

Article

Exploring the Influence of Natural and Agricultural Land Use Systems on the Different Lability Organic Carbon Compounds in *Eutric Endocalcaric Arenosol*

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Abstract: It is important to ensure the ratio of stable and labile soil organic carbon (SOC) compounds in the soil as this influences ecosystem functions and the sustainability of soil management. The aim of this investigation was to determine the changes in SOC compounds and soil quality improvement in Arenosol soil after the conversion of arable land to natural and agricultural land use. The land use types included pine afforestation (PA), uncultivated abandoned land (UAL), unfertilised and fertilised cropland (CLunf, CLf), and unfertilised and fertilised grassland (GRunf, GRf). To assess the lability of organic carbon (OC) compounds, levels of mobile humic substances (MHSs), mobile humic acids (MHAs), mobile fulvic acids (MFAs), active C pool (POXC), and water-soluble C (WEOC) compounds were determined. It was found that faster OC accumulation occurs in PA soil than in CLf, and is somewhat slower in grassland uses (GRf and UAL). As the amount of SOC increased, more MHS formed. A significant increase in their quantity was found in PA (+92.2%) and CRf and UAL (+51.5–52.7%). The application of mineral fertilisers promoted the formation of MHSs in CLf and GRf. PA, GRunf, and GRf soils had more suitable conditions for MHA formation (MHA/MFA > 1.3), whereas CLunf soil contained more MFAs. The POXC pool was insensitive to land-use changes in the Arenosol. After land-use conversion, POXC amounts were significantly ($p < 0.05$) higher in natural ecosystems (UAL and PA) and fertiliser perennial grasses than in CL. The amount of WEOC increased the most in UAL, PA, and GRf (7.4–71.1%). The sequence of decrease in land use was GRf, UAL, and PA > CLunf, CLf, and GRunf. The decreasing order of the carbon management index (CMI) of different land uses (PA > UAL > GRf > GRunf > CLunf) confirms that faster OC accumulation in Arenosol soil occurred in PA and grassland land uses (GRf and UAL). The values of the carbon lability index (CLI) variation (CLunf > GRunf GRf > UAL > PA) show that in PA, UAL, and GRf land uses, mobile organic matter (OM) forms are relatively less formed, which stabilises OC accumulation in the soil. The CMI showed that UAL and GRf were the most suitable soil uses for Arenosol soils.

Keywords: water extractable organic carbon (WEOC); permanganate oxidizable carbon (POXC); soil organic carbon (SOC); CMI; land-use change



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1. Introduction

Soil organic carbon (SOC) represents the largest and most dynamic carbon pool within Earth's surface ecosystems, exerting a significant influence on soil quality and climate change dynamics [1–6].

The main indicators of soil quality for estimating carbon sequestration are humus, quantity, and quality [4,7]. Mineralisation and humification are the major processes controlling the evolution of soil organic matter (SOM). Soil humus and carbon are the main indicators of soil conditions because of their direct influence on many soil processes and

functions, including aggregate formation, water infiltration and retention, nutrient cycling, and biodiversity promotion [5]. Carbon in soil can be stored in stable C compounds and others, which are unstable and mineralizable or easily accessible by microorganisms but still comprise the total organic carbon content of the soil. It is not sufficient to study SOC accumulation and stocks, but it is particularly important to investigate labile organic carbon forms to obtain a more detailed picture of the carbon cycle [4,7,8].

According to the literature, land use effects and soil conditions can be better understood by investigating the labile carbon pool [1,3–5,8–12]. Labile organic carbon in the soil is a conceptual pool of SOC that is primarily involved in organic carbon metabolism and decreases relatively rapidly following disruptive management practices such as tillage and extended fallow periods as is readily oxidised by microbial communities [5]. Conversely, with the application of sustainable agrotechnical practice, the amount of labile organic carbon may increase.

Studies focusing on dissolved organic carbon (DOC) play a crucial role in understanding soil processes [3,13]. Although numerous investigations have been conducted recently, further research is needed to delve deeper into the evolution, stability, and dynamics of DOC in soil. This exploration is essential for gaining insight into its involvement in various processes, such as SOC translocation, mineralisation, humification, and interactions with both organic and inorganic compounds. DOC is the most active and mobile form of SOC. While “DOC” is commonly used to denote organic material dissolved in situ, the term “WEOC” (water-extractable organic carbon) provides a more specific designation, offering insights into the type of DOC fraction under consideration [13,14].

