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Changes in Organic Carbon in Mineral Topsoil of a Formerly Cultivated Arenosol under Different Land Uses in Lithuania

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Abstract: This study aims to determine the differences in the organic carbon, humic acid (HA), and fulvic acid (FA) concentrations in the A and AB horizons, depending on land use, in order to determine the influence of the land use on the soil organic carbon (SOC) sequestration rate in the A horizon, and to assess the impact of the land use on the quality of the humic substances (HS) (the humification rate (HR) and the HA/FA ratio). On the basis of the data of 1995–2018, it would be expedient to convert cropland (CL) areas to fertilized managed grassland (MGfert) in order to increase the SOC accumulation (28%) in the Arenosol. In the unfertilized managed grassland (MGunfer) areas, the SOC accumulation in the A horizon was similar to that in the MGfert (p > 0.05); however, significantly less (−45.0%) HAs were formed, the HR decreased 2.8%, and the HA/FA ratio was 1.12%. This means that less stable humic substances were formed in the MGunfer soil. In the Arenosol, the fastest SOC sequestration took place in the AL and PP areas, the annual SOC stocks increased by 393 and 504 kg ha\(^{-1}\) year\(^{-1}\), respectively, and the HR increased to 19.1–21.3% (CLfert: 11.9%). However, these types of land use produce more FAs (14.5 and 32.5% more, respectively, compared to the MGfert, and 36.3 and 57.7% more, respectively, compared to the CLfert), which can lead to soil acidification and can accelerate eluvial processes. Because of the faster leaching of the FAs from the upper layers of the A horizon to the AB horizon, the humus type changes from humate–fulvate in the A horizon, to fulvate–humate in the AB horizon.

Keywords: humic acids; fulvic acids; humification rate; soil horizon

1. Introduction

By the renunciation of the use of infertile cropped land for agricultural production, and by the conversion of it into other types of land use, the main goal is to stop soil degradation by increasing the SOC sequestration in the soil, as organic carbon is an important component for the functioning of agro-ecosystems [1–3]. SOC is the carbon that is stored in soil organic matter (SOM). The SOM has two fundamental groups. One group represents about 10 to 15% of the SOC reserves in mineral soils, which consist of the decomposition products of organic residues and the microorganisms’ metabolisms [4]. Another group represents 85 to 90% of the SOC reserves, and it is composed of humic substances, with an emphasis on humic acid, fulvic acid, and humin [5]. According to the classic approach, humic substances have been classified into three fractions on the basis of water solubility: humic acid (HA)-insoluble under acidic conditions (pH < 2), but soluble at a higher pH; fulvic acid (FA)-soluble at all pH conditions; and humin, for which the fraction is not soluble in water at any pH value [6]. As the organic carbon content in soil increases, the sorption properties and the water regime improve significantly, and CO\(_2\) emissions decrease [7–9]. The efficiency of the conversion of cropped land areas to another type of land use to accumulate SOC depends on both the soil conditions and the climatic factors that influence the formation of the plant biomass, its further destruction in the soil, and the conditions for the formation of HS [10–12]. It has been found that global warming can accelerate the
mineralization of organic matter (OM), which, in turn, increases the CO₂ emissions from the soil profile [13]. Other researchers [14] point out that climate change may increase the OM mineralization in the upper soil layers, and that, therefore, it is important to focus the sequestration of HS in deeper horizons. The SOC accumulation and distribution in the soil profile is associated with various factors, which include the climate, the topography, the parent material, the soil properties (soil aggregation, texture, mineralogy), the interaction with organisms (vegetation, animals, soil biota), and the land use and management [15–20]. The transfer of organic carbon to deeper soil horizons may be due to the leaching of mobile organic compounds from the upper layers [21,22]. Depending on the soil, the climatic conditions, and the agrotechnical measures, the leaching of organic carbon may vary from 8 to 10 kg ha⁻¹ year⁻¹ [23] till 170 to 310 kg ha⁻¹ year⁻¹ [24]. The soil controls the accrual of the SOC, depending upon the rate of carbon mineralization, the amount and stage of the decomposition of plant residues, and the added organic input additions. The turnover times for various organic materials show that humus-carbon mineralizes slowly, and that, in this way, it accumulates in the soil [25]. The SOC stocks in arable soils can be increased by applying various types of organic fertilizers (manure, biochar, green manure) or by minimizing the tillage [26–28]. The conversion of arable land use into another type can affect the SOC stocks differently.

The scientific literature shows that the sequestration of HS takes place more actively in forest lands [29,30]. In certain soil and climatic zones, the SOC sequestration is more rapid in soils and meadows, where abundant perennial grass root volume is formed [31,32]. The authors of [33] found that, after the conversion of cropped land into cultivated meadow, the input of the plant residues and roots to the soil increases, which thus stabilizes the SOC stock in the topsoil, whereas a decrease in the SOC stocks is seen in the conversion of forest land to pasture, which is associated with lower OM deposition in the soil [34].

Changes in land-use systems can give rise to changes in the chemical, microbial, and physico-chemical properties of the soils, and can affect the quantity and quality of the OM that is incorporated into the system [35]. After the conversion of the land, changes also occur in the quality of the SOM. The higher input of plant residues in grassland was reflected in the changes in the chemical structure of the HAs. There is also conflicting evidence that not always converting cropland to plantation does not contribute to SOC sequestration in the short term. According to the authors of [36], the SOC stock of the 0–60 cm soil layer in the fertile alluvial plain decreased by 27.4–50.9% in the seventh year following the conversion of cropland to plantation. Similar data have been published by other researchers [37], who have found that, in semiarid Mediterranean conditions, the impact of the soil management on the humic composition was relatively low for subacid sandy soils. When assessing the impact of the land use on the SOC sequestration, it is important to evaluate both the changes in the organic carbon concentration in the humus horizon, and the change in its thickness during the period of the land-use conversion. The SOC stocks across the A horizon more accurately reflect the land-use potential to accumulate OM in soil, compared to the organic carbon concentration, as the thickness of the A horizon may increase because of the leaching of HS from the upper layers. An analogous opinion has been published by other researchers [38]. In addition, when transported to deeper soil horizons, organic carbon contributes to the subsoil carbon storage and the stability of the HS [39]. The SOC has different stocks and fractions, with varying degrees of decomposition rates and stabilities. HS are traditionally defined according to their solubilities. HAs are macromolecules, and they differ from the other HS fractions (fulvic acid and humins) in that they are soluble in alkaline media, partially soluble in water, and insoluble in acidic media [40]. Fulvic acids (FAs) mainly exist in soil as small molecules that form molecular aggregates or associations in solutions, and that are soluble in water at all pH values [41]. The carbon in the fulvic acid fraction has great solubility in acid and basic environments, it can be easily leached, and it is also distributed more evenly between the soil layers [42]. Therefore, the carbon in the fulvic acid fraction presents lower concentrations between the humic soil fractions [43]. The carbon in the humin fraction is associated with the mineral
soil fraction, and it shows strong resistance to microbial activity [44]. The carbon in the humic acid fraction and in the humin is more recalcitrant, with a greater stability and presence in unchanged soils [45,46].

