus*
	Forbs	39	*Aegopodium podagraria, Alchemilla vulgaris, Fragaria vesca, Geum rivale, Ranunculus acris, Ranunculus polyanthemos, Trollius europaeus, Veronica chamaedrys*
	Sedges	1	*Carex macroura*

The herb-shrub layer in all studied forest areas on ash is sparse. The undergrowth layer in forest communities is poorly expressed both on ash and in control. The coverage of the herb-shrub layer on the ash dumps is more than two times lower than on the control ones. At all sites on the ash and in the control, cereals and forbs predominate, but in the control, the species diversity of cereals is higher, and the set of dominant forbs is different. In the horizontal structure of communities on ash, a contagious nature of the distribution of individuals of some species is observed. The moss-lichen cover is weakly expressed.

The stocks of living aboveground herb-shrub layer phytomass of forest communities on ash dumps average 8–21 g/0.25 m^2, which is significantly less than in background areas, where they exceed 100 g/0.25 m^2 (Table 4).

Table 4. Above-ground biomass of the herb-shrub layer of forest phytocenoses. (in an air-dry state).

Indicators	Ash Dump			Background Forests
	SUPP	VTPP	NTPP	
Aboveground phytomass, g/0.25 m^2	21.73 ± 1.98	20.43 ± 3.17	7.95 ± 3.35	105.75 ± 6.61
Limits of variation	10.18–35.21	5.87–62.55	3.70–14.00	71.55–144.26

Thus, in the process of self-overgrowing ash dumps in the southern taiga over 50–60 years, mixed forest phytocenoses were formed, which are close in composition to zonal secondary forests.

3.2. Soil and Ash Substrate Parameters

Young soils have been formed under the forest communities on the studied ash dumps. The soils of the VTPP ash dump have the following horizons: O—litter with a thickness of about 2 cm; A—5 cm thickness, graw color, weakly textured; and C—from the depth of 7 cm opened to a depth of 40 cm, structureless ash substrate.

The soils of the SUPP ash dump are characterized by the following horizons: O—litter with a thickness of about 0.5 cm; AT—2.5 cm thickness; A—7 cm thickness brownish-graw, weakly textured; and C—from the depth of 10 cm opened to a depth of 40 cm.

The soils of the NTPP ash dump have the following morphological structure: O—litter with a thickness of about 1 cm; A—from 2 to 9 cm thickness brownish-grew, good textured; AC—8–11 cm thickness grew, structureless; and C—from the depth of 14–18 cm light grey structureless ash substrate opened to the 40 cm point.

As it was seen, less differentiated soils were formed on the VTPS ash dump and had only litter and humus horizons on the parent material (ash substrate). More differentiated variants were observed on SUPP and NTPS ash dumps; they additionally have AT or AC horizons. Soils formed on ash substrates in forest communities can be classified as technosols [44].

Since plant communities on the dumps of the Urals in the first century influenced almost only the upper 20-cm layer [3], it can be assumed that the thickness of young soils formed in the upper layer of ash dumps is near 20 cm, and deeper they are underlain by weathered ash. First, we will focus on the characteristics of ash, which serves as a soil-forming rock for soils formed in forest areas of ash dumps. Earlier, we found that the ash of the SUPP and VTPP ash dumps [30,31] has a sandy texture. Analysis of the particle size distribution of the ash dump of NTPP at a depth of 20–40 cm also shows (Table 5) that it has a sandy texture, since particles with a diameter of >0.01 mm, the share of which exceeds 90%, dominate in its composition. Fine sand prevails among these particles. The contribution of silty particles is extremely low and does not exceed 1%.

Table 5. Particle size distribution in ash substrate of NTPP.

Replications	Percentage Share of Fraction (mm)						
	1.00–0.25	0.25–0.05	0.05–0.01	0.01–0.005	0.005–0.001	<0.001	<0.01
1	2.0	65.3	27.0	1.3	4.0	0.4	5.7
2	0.2	54.5	36.0	7.5	0.9	0.9	9.3
3	1.0	60.4	29.5	8.7	0.4	0.0	9.1

Thus, the ash of all the studied ash dumps has a similar texture and is characterized by an extremely low content of fine silt particles. In principle, the absence of particles with a large total surface can make it difficult to consolidate organic substances in the form of organo-mineral complexes, that is, the storage of carbon by the ash substrate.

