

Article

The Role of the Lithological Factor of Soil Formation in the Short-Term Transformation of Fallow Land in North-West Russia

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Abstract

The role of fallow lands in the regional carbon balance is critical; due to the transition of soils from an arable to a fallow state, soils can turn from a carbon sink into a source. The accumulation and long-term storage of soil organic carbon (SOC) directly affects the ability of terrestrial ecosystems to absorb climatically active gases and store these in soil, making the study of post-agrogenic transformation a priority. Using ^{13}C NMR spectroscopy and analysis of mineral-associated organic matter (MAOM), this study investigated fallow soils in the North-West of Russia (Leningrad region) developing on parent materials of different lithological composition. The results show that the degree of hydromorphism and lithological composition are the main factors determining the trajectory of soil transformation at both the morphological and molecular levels. In the waterlogged Gleyic Anthrosol (V2) formed on the territory of the Vuoksa River, almost all organic carbon (96.8% of SOC) was found in the MAOM fraction, indicating strong mineral stabilization under anaerobic conditions. Here, humic acids (HAs) retained aliphatic structures and low maturity, inheriting traits of precursors of humification. In contrast, the Endocalcaric Luvisol (V5) forming on carbonate material was characterized by the most mature HAs composition, due to high aromaticity ($\text{AR}/\text{AL} = 0.79$), increased oxygen and carboxyl group concentration, and ensures high resistance to biodegradation. Soils of fallow lands on outwash sands under meadow vegetation (V4) were characterized by the largest soil organic matter (SOM) stock (21.4 kg/m^2); however, HAs extracted from these soils had a high degree of oxidation and a relatively high concentration of aliphatic structural fragments. The soil under a hayfield (V3) was characterized by a relatively high concentration of aromatic structural fragments ($\text{AR}/\text{AL} = 0.69$), but with a low nitrogen concentration in its HAs composition, due to anthropogenic activity and the removal of plant biomass that makes a significant contribution to the structure of HA molecules. This study shows that in a young fallow state (up to 10 years), local factors, primarily the carbonate content in the soil or waterlogging, set the trajectory of SOM transformation, which is crucial for predicting soil evolution and the sequestration potential of territories.

Keywords: ^{13}C NMR spectroscopy; carbonate soils; mineral-associated organic matter/MAOM; humic acids

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1. Introduction

Agriculture has a significant impact on soil, which is expressed in changes in physical, chemical, and biological parameters compared to natural analogues [1]. Thus, the use of various agrotechniques is aimed at increasing the content of SOM, soil exchange capacity, stable aggregate structure, and biological and biogeochemical activity [2]. Long-term agriculture leads to radical transformation of soils, the formation of new arable horizons, changes in the trajectory of soil-forming processes, and the formation of a specific microbiome [3]. The cessation of active anthropogenic impact, as a result of economic crises, urbanization, and low product profitability, leads to the abandonment of these lands, which become fallow territories [4]. The transition to a fallow state leads to the development of post-agrogenic succession, which results in natural overgrowth, loss or accumulation of SOM, and waterlogging, as well as soil transformation towards zonal analogues [5]. These processes largely depend on the duration that the land is in a fallow state and on the local geological and geomorphological parameters of the territory. It has previously been noted that the short-term conversion of soils to a fallow state has a positive effect on the parameters of carbon and nitrogen binding from the atmosphere, and it also influences the transformation of the soil microbiome [6]. At the same time, with an increase in the duration of the fallow state, the rates of accumulation of biogenic substances and the quality of SOM may change fundamentally; these territories may be subject to the penetration of invasive species, negatively affecting the biodiversity of the ecosystem [7]. The territory of North-West Russia represents a unique combination of soils forming on rocks of different lithological composition, which creates a wide range of conditions for soil formation and post-agrogenic transformation of fallow lands [8]. This territory is characterized by a long history of agriculture; nevertheless, at present, most of the lands that were previously actively cultivated have been converted to a fallow state [4]. The age of the fallow period plays a critical role in land transformation, since the most active processes that subsequently determine the trajectory of the entire post-agrogenic succession occur in the first decades after the cessation of agricultural use [9]. Of particular interest for studying the early stages of post-agrogenic transformation is the territory of the Karelian Isthmus, bordering Finland. Over a long history of land use and reclamation, unique landscapes have been formed here, which are currently undergoing active post-agrogenic succession [10].

At the beginning of the 20th century, a curtailment of drainage works was noted in the territory of the North-West, with the exception of the Karelian Isthmus, which was associated with the conclusion that drainage leads to shallowing of rivers and harms navigation [11]. Despite the inconvenience of farming on high kames, due to lack of land in the southern regions of Finland, they were used for grazing livestock, haymaking, and growing agricultural products. At the same time, the nearest reserve for expanding agricultural land areas remained the northern regions of the Karelian Isthmus. It was these areas that were intensively drained, and some lakes were drained into rivers and the Gulf of Finland. Nevertheless, a significant portion of agricultural land formed during the Soviet era is currently abandoned, and agricultural lands have been converted to fallow state and are in the process of waterlogging and afforestation [5]. According Gai et al. [12], the transition from aerobic to anaerobic conditions leads to a reduction in the rates of SOM transformation, which is caused by a decrease in microbiological activity, while the rates of CO₂ emission initially depended on the quality of humification precursors. Waterlogging and the transition to anaerobic conditions, as in the case of former arable lands, may be accompanied by a decrease in the physical protection of soil aggregates, which contributes to the transformation of stable forms of carbon in the soil [13].

In addition to the active development of agriculture in the northern part of the Leningrad region, the southern part of the region, confined to the Izhora Upland composed of carbonate materials, was subjected to agricultural development much earlier, due to

the high fertility of these soils. This territory is characterized by the distribution of various types of Endocalcaric Luvisol and Umbric Podzols forming on parent materials containing carbonates [8]. The carbonates in the parent materials have a significant influence on the soils, as the presence of lime in the soil accelerates the transformation of plant and animal residues and also enhances the processes of SOM humification [14]. The presence of carbonates in the soil leads to the physical and chemical stabilization of SOM and also contributes to the retention of various macro- and microelements in the soil [15,16]. Weathering of carbonates leads to aggregation and intensification of organo-mineral interactions and the formation of microaggregates, thereby contributing to the formation and physical stabilization of soil aggregates [17]. Arable soils forming on parent materials containing carbonates make a significant contribution to the regional carbon budget and play an important role in the sequestration of organic and inorganic carbon in the soil [18]. The conversion of agricultural soils formed on carbonate parent rocks to a fallow state may contribute to a reduction in CO₂ emissions into the atmosphere, due to a decrease in anthropogenic influence and in the application of physiologically acidic fertilizers that lead to the mineralization of carbonates in the soil. Thus, over the past 50 years, as a result of various agricultural practices, 0.41 Gt of carbon has been lost, and this figure may increase to 1.13 Gt by 2050 [19]. Thus, the North-West of Russia represents a model object for the transformation of soils as a result of the conversion of lands to a fallow state; this is due to long-term agricultural development, as well as the high diversity of soil-forming rocks.

Arable lands have a significant impact on the carbon balance in the ecosystem, as they can accumulate a substantial amount of organic carbon [20]. The accumulation and long-term storage of SOC directly affects the ability of terrestrial ecosystems to absorb carbon dioxide from the atmosphere; however, changes in land use types can convert soils from a sink of climatically active gases into a source [21]. According to Romanovskaya et al. [22], soils in Russia that have been withdrawn from agricultural use are capable of accumulating up to 29 million tons of C year⁻¹, while the rate of SOC accumulation is about 97–108 g C m⁻² year⁻¹. Nevertheless, there is a gap in the research on the qualitative composition of SOM, which is necessary for calculating the long-term sequestration of SOC. According to Gai et al. [12], it was found that the conversion of soils to a fallow state leads to a change in the soil microbiome, which contributes to a long-term increase in carbon and nitrogen content in soils, while natural biogeochemical cycles are disrupted and the quality of SOM changes. Degradation of the arable layer, accompanied by a decrease in the content of SOM (in short and medium-term period), negatively affects the fertility status of fallow land soils and can also make a significant contribution to climate change [23]. The combined influence of the fallow period and the lithological composition of the rocks determines the rates and trajectory of accumulation and transformation of SOM. It has previously been found that the selective retention of aromatic structural fragments is determined by the mineralogical composition of clay and the carbonate content in the soil, just as SOM stocks increase with a relatively high calcium content, due to the formation of water-stable organo-mineral aggregates in the soil [24].

The current understanding of the carbon cycle in soils is based on the concept of dividing all SOC into fractions with different degrees of availability to microorganisms and, consequently, different residence times in the soil [25]. The most common classification divides SOC into two main groups: particulate (free and occluded) organic matter (POM) and MAOM [26]. This division allows quantitative assessment of the proportion of different carbon pools and their relative stability, being a key element for understanding the processes of its stabilization [27]. POM acts as a “fast” or “active” carbon pool, playing a key role in the short-term nutrient cycle and serving as an important energy source for the soil microbiome [25]. MAOM, in turn, represents a significantly more stable fraction of

SOM [25]. It includes SOM that is strongly bound to the surface of mineral particles, especially clay minerals and iron and aluminum hydroxides [27]. Changes in land use actively influence the distribution of carbon between the POM and MAOM fractions; this is due to the formation of the POM pool from fresh or partially decomposed plant residues, and it is actively subject to transformation as a result of changes in land use, whereas MAOM is formed from microbial products or plant residues processed by microbes. This pool is practically not susceptible to changes in land use and is determined by the content of clay minerals in the soil [24]. Thus, Lin et al. [24] note that the SOC formed on parent rocks containing dolomite is 108% higher than in soils formed on sandy deposits, and 39% higher than in those formed on limestone. In this regard, the analysis of carbon stocks and stabilization rates in soils removed from agriculture, as well as mechanisms for increasing carbon sequestration rates, are priority research directions necessary for developing strategies for climate change adaptation [28,29]. The research hypothesis is that in soils at the early stages of the fallow state (up to 10 years), the properties of the soil-forming rocks and the hydrological parameters of the territory determine the trajectory of SOM transformation, influencing pH, oxygen availability, and organo-mineral interactions. It is assumed that in soils formed on carbonate rocks under conditions of good aeration, the proportion of aromatic and oxygen-containing structural fragments will increase, while in soils subject to waterlogging, oxidative transformation will be limited, which will contribute to the preservation of aliphatic structural fragments inherited from humification precursors. The aim of the present work was to assess how contrasting parent material parameters and hydrological conditions are associated with SOM transformation in former arable horizons of young fallow soils in North-West Russia. To address this objective, we quantified soil carbon and nitrogen concentration and stocks, determined the proportions of MAOM and MAON, and compared the elemental and molecular composition of bulk SOC, MAOM, and HAs.

2. Materials and Methods

2.1. Study Area

The study area is located within the North-West Russia, in the Leningrad region. This territory has undergone relatively rapid geological changes over the past few thousand years, which can even be traced over historical time; seabed areas were replaced by land, and the configuration of rivers and lakes changed. Initially, the territory was predominantly covered by forests, and the local population was concentrated along the shores of water bodies, engaging in fishing and hunting.

Within the framework of the study, work was carried out in two districts of the region, namely, in the Vuoksa River basin and at the marginal part of the Izhora Upland. The Vuoksa basin is located in the northeastern part of the Karelian Isthmus, the territory between Lake Ladoga and the Gulf of Finland. The Vuoksa is a lake–river system that flows from the inland areas of Finland and drains into Lake Ladoga.

The local population has long actively transformed watercourses; dams and canals were built, part of the basin was flooded, and part, on the contrary, was drained. The latter prevailed because local residents sought to maximize the area of agricultural land. There was a shortage of suitable land because significant areas of the territory were occupied by rocky areas and swamps.

The Izhora Upland is located south of the Russian part of the Gulf of Finland. Compared to the Vuoksa basin, it demonstrates the opposite, stability, with a predominance of fertile soils. In this regard, the upland was the first to be agriculturally developed. Currently, it is almost entirely occupied by settlements and agricultural lands, most of which remain abandoned.

The climate in the Leningrad region belongs to the maritime climatic region of the Karelian Isthmus (Dfc—without dry season, cold summer) according to the Köppen–Geiger classification [30]. The territory is characterized by an average annual temperature of $+3\text{ }^{\circ}\text{C}$ and an annual precipitation of 525 mm; the humidification coefficient is >1 . According to the soil-geographical zoning of Russia [31], the territory is confined to the northern margin of the Baltic province of weakly humified Umbric Podzols and Stagnic Podzol.

The territory of the Leningrad region covers 83 thousand km^2 , and it includes serious differences in soil cover and climatic features among different districts of the region. The Izhora Upland is characterized by an average temperature of $+4.5\text{ }^{\circ}\text{C}$, and the average precipitation is 650–700 mm. The territory has a milder climate compared to the Karelian Isthmus, which is due to the influence of the Gulf of Finland; this is reflected in a greater amount of precipitation, a longer growing season, and a warm winter. The study area is shown in Figure 1.