Moreover, the HA/FA ratio can be considered as an index of the humification of the SOM. This index of humification indicates the potential mobility of the carbon in the soil system and a lower intensity of humification. The lower HA/FA ratio means the lower humification index of the SOM, which may be driven by edaphic processes, soil management, and the recent input of OM [47,48]. The ratio of alkali-extractable carbon, mainly HAs and FAs, and SOC, has been called the “humification ratio”. The polymers in humic compounds other than FAs and HAs (i.e., humin) are generally stable and are resistant to microbial attack [49]. Therefore, a low (HA+FA)/SOC ratio usually indicates a high degree of humification. According to the authors of [50], HAs and humin determine the relative stability of the soil, and, therefore, changes in the HS quality should be considered when assessing the impact of land-use changes on the stability of organic carbon compounds.

We hypothesized that the conversion of arable land to forest plantation or grassland (managed grassland, abandoned land) would increase the ability of the soil to uptake and hold the soil organic matter in the Arenosol, which would affect the soil-forming processes of the deeper A horizon, and the amount of resistance to the decomposition humic substances would also increase. The aim of the research was to determine the quantitative and qualitative differences in the SOC accumulation and in the formed humic substances after the conversion of cropped land to other land uses (abandoned land, pine plantation, fertilized managed grassland, unfertilized managed grassland) in the humic (A) and AB horizons in the Arenosol.

2. Materials and Methods

2.1. Experimental Site Description

The long-term experiment (began at the beginning of 1995) was conducted at the Lithuanian Research Centre for Agriculture and Forestry (54°33′49.8″ N; 25°05′12.9″ E) on Endocalcaric Arenosol. The study was conducted in Lithuania (the East Baltic region), which is a part of Central Europe. From the geomorphological point of view, the survey sites were located in the area, the surface of which consists of binary rocks: fluvial and Grūda stage washed moraine sandstone. The relief is a slightly undulating plain. These regions are characterized by a moderate climate, with a mean long-term (1981–2010) annual precipitation value of 685 mm, and an annual mean air temperature of 6.7 °C (the standard climate norm (SCN)) [51]. These hydrothermal conditions are conducive to the precipitation filtration and leaching of biogenic elements from the upper soil layers. The soil was formed on fluvial deposits, and it has the following profile: Ap-AB-B1-B2-1C-C2 [52]. Over a period of 23 years, the Ap changed into Ah in the managed grassland, the abandoned land, and the pine plantation. Moreover, during the experiment period, a 3–4 cm forest floor horizon (O-Ah-AB-B1-B2-1C-C2) was formed in the pine plantation. At the depth of 80–100 cm, the carbonate gravel horizon begins, with the number of carbonates increasing around 7.69–10.07%. The upper part of the profile consists of noncarbonate sand, and the lower parts consist of carbonate pebbles and cobbles. At the beginning of the experiment, the upper part of the profile was transformed by agrogenic activity.

2.2. Field Investigation

The experiment included four sites of different land uses: cropland (CL); managed grassland (MG); abandoned land (AL); and pine plantation (PP). The total plot of each land use site was 400 m² (20 × 20 m). The CL and MG sites were divided into two subplots: unfertilized sites and fertilized sites (CLfert, CLunfert, MGfert, MGunfert) (200 m²).

Cropland site: From 1995 to 2018, various agricultural plants were cultivated in the CL. During this period, the crop rotation was used to improve the physical, chemical, and biological conditions of the soil (Table 1). In the CLfert subplot, the plants were fertilized...
with mineral NPK fertilizers, according to the nutrient needs of the plants and the available plant phosphorus and potassium concentration statuses in the soil: the average for N was 0–100 kg ha\(^{-1}\), the average for P was 13–26 kg ha\(^{-1}\), and the average for K was 25–100 kg ha\(^{-1}\). In 1995 and 2000, the fertilized cropland soil was fertilized with 40 t ha\(^{-1}\) of manure. No further organic fertilization was applied.

Table 1. Crop rotation plants during 1995–2018.

| Crop Species % | Plants Species | Growing Year |
|----------------|---------------|--------------|
| 29.2           | Cereals       | 1995, 1999, 2003, 2010, 2014, 2017 |
|                | Secale cereale L. | 2001         |
|                | Triticosecale Witbank |        |
| 12.5           | Cereal crops with perennial legume undercrop | 1997, 2008, 2018 |
|                | Hordeum vulgare L., Triticum aestivum L. |        |
| 16.7           | Polygonaceae  | 2007, 2011, 2012, 2015 |
|                | Fagopyrum esculentum Moench |        |
| 12.5           | Perennial legume plants | 1998, 2002, 2009 |
|                | Trifolium pratense |        |
| 12.5           | Row plants    | 1996, 2000, 2004 |
|                | Solanum tuberosum L. |        |
| 12.5           | Other plants  | 2006         |
|                | Brassica napus L. |        |
|                | Lupinus angustifolius L. | 2013 |
|                | Lupinus angustifolius L and |        |
|                | Hordeum vulgare L. for green manure | 2016 |
| 4.1            | Fallow        | 2005         |

Managed grassland: A grass–legume mixture was grown in the MG site. From 1995 to 2006, it included hybrid lucerne (Medicago varia L.) (40%), and four species of grasses: 20% red fescue (Festuca rubra L.); 20% bromegrass (Bromus inermis Leyss.); 10% cock’s-foot grass (Dactylis glomerata L.); and 10% meadow-grass (Poa pratensis L.). In 2007 and in 2015, the grasses were reseeded. The same grass mixture was grown from 2007 to 2018, since the 2007 cock’s-foot was replaced by timothy (Phleum pratense L.). The grasses in the MGfert site had been fertilized with N\(_{90}^+\)P\(_{30}^+\)K\(_{120}^+\) since 1995.