The bulk ash composition of the studied ash dumps (Table 6) is dominated by compounds of silicon (SiO_2__40–51%) and aluminum (Al_2O_3—15–32%), as well as either iron (Fe_2O_3—6–8%) in the ash of SUPP and VTPP or calcium compounds (CaO—8%) in the ash of NTPP. In general, the ash of all the ash dumps under consideration is an aluminosilicate formation, but the content of compounds of individual elements in it varies.

Table 6. Gross composition of ash from ash dumps [13,31,32].

Ash Dump	Average Content, %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5
STPP	51.0	30.9	5.88	4.73	1.32	1.36	3.91	0.71	0.22
VTPP	40.30	14.94	8.16	3.54	2.32	1.01	2.52	1.02	0.23
NTPP	40.5	32.4	5.5	7.8	0	nd *	nd	nd	nd

*—not detected.

The study of the physico-chemical characteristics of ash in 15 soil sections also shows its diversity (Table 7). For example, the average pH values for a thickness of 20–40 cm vary significantly within sections from 4.6 to 8.4, i.e., the ash is both acidic or close to neutral, and there is an alkaline reaction in the medium. Attention is drawn to the fact that even within the same forest area on the ash dump of VTPP and NTPP, the pH values differ by 1–2 units. Ash initially contains organic carbon and nitrogen in the composition of unburned coal particles, the amount of which is 0.4–3.3% and 0.03–0.07%, respectively.

Table 7. Limits of ash physico-chemical characteristic variation.

Ash Dump	pH	TOC	TN	Ca^{2+}	Mg^{2+}	P_2O_5	K_2O
		%		mmol/100 g		mg/100 g	
STPP	4.58–5.28	2.51–3.33	0.03–0.04	0.3–0.5	0.4–0.5	17.6–26.8	1.5–1.9
VTPP	5.85–8.23	0.70–2.54	0.03–0.07	0.5–8.1	0.3–0.7	11.5–23.8	1.6–8.9
NTPP	7.15–8.41	0.38–2.23	0.03–0.04	1.2–4.0	0.6–2.0	17.2–21.5	2.0–9.0

The content of exchangeable calcium in the ash also varies significantly—from 0.3 to 8 mmol/100 g, and exchangeable magnesium—from 0.3 to 2 mmol/100 g. The amount of mobile phosphorus compounds in most of the sections is in the range of 12–27 mg/100 g, i.e., plants are well provided with this nutrient. At the same time, the amount of mobile potassium compounds in the ash is low and amounts to 2–9 mg/100 g.

Thus, the ash of the forest areas of the studied ash dumps is heterogeneous in physico-chemical properties, and heterogeneity manifests itself both between ash dumps and within the same ash dump.

Weighted average physico-chemical characteristics of young soils formed in the upper 20 cm thickness of ash dumps (Table 8) indicate their diversity in the reaction of the medium (pH varies from 5.1 to 7.4), the content of organic carbon (varies from 3.3 to 6.0%), total nitrogen (varies from 0.11 to 0.32%), exchange cations of calcium (0.7–8.7 mmol/100 g), magnesium (0.4–1.5 mmol/100 g), mobile phosphorus compounds (10–26 mg/100 g), and potassium (0.7–28 mg/100 g). Thus, the technosols of ash dump forest areas are heterogeneous in physico-chemical properties, just like the ash that serves as a soil-forming rock for them.

Table 8. Weighted average physico-chemical characteristics of technosols.