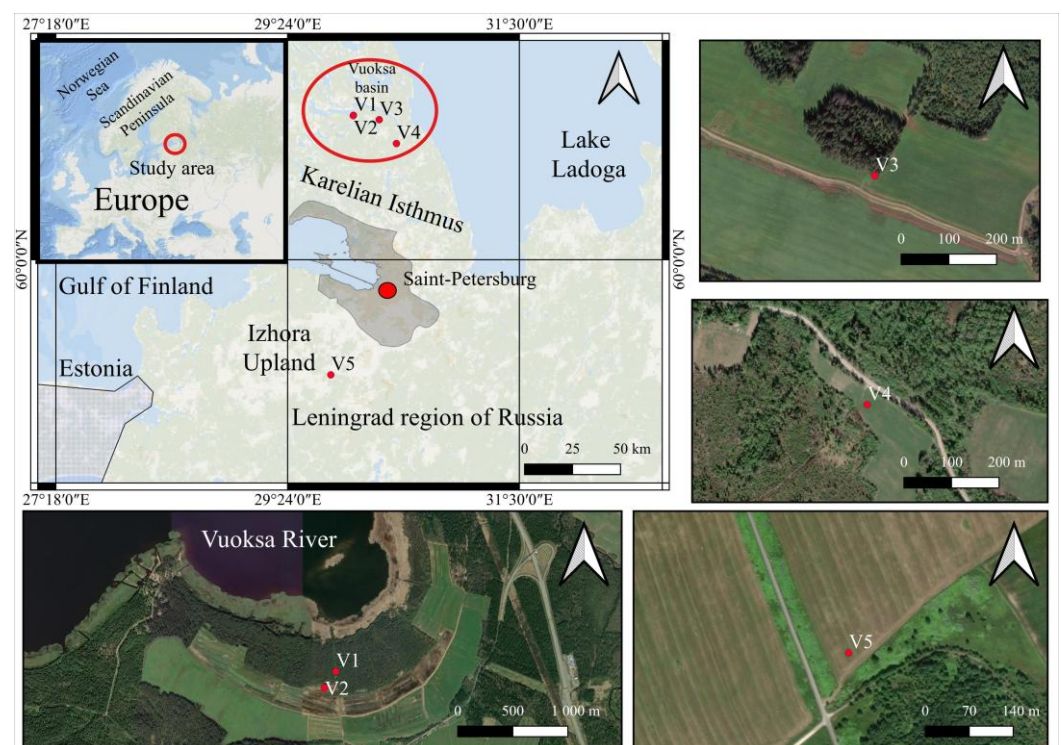


Figure 1. The study area of the present work. V1—Gleyic Retisol (Histic), V2—Gleyic Anthrosol (Loamic), V3—Entic Podzol (Aric), V4—Entic Podzol (Aric, Placic), V5—Endocalcaric Luvisol (Aric).

The studied waterlogged territory in the basin of Vuoksa River (Karelian Isthmus) was created as a result of the drainage of a swampy lowland in the mid-20th century and was intensively used for pasture livestock farming and forage crop rotations until the 1990s. The parent rocks are represented by lacustrine-glacial loams, underlain by moraine deposits of the Valdai glaciation. The soil cover is dominated by anthropogenically transformed Histic Gleysols with signs of drainage, which are at different stages of post-agro-genic evolution. The thickness of the anthropogenically transformed horizon is 25–40 cm, with inclusions of organic material and signs of secondary gleying processes in the lower part of the profile. At the time of this study, the territory was at different stages of natural waterlogging and overgrowth with shrubs, with the formation of young birch–alder stands. Of particular interest is the observed process of degradation of the reclamation system and the restoration of the hydrological regime, which determines the current direction of soil-forming processes. In this district, in addition to the waterlogged territory

of the Vuoksa basin, we studied soils of fallow lands on the territory of an outwash plain, which currently serves as a hayfield (V3), and the territory of a drained meadow (V4), subject to overgrowth with shrubs. In the Izhora Upland (Gatchinsky District), Endocalcaric Luvisol (Aric) (V5) was studied; the age of the transition to fallow state was 2 years. A characteristic feature of this district is the presence of parent materials containing carbonates. The description of the studied soils is presented in Table 1.

Table 1. The morphological organization of studied soils.

Soil ID	Horizon *	Depth, cm	Description	Location	Soil Color **	Soil Name ***
V1	Oe	0–1	Partially decomposed litter	Soil located on forested waterlogged territory; 10 years in fallow state. N 60°38'53.2" E 29°59'49.0"	7.5YR 3/1	Gleyic Retisol (Histic)
	Ap	1–20	Accumulation of organic matter, subangular blocky structure, presence of roots.		7.5YR 5/1	
	Ew	20–40	Iron spots, presence of roots, change of particle-size distribution, from loam to sandy loam.		7.5YR 5/2	
	Cr	40–65	Presence of non-decomposed organic matter, presence of roots, presence of iron in reduced state.		Gley 2 4/10BG	
V2	Oe	0–1	Partially decomposed litter.	Soil located on waterlogged territory; 5 years in fallow state. N 60°38'48." E 29°59'42.1"	7.5YR 3/1	Gleyic Anthrosol (Loamic)
	Ap	1–22	Accumulation of organic matter, subangular blocky structure, presence of roots, presence of non-decomposed organic mater, stagnic conditions.		7.5YR 5/6	
	Br	22–37	Presence of iron in reduced state, presence of non-decomposed organic matter.		7.5YR 4/2	
	Cr	37–63	Presence of iron in reduced state, presence of non-decomposed organic matter, dense.		Gley 2 4/10BG	
V3	Ap	0–25	Accumulation of organic matter, presence of roots.	Territory of fallow lands used for hayfields. Active hayfields. N 60°37'43.8" E 30°13'50.2"	7.5YR 4/2	Entic Podzol (Aric)
	Bs	25–45	Iron spots, sandy materials.		7.5YR 6/6	
	Bs/C	45–67	Iron spots, sandy materials,lighter.		7.5YR 8/6	
	C	67–95	Iron spots, sandy materials,lighter.		7.5YR 7/1	
V4	Ap	0–25	Accumulation of organic matter, presence of roots, lenses of sands.	Territory of fallow land undergoing self-overgrowth; 3 years in fallow state. N 60°31'21." E 30°23'11."	7.5YR 4/2	Entic Podzol (Aric, Placic)
	Bs	25–40	Iron spots, lenses of sands, animal passages.		7.5YR 6/6	
	C	40–80	Iron spots, stagnic conditions.		7.5YR 7/3	
V5	Ap	0–23	Accumulation of organic matter, presence of roots, subangular blocky structure.	Territory of fallow land undergoing self-overgrowth; 2 years in fallow state. N 59°28'27.6" E 29°47'31.4"	7.5YR 5/1	Endocalcaric Luvisol (Aric)
	Ah	23–30	Loss of silicate clay.		7.5YR 6/1	
	Ck ₁	30–42	Accumulation of silicate clay, presence of pedogenic calcium.		7.5YR 7/1	
	Ck ₂	42–75	Presence of pedogenic calcium, dense.		7.5YR /3	
	Ck ₃	75–...	Hard bedrock enriched by calcium.		7.5YR 7/2	

* Jahn et al. [32], ** Munsell soil color chart [33], *** IUSS WRB [34].

Within the framework of this study, the soils shown in Figure 2 were used.

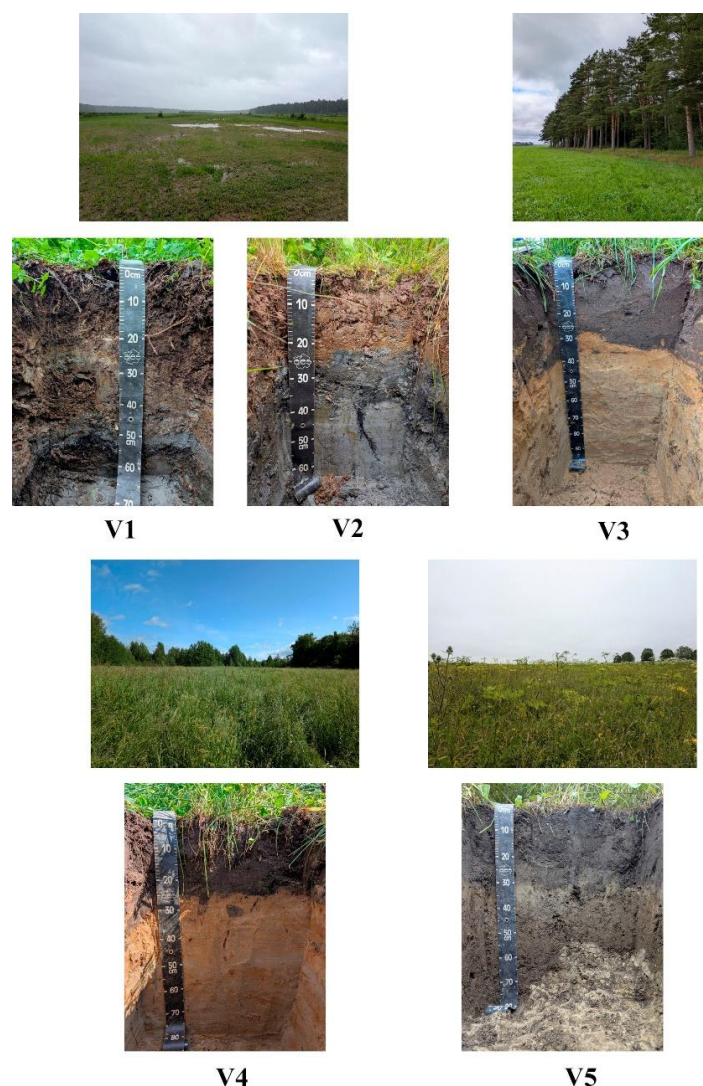


Figure 2. Soils of fallow land of the Leningrad region. V1—Gleyic Retisol (Histic), V2—Gleyic Anthrosol (Loamic), V3—Entic Podzol (Aric), V4—Entic Podzol (Aric, Placic), V5—Endocalcaric Luvisol (Aric).

2.2. Sampling Strategy

Soil sampling was performed during the summer period of 2025. The selection of these fallow land and active hayfield sites was due to the different ages of the fallow state, hydrological conditions, vegetation cover, and the high diversity of parent materials, which have a great influence on the soil formation process. This study included two waterlogged sites developed on lacustrine-glacial loams, representing forested and non-forested stages of post-agrogenic development (V1 and V2) 10 and 5 years after abandonment, respectively. Two sites were on an outwash plain, comprising an actively managed hayfield (V3), a meadow abandoned 3 years previously (V4), a site developed on carbonate-containing parent material, abandoned 2 years previously (V5). Over a short time interval, a more dynamic change in soil parameters and the molecular structure of HAs was observed compared with soils that had remained fallow for more than 20–30 years. Soil samples were collected from all diagnosed horizons to assess carbon and nitrogen concentration and stocks. Soil material was collected from different parts of each genetic horizon within the same soil pit. Soil samples from the upper humus-accumulative horizons were used to analyse the molecular composition of HAs and the MAOM concentration. For POC and MAOM analyses, soil samples were collected separately as intact soil

blocks, with three replicate blocks collected at each landscape position. Samples intended for chemical analysis were kept at +4 °C to determine key soil parameters. Soil was ground and passed through a 2 mm sieve to obtain the fine earth fraction. Soil bulk density was determined using the core method, in which undisturbed soil samples were collected with a cutting ring of known volume.

2.3. Laboratory Methods

The pH value was measured via the potentiometric method in an aqueous suspension using a soil-to-solution ratio of 1:2.5, with all determinations performed in triplicate [35]. Soil carbon and nitrogen concentrations were determined in triplicate using a CHN analyzer (EA3028-HT EuroVector, Pavia, Italy). Carbon and nitrogen stocks (volumetric concentration) were calculated according to the following equation:

$$C_{stock} = \rho * C * H * 0.1 \quad (1)$$

where C_{stock} is the carbon stock (kg/m^2), ρ is the horizon density (g/cm^3), C is the carbon concentration (%), 0.1 is the conversion factor, and H is the depth (cm).

$$N_{stock} = \rho * N * H * 0.1 \quad (2)$$

where N_{stock} is the nitrogen stock (kg/m^2), ρ is the horizon density (g/cm^3), N is the nitrogen concentration (%), 0.1 is the conversion factor, and H is the depth (cm).