Active soil carbon (POXC) serves as an indicator of soil health and is determined via permanganate oxidation [15]. The quantity of POXC, commonly assumed to represent soil carbon, is deduced from the reduction of MnO_4 in solution (Mn^{7+} to either Mn^{4+} and/or Mn^{2+}), making it an indirect measure of organic carbon lability, quality, and microbial decomposition [7,8,11]. Recently, interest in this method has grown [1,5,8,11] due to its cost-effectiveness, rapid analysis, independence from drying temperature prior to analysis [15], lack of requirement for sample density [16], and reliability through a standardised approach. This technique assesses the active pool of SOC, aiming to capture early alterations in carbon cycling [17], correlating with commonly used soil quality indicators [18,19] and aiding in the identification of management strategies that foster SOC accumulation or loss [20] and soil biological activity [5,8,11,21].

Nevertheless, none of these studies addressed the relationship between POXC and different soil uses or after changes in soil use. In addition, there is insufficient knowledge about the functioning of deep soil horizons or how management practices might affect labile C pools at depth. Advancing current knowledge about POXC in agroecosystems might also lead to an innovative approach when addressing soil health assessments and might contribute to the sustainability of soil [5,11].

Mineral fertilisers boost vegetation and nitrogen accumulation and improve the soil C ratio, reducing mineralisation and increasing humification and SOC levels. They enhance stable SOM fractions, crop yields, straw residue, and root biomass, improving SOC content, soil aggregation, and plant growth. However, not all SOM parameters in sandy soils are equally improved. Mineral fertilisers can reduce humification, support mineralisation, and decrease humus quality and organic matter stability. The necessity for organic fertiliser remains, and SOM quantity, quality, and stability are crucial for soil structure stability under long-term mineral fertilisation. The relationship between SOM parameters and soil structure grows with an experiment’s duration [2,22].

The carbon management index (CMI) assesses the relative effectiveness of various management approaches in influencing soil organic carbon (SOC) pools and carbon sequestration. Originating from [17], CMI offers a sensitive gauge of changes in soil carbon dynamics compared with a stable reference soil. Essentially, CMI aids in monitoring the differences in carbon dynamics among treatments over extended periods. A higher CMI

value signifies system rehabilitation, improvement, and sustainability, whereas a lower value suggests decline [1,2,4,8].

Researchers [4] further emphasise that a high CMI value indicates positive impacts on total organic carbon (TOC) content and soil quality, suggesting that a CMI value exceeding 100 reflects beneficial effects, while values below 100 indicate adverse impacts. The lability index (LI) gauges the relative lability of soil organic matter (SOM) in altered land use compared to reference soil, whereas the carbon pool index (CPI) quantifies changes in TOC resulting from land-use changes, with lower CPI values indicating greater carbon loss [8,23].

Recent studies on the carbon management index underscore the significance of soil carbon management in sustainable agriculture, climate change mitigation, and ecosystem resilience [1,8,11,23]. Advancing our understanding of soil carbon dynamics and management strategies is crucial for developing practical solutions to enhance soil health and ecosystem services while addressing global environmental challenges.

Arenosols have a loamy sand or coarse texture to a depth of 100 cm from the soil surface, they contain less than 35 percent (by volume) of rock fragments or other coarse fragments. They are easily erodable sandy soils with slow weathering rates, low water and nutrient holding capacity, and low base saturation [24,25]. Arenosol soils lack detailed studies on C sequestration. This study therefore aims to fill this gap.

This study aimed to determine the differences in the organic carbon mobile compounds in the soil after the conversion of arable land use to other types of land use and to evaluate which type of land use increases the amount of SOC in Arenosols.

2. Materials and Methods

2.1. Study Area and Soil Sampling

To determine the most effective methods for enhancing soil fertility and SOC sequestration in Arenosol soils, an experiment was established in 1995. The experimental plot has been used for a long time (about 50 years by 1995) as arable land for the cultivation of annual agricultural crops. This experiment investigated the influence of natural and agricultural ecosystems on soil properties (Figure 1). Four land uses were studied: cropland cultivation (CL), cut grassland cultivation (GR), uncultivated abandoned land (UAL), and pine afforestation (PA). The total size of each land-use site was 400 m² (20 m × 20 m). Soil samples were collected from each of the six plots at two soil depths (0–15 and 15–25 cm), with four replicates ($n = 48$), using an auger at four random locations (replicates) from each treatment plot (from different land use divided into fertilised and non-fertilised plots).