Ash Dump	Section	pH	TOC	TN	Ca^{2+}	Mg^{2+}	P_2O_5	K_2O
			%		mmol/100 g		mg/100 g	
SUPP	1	5.12	4.16	0.13	1.9	1.0	21.0	7.6
	2	5.50	3.96	0.11	2.9	0.9	23.8	10.1
	3	5.29	5.76	0.16	2.6	1.5	14.7	8.5
VTPP	4	5.83	5.59	0.24	0.8	0.4	22.9	27.6
	5	6.15	4.64	0.32	0.8	0.4	26.3	21.3
	6	6.09	6.02	0.21	0.7	0.6	10.8	2.3
	7	5.92	5.91	0.18	0.8	0.6	19.2	2.3
	8	6.53	5.17	0.18	7.7	0.9	10.6	19.3
	9	6.45	5.10	0.16	8.7	0.9	9.6	12.0
	10	7.13	4.12	0.16	7.0	0.9	12.9	19.3
	11	7.03	4.26	0.26	3.1	1.5	24.1	17.4
NTPP	12	7.38	6.22	0.31	5.2	1.1	11.4	15.4
	13	7.38	5.35	0.23	5.2	1.1	11.4	15.4
	14	6.73	3.28	0.24	3.4	0.8	19.2	6.1
	15	6.75	3.39	0.28	2.5	0.9	21.2	6.2

Soils in forest communities of ash dumps, compared to soils in forests of natural habitats formed on the surface of rocks (Table 9), have a more alkaline reaction to the environment, in some cases, a lower content of TOC and TN, sometimes a higher content of exchangeable calcium, and several times higher amounts of mobile phosphorus and, in most cases, potassium.

Table 9. Limits of variation of the weighted average physico-chemical characteristics of the upper 20 cm soil layer of southern taiga forests.

n	pH	TOC	TN	Ca^{2+}	Mg^{2+}	P_2O_5	K_2O
		%		mmol/100 g		mg/100 g	
7	4.47–5.15	4.08–7.97	0.18–0.29	1.7–2.7	0.7–1.5	0.6–2.0	3.1–5.8

Organic carbon stocks in young soils formed on ash dumps (Figure 2) range from 23 to 83 t/ha (on average 43.7 t/ha), i.e., vary by more than three times. There are no significant differences between the accumulation of carbon in young soils from different ash dumps. Even within the same ash dump, the values differ by 17–48 t/ha.

Calculations of correlation coefficients between the physico-chemical characteristics of ash dump young soils show that the content of exchangeable calcium in them is positively related to the pH value (K = +0.52) and negatively related to the content of mobile phosphates (K = −0.63). In turn, there is a positive correlation between the pH value and the content of total nitrogen (K = +0.55). The content and stocks of carbon in technosols are most influenced by the amount of mobile phosphorus compounds (K is equal to −0.58 and −0.53, respectively). All indicated values of the correlation coefficients are significant at the level of $p < 0.05$ and are average.

The organic carbon distribution along the profile, given in the example of sections on different ash dumps (Figure 3), is regressive-accumulative in nature, with a maximum in the A0 horizon and a further sharp decrease in content with depth.