The particle size distribution of the samples was determined by sedimentation, based on Stokes' law, using the pipette method in one replicate [36]. In non-calcareous soil horizons, extractable P_2O_5 and K_2O were determined using the Kirsanov method modified by CINAO [37], with extraction in 0.2 mol/L HCl at a soil-to-solution ratio of 1:5, followed by colorimetric determination of phosphorus and flame photometric determination of potassium, with results expressed as P_2O_5 and K_2O , respectively. In carbonate-containing soil horizons, extractable P_2O_5 and K_2O were determined using the Machigin method modified by CINAO [38], with extraction in 10 g/L ammonium carbonate solution at pH 9.0 and a soil-to-solution ratio of 1:20, followed by colorimetric determination of phosphorus and flame photometric determination of potassium, with results expressed as P_2O_5 and K_2O , respectively. N-NH_4^+ and N-NO_3^- were extracted from air-dried soils using 0.01 mol/L CaCl_2 at a soil-to-solution ratio of 1:10, with shaking for 2 h at 20 ± 1 °C, followed by centrifugation, according to GOST R 53219–2008 (modified ISO 14255:1998) [39]. N-NH_4^+ was determined spectrophotometrically by the modified Berthelot reaction at 660 nm, whereas N-NO_3^- was determined after cadmium reduction to nitrite and subsequent formation of an azo dye at 543 nm, using segmented flow analysis.

MAOM and POM fractions were isolated from air-dried soil samples sieved to 2 mm. Particle-size fractionation was performed according to the protocol of Muratore and Welsh [40]. Briefly, 5 g of soil was placed in conical centrifuge tubes and mixed with 15 mL of 0.5% sodium hexametaphosphate solution, followed by 24 h of agitation on a rotary shaker. After mixing, the soil suspension was poured onto a 0.053 mm sieve and rinsed with 200 mL of 0.5% sodium hexametaphosphate solution. The suspension that passed through the 0.053 mm sieve was collected, centrifuged at 10,000 rpm for approximately 10 min, and then dried at 105 °C; this fraction represents the fine MAOM (fMAOM) fraction. The fraction retained on the 0.053 mm sieve was also collected and dried at 60 °C; this fraction represented the POM fraction [40]. The mass of the MAOM fraction was determined as the difference between the mass of the initial soil subsample and that of the POM fraction.

In the dried MAOM-containing fractions (<0.053 mm; fMAOM), SOC and TN concentrations were measured using a CHN analyzer (EA3028-HT EuroVector, Pavia, Italy). After carbon and nitrogen determination in the <0.053 mm fraction, the values obtained

were recalculated to estimate the proportions of MAOC (% of SOC) and MAON (% of TN) in the bulk soil.

2.4. Analysis of HAs and MAOM

HAs were extracted from the studied soils following the procedure recommended by the International Humic Substances Society (IHSS) [41]. Carbonate content in the soil was determined by the acidometric method. The elemental composition of humic substances refers to the percentage concentrations of C, H, N, and O and were determined with a CHN analyzer (EA3028-HT EuroVector, Pavia, Italy). A van Krevelen diagram was employed for the graphical analysis of elemental composition. Elemental composition data were corrected for moisture and ash content.

Oxygen concentration was calculated from the difference, as follows:

$$O = 100 - (C + H + N + ash) \quad (3)$$

where C, H, N represent elemental concentrations, ash is the ash concentration in studied HAs.

The H/C ratio was calculated according to the following equation:

$$H/C = (H, \%/C, \%) * 11.9 \quad (4)$$

where C, H are the elemental concentrations.

The O/C ratio was calculated according to the following equation:

$$O/C = (O, \%/C, \%) * 0.75 \quad (5)$$

where O, C are the elemental concentrations.

The degree of oxidation (w) was calculated according to the following equation:

$$w = 2 * ((O, \%/16) - (H, \%/1.01)) / (C, \%/12.01) \quad (6)$$

where C, H are the elemental concentrations.

Solid-state ^{13}C -NMR spectra of HAs were recorded on a Bruker Avance 500 NMR spectrometer (MA, USA) with a 3.2 mm ZrO_2 rotor. After obtaining the HAs spectra, the results were analyzed in the MestReNova software package ver. 12.0.0-20080 (Mestrelab Research, Santiago de Compostela, Spain). Eight groups of structural fragments were identified in the obtained spectra, as follows: 0–46 ppm, alkyl C; 46–60 ppm, O,N-alkyl; 60–105 ppm, CH_2OH and CHOH ; 105–144 ppm, aromatic C; 144–164 ppm, O,N-aromatic; 164–183 ppm, COO-R ; 183–190 ppm, aromatic C=O ; 190–204 ppm, C=O . The hydrophobicity ($\text{AL h,r} + \text{AR h,r} = \text{C,H-Alkyl} + \text{C,H Arom}$) and humification indices ($\text{C,H-AL/O,N-AL} = \text{C,H-Alkyl}/(\text{O,N-Alkyl} + \text{CH}_2\text{OH})$) were calculated on their basis. To summarize the results of ^{13}C NMR spectroscopy among the SOM, MAOM, and HA fractions, there were 4 functional groups: alkyl (0–47 ppm), O-alkyl (47–110 ppm), aromatic (110–160 ppm), carbonyl (160–220 ppm), which allowed the precise identification of the main differences both among the SOM fractions and among the studied samples.

Based on ^{13}C NMR spectroscopy for each sample of MAOM, the integral indexes were calculated (Equations (7)–(9)). The integral index (RI) indicates the degree of resistance of SOM to microbial decomposition. Higher RI values correspond to more recalcitrant (resistant) OM, suggesting greater potential for long-term carbon sequestration in soil [42]. The aromaticity index (AI) is a parameter reflecting the proportion of aromatic carbon within the total organic carbon pool of a sample. A high AI indicates the predominance of stable, condensed aromatic structures. A low AI is characteristic of fresh SOM (plant residues, composts) enriched in carbohydrates and proteins, which are readily decomposed by microorganisms [43]. The alkyl-C/O-alkyl-C ratio (A/O-A ratio) was used to assess the degree of SOM decomposition in soil. A low A/O-A ratio indicates a low degree of SOM

decomposition, with predominance of fresh, labile plant residues. A high A/O-A ratio reflects a high degree of SOM transformation and decomposition, accompanied by accumulation of microbial products and more stable carbon forms [42]:

$$RI = \frac{(alkyl\ C) + (Arom - C)}{(O\ alkyl - C) + (Carboxil - C\ and\ Carbonyl - C)} \quad (7)$$

$$AI = \frac{Arom - C}{(alkyl\ C) + (O\ alkyl - C) + (Arom - C)} \quad (8)$$

$$A/O - A = \frac{alkyl\ C}{O\ alkyl - C} \quad (9)$$

2.5. Statistical Analysis

Results are presented as the mean $\pm$ standard deviation (SD). Normality was tested using the Shapiro–Wilk test. Pairwise comparisons between soil samples were carried out using Tukey’s multiple comparisons test, with the significance level set at $\alpha = 0.05$. Pearson’s correlation analysis was applied to the physicochemical parameters of the studied soils. Principal component analysis (PCA) was used to assess the influence of the lithological factor and land use on SOM formation. Statistical analysis and visualization were performed using GraphPad Prism 9 (GraphPad Software LLC) and Origin ver. 2024 Pro (OriginLab Corporation).

3. Results and Discussions

3.1. Transformation of Soils of Fallow Land Wih Different Parent Materials

The lithological composition of parent materials makes a significant contribution both to soil formation and to their post-agrogenic transformation. Compared to old fallow soils, morphological changes were less pronounced in young analogues (0–10 years) [44]. However, with increasing age, litter formation was noted (V1–V2); for soils forming on waterlogged territories, active gleying processes were noted. The heavy texture class of the parent materials serves as a natural barrier, leading to increased expression of hydromorphism. For soils forming on outwash sands (V3–V4), the development of stagnic conditions was noted. As a result of changes in the hydrological regime, pseudo-fibers (thin, horizontal or undulating, iron-enriched bands in sandy soils, locally compacted and partially cemented by iron oxides and hydroxides) had formed, and local gleying processes were observed. For the soil forming on parent materials containing carbonates (V5), the lowest degree of transformation was revealed, which was due to the high degree of lithorefectivity of these soils. Lithorefectivity plays an important role in the transition of soils to a fallow state and can change the trajectory of the soil-forming process [45].

In addition to morphological changes, changes in the physicochemical parameters of the soils were noted (Table 2). The physicochemical parameters of soils can undergo quite substantial changes in relation to morphological organization. Soil acidity is the most dynamic parameter, due to changes in soil formation conditions as a result of the transition to a fallow state. Regarding the particle size distribution, it was found that the waterlogged soils (V1–V2), as well as the soil forming on the Izhora Upland (V5), were characterized by a relatively high concentration of silt and clay particles, while the soils forming on the territory of the outwash plain (V3–V4) were characterized by a light particle size distribution (sands and sandy loams). This diversity is due to the high heterogeneity of the lithological composition of the parent materials [8]. Among all the studied objects, significant differences for pH parameter were observed, which was confirmed by Tukey’s test. Thus, it was found that the studied soils could be divided into three groups, namely, with an acidic reaction (3.4–4.2 pH for V1–V2), slightly acidic/close to neutral (V3–V4 with pH 5.5–6.5), and also, separately, the soil profile of V5 (6.8–7.5 pH), in which a transition

from a slightly acidic reaction to a slightly alkaline one was observed, due to the presence of carbonates in the parent materials and their dissolution. The change in soil acidity is largely due to the change in plant communities. Changes in pH at the arable-meadow stage were almost imperceptible, due to the high ash concentration of plant litter, while the change from meadow to forest plant communities was accompanied by a significant change in soil pH [46,47]. The concentration of SOC naturally decreases with depth; the highest concentration ($6.23 \pm 0.12\%$ of C) was noted in the fallow soil under the meadow (V4). Young fallow land areas are characterized by active accumulation of SOM, due to an increase in plant biomass and their subsequent humification [48]. The lowest concentration ($3.36 \pm 0.05\%$ of C) of SOM was noted in the soil under the hayfield (V3); this was due to active farming and soil depletion as hay was removed from the territory. Similar results ($3.14 \pm 0.03\%$ of C) were noted for the soil subject to waterlogging (V2). A high degree of soil hydromorphism negatively affects plant growth and also leads to inhibition of soil microorganisms involved in the transformation of SOC. At the same time, the soil (V1) forming in a forested area was characterized by more active formation of SOC, due to the accumulation of coarse humus forms and their weak degree of transformation under anaerobic conditions. According to the Tukey's test performed with regard to the carbon content in the upper humus-accumulative horizons, significant differences were identified between the objects V1, V2, V4, and V5; sample V3 did not have significant differences from samples V2 and V5. Our findings are supported by the results of the study by Likhanova et al. [49], which also reported that under waterlogged conditions, the rate of SOM accumulation increased, mainly due to coarse humus forms. Aerobic conditions promote more rapid transformation of SOM, due to more active microbiological activity [13]. According to previously conducted studies on plots in a long-term fallow state, it was found that the SOM may increase in the first decades due to active humification processes; subsequently, as a result of changes in plant communities, it decreases, and only after 80 years of the fallow state is an increase again observed [44].

Regarding total nitrogen, its regular relation with the concentration of SOM was noted; the highest concentration was noted in the arable (V3 Ap) and old arable (V1 Ap, V5 Ap) horizons of the soils, while the highest nitrogen concentration was noted in the old arable horizon of the soil (V4 Ap— $0.35 \pm 0.01\%$) under meadow vegetation.

Table 2. The physico-chemical characteristics of studied soils.