Abandoned land and pine plantation: No agrotechnical activities were performed in the AL and PP sites. During the study period, a natural vegetation phytocenosis, which is typical of the sandy soils in this region, was formed on the AL site. The botanical composition of the phytocenosis varied, depending on the hydrothermal conditions of the growing season. In the AL site in July, the grass was cut, and the biomass was left on the soil surface [53,54]. Scot’s pine (Pinus sylvestris L.) was grown in a PP site. In 1995, 10,000 seedling ha\(^{-1}\) had been planted. After thinning in 2009 and in 2015, the tree density was 3509 trees ha\(^{-1}\).

2.3. Soil Texture and Chemical Properties

The chemical and physical properties of the soil were determined before the experiment was set up (1995), and in 2018. The particle sizes of the mineral soil samples were determined in the A (0–20 cm) and AB horizons, according to the FAO [55]. In the A horizon, the content of the sand particles (2000–63 \(\mu\)m) was 80.7–83.8%, the content of the silt particles (63–2 \(\mu\)m) was 11.8–14.3%, and the content of the clay particles was 4.5–5.4%. The amount of sand particles ranged from 80.7 to 83.8% in the A horizon, to from 85.5 to 90.2% in the AB horizon, and the silt particles ranged from 11.2 to 14.3% to 3.5 to 9.7%,
respectively. The amount of clay particles in the AB horizon changed marginally compared to in the A horizon. According to the texture and diagnostic horizon properties, the soil belongs to the coarse sand, Arenosol \[52\].

Until 1995 (for more than 50 years), the soil of the experimental area was used as cropped land, various agricultural crops were cultivated, and mineral and organic fertilizers and liming (the last time in 1984) were applied. Under the influence of the agrotechnical measures that were applied, before the establishment of the experiment (1995), the soil reaction was neutral or nearly neutral (pH \(K\text{Cl} 6.0–6.8\)), it was moderately rich in mobile phosphorus (157–188 mg \(P_2O_5 \text{ kg}^{-1}\)) and potassium (170–194 mg \(K_2O \text{ kg}^{-1}\)), and the organic carbon concentration ranged from 9.5 to 9.9 g kg\(^{-1}\) (Table 2). The carbon-and-nitrogen ratio (C:N) in 1995 ranged from 12.5 to 13.6, and it was favorable for the transformation of the organic matter in the soil (Table 2). After the land-use conversion from cropland to other types of land use, which took place over 23 years, the chemical soil properties differentiated, depending on the applied agronomic measures of the land use. The soil pH decreased to 5.5–5.9 pH at the PP and MGfert sites. Without fertilizer application, the mobile phosphorus and potassium concentrations decreased in the CLunfert, MGunfer, and PP soils. The organic carbon concentrations in the PP, AL, and MGfert soils increased. In 2018, the C:N ratio ranged from 11.7 to 14.4.

Table 2. Arenosol topsoil (0–25 cm) chemical properties (1995 and 2018).

| Under Land Use | Year | SOC g kg\(^{-1}\) | Available \(P_2O_5\) mg kg\(^{-1}\) | Available \(K_2O\) mg kg\(^{-1}\) | pH\(K\text{Cl}\) | C:N Ratio |
|---------------|------|-----------------|-----------------|-----------------|----------------|------------|
| PP            | 1995 | 9.7 ± 0.08      | 168 ± 4.88      | 192 ± 4.67      | 6.0 ± 0.08    | 12.9       |
|               | 2018 | 12.2 ± 0.10     | 133 ± 11.5      | 128 ± 9.7       | 5.5 ± 0.38    | 14.4       |
| AL            | 1995 | 9.9 ± 0.08      | 157 ± 4.88      | 170 ± 4.67      | 6.0 ± 0.08    | 13.6       |
|               | 2018 | 11.0 ± 0.75     | 158 ± 18.5      | 163 ± 11.8      | 6.3 ± 0.06    | 12.9       |
| MGunfert      | 1995 | 9.9 ± 0.08      | 177 ± 4.88      | 174 ± 4.67      | 6.8 ± 0.08    | 13.3       |
|               | 2018 | 9.8 ± 0.40      | 71 ± 13.5       | 80 ± 5.7        | 6.1 ± 0.10    | 12.1       |
| MGfert        | 1995 | 9.9 ± 0.08      | 177 ± 4.88      | 174 ± 4.67      | 6.8 ± 0.08    | 13.3       |
|               | 2018 | 14.2 ± 0.43     | 208 ± 18.5      | 168 ± 9.1       | 5.9 ± 0.40    | 13.4       |
| CLunfert      | 1995 | 9.5 ± 0.08      | 188 ± 4.88      | 194 ± 4.67      | 6.0 ± 0.08    | 12.5       |
|               | 2018 | 8.9 ± 0.15      | 118 ± 19.3      | 98 ± 5.5        | 6.4 ± 0.15    | 13.5       |
| CLfert        | 1995 | 9.5 ± 0.08      | 188 ± 4.88      | 194 ± 4.67      | 6.0 ± 0.08    | 12.5       |
|               | 2018 | 8.3 ± 1.10      | 229 ± 26.8      | 185 ± 23.3      | 6.4 ± 0.25    | 11.7       |

Note. Abbreviations: PP: pine plantation; AL: abandoned land; MGunfert: managed unfertilized grassland; MGfert: managed fertilized grassland; CLunfert: unfertilized cropland; CLfert: fertilized cropland; SE: standard error. AL, MGunfert, and CLunfert subplots were unfertilized; MGfert and CLfert subplots were fertilized.

The soil C:N of intensely cultivated soils is generally expected to produce a lower soil C:N compared to the uncultivated soils, based on the same source \[56\]. Accordingly, the soil C:N classification is: optimal conditions (9 ≤ C:N ≤ 12); dominant oxidation (C:N < 9); and nitrogen deficiency (C:N > 12).