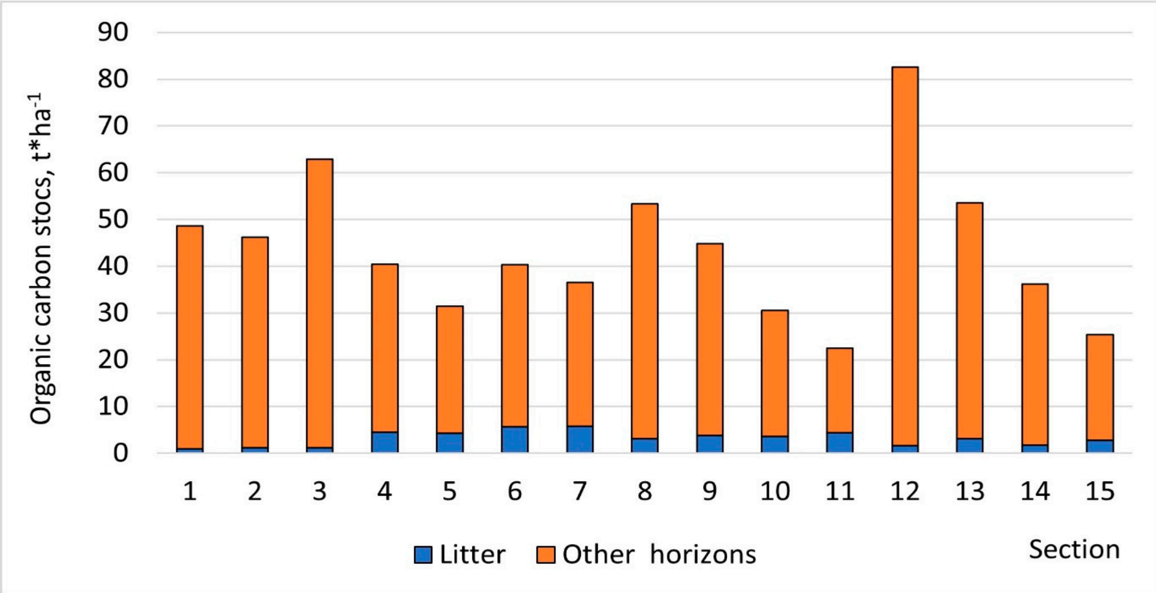

Figure 2. Carbon stocks in technosols of ash dump forest areas: soil sections 1–3—SUPP ash dump; 4–11—VTPP ash dump; 12–15—NTPP ash dump.

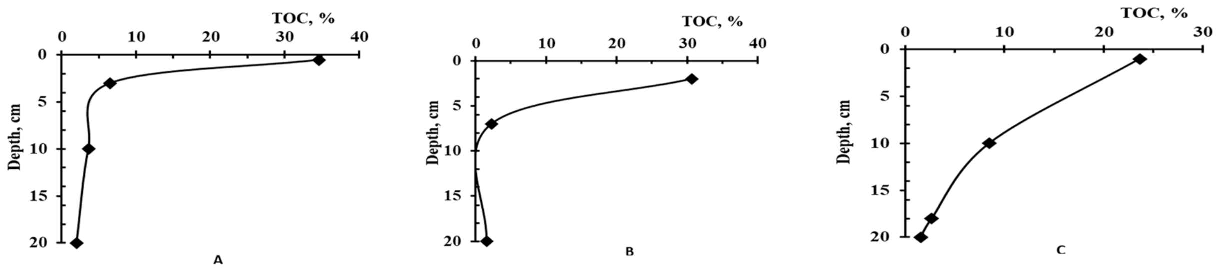

Figure 3. Distribution of TOC along the soil profile: (**A**)—Section 2; (**B**)—Section 5; (**C**)—Section 12.

Since the largest amount of carbon in forest soils accumulates in litter, which is the main source of organic matter for mineral horizons, let us dwell in more detail on its characteristics (Table 10). The carbon content in the litter of young soils from ash dumps varies from 23 to 44%; nitrogen is also contained in high quantities, amounting to 0.9–1.9%. The values of the ratio of carbon to nitrogen content, which are in the range of 16–32, allow us to classify humus as mor and moder [45], i.e., humic acids of technosol litters have weak or very weak contact with the soil mineral part.

The reaction of the litter medium is predominantly slightly acidic; pH values vary from 5.4 to 6.6, within narrower limits than in the other soil horizons. The litter contains a high amount of mobile phosphates (from 40 to 114 mg/100 g) and varies from low to high amounts of mobile potassium (7–128 mg/100 g), as well as from 5 to 25 mmol/100 g of exchangeable calcium ions and from 1 to 13 mmol/100 g of exchangeable magnesium ions.

Carbon stocks in the litter of forest area technosols (Figure 2) range from 1.0 to 5.8 t/ha (on average, 3.2 t/ha), while lower values fall on SUPP and NTPP ash dumps (1.0–3.1 t/ha) with low-thickness (not exceeding 1 cm) litter, while higher values correspond to VTPP ash dumps (3.2–5.8 t/ha) with 2-cm thickness litter. The contribution of the litter to the organic carbon soil stocks varies widely—from 2 to 16%, averaging 7.3%.

Statistically significant (at the level of $p < 0.05$ values) correlation coefficients between the physico-chemical characteristics of the litter indicate the presence of a middle negative relationship between the content of exchangeable calcium and nitrogen in it (K = −0.53) and, accordingly, a positive relationship between the amount of Ca and the ratio of C and N (K = 0.55). A middle positive correlation was also revealed between the content of mobile phosphates and nitrogen (K = 0.57) and, accordingly, a negative one—between the amount of P_2O_5 and C:N (K = −0.62) in it. The carbon stocks in the litter are most affected by the content of calcium and magnesium exchange cations (K is equal to −0.68 and −0.69, respectively), which means that in their presence, the best decomposition occurs. We were unable to detect a correlation between the studied litter parameters and carbon accumulation in the whole profile of ash dump young soils.