Soil ID	Horizon	pH	Particle Size Distribution, %			SOC %	N	C/N	P ₂ O ₅	K ₂ O	N-NH ₄ ⁺	N-NO ₃ ⁻	CaCO ₃ %
			Sand	Silt	Clay								
V1	Ap	3.70 ± 0.01	41.50	51.44	7.06	4.54 ± 0.02	0.22 ± 0.01	24.14	75	51	14.81	4.55	-
	Ew	3.80 ± 0.01	9.82	84.48	5.70	1.04 ± 0.01	0.05 ± 0.01	24.34	208	33	8.02	0.88	-
	Cr	4.00 ± 0.01	33.82	59.68	6.50	1.08 ± 0.01	0.04 ± 0.01	31.59	271	28	22.44	0.12	-
V2	Ap	3.40 ± 0.01	43.20	49.52	7.28	3.14 ± 0.03	0.13 ± 0.01	28.25	71	40	10.86	0.03	-
	Br	4.20 ± 0.01	35.86	58.36	5.78	1.95 ± 0.03	0.09 ± 0.01	25.34	175	39	13.84	0.33	-
	Cr	3.80 ± 0.24	44.68	52.54	2.78	0.24 ± 0.02	0.01 ± 0.01	28.08	183	18	14.55	0.18	-
V3	Ap	6.50 ± 0.01	84.88	13.38	1.74	3.36 ± 0.05	0.20 ± 0.01	19.65	177	33	10.67	0.79	-

	Bs	6.30 ± 0.01	92.94	5.02	2.04	0.35 ± 0.02	0.05 ± 0.01	8.19	67	36	7.11	0.06	-
	Bs/C	6.20 ± 0.02	90.26	9.12	0.62	0.15 ± 0.01	0.04 ± 0.01	4.39	81	46	8.66	0.03	-
	C	5.80 ± 0.15	94.84	4.44	0.72	0.04 ± 0.01	0.04 ± 0.01	1.17	53	35	7.31	0.02	-
V4	Ap	5.50 ± 0.08	81.02	14.20	4.78	6.23 ± 0.12	0.35 ± 0.01	20.83	274	42	21.53	0.52	-
	Bs	6.10 ± 0.04	93.32	6.16	0.52	0.60 ± 0.01	0.06 ± 0.01	11.70	68	17	8.34	0.03	-
	C	6.40 ± 0.01	80.36	17.00	2.64	0.25 ± 0.01	0.02 ± 0.01	14.62	37	47	6.30	0.10	-
V5	Ap	6.80 ± 0.02	34.74	50.42	14.84	3.43 ± 0.03	0.22 ± 0.01	18.24	166	72	14.36	0.70	2.48
	Ah	7.00 ± 0.02	27.96	65.74	6.30	1.58 ± 0.01	0.11 ± 0.01	16.80	105	52	9.96	0.49	2.04
	Ck ₁	6.80 ± 0.02	37.68	44.34	17.98	0.39 ± 0.06	0.05 ± 0.01	9.13	40	63	6.92	0.21	2.15
	Ck ₂	6.90 ± 0.03	37.52	30.90	31.58	0.55 ± 0.06	0.07 ± 0.01	8.87	51	100	8.08	0.27	2.93
	Ck ₃	7.50 ± 0.04	27.90	54.60	17.50	0.29 ± 0.01	0.05 ± 0.01	6.79	45	57	6.14	0.33	11.90

Regarding the C/N ratio, it was found that soils under conditions of increased soil hydromorphism (V1-V2) were characterized by a wide range of values of this index (24.14–31.59). This indicates low rates of SOM mineralization; as a result of waterlogging, SOM is mainly conserved and retains the molecular structures of humification precursors [13,49]. In the soils forming on sandy deposits, after the transition to a fallow state, in most cases, there was a more intensive accumulation of SOM as well as nitrogen, which is associated with active rates of SOM humification [50,51]. However, in soil variants confined to areas characterized by long periods of waterlogging, the transition to a fallow state leads to a deterioration of both physical and chemical parameters compared to active arable analogues. For soils under the hayfield (V3), an optimal range of values was noted; in the upper humus-accumulative horizon (C/N—19.65), SOM transformation processes actively occurred, while in the underlying horizons, the C/N ratio gradually decreased (8.19 for Bs → 4.39 for Bs/C → 1.17 for C), this distribution is due to a decrease in the SOM in the underlying horizons, which is typical for soils developing on outwash plains. In the soils developing under meadow vegetation (V4), the C/N ratio (20.83) was characteristic of the upper humus-accumulative horizon. The underlying horizons were characterized by lower values (11.70 and 14.62, respectively), which indicates processes of movement of labile SOM under a leaching water regime and its subsequent conservation. The soils of fallow land developing on parent materials containing carbonates were characterized by the relatively narrow C/N ratio in the humus-accumulative horizons (Ap-Ah, 18.24 and 16.80, respectively). This was due to the favorable physical parameters of this soil, as well as the neutral pH value, which favorably affects microbial activity. According to a study by Zhao et al. [52], soils forming on parent materials containing carbonates are able to actively accumulate SOC and nitrogen only for the first 20 years, after which the accumulation rates decrease. The underlying horizons were characterized by a sharp decrease in the C/N ratio. In general, short fallow time did not have a significant effect on the C/N ratio, the level of soil hydromorphism was an important factor.

The content and dynamics of biogenic elements are important indicators of soil fertility; therefore, the analysis of phosphorus and potassium, as well as ammonium and nitrate nitrogen content is necessary to assess the rate of soil transformation during the transition to a fallow state. Regarding phosphorus, a strong heterogeneity was found both among the studied soils and within the profiles. In the soils of fallow land formed in waterlogged conditions, it was found that the phosphorus content increased with depth, which contradicts classical ideas, according to which accumulation occurs due to biotic interactions and is concentrated in the upper humus-accumulative horizon. The increase in the content of mobile phosphorus in the soil is associated with anaerobic conditions, in which phosphorus changes from an insoluble form to a soluble one when the valence of iron changes from Fe^{3+} to Fe^{2+} [53]. The solubility of chemical elements is largely determined by pH value and oxidative conditions due to chelation and complexation [54]. In the soil variants forming on outwash sands, maximum phosphorus content values were found in the upper humus-accumulative horizons, due to the application of mineral fertilizers; with increasing depth, the phosphorus content sharply decreased. Regarding the soil variant forming on parent materials containing carbonates, a classical distribution of phosphorus down the profile was noted [5], with a maximum value in the upper humus-accumulative horizon and a gradual decrease with depth. It has been found that over short periods of fallow state (2–3 years), phosphorus can remain in relatively high concentrations in the soil, but changes in the degree of soil hydromorphism, as in the cases of waterlogged soils, lead to its loss from old arable horizons. According to Kalinina et al. [48], under a leaching water regime, significant phosphorus losses are observed in soils with increasing fallow age, which is due to an increase in soil acidity and leaching processes.

Regarding potassium, a strong correlation ($r = 0.79$, $p < 0.001$) was found with the concentration of clay, due to the content of potassium in exchangeable form within clay minerals. The highest potassium content was characteristic of the soils of fallow lands developing on parent materials containing carbonates (V5); the range of values here was from 52 to 100 mg/kg. In the waterlogged soils (V1–V2) developing on loamy deposits, a range of 28–51 mg/kg was characteristic, while for soils forming on sandy deposits, the lowest values of 17–47 mg/kg were observed. With increasing fallow time, the content of K, P, and Ca may decrease due to leaching [54].

Regarding ammonium nitrogen, it was found that the highest values were in the old arable horizon of the soil developing on outwash sands (V4 Ap) and the underlying horizon of the soil on the territory of Vuoksa basin (V1 Cr). The soil of fallow land forming on outwash sands was characterized by active transformation of SOM, which leads to active accumulation of the ammonium form of nitrogen; however, the nitrification process here is practically undeveloped, which may be due to the acidic reaction and the inhibition of nitrifying bacteria. For the forested area of the Vuoksa basin (V1), active accumulation of the ammonium form of nitrogen and nitrate was noted. The 10-year stage of the fallow state, accompanied by the development of forest cover, has a positive effect on the formation of the nitrogen cycle in this area. In the underlying Cr horizon, the active conservation of ammonium nitrogen occurs under anaerobic conditions, while in the upper humus-accumulative horizon, ammonification and subsequent nitrification processes actively occur. Under conditions of increased hydromorphism in the Vuoksa basin area (V2), a lower intensity of nitrification was noted, associated with the development of anaerobic processes in the upper soil horizons, while active conservation of ammonium nitrogen occurred in the underlying horizons. In the territory used as a hayfield (V3), where aerobic processes are developed, nitrate accumulation occurred to a lesser extent. This is due to the assimilation of nitrogen by plants and microorganisms, which was noted in the soils of fallow land developing on parent materials containing carbonates. Thus, the transition

to a fallow state over a short period of time can create conditions for active ammonification, which was noted for the soil profile under meadow vegetation (V4); however, due to the disturbed nitrogen cycle as a result of agricultural activity, nitrification here occurs much more slowly than in fallow soils that have already undergone afforestation and where the nitrogen cycle has been restored. In long-term fallow variants, the content of ammonium and nitrate nitrogen increases in the soils up to background values, due to changes in the composition of the soil microbiome [44].

Important parameters associated with the transition of soils to a fallow state are the stocks of carbon and nitrogen in the soils (Figure 3). The maximum carbon stock value (Figure 3A) for the upper humus-accumulative horizon (0–30 cm) was noted in the soils in a young fallow state (V4); the change of vegetation to meadow communities led to active accumulation of SOM. This soil was characterized by the largest stocks in the 0–100 cm layer, indicating the migration of organo-mineral compounds in the soil. The lowest stocks were in the waterlogged soils V1–V2 (9.30–9.61 kg/m²), where the acidic reaction and the high degree of soil hydromorphism negatively affected the accumulation of SOM in the upper soil layer. However, the profile of the forested soil in the territory of Vuoksa basin V1 was characterized by relatively high carbon stocks at a depth of 0–100 cm. This is due to the development of anaerobic processes and the conservation of SOM in the Cr horizon of the soils; the same trend was noted in the second soil profile on the waterlogged territory (V2). As a result of the action of anaerobic processes, SOM is predominantly conserved, which is also reflected in the molecular composition and the dominance of aliphatic structural fragments, characterized by the composition of humification precursors [13]. In the sandy soil under the hayfield (V3), most of the SOM was concentrated in the upper layer of 0–30 cm, while the underlying horizons practically did not participate in the accumulation of SOM; this soil was characterized by the lowest carbon stock in the 0–100 cm layer. Long-term use of land as hayfields negatively affects the accumulation of SOM, due to the constant and prolonged removal of plant residues; therefore, the main contribution to the accumulation of organic substances is made by the root system rather than the aboveground phytomass. This thesis is confirmed by the results for plot V4, where, as a result of self-overgrowing, a significant amount of plant residues accumulates and is transformed in the soil. Our data regarding waterlogged soils are confirmed by studies by various scientists [55,56] reporting that periodic waterlogging conditions leads to the accumulation of coarse humus forms in the soil and the formation of peat horizons. The soils of fallow land on parent materials containing carbonates (V5) were characterized by relatively high carbon stocks, in both the 0–30 and 0–100 cm layers (12.18 and 17.05 kg/m², respectively). According to Kalinina et al. [50], transition to a fallow state leads to an increase in carbon stocks in the upper soil layers. In the initial stages, carbon stocks may decrease relative to arable analogues, but with increasing fallow time, the stock values will tend towards background analogues.

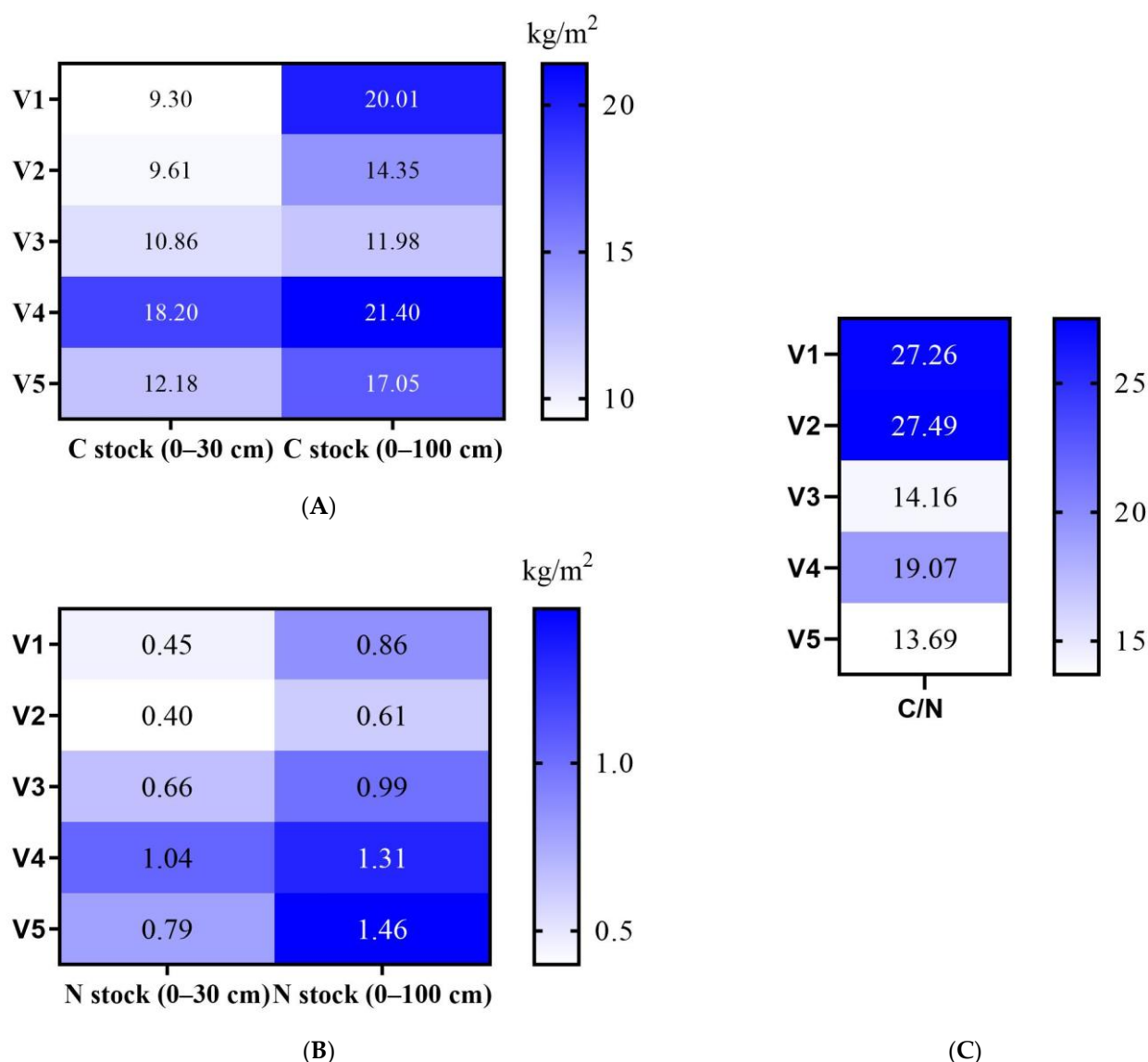


Figure 3. Carbon (A) and nitrogen (B) stocks on depth 0–30 cm and 0–100 cm for studied soils as well as C/N ratio (C). V1—Gleyic Retisol (Histic), V2—Gleyic Anthrosol (Loamic), V3—Entic Podzol (Aric), V4—Entic Podzol (Aric, Placic), V5—Endocalcaric Luvisol (Aric).