2.4. Soil Sampling and Analysis

Prior to soil sampling, profiles were excavated at three locations in each type of land use (in a 20 m × 20 m grid), to a depth of 50 cm, in order to accurately determine the depths of the A and AB horizons in each type of land use, and to determine the soil bulk density and the soil chemical properties. Composite soil samples were taken in 2018 from mineral topsoil for an analysis of the soil humic substances (organic carbon, HAs, and FAs) in each type of land use, with three replicates from three depths: 0–20 cm (A horizon: Layer 1); from 20 cm to the beginning of the AB horizon (A horizon: Layer 2); and from the AB horizon (Table 3). Such sampling allowed for a more accurate estimation of the distribution of the humic substances in the A horizon 23 years after the land conversion, and for the
assessments of their accumulation differences to the AB horizon in different types of land use, as well as for a more accurate calculation of the HS (organic carbon, HAs, FAs) stocks in the A horizon, taking into account their concentration differences at different depths of the A horizon, as well as the thickness of the A horizon. The soil samples were air-dried, gently crushed, and were passed through a 2 mm mesh sieve. During the soil sample preparation, coarse material (roots and litter) was removed.

**Table 3.** Soil sampling over A and AB horizons of Arenosol in different land-use sites.

| Under Land Use | Soil Sampling over Depths (cm) |
|---------------|-------------------------------|
|               | A Horizon: Layer 1 | A Horizon: Layer 2 | AB Horizon |
| PP            | 0.0–20.0             | 20.0–32.0           | 32.0–37.0 |
| AL            | 0.0–20.0             | 20.0–30.0           | 30.0–36.3 |
| MGUnfert      | 0.0–20.0             | 20.0–28.8           | 28.8–34.6 |
| MGfert        | 0.0–20.0             | 20.0–29.0           | 29.0–34.5 |
| CUnfert       | 0.0–20.0             | 20.0–28.8           | 28.8–35.5 |
| Cfert         | 0.0–20.0             | 20.0–25.2           | 25.2–32.5 |

Note. Abbreviations: PP: pine plantation; AL: abandoned land; MGUnfert: managed unfertilized grassland; MGfert: managed fertilized grassland; CUnfert: unfertilized cropland; Cfert: fertilized cropland. AL, MGUnfert, and CUnfert subplots were unfertilized; MGfert and Cfert subplots were fertilized.

The soil bulk density was determined at the beginning of the experiment (1995) and in 2018 by the Core method by using a metal ring pressed into the soil (intact core), and by determining the weight after drying [57].

The soil particle-size distribution was obtained using the particle-size analysis method (ISO: 11277:2009).

The total N of the soil was determined (ISO: 11261:1995), by the Soil Quality—Determination of Total Nitrogen—Modified Kjeldahl Method.

The plant available P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O were extracted using 0.03 M of ammonium lactate (the Egner–Riehm–Domingo (A–L) method [58]).

The SOC concentration of the soil was determined by ISO: 10694:1999 (the Duma method, after dry combustion). For the humic and fulvic acid analyses, the SOM was fractionated into HA and FA fractions, according to the Ponomareva and Plotnikova [59] version of the classical Tyurin method. The organic C contents of the isolated HA and FA was determined by the spectrophotometric procedure, at a wavelength of 590 nm, by using glucose as a standard after wet combustion, according to Nikitin [60].

Ten grams of each soil sample, air-dry sieved (≤ 2 mm), was weighed into a 250 mL plastic centrifuge bottle, 200 mL 0.5 M of NaOH was added, and it was shaken overnight. Then, the sample was centrifuged at 2000× rpm for 20 min to allow the sedimentation of the insoluble humin, and all of the supernatant was decanted into a clean centrifuge bottle. The solution was adjusted to a pH of 2.0, with 6 M HCl, and was then centrifuged at 2000× rpm for 20 min in order to cause the sedimentation of the HA. The solution of FA was decanted into a 250 mL volumetric flask. Continuing procedure: Then, the sediment of HA was washed with 30 mL 0.5 M HCl and centrifuged, supernatant was added to the volumetric flask, and made up to the mark with water and mixed. The optical density was read at 465 nm, and it was diluted, if necessary, to bring on scale. The HA was washed out of the centrifuge bottle into a preweighed oven-dry 100 mL glass beaker. The sample was carefully evaporated to dryness on a hotplate, avoiding loss by spitting, and was cooled in desiccator and reweighted. The difference in weights gave the weight of the HA plus ash. The sample was combusted in a muffle furnace at 500 °C overnight to burn off the HA fraction, it was cooled in a desiccator, and then the beaker containing the residual ash was reweighed.

The soil organic carbon (SOC) stocks in the A horizon were calculated as follows [61,62]:

\[
\text{SOC stock (t ha}^{-1}\text{)} = (\text{SOC}_{\text{con}1} \times \text{BD} \times \text{depth}_{1} \div 10) + (\text{SOC}_{\text{con}2} \times \text{BD} \times \text{depth}_{2} \div 10),
\]

where SOC<sub>con1</sub> is the SOC concentration (g kg<sup>−1</sup>) in the 0–20 cm layer; SOC<sub>con2</sub> is the SOC concentration (g kg<sup>−1</sup>) from 20 cm to the AB horizon layer; BD is the bulk density of
the soil (t m$^{-3}$); depth1 is the thickness of the 0–20 cm soil layer; depth2 is the thickness of the layer from 20 cm to the AB horizon; and 10 is the coefficient to calculate the SOC stocks in t ha$^{-1}$. The HA and FA stocks in the A horizon were calculated analogously.

In order to quantitatively evaluate the OM and HS, the following parameters were calculated [63]:

The humification rate (HR) (HR = 100 × (HAs + FAs)/ SOC), where HAs is the humic acid concentration (g kg$^{-1}$); FAs is the fulvic acid concentration (g kg$^{-1}$); and SOC is the soil organic carbon (g kg$^{-1}$).

The humic and fulvic acid ratio (HA/FA), where HAs is the humic acid concentration (g kg$^{-1}$) in the soil; and FAs is the fulvic acid concentration (g kg$^{-1}$) in the soil.

The HA/FA ratio, as an index for the polymerization and condensation of the OM decomposition products, was calculated to assess the changes in the SOC quality [64,65]. The relationship between the concentrations of humic and fulvic acids (the HA/FA ratio) is indicative of the potential mobility of the C in the soil system. The humification rate (HR) was also calculated for each land use in order to further characterize the HS quality [64,66]. The humification ratio offers an alternative way to evaluate the quality and stability of the humus.