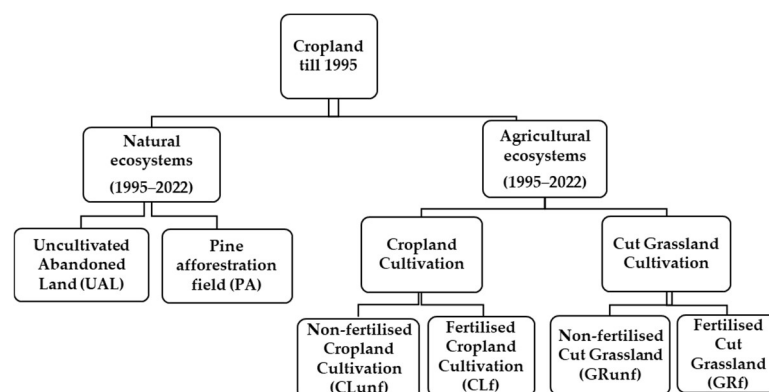


Figure 1. Scheme of conversion of arable land use to other land uses (experiment performed in the Lithuanian Centre for Agriculture and Forestry, Voke branch).

The soil was identified according to the International Soil Classification System (IUSS Working Group WRB 2022) [26]. It was conducted in Arenosol soil formed on fluvioglacial deposits, with the following profile: Ah-AB-B1-B2-2C α 1-2C α 2. The relief is a slightly undulating plain. Carbonates were identified at depths of 80–100 cm. The soil texture

of horizon A (classified by FAO) comprised sand—81.0–83.7%, silt—11.2–13.7%, and clay—4.5–5.0%; B1, B2 horizons, respectively, 84.5–86.8%, 4.55–7.95%, and 7.50–8.65%; C1, C2 horizons—91.4–98.4%, 1.2–3.53%, and 0.4–5.04%.

During the long-term experiment, various biological and agroecological properties were analysed separately [27]. At the beginning of the experiment, the pH_{KCl} of the humus layer ranged from 6.0 to 6.8, SOC was between 9.5 and 9.9 g kg^{-1} , and there was 157–188 $\text{mg P}_2\text{O}_5 \text{ kg}^{-1}$ and 170–194 $\text{mg K}_2\text{O kg}^{-1}$. After 25 years, the pH_{KCl} of the humus layer ranged from 5.5 to 6.4, SOC level changed depending on the land use and applied agrotechnical measures, and was between 8.3 and 14.2 g kg^{-1} , P_2O_5 was between 71 and 229 mg kg^{-1} , and K_2O was between 80 and 185 mg kg^{-1} (Table 1).

Table 1. Soil chemical characteristics (1995–2020) and Ah horizon depth.

	Years	CLf	CLunf	GRunf	GRf	UAL	PA
pH_{KCl}	1995	6.0 ± 0.08	6.0 ± 0.08	6.8 ± 0.08	6.8 ± 0.08	6.0 ± 0.08	6.0 ± 0.08
	2020	6.4 ± 0.20	6.4 ± 0.11	6.1 ± 0.03	5.9 ± 0.28	6.3 ± 0.18	5.5 ± 0.15
Available P_2O_5 mg kg^{-1}	1995	188 ± 4.9	188 ± 4.9	177 ± 4.9	177 ± 4.9	157 ± 4.9	168 ± 4.9
	2020	229 ± 33.0	118 ± 6.5	71 ± 3.7	208 ± 12.0	158 ± 26.3	133 ± 10.0
Available K_2O mg kg^{-1}	1995	194 ± 4.7	194 ± 4.7	174 ± 4.7	174 ± 4.7	170 ± 4.7	192 ± 4.7
	2020	185 ± 14.0	98 ± 6.7	80 ± 2.8	168 ± 12.8	163 ± 17.2	128 ± 7.5
SOC g kg^{-1}	1995	9.5 ± 0.08	9.5 ± 0.08	9.9 ± 0.08	9.9 ± 0.08	9.9 ± 0.08	9.7 ± 0.08
	2020	8.3 ± 0.4	8.9 ± 0.8	9.8 ± 0.3	14.2 ± 0.9	11.0 ± 0.6	12.2 ± 2.1
Ah horizon depth, cm	1995	28 ± 0.0	28 ± 0.0	28 ± 0.0	28 ± 0.0	28 ± 0.0	28 ± 0.0
	2020	25.2 ± 0.67	28.8 ± 0.67	28.8 ± 2.00	29.0 ± 1.22	31.0 ± 0.22	32.0 ± 1.41

Note. CLf—fertilised crop cultivation; CLunf—non-fertilised crop cultivation; GRunf—non-fertilised cut grassland cultivation; GRf—fertilised cut grassland cultivation; UAL—uncultivated abandoned land; PA—pine afforestation field. ± Standart error.