The nitrogen stock data in the studied soils are presented in Figure 3B. The highest nitrogen stocks in the 0–30 cm layer, as in the case of carbon, are characteristic of the young fallow territory (V4). Where meadow vegetation develops, as a result of the transformation of a large amount of plant residues, a significant amount of nitrogen enters the soil. However, the highest nitrogen stocks in the 0–100 cm layer correspond to the soil developing on parent materials containing carbonates (V5), with up to 45% of N concentrated precisely in the underlying horizons. The lowest stocks were noted in the soils of Vuoksa basin territory, both in the 0–30 cm and 0–100 cm layers, which may be due to the waterlogging process. According to Kalinina et al. [48,50], in the initial stages of the fallow state, there is practically no change in nitrogen stocks in the soil; in the upper humus-accumulative horizons, active accumulation of nitrogen is noted with increasing fallow time, while denitrification processes occur in the underlying horizons. This process can continue for about 50 years of fallow state, after which nitrogen stocks will again approach background analogues.

During the analysis of SOM quality according to the C/N ratio (Figure 3C), it was found that the narrowest ratio corresponded to the soil developing on parent materials containing carbonates (V5), the high availability of nitrogen in the SOM may contribute to the formation of stable forms of carbon in the soil. In contrast, the widest ratio corresponded to the fallow land soils forming on the waterlogged territory, where the high level of soil hydromorphism led to the accumulation of predominantly labile carbon forms. For the agricultural soil under the hayfield (V3), a relatively narrow C/N ratio was noted, apparently due to the periodic application of mineral and organic fertilizers; a relatively small amount of SOM accumulates here, but it is of high quality. The soils of fallow land under meadow vegetation, characterized by high levels of carbon and nitrogen stocks, showed a relatively wide C/N ratio, which may indicate a slightly degraded state of SOM as a result of the transition to fallow state. Changes in the composition of plant communities, as well as active rates of humification, lead to significant changes in the qualitative composition of SOM; thus, the formation of forest communities leads to an increase in the labile carbon pool in the soil [57,58], while in the early stages of fallow state with the formation of meadow vegetation, an increase in the stable SOM pool occurs [50,51], due to the chemical composition of plant litter and its ash concentration.

As a result of the analysis of the physicochemical parameters of soils of arable and fallow land, it was found that soils over a short period of time in a fallow state are capable of undergoing substantial transformation caused by environmental factors. Under waterlogging conditions, soils acquire an acidic reaction, gley processes develop, SOM accumulates, and coarse humus forms. On the other hand, in well-aerated soils developing on outwash sands, highly productive plant communities form in fallow areas, which leads to the accumulation of significant amounts of SOM and nitrogen. The fallow land soil on parent materials containing carbonates was characterized by high quality of SOM as well as availability of biogenic elements. The soil under the hayfield was characterized by a relatively low degree of availability of biogenic elements as well as low SOM stocks.

3.2. The Amount of Mineral-Associated Carbon and Nitrogen

The analysis of the distribution of SOC and TN between the labile (POM) and stable (MAOM) fractions revealed significant heterogeneity among the studied fallow land soils of the Leningrad region. The proportion of MAOC in the total SOC pool varied widely, from 41.9% in Endocalcaric Luvisol (V5) to an extremely high 96.8% in Gleyic Anthrosol (V2) (Table 3). Gleyic Anthrosols are characterized by a high degree of mineral protection. Despite the relatively low absolute SOC concentration (3.14%), almost all of the carbon in this soil was in a protected mineral form (MAOC = 3.04%). This indicates a deep degree of transformation of the original SOM and its strong binding to the mineral matrix, which is characteristic of long-term pedogenesis processes or specific conditions of past anthropogenic impact. The high concentration of MAON (79.4% of TN) in this soil confirms that nitrogen was also predominantly stabilized within organo-mineral complexes. In the remaining soils, the concentration of MAOC ranged from 42–59%, indicating the presence of a significant pool of labile carbon (POM), probably represented by plant litter residues accumulating during post-agrogenic (secondary) succession. It is interesting to note that the Podzols (V3, V4) demonstrated higher absolute accumulation of both SOC and MAOC.

In all studied soils, the C:N ratio in the MAOM fraction (fMAOM C:N) was lower than that in the bulk soil (Soil C:N). The difference ranged from 3 units (V1, V3) to 5 units (V2). A decrease in the C:N ratio upon transition to the mineral-associated fraction is a sign of microbial processing of SOM. During the decomposition of labile components (rich in carbon), microorganisms immobilize nitrogen, and their metabolic products (microbial necromass), rich in nitrogen and possessing a high sorption capacity, form the MAOM

pool [59]. An exception in terms of absolute values is the Gleyic Anthrosol soil (V2), where a high C:N ratio in the MAOM fraction (33) with a low nitrogen concentration may indicate a specific composition of stabilized compounds or a limitation of the nitrogen fixation process in a particular ecological niche.

Table 3. The amount and proportion of MAOC and MAON in the studied soils. Stoichiometric C:N ratios in the soil and the fraction containing MAOM (<0.053 mm). V1—Gleyic Retisol (Histic), V2—Gleyic Anthrosol (Loamic), V3—Entic Podzol (Aric), V4—Entic Podzol (Aric, Placic), V5—Endocalcaric Luvisol (Aric). *—fraction <0.053 mm.

Soil ID	SOC, %	MAOC, %	MAOC, % of SOC	TN, %	MAON, %	MAON, % of TN	Soil C:N	fMAOM * C:N
V1	4.54 ± 0.02	2.58 ± 0.03	56.8 ± 0.8	0.22 ± 0.01	0.16 ± 0.01	74.9 ± 0.1	24	18
V2	3.14 ± 0.03	3.04 ± 0.07	96.8 ± 2.1	0.13 ± 0.01	0.11 ± 0.01	79.4 ± 0.1	28	33
V3	3.36 ± 0.05	1.77 ± 0.03	52.7 ± 0.9	0.20 ± 0.01	0.12 ± 0.01	57.3 ± 0.1	19	18
V4	6.23 ± 0.12	3.65 ± 0.18	58.6 ± 2.9	0.35 ± 0.01	0.25 ± 0.01	69.6 ± 0.1	21	17
V5	3.43 ± 0.03	1.44 ± 0.01	42.0 ± 0.4	0.06 ± 0.01	0.12 ± 0.01	53.2 ± 0.1	18	14

Solid-state NMR spectroscopy data made it possible to detail the chemical nature of SOM in different soils and fractions (Figure 4). Analysis of the carbon distribution by functional groups shows a clear differentiation between bulk SOM, MAOM, and HAs.

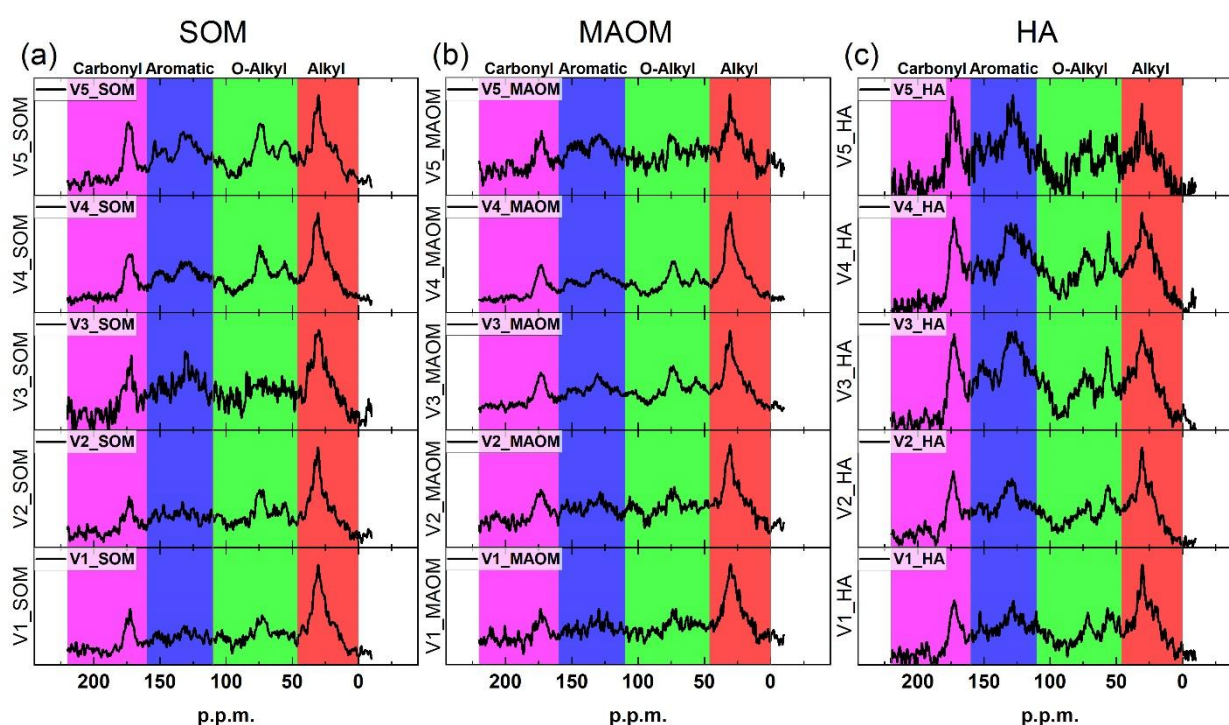


Figure 4. ^{13}C NMR spectra of SOM (a), MAOM (b), HA (c) isolated from studied soils of fallow and arable lands of Leningrad region. V1—Gleyic Retisol (Histic), V2—Gleyic Anthrosol (Loamic), V3—Entic Podzol (Aric), V4—Entic Podzol (Aric, Placic), V5—Endocalcaric Luvisol (Aric).

In all studied soils, the transition from SOM to the MAOM fraction was accompanied by an increase in the proportion of alkyl carbon (0–45 ppm) and a decrease in the proportion of O-alkyl carbon (45–110 ppm), with the exception of the Entic Podzol (Aric) (V3), where the changes were less pronounced (Figure 5). The increase in the concentration of alkyl structures (lipids, waxes, polymethylene chains) in MAOM indicates the selective preservation of biochemically resistant compounds in the soil mineral matrix [60,61]. At

the same time, an enrichment of MAOM with aromatic structures (110–160 ppm) was observed compared to SOM in soils V5, which reflects the participation of condensed aromatic systems in the formation of stable organo–mineral complexes. The spectra of HAs isolated from the studied soils demonstrate a molecular composition that differs in several aspects from both SOM and MAOM. A characteristic feature of HAs is a systematically higher concentration of aromatic carbon compared to SOM and MAOM (Figure 4). For all soils, the proportion of aromatic compounds in HAs exceeded that in SOM and MAOM, ranging from 31.70% (V1) to 41.34% (V5). The maximum aromaticity of HAs was found in the V5 (Endocalcaric Luvisol), which indicates a notable condensation of aromatic compounds. SOM formed on carbonate parent rocks is characterized by elevated values of aromatic structural components, due to a decrease in the proportion of aliphatic peripheral fragments under changing humification conditions in the presence of carbonates [62].