2.5. Statistical Analysis

All the data presented in the tables are the mean values of the three replicates for each sampling point. A one-factor analysis of variance (ANOVA) was performed to determine the treatment effects (different land-use types and different soil layers) of the resulting data. The means of the main effects (the SOC concentration, the HA and FA concentrations, the SOC, HA, and FA stocks) were compared by Duncan’s multirange test at $p < 0.05$. Standard error (SE) was used to estimate the changes in the Horizon A thickness over the study period. Relationships between the organic carbon concentration and the granulometric composition of the soil were explored by using simple linear regression, and the coefficient of correlation (r) was used as an indicator that the equation fits for the data.

3. Results

3.1. SOC Concentration and Stocks

In the year of the experiment installation (1995), the SOC concentrations in the topsoil at all the sites of the different land uses were similar and amounted to 9.5–9.9 g kg$^{-1}$. After 23 years of different land use, both the SOC concentration in the A horizon and its thickness changed. The thickness of the A horizon increased most at the PP (+4.0 ± 0.58 cm) and AL (+3.0 ± 0.58 cm) sites. A small increase in the A horizon (0.8–1.0 cm) was also found in the MG and unfertilized CL areas. The thickness of the A horizon in the fertilized CL area decreased by 2.8 ± 1.09 cm over 23 years.

A total of 23 years after the conversion of the land use from CL to MG, AL and PP, the SOC concentrations in the soil changed, depending on the vegetation cover and the plant cultivation agrotechniques that were used. In 2018, in the 0–20 cm layer of the A horizon, a significantly higher SOC concentration (12.77 g kg$^{-1}$) was found at the MGfert site. In the other types of land use (PP, AL, MGunfert, CLunfert, and CLfert), the Corg concentrations ranged from 10.63 to 12.73 g kg$^{-1}$. The differences between these land-use types were insignificant statistically (Table 4).

At 20 cm deeper, and before the beginning of the AB horizon, the SOC concentrations ranged from 8.10 to 8.20 g kg$^{-1}$ in the CL soil, to from 9.97 to 10.10 g kg$^{-1}$ in the MG soil, and, compared to the 0–20 cm layer, they decreased by 1.90–3.53 g kg$^{-1}$, or 15.8–27.7%, on average. The decrease in the SOC concentration below 20 cm, compared to the 0–20 cm layer, is marked, but a statistically significant difference between these horizons was found only in the CLfert. The SOC concentration in the AB horizon decreased even more compared to that in the 0–20 cm layer: 3.20–5.86 g kg$^{-1}$, on average. A larger difference between these layers was found in the PP soil (−5.86 g kg$^{-1}$; $p < 0.05$) and the CLunfert soil (−5.66 g kg$^{-1}$; $p < 0.05$). However, despite the different SOC accumulations, after
23 years, no significant differences in the SOC concentrations in the AB horizons of the different types of land use were found.

Table 4. SOC concentrations (g kg\(^{-1}\)) in A and AB horizons in soils of different types of land use (2018).

| Under Land Use | SOC Concentration (g kg\(^{-1}\)) | A Horizon: Layer 1 | A Horizon: Layer 2 | AB Horizon |
|----------------|----------------------------------|--------------------|--------------------|------------|
| PP             | 12.73 AB c                       | 9.20 ABC abc       | 6.87 AB a          |
| AL             | 11.73 AB c                       | 9.13 ABC abc       | 7.13 AB a          |
| MGUnfert       | 12.00 AB c                       | 10.10 B c          | 6.60 AB a          |
| MGfert         | 12.77 B c                        | 9.97 AB abc        | 7.67 B a          |
| CLUnfert       | 10.63 AB c                       | 8.10 ABC c         | 4.97 AB a          |
| CLfert         | 10.70 AB b                       | 8.20 AB a          | 7.50 AB a          |

Note. Abbreviations: PP: pine plantation; AL: abandoned land; MGUnfert: managed unfertilized grassland; MGfert: managed fertilized grassland; CLUnfert: unfertilized cropland; CLfert: fertilized cropland. AL, MGUnfert, and CLUnfert subplots were unfertilized; MGfert and CLfert subplots were fertilized. Capital letters indicate differences among land uses within the same soil layer (in columns); lowercase letters indicate differences among soil layers within the same land use (in rows).

A relationship analysis of the soil texture and SOC concentration shows that the SOC concentration in the Arenosol depends not only on the type of land use, but also on the texture of the soil. A strong positive relationship between the SOC concentration and the silt particle content (\(r = 0.77\)) in the soil was found. The SOC concentration was not correlated with the clay, while the relationship with the sand particle content was negative (\(r = -0.83\)) (Figure 1).

The calculations of the SOC stocks in the whole A horizon, 23 years after the conversion of the arable land to other types of land use, indicate that, compared to the CLfert, during this period, they increased significantly in the PP soil (+11.6 t ha\(^{-1}\); \(p < 0.05\)) and in the herbaceous land uses (MG and AL; +5.3–9.0 t ha\(^{-1}\); \(p < 0.05\)). The SOC accumulation in the MG and AL sites was similar to in the PP site, and no significant differences were found between them (Figure 2). The use of mineral fertilizers in the CL and MG areas slightly reduced (\(p > 0.05\)) the SOC accumulation in the A horizon, compared to the unfertilized soil in these types of land use.

Figure 1. Dependence of organic carbon concentration (g kg\(^{-1}\)) on soil particle size. (a) sand particle (2000–63 µm); (b) silt particle (63–2 µm); (c) clay particle (<0.002 mm).
3.2. Organic Carbon Quality

As a result of the conversion of cropland to other types of land use, not only amount of organic carbon, but also the quality of their chemical composition has changed. Depending on the type of land use, the concentration of humic acids in the Arenosol was 6.25–12.69% of the total SOC concentration in the A horizon. The lowest HA concentration was found in the CL area: it averaged 0.70–0.77 g kg\(^{-1}\) in the 0–20 cm layer (Table 5). The HA concentration in the 0–20 cm layer was significantly higher (1.97 g kg\(^{-1}\), \(p < 0.05\)) in the PP soils compared to in the CLfert soil.