Table 10. Characteristics of technosol litter.

Ash Dump	Section Number	Thickness	pH	TOC	TN	C:N	Ca^{2+}	Mg^{2+}	P_2O_5	K_2O
		cm		%			mmol/100 g		mg/100 g	
SUPP	1	0.5	6.40	28.55	1.13	25.3	12.5	10	80.7	33.1
	2	0.5	6.56	34.61	1.10	31.5	20.0	12.5	50.9	33.3
	3	0.5	6.55	34.33	1.18	29.1	25.0	7.5	40.1	31.7
VTPP	4	2	6.39	31.95	1.43	22.3	4.8	2.0	98.2	184
	5	2	6.39	30.69	1.87	16.4	4.8	1.9	99.5	127.8
	6	2	5.40	40.30	1.76	22.9	4.7	2.0	54.1	8.3
	7	2	6.16	41.30	1.49	27.7	5.0	2.3	69.7	7.4
	8	2	6.78	22.56	0.99	22.8	10.3	1.5	22.7	112.8
	9	2	5.90	27.46	0.88	31.2	10.0	1.7	25.1	85.7
	10	2	5.98	25.71	1.07	24.0	8.7	1.7	22.4	115.1
	11	2	6.87	31.84	1.79	17.8	5.8	1.8	97.6	106.7
NTPP	12	1	5.91	23.64	1.49	15.9	5.3	2.3	82.5	24.2
	13	1	5.99	44.11	1.63	27.1	5.3	1.2	85.4	25.9
	14	1	5.85	24.46	1.57	15.6	9.0	3.8	101.2	19.4
	15	1	5.99	39.78	1.86	21.4	9.7	3.0	114.3	18.2

3.3. Technosol Humus Parameters

Indicators of the composition of humus, which corresponds in this work to the concept of the "humus substance system" [46] of young soils in forest communities of VTPP and SUPP ash dumps, are presented in Table 11. The proportion of carbon attributable to humic acids (HA) in the composition of technosols humus has maximum values equal to 13–19% in the AT or A horizons and minimum values ranging between 1–5% in the C horizon.

Table 11. Composition of humus from ash dump technosols and of sod-podzolic soil humus horizons (% to TOC).

Horizon	Depth, cm	TOC, %	Humic Acid Fractions			∑HA	∑FA	Humins	C_{HA}:C_{FA}
			1	2	3				
Technosol of SUPP ash dump									
O	0–0.5	28.55	8.3	0.3	5.2	13.8	16.1	70.1	0.86
AT	0.5–3	9.57	8.6	0.6	9.7	18.9	25.3	55.8	0.75
A	3–10	3.36	3.0	0.1	0.8	3.9	12.7	83.4	0.31
C	10–20	2.14	0.6	0.2	0.2	1.0	6.4	92.6	0.16
Technosol of VTPP ash dump									
O	0–2	30.69	5.9	0.2	4.2	10.3	12.4	77.3	0.83
A	2–7	2.23	5.9	2.4	4.6	12.9	23.9	63.2	0.54
C	7–20	1.39	0.7	3.2	1.2	5.1	12.8	82.1	0.40
Sod-podzolic soils of the Middle Urals (n = 24) [47]									
A	$\bar{x}$	4.08	16.9	2.2	4.5	23.6	32.5	43.9	0.73
	s	1.46	6.2	2.1	3.3	6.2	9.6	16.2	0.13

$\bar{x}$—average value. s—standard deviation.

In almost all horizons of the profiles, free humic acids associated with mobile sesquioxide oxides (HA1) predominate among the HAs; humic acids associated with clay particles and stable sesquioxides (HA3) also have a relatively high representation; humic acids associated with calcium (HA2) are present in minimal quantities.

Fulvic acids (FA) predominate over humic acids in the composition of humus—carbon in them accounts for from 6 to 25%. The values of the integral indicator of the ratio of carbon of humic acids and fulvic acids decrease with depth; the humus in the litter and AT horizon is humate-fulvate (C_{HA}:C_{FA} = 0.8–0.9). In the A and C horizons, it is fulvate (C_{HA}:C_{FA} has values $\leq$ 0.5).