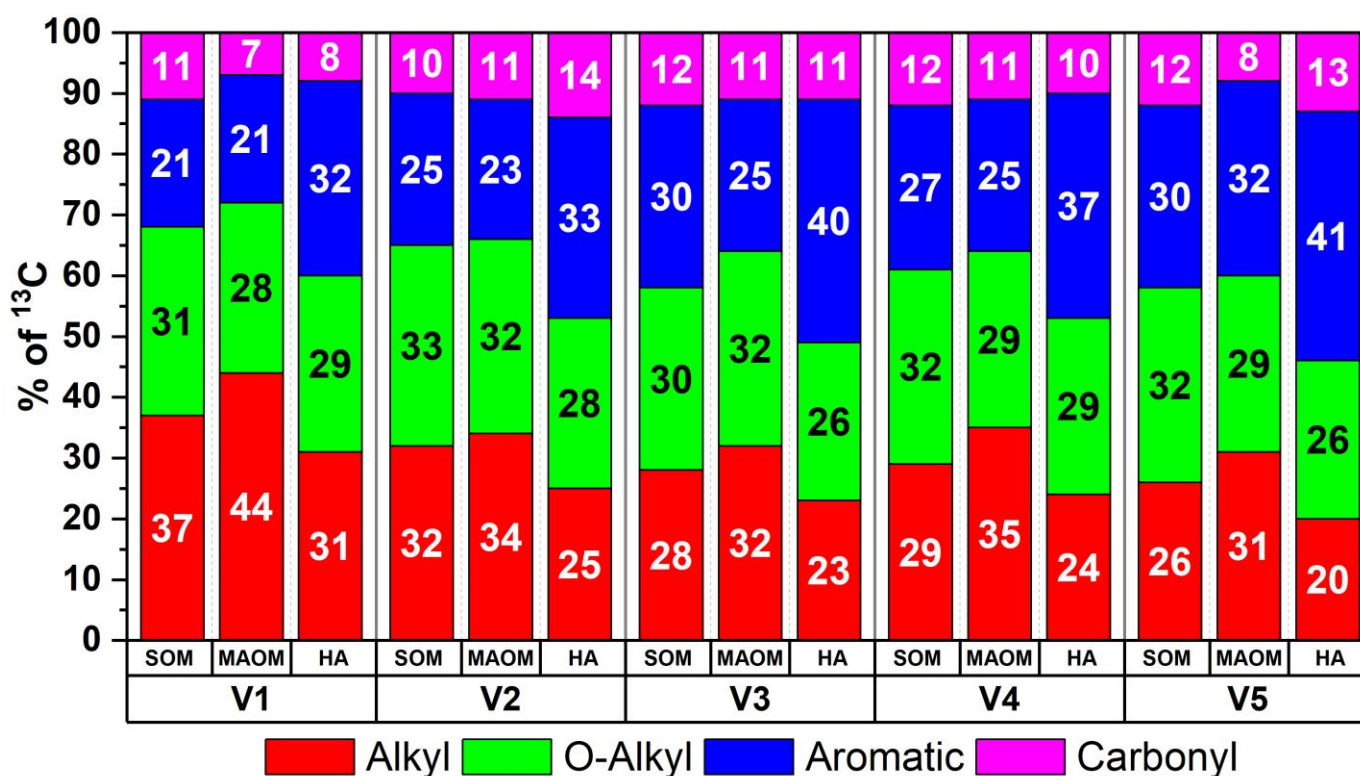


Figure 5. Molecular composition (% of ^{13}C) of SOM, MAOM and HAs. V1—Gleyic Retisol (Histic), V2—Gleyic Anthrosol (Loamic), V3—Entic Podzol (Aric), V4—Entic Podzol (Aric, Placic), V5—Endocalcaric Luvisol (Aric). Alkyl—0–45 ppm, O-Alkyl—45–110 ppm, Aromatic—110–160 ppm, Carbonyl—160–220 ppm.

The degree of humification (A/O-A index) showed a clear tendency to increase upon transition from bulk SOM to the mineral-associated fraction (Figure 6). In all five soils, the A/O-A value in the MAOM fraction exceeded the corresponding value for SOM. The greatest increase in the index values was observed in soils V1 (from 1.20 to 1.58) and V4 (from 0.93 to 1.19). This indicates that mineral protection of SOM is accompanied by selective accumulation of alkyl structures relative to labile O-alkyl components originating mainly from plant residues [63]. The RI index, as an integral indicator of SOM stability, demonstrated the most consistent dynamics when analyzing the fractional composition of SOM. In all the studied soils, the RI value in the MAOM fraction exceeded the corresponding value for SOM. The increase in the index ranged from 0.07 units in V2 (from 1.28 to 1.35) to 0.43 units in V1 (from 1.36 to 1.85). The highest RI values in the MAOM

fraction were recorded in soils V1 (1.85) and V5 (1.70), which indicates the maximum degree of mineral stabilization of SOM. The stability of HAs was comparable to that of MAOM, and in some cases (V3), even exceeded it (RI in HA = 1.71 versus MAOM = 1.31). Despite differences in molecular composition (predominance of aromatic carbon in HAs versus alkyl carbon in MAOM), both fractions are characterized by a high degree of resistance to biological decomposition, although this is achieved through different pathways [25,64].

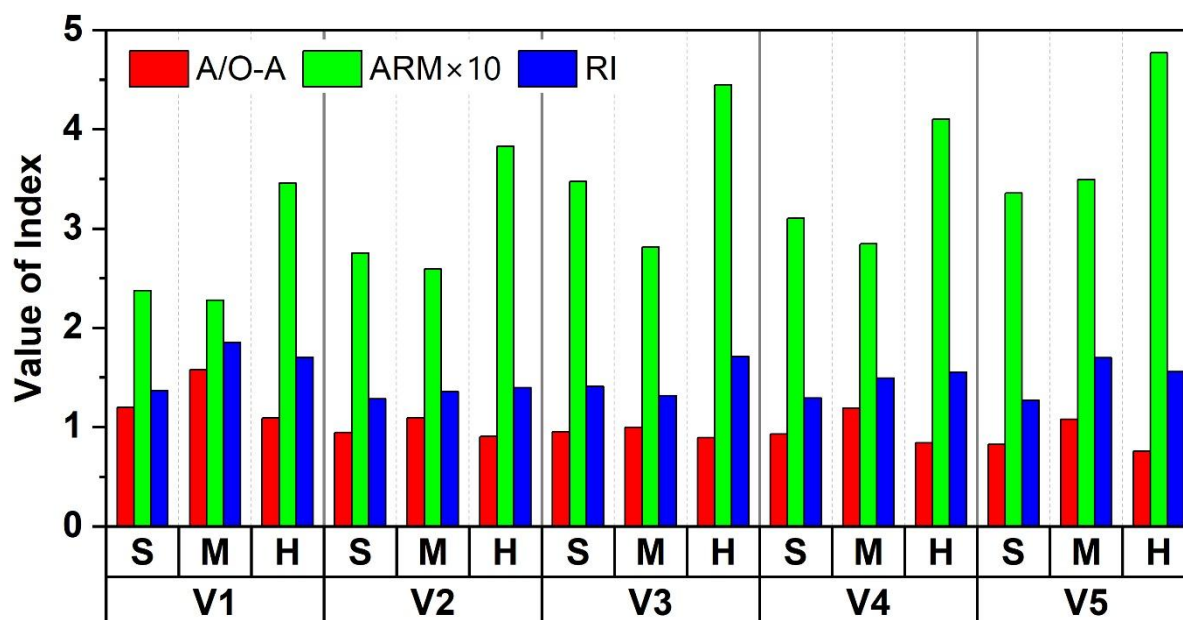


Figure 6. Quality indices calculated from NMR spectra (The aromaticity index (ARM) was multiplied by 10 for ease of visualization). S—SOM, M—MAOM, H—humic acids. V1—Gleyic Retisol (Histic), V2—Gleyic Anthrosol (Loamic), V3—Entic Podzol (Aric), V4—Entic Podzol (Aric, Placic), V5—Endocalcaric Luvisol (Aric).

The composition of SOM differs mainly in the nitrogen concentration, in soil V1 (Gleyic Retisol, Histic), a sharp decrease in N concentration was recorded in the MAOM fraction (0.44–0.71%) compared to SOM (1.02–1.54%), i.e., 43–57% less (Table 4). In contrast, in soil V2, the nitrogen concentration in MAOM (1.97–2.06%) exceeded that in SOM (0.74–1.27%) by more than 1.5 times. In soils V3–V5, the differences in nitrogen concentration between fractions were less pronounced.

Table 4. Elemental composition of SOM and MAOM of the studied soils, mass % on an ash-free basis after HF acid treatment. C—carbon; N—nitrogen; H—hydrogen; O—oxygen.

Soil ID	SOM				MAOM			
	N, %	C, %	H, %	O, %	N, %	C, %	H, %	O, %
V1	1.28 ± 0.37	45.63 ± 0.01	5.39 ± 0.75	47.70 ± 0.39	0.57 ± 0.19	44.18 ± 0.03	7.64 ± 0.49	47.60 ± 0.27
V2	1.01 ± 0.37	45.43 ± 0.26	5.13 ± 0.84	48.34 ± 0.21	2.02 ± 0.06	48.81 ± 0.23	5.31 ± 0.13	43.86 ± 0.16
V3	1.44 ± 0.05	46.11 ± 0.28	4.66 ± 0.20	47.83 ± 0.13	1.77 ± 0.13	47.72 ± 0.02	4.56 ± 0.13	45.96 ± 0.02
V4	1.97 ± 0.09	54.49 ± 0.26	4.19 ± 0.26	39.35 ± 0.54	1.76 ± 0.13	54.68 ± 0.20	5.09 ± 0.98	38.48 ± 0.64
V5	2.48 ± 0.11	49.24 ± 0.14	4.43 ± 0.26	43.85 ± 0.01	1.93 ± 0.19	47.17 ± 0.55	5.94 ± 0.22	44.96 ± 0.53

Atomic ratios calculated based on elemental analysis data allow for the assessment of changes in the molecular structure of SOM [65]. The O:C ratio is an indicator of the

degree of oxidation of SOM. In the studied (Figure 7) MAOM samples, the O:C ratio varied from 0.52–0.53 (V4) to 0.81 (V1). Low O:C values in soil V4 indicate a predominance of reduced, condensed molecular structures with a high degree of aromaticity, which is consistent with the NMR data on the maximum concentration of aromatic carbon in this soil. Changes in the H:C ratio in SOM and MAOM are multidirectional, which is due to both the different lithological composition of the rocks and the different hydrological regime of the soils. In soil V1, the H:C ratio in the MAOM fraction (1.98–2.17) significantly exceeded that in SOM (1.28–1.56), which confirms the selective accumulation of aliphatic structures (inherited from humification precursors) in the MAOM. In soils V2–V5, the differences in H:C between SOM and MAOM were smaller magnitude, indicating a more balanced composition of stabilized compounds.

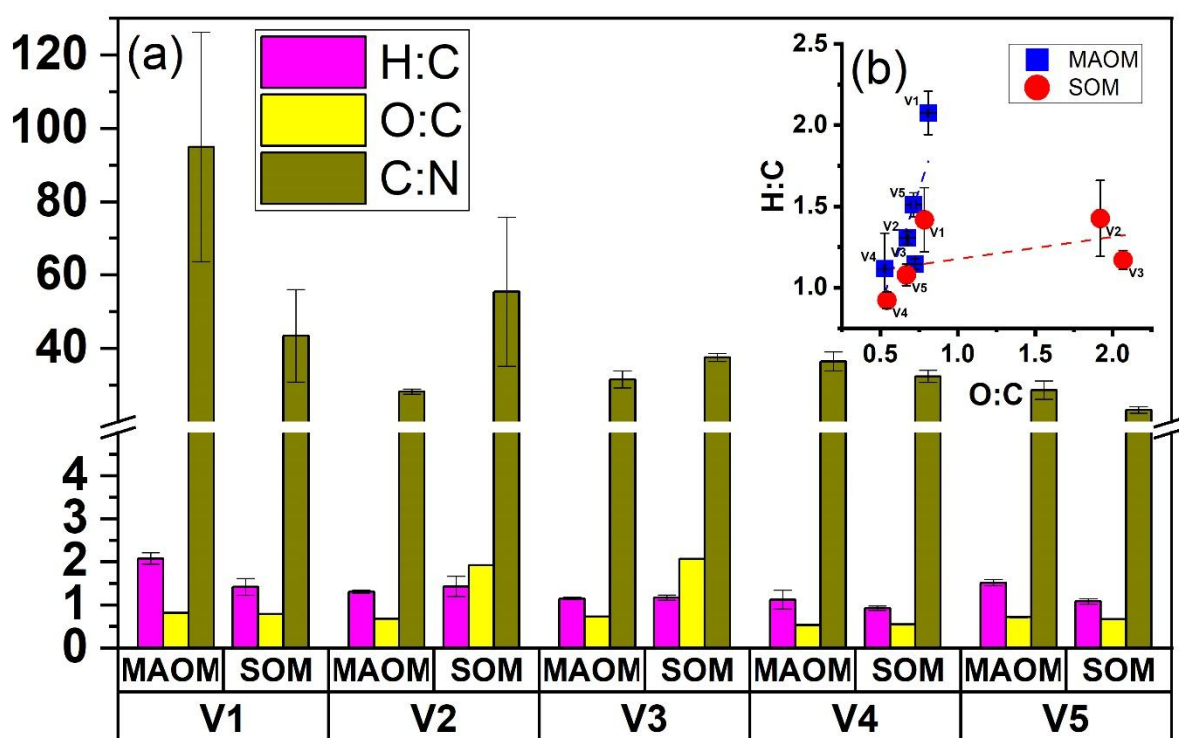


Figure 7. (a)—Molar ratios in the elemental composition of MAOM and SOM. (b)—Van Krevelen diagrams for MAOM and SOM. Calculations were performed for SOM and MAOM on an ash-free basis after HF acid treatment.