The experiment was conducted in a temperate climate zone and the subregion of Atlantic–European continental mixed and broadleaved forests [28]. This region is characterised by a moderate climate with a mean long-term (1991–2020) annual precipitation of 678 mm and an annual mean air temperature of 7.2 °C (the standard climate norm—SKN) (LHMT Climate and Research Department) [29].

Annual agricultural plants that are more suitable for light-textured soils were grown on the crop rotation sites. The crops were cultivated according to the recommended practices for the region. From 1995 to 2022, the crop rotation included: 23.8% cereal crops (*Secale cereale* L., *Hordeum vulgare* L., *Triticosecale wittmack*, *Triticum aestivum* L.), 14.3% cereal crops with perennial grasses under crop, 19% buckwheat family (*Fagopyrum esculentum* Moench), 14.3% perennial leguminous grasses (*Trifolium pratense*), 14.3% row plants (*Solanum tuberosum* L.), and 14.3% other (*Brassica napus* L., *Lupinus angustifolius* L.). At the cropland site, the agrotechnics of plant cultivation recommended in Lithuania were applied: autumn soil ploughing (22–24 cm deep), spring soil cultivation (2 times, 8–10 cm deep), fertilising with mineral fertilisers, and sowing. Plant protection measures were applied depending on the prevalence of diseases and pests, using pesticides registered in Lithuania. At the fertilised crop cultivation site (CLf), mineral NPK fertilisers were applied based on plant nutrient requirements and soil phosphorus and potassium concentrations. Single-component mineral fertilisers (ammonium nitrate, superphosphate, potassium chloride) were used for fertilising. Depending on the plants' needs, the level of fertiliser application was N 0–100 kg ha^{-1} , P 13–26 kg ha^{-1} , and K 25–100 kg ha^{-1} . In 1995 and 2000, when growing potatoes in crop rotation, CLf site soil was fertilised with 40 t ha^{-1} of cattle manure. Manure was applied in the fall to a depth of 22–24 cm. No further organic fertilisation was applied.

At the cut grassland site (GRunf and GRf), a grass–legume mixture, which included four species of grasses (20% red fescue, *Festuca rubra* L.); 20% brome grass, *Bromus inermis* Leys.); 10% cock's-foot grass, *Dactylis glomerata* L.; 10% meadow-grass, *Poa pratensis* L.),

and one species type of legume (40% lucerne, *Medicago varia* L.) was applied. In 2007–2022, the cock's-foot grass was replaced with timothy (*Phleum pratense* L.). Grasses were reseeded in 2007 and 2015. At the beginning of vegetation, grasses were fertilised with 90 kg N ha⁻¹, 26 P kg ha⁻¹, and 125 K kg ha⁻¹. After the first biomass harvest, grasses were fertilised with 30 N kg ha⁻¹. Plant succession began in the experimental plots after the cessation of the agricultural practices.

Soil use was uncultivated in the abandoned land (UAL), but sporadic woodcutting was performed as needed in such a way as to avoid overgrowth of trees (self-afforestation). During the study period, a natural vegetation phytocenosis typical of Arenosol soils in this region formed on the site of abandoned, ex-arable land. In addition, the species composition of plants changed depending on the duration of the abandonment, climatic factors, and growing season. As the abandonment duration increased, the number of perennial grass species also increased. In comparison with the first year of abandonment, the number of perennial plant species doubled by 2022. This mostly consists of plants belonging to the *Poaceae* family. Over a 27-year period, only plants of three families (*Asteraceae*, *Poaceae*, and *Fabaceae*) were constantly present in the phytocenosis.

Scots pine (*Pinus sylvestris* L.) grows in pine-afforested (PA) fields. No agrotechnical activity was performed at the PA site. In 1995, 400 pine trees (10,000 ha⁻¹) were planted on the site of the pine plantation (400 m²), as it is known that not all seedlings survive. After the pine seedlings grew (in 2004), tree thinning was carried out, forming the recommended density of trees (3700–4000 ha⁻¹) for pine plantations in the Lithuanian region.

2.2. Soil Chemical Analysis

pH was determined in KCl 1 M, (*w/v* 1:5); available phosphorus (P₂O₅) and potassium (K₂O) were determined according to the Egner–Riem–Domingo (A–L) method.