**Table 5.** Humic acid concentrations (g kg\(^{-1}\)) in different layers of soil of different types of land use.

| Under Land Use | A Horizon: Layer 1 | A Horizon: Layer 2 | AB Horizon |
|----------------|--------------------|--------------------|------------|
| PP             | 1.97 D b           | 0.77 ABC a         | 0.20 C a   |
| AL             | 1.60 BCD c         | 0.73 ABC b         | 0.13 ABC a |
| MGUnfert       | 1.10 AB c          | 0.50 ABC abc       | 0.10 A a   |
| MGfert         | 1.60 BCD c         | 0.87 C abc         | 0.10 A a   |
| CLunfert       | 0.70 A c           | 0.53 ABC c         | 0.10 A a   |
| CLfert         | 0.77 A c           | 0.30 A abc         | 0.10 A a   |

Note. Abbreviations: PP: pine plantation; AL: abandoned land; MGUnfert: managed unfertilized grassland; MGfert: managed fertilized grassland; CLunfert: unfertilized cropland; CLfert: fertilized cropland. Capital letters indicate differences among land uses within the same soil layer; lowercase letters indicate differences among soil layers within the same land use.

The conversion of CL to grassland use (MG and AL) induced the formation of HAs in the soil; however, only in the MG site that was fertilized with mineral fertilizers and in the AL soil did their concentrations increase significantly (\(p < 0.05\)). The deeper HA concentrations (from 20 cm to the beginning of the AB horizon) decreased in all the types of land use to 0.30–0.87 g kg\(^{-1}\), or 24–74%. Compared to the CL area, significantly more (\(p < 0.05\)) HAs were formed in this layer only in the MGfert soil. Their concentrations in the
other types of land use (MGunfert, AL, PP) were increased; however, the differences were insignificant \((p > 0.05)\). The HA concentrations in the AB horizon decreased by 86–94\%, compared to those in the 0–20 cm layer. Significantly higher HA concentrations \((p < 0.05)\) in this layer were found only in the PP area, compared to the CL.

The HA stocks averaged 2.31–2.60 t ha\(^{-1}\) in the A horizon of the CL soil (Figure 3). The accumulation of HAs in the soil was mostly increased by the conversion of CL to PP. A total of 6.10 t ha\(^{-1}\) of HAs was accumulated in the A horizon of this land use. Compared to the CLfert, their stocks increased 2.6 times \((p < 0.05)\). The conversion of CL to herb land use led to the formation of HAs only in the MG site that was fertilized with mineral fertilizer and in the AL soil \((p < 0.05)\). Compared to the CLfert soils, their concentrations increased 2.30 and 2.40 times, respectively.

![Figure 3. Humic and fulvic acids stocks (t ha\(^{-1}\)) in A horizon. Note. Abbreviations: CLfert: cropland fertilized; CLunfert: cropland unfertilized; AL: abandoned land; MGfert: managed fertilized grassland; MGfert: managed fertilized grassland; AL: abandoned land; PP: pine plantation. Lower-case letters indicate HA and FA stock differences among land uses.](image)

Depending on the type of land use, the FA concentration in the upper 0–20 cm layer varied in the range of 0.40–0.73 g kg\(^{-1}\) (Table 6). The formation of FAs in the soil was stimulated only by the conversion of arable land to PP. Compared to the CLfert, their concentration in the 0–20 cm layer increased by 46\%. Below 20 cm, the FA concentration decreased significantly, by 17.6–42.1\% \((p < 0.05)\), only in the herb land use (MG, AL). A significant decrease in the amount of FAs, compared to the 0–20 cm layer, was found only in the AB horizon (except for the CLunfert). However, no significant differences were found between any types of land use in this layer after 23 years.

Because of the different thicknesses of the A horizon, the FA accumulation in the different types of land use varied. Their reserves in the CL area amounted to 1.52–1.68 t ha\(^{-1}\). The conversion of CL to MG increased the FA stocks; however, the difference from the CL area was insignificant \((p > 0.05)\). Their concentrations increased significantly only in AL and PP soils, compared to the CL area \((p < 0.05)\).
Table 6. Concentration of fulvic acids (g kg\(^{-1}\)) in different layers of soil of different land uses.

| Under Land Use | Fulvic Acid Concentration (g kg\(^{-1}\)) |
|---------------|-----------------------------------------|
|               | A Horizon: Layer 1 | A Horizon: Layer 2 | AB Horizon |
| PP            | 0.73 D c            | 0.50 D c            | 0.23 B a   |
| AL            | 0.63 BCD c          | 0.37 AB b           | 0.17 AB a  |
| MGunfert      | 0.53 AB c           | 0.40 BCD b          | 0.13 AB a  |
| MGfert        | 0.57 BCD c          | 0.47 BCD b          | 0.20 AB a  |
| CLunfert      | 0.40 A c            | 0.33 AB c           | 0.13 AB c  |
| CLfert        | 0.50 AB c           | 0.40 ABCD c         | 0.10 AB a  |

Note. Abbreviations: PP: pine plantation; AL: abandoned land; MGunfert: managed unfertilized grassland; MGfert: managed fertilized grassland; CLunfert: unfertilized cropland; CLfert: fertilized cropland. AL, MGunfert, and CLunfert subplots were unfertilized; MGfert and CLfert subplots were fertilized. Capital letters indicate differences among land uses within the same soil layer; lowercase letters indicate differences among soil layers within the same land use.

The ratio of HAs to FAs in the 0–20 cm layer depended on the type of land use. It was the lowest in the CL soil (1.18–1.54) (Figure 4). When the CL was converted to herb land use or to PP, more HAs were formed in the soil, and the HA/FA ratio increased to 2.54–3.2. Relatively more HAs are formed in the MGfert soil and, thus, the HA/FA ratio is found to be the highest (3.20) in this case. At deeper levels, from 20 cm to the beginning of the AB horizon, the HA/FA ratio decreased to 0.5–1.97.

The ratio of HAs to FAs in the 0–20 cm layer depended on the type of land use. It was the lowest in the CL soil (1.18–1.54) (Figure 4). When the CL was converted to herb land use or to PP, more HAs were formed in the soil, and the HA/FA ratio increased to 2.54–3.2. Relatively more HAs are formed in the MGfert soil and, thus, the HA/FA ratio is found to be the highest (3.20) in this case. At deeper levels, from 20 cm to the beginning of the AB horizon, the HA/FA ratio decreased to 0.5–1.97.