The elemental analysis data are generally consistent with the results of NMR spectroscopy (see Figure 4). Thus, the high H:C ratio (1.98–2.17) and low O:C ratio (0.81) in the MAOM of soil V1 (Gleyic Retisol, Histic) support the NMR data on the maximum concentration of alkyl carbon (43.78%) and the high humification index A/O-A (1.58). The atomic H:C and O:C ratios in the coordinates of the van Krevelen diagram (Figure 7b) show that the stabilization of SOM in the mineral matrix is accompanied by the selective fixation of molecules with a certain degree of oxidation and aliphaticity, depending on soil and environmental conditions [66]. Thus, we can note that SOM formed under conditions of waterlogging is characterized by a high potential for carbon sequestration, which is due to both low rates of SOM transformation and the formation of an organo–mineral matrix in which a significant amount of carbon is enclosed.

3.3. The Elemental Composition in HAs of Studied Soils

The elemental composition of HAs reflects the main processes occurring at the molecular level (oxidation, reduction, hydrogenation, dehydrogenation) and serves as basic information about the structure of humic substances. Within the framework of the analysis, HAs were isolated from the upper humus-accumulative soil horizons, where the processes of humification and formation of humic substances occur most actively.

All studied samples demonstrated a composition typical of humic acids [67]: C—51.91–53.76%, H—4.62–5.15%, N—2.84–3.32%, and O—38.28–40.15% (Table 5). The studied HAs are characterized by relatively small differences in elemental composition; however, these differences reflect the conditions of soil-forming processes. The highest carbon concentration was noted in HAs of hayfield soils (V3) and in the waterlogged territory (V2), the lowest concentration was observed in HA samples of soils forming on parent materials containing carbonates and fallow land under meadow vegetation. A decrease in the intramolecular carbon concentration may indicate an increase in the functionality of structural fragments within the HAs [68]. Regarding nitrogen, it was found that the highest concentration corresponded to the HA samples from soils on parent materials containing carbonates (V5). The presence of carbonates and clay particles leads to the formation of a favorable environment for ammonifying microorganisms and further accumulation of nitrogen in precursors of humification [69]. The lowest nitrogen concentration was noted in the HA sample from hayfield soil (V3). As a result of agricultural activities, nitrogen-enriched humification precursors enter the soil to a lesser extent. Regarding hydrogen, it was found that the highest concentrations were in HA samples from the waterlogged territory (4.62–5.15%). A relatively high proportion of hydrogen concentration indicates low maturity of HAs. A high degree of soil hydromorphism leads to the conservation of SOM rather than its transformation; therefore, soil HAs inherit the characteristics of precursors of humification [70]. In contrast, the lowest hydrogen concentration was noted in the HA sample from soil forming on parent materials containing carbonates (V5), which was associated with a high degree of SOM transformation and HAs maturity [71]. The highest oxygen concentration was observed in HAs from soil forming on parent materials containing carbonates (V5), indicating their high degree of oxidation and the presence of carboxyl and hydroxyl functional groups. The lowest oxygen concentration was in the the HA sample from soil on the waterlogged territory (V2), due to reduction conditions in the soil.

Table 5. The elemental composition of HAs isolated from studied soils. V1—Gleyic Retisol (Histic), V2—Gleyic Anthrosol (Loamic), V3—Entic Podzol (Aric), V4—Entic Podzol (Aric, Placic), V5 - Endocalcaric Luvisol (Aric). W—the degree of oxidation; C—carbon; N—nitrogen; H—hydrogen; O—oxygen.

Soil ID	C, %	N, %	H, %	O, %	C/N	H/C	O/C	w	Ash Concentration, %
V1	53.00	3.07	4.98	38.96	20.17	1.12	0.55	−0.01	0.01
V2	53.47	3.10	5.15	38.28	20.15	1.15	0.54	−0.07	0.51
V3	53.76	2.84	4.76	38.63	22.05	1.05	0.54	0.02	0.50
V4	52.49	3.11	4.77	39.62	19.66	1.08	0.57	0.05	0.94
V5	51.91	3.32	4.62	40.15	18.23	1.06	0.58	0.10	0.80

Based on the C/N ratio, it was found that HA samples from waterlogged soils (V1–V2) were characterized by a relatively wide ratio; this was also noted for carbon and nitrogen stock values. Reduction conditions in the soil, which are confirmed by high values of the oxidation index (w —(−) 0.1 and (−) 0.7), lead to the conservation of SOM and its low transformation rate, which is reflected in the wide H/C ratio (1.12–1.15). As a result of

waterlogging of the territory, the humification process here proceeds least actively, and therefore, soil HAs acquire the characteristics of the original precursors of humification [72]. The widest C/N ratio was noted in HAs from hayfield soil (V3), due to rapid nitrogen mineralization as a result of agricultural activity. Despite the wide C/N ratio, HAs were characterized by a relatively narrow H/C ratio, which indicates active transformation of SOM. HAs from soils of fallow lands with meadow vegetation (V4) were characterized by a relatively narrow C/N ratio, which indicates a relatively high degree of nitrogen enrichment of HAs; the H/C value (1.08) was relatively low, higher than in the HAs sample from hayfield soil (V3), but lower than in HAs from waterlogged soils (V1–V2). This distribution is due to the active rate of plant residue formation and their further humification under Podzolic soil formation [44]. HAs from soils forming on parent materials containing carbonates of the Izhora Upland, according to the elemental analysis, were characterized as the most mature, which is due to the active rate of SOM humification. According to the obtained indices, these HAs were characterized by a high degree of nitrogen enrichment as well as a high degree of oxidation, which indicates aerobic conditions under which soil microorganisms are able to actively participate in the transformation of SOM [73]. To visualize the intramolecular processes occurring in HAs, a van Krevelen diagram was constructed in H/C–O/C coordinates (Figure 8).

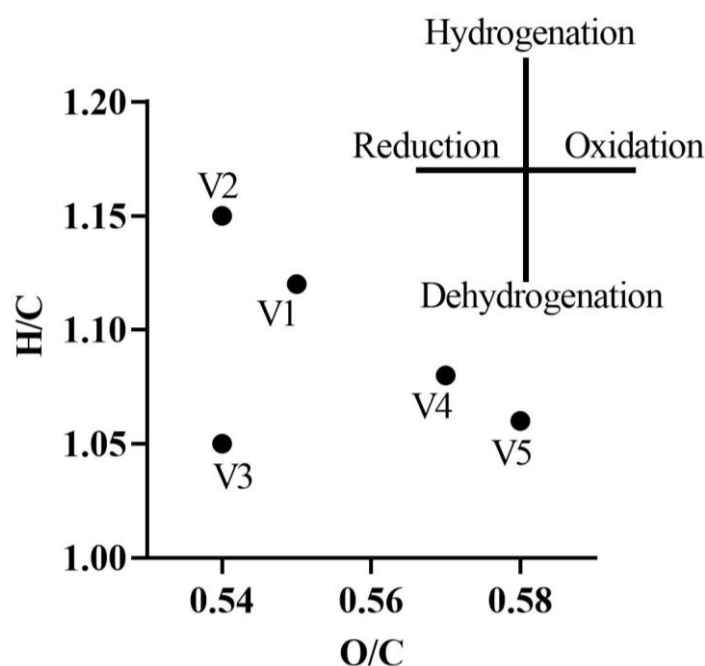


Figure 8. Distribution fields of elemental composition indices in H/C–O/C coordinates of HAs. V1—Gleyic Retisol (Histic), V2—Gleyic Anthrosol (Loamic), V3—Entic Podzol (Aric), V4—Entic Podzol (Aric, Placic), V5—Endocalcaric Luvisol (Aric).

Figure 8 shows the grouping of HA samples from soils on the waterlogged territory (V1–V2); these are located in the upper-left part of the diagram, corresponding to processes associated with reduction conditions and the formation of an aliphatic periphery in the HA structure, comprising immature humic substances. In the lower-right part are the most mature HA samples, namely, HAs from soils of fallow land under meadow vegetation and soils on parent materials containing carbonates. These samples are in the oxidation zone and are characterized by high transformation rates. The HA sample from hayfield territories occupies a separate position in the lower-left part of the graph, which indicates high rates of intramolecular transformation, but it is located in a zone close to reduction conditions. This position, together with the wide C/N ratio, may be a consequence

of agricultural activities, as a result of which fresh plant residues enter the soil to a lesser extent, while the SOM already present undergoes deep transformation [74].

During the analysis of the elemental composition, it was found that a high degree of soil hydromorphism led to low rates of SOM humification, reflected in the similarity of the HAs structure to humification precursors and the presence of an aliphatic periphery [72]. Agricultural use leads to an increase in the C/N ratio due to active nitrogen mineralization; nevertheless, soil HAs, due to active humification rates under aerobic conditions, are characterized by a relatively high degree of maturity compared to the studied HAs. HAs from fallow land soils forming on outwash sands and parent materials containing carbonates are characterized as the most humified, due to the high biological activity of soils and active rates of SOM transformation under aerobic conditions, as confirmed by data obtained previously [10].

3.4. Molecular Structure of Humic Acids Formed in Studied Soils of Fallow and Arable Lands

The obtained data on the molecular composition of HAs confirm the elemental composition of the HAs (Figure 3). Thus, it was found that HAs from soils of the waterlogged territory (V1–V2) were characterized by the highest concentration of aliphatic structural fragments (AL = 62–64%), due to the low maturity of HAs, which have structural features of the original SOM entering the soil. Anaerobic conditions lead to the conservation of SOM and its prolonged transformation under waterlogged conditions [72]. Regarding HAs isolated from hayfield soil (V3), as noted, these HAs were characterized by a relatively high level of maturity; the concentration of aromatic structural fragments was 41%. Agricultural activity leads to a decrease in nitrogen concentration in HAs due to rapid mineralization, but it causes a decrease in the concentration of alkyl C and -OCH groups, which leads to deeper transformation of organic compounds already present in the soil and an increase in the concentration of aromatic structural fragments (Table 6). The HA sample from soil under meadow vegetation contained 39% aromatic structural fragments, which was average among the studied HA samples. Compared to the HA sample from hayfield soil, with a similar composition of parent materials, a decrease in the concentration of aromatic structural fragments was noted, due to the incorporation of fresh SOM as a result of the formation of meadow vegetation. Due to this, the concentration of nitrogen and oxygen-containing structural fragments in the HAs increase. The highest concentration of aromatic structural fragments was noted in HAs from soils forming on parent materials containing carbonates (44%), indicating a high maturity of SOM relative to the other studied HAs samples.

Table 6. Concentration of structural fragments in the HAs of studied soil of fallow and arable lands. V1—Gleyic Retisol (Histic), V2—Gleyic Anthrosol (Loamic), V3—Entic Podzol (Aric), V4—Entic Podzol (Aric, Placic), V5—Endocalcaric Luvisol (Aric). AR - sum of aromatic fragments (Arom C, O,N-Arom, Arom=O); AL—sum of aliphatic fragments (Alkyl C, O,N Alkyl, CH₂OH, COO-R, C=O); AL h_r + AR h_r, % - degree of hydrophobicity; C,H-AL/O,N-AL - degree of humification of organic matter.