The SOC content was determined using H₂SO₄ and K₂Cr₂O₇ digestion methods [30] at 160 °C for 30 min. Spectrophotometric measurements at a wavelength of 590 nm were performed using glucose as a standard. Before the analysis, soil samples were air-dried, sieved through 2 mm and 0.25 mm sieves, and homogenised after manually removing visible roots and plant residues. Mobile humus substances (MHSs) including mobile humic acids (MHAs) and mobile fulvic acids (MFAs) were extracted using a 0.1 M NaOH solution [31].

Water-extractable (cold) organic carbon (WEOC) was analysed with an ion chromatograph (SKALAR, Skalar Analytical B.V., Breda, The Netherlands). Samples were shaken with distilled water at a 1:5 ratio for 1 h, then filtered through a blue band filter for further analysis. CO₂ was measured with an infrared detector during UV digestion before automatically adding H₂SO₄ [13,14].

Permanganate oxidizable carbon/active carbon (POXC) was determined by adding 2.0 mL KMnO₄ and 18.0 mL H₂O to 2.5 g of soil, shaking for 2 min, and settling for 10 min. Samples were then diluted with 0.5 mL supernatant and 49.5 mL H₂O. The absorbance of each sample was measured at 550 nm using a spectrophotometer, ensuring the sensitivity and linearity of the permanganate-oxidizable carbon method [7,32].

The CPI, LI, and CMI were calculated based on the method of Blair (1995) [1,4,7,8,23].

- Carbon Pool Index (CPI)

$$\text{CPI} = \text{SOC} / \text{SOC reference} \quad (1)$$

- Carbon Lability Index (LI)

$$\text{L (Lability)} = \text{POXC} / \text{unhydrated C} \quad (2)$$

$$\text{LI} = \text{Lability} / \text{Lability in reference soil} \quad (3)$$

- Carbon Management Index (CMI)

$$\text{CMI} = \text{CPI} \times \text{LI} \times 100 \quad (4)$$

2.3. Statistical Analysis

All data were analysed using SAS Enterprise software, version 7.1 (SAS Institute Inc., Cary, NC, USA). The differences between the experimental treatments were tested using two-way analysis of variance (ANOVA). The probability level was set at 0.05 and grouped according to letters by Duncan's test. Standard error (SE) values were used to estimate the deviations of soil chemical parameters from the mean values. Correlations were performed according to Pearson.

3. Results

3.1. Distribution of SOC Amounts for Different Land Uses and Depths

The conversion of arable land to other types of land use altered SOC sequestration processes in an Arenosol soil. After 27 years of different land uses, the greatest SOC content increase was seen after the conversion of arable land use to PA: the amount of SOC in the 0–15 cm layer was on average 17.3 g kg^{-1} , and in the 15–25 cm layer, 13.9 g kg^{-1} ($p < 0.05$) (Table 2). A significant SOC increase was also found in UAL and GRf land uses (+36.7–41.3% compared to CLf, $p < 0.05$) in the 0–15 cm layer and +25.1–28.2% in the 15–25 cm layer. Without fertiliser application, SOC accumulation in GR was similar to that in CLf. It should be noted that the application of mineral NPK fertilisers significantly ($p < 0.05$) increased the formation of humus substances in CL and GR; the amount of SOC increased by 12.8% and 27.3% in the 0–15 cm layer and by 13.0% and 8.4% in the 15–25 cm layer, respectively. When no fertiliser was used in the CL, compared to the fertilised CL, the decrease in SOC content (−30.4%) was more pronounced in the 0–15 cm layer, while in deeper layers, the changes were insignificant. Significant differences in SOC content at different depths were found only in PA, UAL, GRf, and CLf soils. The differences between depths were insignificant for CLunf and GRunf land uses.

Table 2. Accumulation of SOC and mobile humic substances in different land-use systems.

Land Use	SOC		MHS		MHA		MFA		MHA/MFA	
	g kg ⁻¹									
	0–15 cm	15–25 cm	0–15 cm	15–25 cm	0–15 cm	15–25 cm	0–15 cm	15–25 cm	0–15 cm	15–25 cm
CLf (control)	11.09 e	9.83 f	3.22 de	3.06 def	1.48 e	1.38 ef	1.74 dfe	1.68 dfe	0.880 bc	0.830 bc
CLunf	8.50 g	8.70 g	2.53 fe	2.28 f	0.95 f	0.956 f	1.58 fe	1.32 f	0.610 c	0.730 bc
GRunf	11.9 de	11.6 de	3.89 cd	3.88 cd	2.08 bcd	1.89 cde	1.82 dfe	1.99 cde	1.340 a	0.970 bc
GRf	15.2 b	12.4 d	4.92 b	4.39 bc	2.41 bc	2.16 bcd	2.51 bc	2.23 bcd	0.960 bc	0.970 bc
UAL	15.7 b	12.3 d	4.88 b	3.89 cd	2.32 bcd	1.82 de	2.56 ab	2.07 bcde	0.900 bc	0.870 bc
PA	17.3 a	13.9 c	6.19 a	4.93 b	3.15 a	2.53 b	3.04 a	2.40 bc	1.040 ab	1.050 ab