The HRs of the OM in the different land uses were also unequal. In the upper 0–20 cm layer, the lowest degree of humification (8.2–11.9%) was found in the CL land use (Figure 5). The conversion of CL to MG land use increased the HR of the OM humification only with the use of mineral fertilizers. The highest rates of OM humification (21.3 and 19.1%, respectively) were found in the PP and AL soils. Below 20 cm, depending on the type of land use, the HR decreased to 7.4–13.7%, but the differences between the land uses remained the same. In the horizon of AB, the HR was only 2.6–6.3%, and it decreased 2.4–4.6 times compared to the 0–20 cm layer.

![Figure 4. Ratio between humic and fulvic acids in soils of different types of land use. Note. Abbreviations: CLfert: cropland fertilized; CLunfert: cropland unfertilized; AL: abandoned land; MGunfert: managed unfertilized grassland; MGfert: managed fertilized grassland; AL: abandoned land; PP: pine plantation.](image-url)
The SOC sequestration in soil depends on a variety of factors, which include the soil texture. Different opinions can be found in the scientific literature on the relationship between the soil texture and the SOC sequestration. Some researchers [67,68] have found in their experiments that the SOC sequestration in the soil was related to the content of clay particles. It is said that the association between clay particles and soil organic carbon that forms clay–humic complexes plays a fundamental role in organic carbon protection against microbial oxidation. Other researchers [69] have not confirmed such a relationship in their experiments. Several studies [70] report that other physico-chemical parameters are much stronger predictors of the OM content, with the clay content having relatively little explanatory power. In their view, the exchangeable calcium strongly predicted the OM content in water-limited alkaline soils, whereas, with increasing moisture availability and acidity, iron- and aluminum-oxyhydroxides emerged as better predictors, which demonstrates that the relative importance of the OM stabilization mechanisms scales with the climate and the acidity. Our study data show that the SOC content in the Arenosol had a strong positive relationship with the silt particle content. This can be explained by the fact that there were very low contents of clay (4.7–5.9%) in the Arenosol, and such contents could not significantly change the sorption properties of the soil. The authors of [71] argue that the soil texture is merely one of the factors that contributes to the SOC sequestration in soil. Overall, it is the result of a complex interaction between abiotic and biotic factors.

The conversion of arable land to other types of land use in Arenosol alters the SOC accumulation, depending on the vegetation cover. The first 23 years after the land-use conversion, the sequestration of the SOC in the Arenosol took place the fastest in the PP; the SOC accumulation in this land use increased by 504.0 kg ha\(^{-1}\) per year, on average. The SOC stocks in the AL soils increased less annually compared to the PP soils, and they averaged 392.7 kg ha\(^{-1}\) per year. The SOC accumulation in the MG soil was slower, with an average annual increase in the stocks of 262.9–332.0 kg ha\(^{-1}\) as, unlike in AL, the aboveground grass biomass is used for feed, which reduces the input of the OM residues into the soil and, consequently, the rate of the SOC sequestration. Under similar climatic conditions (Latvia), no positive effect of the cultivated grasses on the SOC sequestration, compared to cropland, was found [72]. The data from our studies coincide with the data...
by the authors of [73] from a long-term experiment: they found that the SOC accumulated mainly in forest and pasture types of land use. Compared with cropland use over 130 years, the SOC stocks increased by 46 and 25%, respectively. The change in the SOC concentrations at three depths (0–20 cm; from 20 cm to AB horizon; AB horizon) indicates that it decreases gradually, as, in most cases, the differences in the concentrations between them were insignificant and were characterized only on the changing trends.

The qualitative analysis of the OM showed that the Arenosol was dominated by HAs with greater resistance to mineralization. The HA formation increased significantly after the conversion of arable land to the PP, AL, and MGfert. Without the use of fertilizers in the MG, the concentration of the HAs in the soil did not change significantly, which can be attributed to the lower amount of plant residues, compared to the fertilized MG land use. In all types of land use, the concentration of HAs decreased significantly in the AB horizon, and it was only by 6–14%, compared to its concentration in the 0–20 cm layer, which confirms their lower mobility in the soil. Having studied the quality of humic substances in arable and grassland soils in Central–Eastern Europe, the authors of [41] argue that labile and humified OM is better protected in grassland soils, and it is consequently less vulnerable to mineralization. The researchers [74] analyzed the influence of three different ecosystems (forest, pasture, and maize crop) on the formation of soil humic substances, and they found that the organic carbon and the humic and fulvic acid contents in the soil decreased in the following order: forest > pasture > maize. All of the attributes that were studied decreased significantly with the increasing soil depth, with the exception of the rate and degree of humification. Similar results were obtained in our experiment.

The FA concentration in the Arenosol was lower compared to that of HAs. Their concentration in the A horizon was 4.73–5.64% of the total SOC. A total of 23 years after the land-use conversion, the concentration of FAs in the topsoil (0–20 cm) increased significantly only in the PP soil, compared to the CLfert. An increase was also found below 20 cm and up to the AB horizon. This confirms that, in the PP soils, there is a more active formation of FAs compared to the other land uses (MG, AL, CL). According to the more formation of FAs in the PP soils, their leaching from the topsoil is going on as well. The authors of [75] argue that the qualitative changes in humus depend on the period that has elapsed after the land-use conversion. For example, they found that the FA content in the AL soil increased with increasing fallow periods for more than 20 years. Differences in the decreases in the HA and FA concentrations in the A and AB horizons prove that FAs leach out more intensively from the upper layers, compared to HAs, which results in a change in the type of humus formation in the subsoil.