The humus substance system formed in young soils of self-overgrowing areas of ash dumps under mixed forests, in comparison with the soddy-podzolic soils prevailing in the territories adjacent to ash dumps, the composition of humus of which was generalized by us for the southern taiga of the Middle Urals [47] (Table 11), is characterized by a significantly lower content of extractable humus acids (HA and FA) and, accordingly, a higher proportion of humins.

At the same time, in the upper horizons of technosols, the proportions of individual fractions of humic acids and fulvic acids are close to those in background soils; HA1 predominates. In addition, the humus composition of the O and AT horizons of technosols, as well as its composition in the humus horizon of sod-podzolic soil, corresponds to the humate-fulvate type.

The obtained materials allow us to conclude that the formation of a humus substance system in the ash substrate under forest communities follows a zonal type, with the predominance of the synthesis of fulvic acids over humic acids, in which the most mobile HAs predominate.

4. Discussion

During the study, it was revealed that in the process of self-overgrowing of the ash dumps of the SUPP, VTPP, and NTPP of the Middle Urals in the conditions of the southern taiga for 50–60 years, mixed forest phytocenoses similar in composition to zonal secondary forests were formed.

Compared to the latter, they are characterized by a smaller height and diameter of trees, lower soil coverage by the herb-shrub layer, as well as lower indicators of species density and floristic richness. The changes in plant communities in ash dumps are associated with the regularities of restorative successions. The identified features of the composition and structure of the communities developed on the ash dump made it possible to evaluate these communities at the time of observation as a stage of progressive succession with improved conditions due to the biotic transformation of the habitat, developing as derivative forests of the zonal type.

The established heterogeneity of the ash in the studied ash dumps in terms of physico-chemical properties, as well as the diversity of the soils formed on it, do not contradict the results of other studies [18,48–51]. In all cases, not dependent on ash peculiarities, the soil-forming process on the ash dump is detected by the accumulation of carbon, nitrogen, and some other macronutrients and accompanied by changes in the medium reaction.

It is most appropriate to compare the results of this carbon accumulation study in young soils of self-overgrowing forest areas of Middle Ural ash dumps with data for soils surrounding them in southern taiga coniferous forests, although much attention is paid to carbon reserves in the soils of forest ecosystems of various natural zones in modern studies [52–56].

The established carbon stocks in the technosols of ash dump forest communities, on average equal to 44 t/ha, are almost two times less than the stocks of C in the soils of zonal coniferous forests of the southern taiga of the Middle Urals, which, according to various authors, range from 88 t/ha [57] to 94.6 t/ha [58]. A wide range of values was revealed (23–83 t/ha) for carbon stocks in the ash dump soils, which is also typical for this indicator in zonal soils (42–132 t/ha [57].

The litter of technosols on ash is characterized by significantly lower C stocks (on average 3.2 t/ha) compared to the litter of southern taiga zonal soils, in which carbon stocks are estimated by various sources at 8.8–11.3 t/ha [59] or 9.0 t/ha [58], which is probably due primarily to the smaller amount of litter in the forests of ash dumps as well as the greater intensity of its decomposition. At the same time, the share of litter in the technosol organic carbon stocks (equal to 7.3% on average) is close to that in zonal soils (5–6%).

Since data on carbon stocks in soils from ash dumps are scarce [60,61], and for forest areas without reclamation measures are practically absent, we have no opportunity to compare our results with similar studies.

Our investigation shows that while carbon stocks in the soils of forest areas of ash dumps and zonal southern taiga forests vary significantly and differ from each other, the composition of the humus substance system formed in them is close and characterized by a weak degree of humification [62]—the proportion of humic acids varies within 10–20%.

In this work, a negative relationship has been established between the amount of mobile phosphates and the content of carbon, as well as its stocks, in technosols of ash dump forests. A similar relationship between soil P content and stored carbon was shown in the long-term pedogenesis series and in zonal forests [63].