Note. CLf—fertilised crop cultivation; CLunf—non-fertilised crop cultivation; GRunf—non-fertilised cut grassland cultivation; GRf—fertilised cut grassland cultivation; UAL—uncultivated abandoned land; PA—pine afforestation field. SOC—soil organic carbon, MHS—mobile humic substance MHA—mobile humic acids, MFA—mobile fulvic acids. MHA/MFA—ratio of MHA and MFA. Letters indicate differences ($p < 0.05$) between land use and the 0–15 and 15–25 cm layers.

3.2. Effects of Land Use on Mobile Humic Substances (MHSs), Mobile Humic Acids (MHAs) and Mobile Fulvic Acids (MFAs)

Higher amounts of SOC resulted in higher amounts of MHSs in the soil. More favourable conditions for the formation of MHSs were found in the PA soil. The amount of MHSs increased by 92.2% in the 0–15 cm layer compared to CLf and by 61.1% in the 15–25 cm depth and was significantly higher than that in other land uses. Fewer humus substances were formed in GRf and UAL soils, but compared to CLf, their amounts were still significantly increased—about 50% in the upper layer and 27.2–43.2% in the 15–25 cm layer. The lowest amount of MHSs was found in the CLunf soil. This is typical for both layers. It can be noted that in all land uses, the MHS content in the 15–25 cm layer was

lower than that in the 0–15 cm layer, but only the PA was significantly different between the two layers. The use of mineral fertilisers promoted the formation of MHSs, and their content in CLf soil increased by 27.3% in the 0–15 cm layer and 34.2% in the 15–25 cm layer, and GR by 26.4 and 13.1%, respectively ($p < 0.05$).

The amount of MHAs in the soil, depending on the type of land use, was 11.2–18.2% of the SOC in the 0–15 cm layer and 11.0–18.0% of the SOC in the 15–25 cm layer, and the amount of MFAs was 15.4–18.7% and 15.3–17.3%, respectively (Table 2). The lowest amount of MHAs in both layers was found in the CLunf soil. More favourable conditions for MHA formation were in PA soil, compared to CLf: the amount in the 0–15 layer increased by 1.67 g kg^{-1} (+112.7%, $p < 0.05$), and in the 15–25 cm layer, by 1.15 g kg^{-1} (+83.5%, $p < 0.05$), and a significantly lower amount of MHAs was found in CLunf soil. Grassland land use (UAL, GRf, GRunf) had the same effect on MHA formation. The amount of MHAs in the 0–15 cm layer increased on average by 40.2–62.7% ($p < 0.05$); in the 15–25 cm layer, it increased by 32.0–56.7% ($p < 0.05$) compared to CLf. It should be noted that mineral fertilisers had a positive effect on the formation of MHAs in both CL and GR soils: their amount increased by 35.7 and 22.5% in the 0–15 cm layer, and by 9.0 and 43.7% in the 15–25 cm layer, respectively, but the increase was not statistically significant. No significant differences in MHA amounts between the upper and deeper Ah horizon soil layers were found in any of the studied land use types.

The type of land use had a slightly different influence on the formation of MFAs than on MHAs. If MHAs were mostly formed in PA soil, then for MFAs, the effects of PA and GRf on their amount were similar. The amount of MFAs in the 0–15 cm layer increased by 44.0–47.3% (Table 2) and in the 15–25 cm layer, by 23.4–42.7% compared to CLf. The CLunf, CLf, and GRunf conditions for the formation of MFAs were similar, and no significant differences in their amounts were found in the studied land uses in both the 0–15 and 15–25 cm layers. After calculating the MHA/MFA ratio in the soil of different land uses, it was found that the conversion of arable land to cultural grassland or PA activates the formation of more valuable MHAs (Table 2); more were found in both the 0–15 and 15–25 cm layers. Fertiliser application in CL and GR promoted the formation of MHSs in unfertilised soil (0–15 cm). CLunf (0–15 cm) had the lowest MHA/MFA ratio compared with all grassland uses and PA. An MHA/MFA ratio closest to 1, considered the most favourable, was determined for GRf, UAL, and PA, with above 1 indicating that more sustainable and quality-assuring humic acids predominated.