Soil ID	Alkyl C	O,N-Alkyl	CH ₂ OH, CHOH	Arom C	O,N-Arom	COO-R	Arom=O	C=O	AR	AL	AR/AL	AL h _r +AR h _r	C,H-AL/O,N-AL
V1	28	10	15	26	9	10	1	1	36	64	0,56	54	1.12
V2	24	10	15	27	10	12	1	1	38	62	0,61	51	0.96
V3	23	8	15	29	11	12	1	1	41	59	0,69	52	1.00
V4	23	9	17	28	10	11	1	1	39	61	0,64	51	0.88
V5	18	9	13	31	12	15	1	1	44	56	0,79	49	0.82

Important parameters for assessing the quality of SOM are the humification indices ($C,H-AL/O,N-AL$) and hydrophobicity index ($AL\ h,r + AR\ h,r$) (Figure 9). According to these indices, the most active rates of humification were observed in the HA sample from the forested area of the Vuoksa basin territory (V1); the highest concentration of hydrophobic molecules was also observed here. This is due to the strong connection of HAs with the original material of precursors of humification. Forest litter is dominated by waxes and lipids, which are characterized by a high degree of hydrophobicity [65]. An increase in the concentration of hydrophobic molecules in the composition of HAs means that soil HAs have lower migration activity, are less soluble, and are also more stable in the environment [42]. Thus, under afforestation and waterlogging conditions, we can observe “young” SOM, which, due to weak transformation under anaerobic conditions, acquires the original characteristics of humification precursors, characterized by a high concentration of hydrophobic “environmentally stable” molecules [75]. A relatively high degree of humification and hydrophobicity was observed in the HAs sample from hayfield soil. Agriculture, as noted above, leads to active mineralization of nitrogen-containing compounds in the HAs’ structure. In addition, a selection of more stable hydrophobic molecules may occur; these are not subject to rapid mineralization compared to hydrophilic compounds in the HAs [76]. The decrease in the concentration of hydrophobic molecules and the decrease in the degree of humification in HAs from the waterlogged territory (V2) was due to the conservation of SOM under anaerobic conditions, and the decrease in the concentration of hydrophobic molecules compared to sample V1 was due to the absence of woody plants, whose humification precursors contain a relatively high content of waxes and lipids [65].

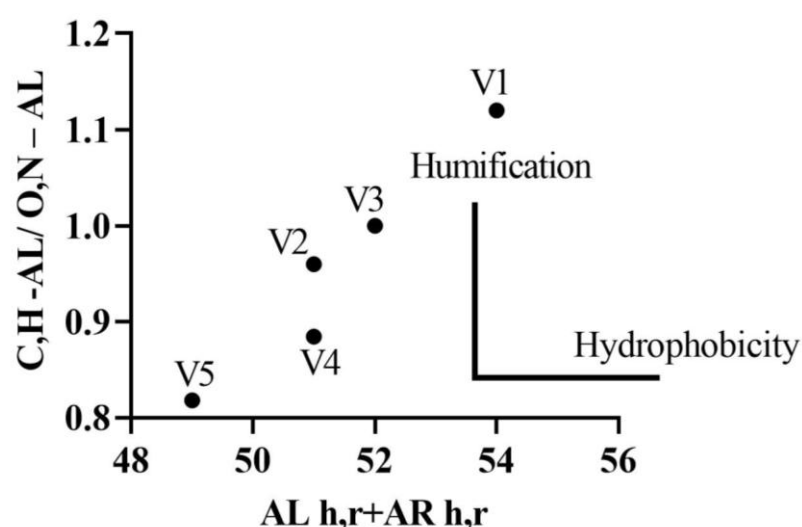


Figure 9. Diagram of integral indices of molecular composition of studied HAs isolated from soils of fallow and arable lands. V1—Gleyic Retisol (Histic), V2—Gleyic Anthrosol (Loamic), V3—Entic Podzol (Aric), V4—Entic Podzol (Aric, Placic), V5—Endocalcaric Luvisol (Aric).

The HAs sample from soil under meadow vegetation (V4) was characterized by a relatively high concentration of hydrophilic compounds in the HA composition, reflected in a relatively high O/C ratio (0.51) as well as the highest concentration of oxygen-containing (CH_2OH , $CHOH$) structural fragments in the HAs. This is due to the incorporation of “young” SOM as a result of the transition to a fallow state.

Despite the high aromaticity ($AR/AL = 0.79$), the HA sample isolated from soils formed on carbonate containing parent materials (V5) was characterized by a low degree of hydrophobicity (49%). As in the case of the HAs isolated from soil under meadow vegetation (V4), these HAs contained a relatively large number of hydrophilic molecules, due

to the high concentration of structural fragments among phenol groups (O,N-Arom) as well as carboxyl groups ($-\text{COO-R}$). These HAs have high functional activity due to the large number of nitrogen- and oxygen-containing groups, which determines a high degree of SOM stabilization [41].

For the statistical analysis of the molecular and elemental analysis of HAs, the principal component analysis (PCA) method was used (Figure 10).

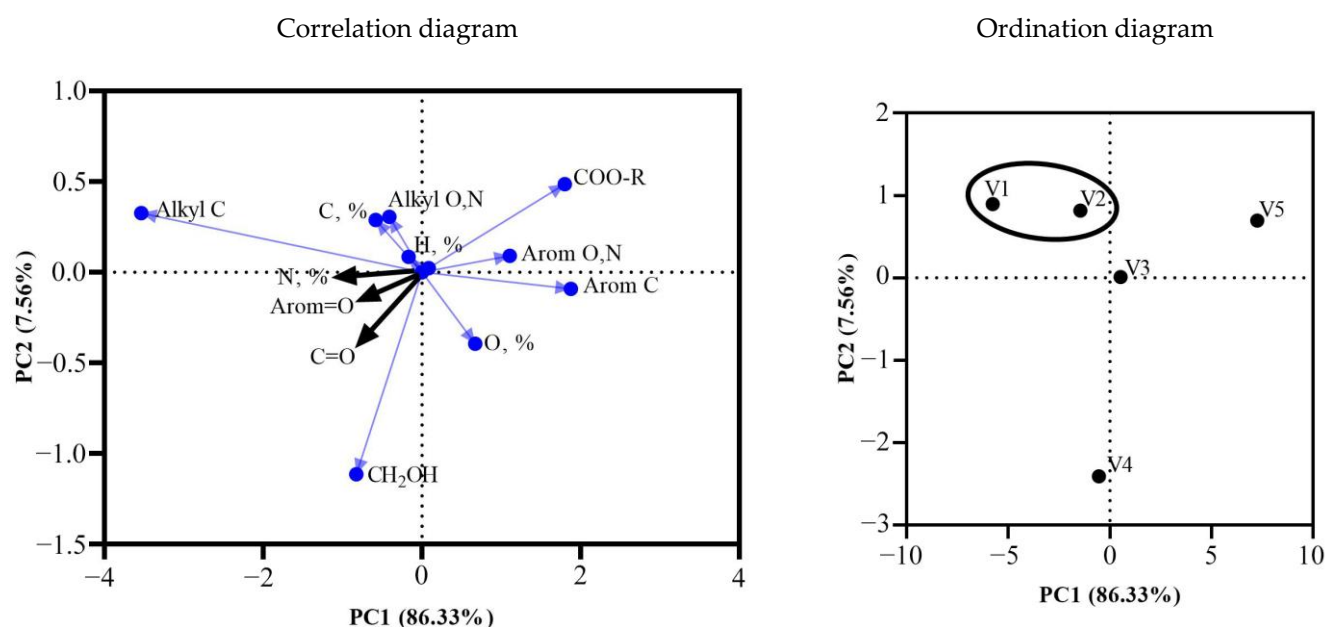


Figure 10. Results of PCA for structural fragments and elemental composition of HAs isolated from studied soils of fallow and arable lands. V1—Gleyic Retisol (Histic), V2—Gleyic Anthrosol (Loamic), V3—Entic Podzol (Aric), V4—Entic Podzol (Aric, Placic), V5—Endocalcaric Luvisol (Aric).

The main component (PC1) separates the profiles along the axis. Positive PC1 is associated with high concentration of oxygen, carboxyl groups ($-\text{COO-R}$), as well as aromatic structural fragments (C,H-Arom, O,N-Arom). Negative PC1 values are associated with high carbon concentration and aliphatic structural fragments (C,H-Alkyl), as well as alcohol groups (CH_2OH). Thus, this component reflects the maturity and degree of oxidation of HAs. HAs samples V1-V2 are located on the left side of the ordination graph, which confirms our data that under anaerobic conditions, HAs carrying the original characteristics of precursors of humification are formed, while under aerobic conditions, active transformation of SOM occurs with the formation of “mature” humic substances. The HA samples formed on sandy and carbonate-containing rocks are distributed in different parts of the graph, which indicates different trajectories of SOM formation depending on the lithological conditions and land use.

4. Limitation of Research

The limitations of this study include the local organization of the research; this is due to the high mosaic pattern of the relief and agricultural practices carried out in Leningrad Oblast. Most of the fallow territories in the region were withdrawn from agricultural use more than 30 years ago; therefore, the studied areas are of particular value from the standpoint of studying soil transformation at the early stages of the fallow state. Nevertheless, as a result of the high connectivity of the territory, the obtained results may be relevant for areas of fallow lands located within the humid zone of the southern taiga.

5. Conclusions

This comprehensive study of physicochemical parameters of soils, stocks of SOM and nitrogen, as well as the molecular structure of HAs and MAOM parameters at five key sites of fallow soils in the Leningrad region reveals the determining role of local soil formation conditions in the direction and rate of post-agrogenic transformation. The main factors influencing soil transformation and the molecular structure of SOM are the degree of hydromorphism and the lithological composition of parent materials. The analysis of physicochemical parameters revealed a clear differentiation in acid–base conditions and particle size distribution in studied soil samples. The most acidic conditions (pH 3.4–4.2) were noted in areas with heavy texture class and signs of gleying processes, for soils formed in waterlogged conditions (V1 and V2), due to anaerobic conditions and low rates of SOM transformation. In contrast, a neutral pH (6.8–7.5) formed in the soil on carbonate materials (V5). Sandy soils under hayfield (V3) and fallow soils (V4) occupied an intermediate position with a slightly acidic reaction. Carbon and nitrogen stocks in the meter-thick layer showed that the maximum amount of carbon was accumulated in the soil profile of fallow territories (V4—21.4 kg/m²), which was associated with the active accumulation of fresh SOM in the early stages of the fallow state and its transformation in aerobic conditions. However, the greatest change from 0–30 cm to the 30–100 cm occurs in V1, due to the downward movement of C in waterlogged conditions. The highest nitrogen stocks were noted in the soil forming on carbonate materials (V5—1.46 kg/m²), due to the high biological activity of soils and the accumulation of mineral-bound nitrogen. Based on the C/N ratio, it was noted that the widest ratio (up to 27.49) was observed in waterlogged areas V1 and V2, where coarse humus forms accumulated and rates of nitrogen accumulation were slowed.

The proportion of MAOC in the total SOC pool varied significantly between soils, from 41.9% to 96.8%. In Gleyic Anthrosol, MAOC was predominant (96.8% of SOC). This value significantly exceeds typical indicators for Umbric Podzol and indicates a deep transformation of SOM during long-term anthropogenic impact, followed by stabilization under fallow conditions. In the remaining soils, the proportion of MAOC ranged from 41.9% (Endocalcaric Luvisol) to 58.7% (Entic Podzol), which falls within the range of values characteristic of soils in the taiga–forest zone. The proportion of MAON in the total TN pool turned out to be higher than the proportion of MAOC in SOC, ranging from 53.2% (Endocalcaric Luvisol) to 79.4% (Gleyic Anthrosol). In all the studied soils, more than half of the total nitrogen was in a stable mineral-associated form. The results of elemental analysis and ¹³C NMR spectroscopy of HAs showed that HAs isolated from soils forming on carbonate materials were characterized as the most “mature,” which was due to the high concentration of aromatic structural fragments (AR/AL = 0.79), high oxygen concentration (37.5%), and carboxyl groups (15%), which determined the high functionality and resistance of HAs to biodegradation. In contrast, in soils with a high level of hydromorphism (V1 and V2), HAs retain the original structural characteristics of humification precursors and characterized by “low” maturity. HAs isolated from fallow land soils on outwash sands (V4) occupied an intermediate position, due to the active formation and humification of SOM. HAs isolated from hayfield soils (V3) were characterized by a high concentration of aromatic structural fragments, but with a low nitrogen concentration in the HAs, which is due to active agricultural activity, during which condensation of natural compounds occurs under conditions of periodic biomass removal.

The conducted study shows that the direction of transformation of lands and SOM in the early stages of fallow state (up to 10 years) is primarily determined by local soil formation factors. The presence of carbonates in the parent materials contributes to the formation of “mature” and oxidized SOM, providing a high potential for fertility and re-

sistance to biodegradation. In contrast, a high degree of hydromorphism leads to the conservation of SOM, which retains the original form of humification precursors. The studied soil environments exhibited contrasting patterns of SOM accumulation and stabilization. Waterlogged soils showed substantial MAOC while retaining predominantly aliphatic fragments, soils formed on carbonate materials contained more mature SOM with structural features indicative of greater resistance to decomposition, whereas sandy soils under meadow vegetation accumulated the largest carbon stocks but contained HAs relatively enriched in carbohydrate and other aliphatic structures, highlighting the distinction between carbon accumulation and molecular maturation. The obtained results emphasize that predicting the short-term evolution of fallow soils is impossible without considering the features of the lithological composition of soils and parent materials, which set the trajectory of SOM transformation at the molecular level.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

SOM	Soil organic matter
HAs	Humic acids
IUSS WRB	International Union of Soil Sciences World Reference Base for Soil Resources
NMR	Nuclear magnetic resonance
MAOC	Mineral-associated organic carbon
MAOM	Mineral-associated organic matter

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