Our study revealed a negative relationship between carbon stocks in the litter and the content of exchangeable calcium ions in the forest soils of ash dumps, which is consistent with previous studies in temperate forests that showed a positive relationship between the calcium content in the litter and the rate of its decomposition [64,65].

Litter calcium supports the growth of white rot fungal species and is an important cofactor for lignin degrading enzymes in decomposer microflora [66], increases microbial activity, abundance, and diversity of fungi and earthworms [67,68], and is also associated with pH, the increase of which increases microbial biomass and the rate of litter decomposition, soil respiration, and mineralization [69–72]. In general, calcium is characterized by a relative accumulation in the mortmass of forests due to its biochemical properties [25]. The negative relationship of carbon stocks on magnesium content in the litter of technogenic forest communities, which we identified, has received virtually no attention in the literature, apparently due to the relatively low content of this element in soils.

Our study has some limitations. The first is related to the use of Tyurin's wet burning method for determining TOC, based on the oxidation of organic matter with a solution of potassium bichromate in sulfuric acid and the subsequent determination of the excess oxidizer by titration with Mohr's salt. Perhaps the use of high-temperature catalytic combustion on a TOC analyzer would give slightly different results. The second limitation is that in this work, carbon stocks and the factors affecting them were studied only in relation to the ash substrate with specific properties, and therefore the results of the work cannot be extended to other anthropogenic substrates.

The results of this study primarily indicate the need to consider the soils of technogenic ecosystems in the global soil carbon budget. In addition, data on the influence of some physico-chemical parameters of the substrate on technosol carbon stocks can contribute to a better understanding of the carbon accumulation process as well as a possible impact on its rate. Improving soil organic matter management is seen as a key solution for climate change mitigation and adaptation by the international community [73]. Further research may be aimed at identifying the characteristics of carbon accumulation in the soils of ash dump forest communities forming in other natural conditions, which will allow assessing the influence of climatic factors on the carbon stocks in the technogenic substrate.

5. Conclusions

During the study conducted at three ash dumps (SUPP, VTPP, and NTPP) composed of fly ash from various brown coals and located within the southern taiga of the Middle Urals, it was revealed that over 50–60 years, forest communities with a significant proportion of late successional species spontaneously formed on them, which indicates the restorative nature of the observed vegetation changes. During this period, poorly differentiated technosols with a thickness of about 20 cm were formed on the ash substrate with varying physico-chemical properties under mixed forests. For the first time, an assessment was made of the contribution of soils in forest areas of ash dumps to carbon sequestration by zonal soils. It was determined that carbon stocks in young soils from ash dumps are equal to 23–83 t/ha, including litter, which accounts for 1.0–5.8 t/ha. The contribution of young soils from ash dump forest communities to carbon sequestration is about 50% of the zonal soils of southern taiga forests.

This work attempted to identify the influence of the physico-chemical properties (pH, TOC, TN, P, K, Ca, and Mg) of the ash substrate and forest litter on the accumulation of carbon in the soil. It was shown for the first time that the amount of mobile phosphorus compounds in soils formed on a technogenic substrate is negatively related to the content and stocks of organic carbon in them, and the content of calcium and magnesium in the litter has the greatest influence (also negative) on the carbon stocks in it. The humus substance system is formed in young soils of ash dump forest areas, like in zonal soils with a low proportion of humic acids in their composition.

Thus, our hypothesis was confirmed with respect to changes in carbon reserves in the young soils of ash dumps in the process of forest community formation, which tends to approach zonal soil variants; however, for half a century, C reserves in technosols did not reach the level of natural forest ecosystem soils. The assumption that the differences in the physico-chemical characteristics of the ash substrate have a significant effect on the accumulation of carbon by technogenic soils was also confirmed, and the influence of phosphorus, calcium, and magnesium on the C stocks was established.

As determined in this study, carbon stocks in the forest soils of fly ash can be considered along with the soil stocks of zonal forests in the carbon regional budget. The identified influences of some physical-chemical parameters of the substrate on technosol carbon stocks can contribute to a better understanding of carbon accumulation in the soil-forming process, both on technogenic substrates and on earth rocks. People can influence the sequestration of carbon by young soils, changing in a certain direction the indicators of the chemical composition of the technogenic substrate, which affect the accumulation of carbon.

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