3.3. The Influence of Land Use on Active Carbon (POXC) and Water Extractable Organic Carbon (WEOC)

Depending on land use, the POXC fraction in Arenosol soil varied from 219 to 432 mg kg^{-1} in the 0–15 cm layer and 217 to 382 mg kg^{-1} in the 15–25 cm layer (Figure 2). In grassland uses (GR, UAL) and PA, the amount of POXC was significantly higher in all studied soil layers than in the CL. The influence of mineral fertilisers on the variation in POXC content in the CL and GR was also determined. The use of fertilisers in the upper layer of the CL had no effect, but in the deeper layer, the POXC amount increased ($p < 0.05$). Fertilisation with mineral fertilisers significantly increased the POXC content in the upper layer of the GR land use.

The CLf land use was characterised by a similar distribution of POXC in the Ah horizon, and significant differences in the amount in the 0–15 and 15–25 cm layers were found only between the ecosystem (GRf and PA) and CLunf variants.

The WEOC fraction is the smallest fraction of SOC as it is the most mobile and the quickest to mineralise. In the soil of the experimental area, the average WEOC content was $0.255\text{--}0.138 \text{ mg kg}^{-1}$ in the 0–15 cm layer and $0.203\text{--}0.134 \text{ mg kg}^{-1}$ in the 15–25 cm layer, which accounted for 1.26–1.63% and 1.40–1.67% of SOC, respectively (Figure 3).

A faster formation of WEOC occurred after the conversion of arable land to UAL, GRf, and PA because of the accumulation of more organic residues on the surface. In the mentioned areas, the WEOC concentration increased by 45.6–71.1% ($p < 0.05$) in the

0–15 cm layer and by 23.4–42.7% ($p < 0.05$) in the 15–25 cm layer compared to CLf. Changes in other land use types (CLunf and GRunf) were insignificant. The WEOC amounts at both depths were essentially similar for all land-use types, except for GRf. In this land use, a significant decrease in its amounts was determined in the 15–25 cm layer compared to the upper layer.

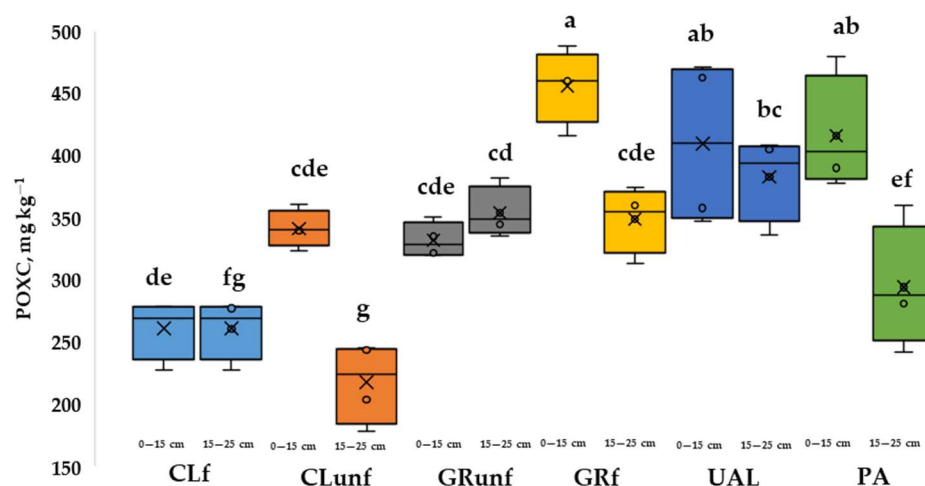


Figure 2. Active Carbon (POXC) distribution in different land uses and layers. Note. CLf—fertilised crop cultivation; CLunf—non-fertilised crop cultivation; GRunf—non-fertilised cut grassland cultivation; GRf—fertilised cut grassland cultivation; UAL—uncultivated abandoned land; PA—pine afforested field. Letters indicate differences ($p < 0.05$) between land use in the 0–15 and 15–25 cm layers. The standard errors are marked.