Because of the variations in the concentrations and thicknesses of the A horizons, the HA accumulation in the A horizon differed significantly more in the different land uses compared to the SOC accumulation. More stocks of HAs (6.21 t ha$^{-1}$) were found in the PP soil, which was affected by the higher concentration and thicker A horizon in this land use. Compared to the CLfert, their stocks on the A horizon increased by 172%. The conversion of arable land to AL also promoted HA accumulation in the soil, but it was 13% lower ($p > 0.05$) compared to their accumulation in the PP soil. Compared to CL land use, grasses boosted HA stocks on the A horizon, but the differences were insignificant after 23 years. FAs also accumulated more in the PP and AL soils. Compared to the CLfert, their stocks on the A horizon increased by 57.7 and 36.3%, respectively ($p < 0.05$). The conversion of arable land to MG encouraged the accumulation of FAs, but the differences were insignificant. It can be stated that grassland and PP both stimulate SOC accumulation in soil, and more valuable humic substances with higher resistances to mineralization are formed. Similar data on the SOC accumulation in different types of land use have been published by other researchers [76]. The results of a long-term experiment (since 1995) in Germany show that the SOC in croplands and grasslands is characterized as easily degradable, but that it is more stable in grasslands under no-till conditions. Forest SOC appears almost nondegradable, and, thus, it is mostly stable in the long term. Mobile humic substances can be translocated to the B and C horizons by percolating water [77].
in the decreases in the HA and FA concentrations in the A and AB horizons prove that FAs leach out more intensively from the upper layers compared to HAs, which results in a change in the type of humus formation in the subsoil. Analogous data on the faster leaching of fulvic acids from the topsoil compared to humic acids have been published by other researchers [77–80]. By analyzing the changes in the HA and FA concentrations, and their stocks in the A horizon, after the conversion of CL to other types of land use, it can be noted that the grasslands and PP in Arenosols stimulated HA synthesis to a higher degree, while the FA concentrations varied less in the different types of land use. This fact may be related to the faster leaching of FAs from the top layer, as is evidenced by the smaller difference in the FA concentration between the 0–20 cm layer and the AB horizon, compared to the differences in the HA concentrations in the mentioned layers. The authors of [37] also studied the conversion of cropped land to forest, and they report that FAs were more leached from the upper layers compared to HAs, and that these processes were more active in sandy soils compared to sandy loam. The variation in the ratio of humic to fulvic acids in different land uses confirms the claim that, in the course of OM mineralization, more humic acids are formed in the forest and grassland land uses compared to the arable land use, which helps to improve the soil properties.

The HA-to-FA ratio characterizes the predominant processes of the OM transformation that reflects the mobility and quality of the SOM [81,82]. An HA/FA ratio near 1 is indicative of good-quality organic material that could enhance the soil physical properties and improve the plant growth [69]. The variation in the ratio of humic to fulvic acids in different land uses confirms the claim that, in the course of OM mineralization, more humic acids are formed in the forest and grassland land uses (HA/FA ratio: 2.68–3.20), compared to the arable land use (HA/FA ratio: 1.18–1.52), which helps to improve the soil properties. This may lead to an increased uptake of organic residues into the forest and grassland soils, which are likely to stimulate the soil microbial community activity to further humify the new C resources [83]. The opposite results were published by the authors of [37], who studied the influence of afforestation on the SOC content and the properties of the SOM in the mineral topsoil in the boreo–nemoral ecotone in Latvia. The results of their experiment did not confirm that afforestation stabilizes and promotes the formation of stable humic substances. In Arenosol, because of the faster leaching of fulvic acids, the HA/FA ratio in the layer deeper by 20 cm decreased to 0.50–1.97, and, in the AB horizon, it decreased to 0.5–0.87. It should be noted that, in the AB horizon, the differences in the HA/FA ratios in the different land uses were smaller compared to the 0–20 cm layer, which confirms the different mobilities of the humic and fulvic acids in the soil.

The humification rate offers an alternative way to evaluate the quality and stability of humus [84]. Humic acids (HAs) are macromolecules that comprise humic substances, and, because of their amphiphilic character, HAs form micelle-like structures in neutral-to-acidic conditions. Fulvic acids are the most reactive fractions, but with a lower chemical stability [6]. This indicates an unfavorable characteristic, which can facilitate cation leaching and the illuviation of humified clays in the form of organic complexes. The authors of [85] consider the FA and the light OM to be more sensitive to the changes that are caused by agricultural soil management than the SOC. The increase in both humus fractions in the soil increases its resistance to physical and chemical degradation [86–88].

Our data on the humification rate of OM also confirms that humification processes are faster in grasslands, compared to in CL (Figure 5). While the HR in the CL soil accounted for 8.2–11.9%, the MG increased to 13.6–16.4%. The HR was even higher in the AL and PP soils (19.1–21.3%, respectively), as the aboveground part of the herb grasses or tree litter mineralized on the soil surface in these types of land uses and replenished the HS reserves in the soil. At a depth greater than 20 cm, the HR decreased to 7.3–13.7%; however, it was also higher in the MGfert, AL, and PP soils. The HA and FA concentrations in the AB horizon decreased significantly, and the HR amounted to only 2.90–6.23%. A stronger influence of the forest and grassland land uses on the OM humification processes and the HA accumulation in soil was also found in other experiments [46,89,90].
5. Conclusions

The results of this study provide a more accurate assessment of the SOC sequestration processes in Arenosol after the conversion of cropped land to other types of land use (grassland and pine plantation) in a temperate climate zone, over a 23-year time period. On the basis of the data on the changes in the SOC accumulation and the OM quality, the ability of different types of land use to accumulate SOC in soil to form more stable and degradable humus substances was assessed. On the basis of the findings of the long-term experiment, it is expedient to change the land use from cropland to managed grassland, with mineral fertilizers in infertile Arenosols, in order to increase the SOC accumulation. Such conversion preserves the agricultural activity and increases the SOC sequestration in the soil by an average of 28%, compared to the fertilized cropland. With or without the use of fertilizers in managed grassland areas, the SOC accumulation in the A horizon takes place similarly; however, significantly less (−45.0%) HAs are formed, the HR decreases from 16.4 to 13.6%, and the HA/FA ratio decreases from 3.20 to 2.08. The evolution of these indicators confirms that, although the rate of SOC sequestration in the nonfertilized MG areas differs marginally from that of fertilized managed grassland, relatively more mobile FAs are formed, which are less resistant to mineralization, and which leach faster from the topsoil. The SOC sequestration is also intensive in the abandoned land and pine plantation areas, with the annual SOC stocks increasing by 393 and 504 kg ha\(^{-1}\) year\(^{-1}\), respectively. Humification processes are more active in the abandoned land and pine plantation areas, and the HR increases to 19.1–21.3%. However, these types of land use produce more FAs (14.5 and 32.5% more, respectively, compared to fertilized managed grassland, and 36.3 and 57.7% more, respectively, compared to fertilized cropland), which can lead to soil acidification, and which can accelerate eluvial processes. Because of the faster leaching of FAs from the upper layers of the A horizon to the AB horizon, the humus type changes from humate–fulvate in the A horizon, to fulvate–humate in the AB horizon.

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