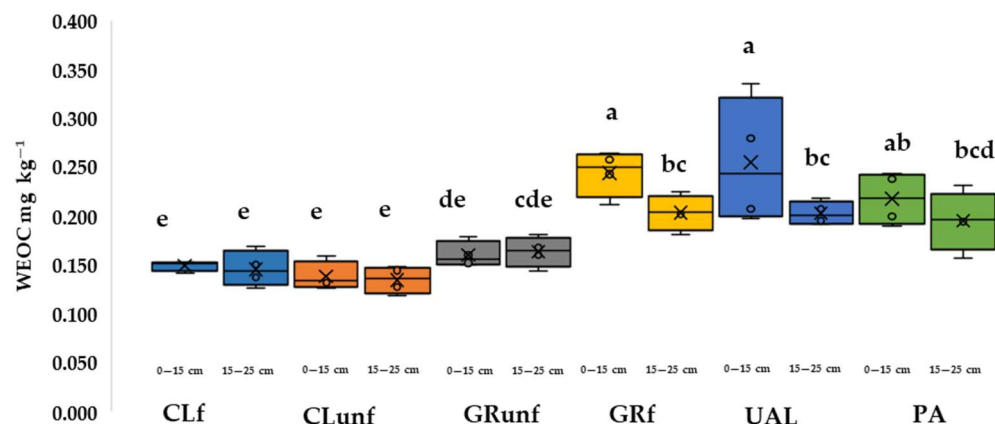


Figure 3. Water extractable organic carbon (WEOC) distribution according to land use and depth. Note. CLf—fertilised crop cultivation; CLunf—non-fertilised crop cultivation; GRunf—non-fertilised cut grassland cultivation; GRf—fertilised cut grassland cultivation; UAL—uncultivated abandoned land; PA—pine afforested field. Letters indicate differences ($p < 0.05$) between land use in the 0–15 and 15–25 cm layers. The standard errors are marked.

3.4. Dependence of Labile Carbon Fractions on Soil Ah Depth and pH

Correlation analysis showed that the thickness of the Ah horizon was moderately correlated with the amounts of MHSs and MHAs ($r = 0.7366$ and $r = 0.6892$, respectively) and strongly depended on the amount of MFAs (correlation $r = 0.9396$ and determination $R^2 = 0.88$, respectively) (Table 3).

The POXC and WEOC contents were least correlated with the Ah layer ($R^2 = 0.4006$ and $R^2 = 0.4034$, respectively).

According to Pearson's correlation coefficient, soil pH was most strongly correlated with MHSs ($R^2 = 0.7428$, $r = -0.8618$) and MHAs ($R^2 = 0.748$, $r = -0.8650$) ($p < 0.001$).

Weaker correlations were found for the POXC ($R^2 = 0.2525$, $r = -0.5025$) and WEOC ($R^2 = 0.3796$, $r = -0.6161$).

Table 3. Correlation of labile carbon compounds: mobile humic substances (MHAs), mobile humic acids (MHAs), mobile fulvic acids (MFAs), active organic carbon (POXC), and water extractable organic carbon (WEOC) with Ah soil depth and pH.

	MHS	MHA	MFA	POXC	WEOC
Ah	$y = 1.306x + 23.552$	$y = 2.1038x + 24.792$	$y = 2.6537x + 23.724$	$y = 0.0298x + 18.153$	$y = 29.091x + 23.494$
	$R^2 = 0.5426$	$R^2 = 0.475$	$R^2 = 0.8828$	$R^2 = 0.4006$	$R^2 = 0.4034$
	$r = 0.7366$	$r = 0.6892$	$r = 0.9396$	$r = 0.6329$	$r = 0.6351$
	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p = 0.0001$	$p = 0.0076$
pH	$y = -0.2626x + 7.078$	$y = -1.7158x + 12.304$	$y = -1.3026x + 9.9071$	$y = -80.928x + 869.08$	$y = -15.196x + 123.32$
	$R^2 = 0.7428$	$R^2 = 0.7482$	$R^2 = 0.5782$	$R^2 = 0.2525$	$R^2 = 0.3796$
	$r = -0.8618$	$r = -0.8650$	$r = -0.7604$	$r = -0.5025$	$r = -0.6161$
	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$	$p = 0.0001$	$p = 0.0044$

3.5. Soil Quality Index—Carbon Management Index

The Carbon pool index (CPI), Carbon lability index (LI), and carbon management index (CMI) were calculated for the comprehensive evaluation of SOC quantity and qualitative composition of land use impacts (Table 4).

Table 4. Effects of land use on Carbon Pool Index (CPI), Carbon Lability Index (LI), and Carbon Management Index (CMI).

Land Use	Carbon Pool Index (CPI)		Carbon Lability Index (LI)		Carbon Management Index (CMI)	
	0–15 cm	15–25 cm	0–15 cm	15–25 cm	0–15 cm	15–25 cm
CLf (control)	–	–			100.0	100.0
CLunf	0.77 e	0.89 e	1.39 a	0.90 b	105.6 ab	77.0 b
GRunf	1.08 d	1.19 cd	1.00 b	1.00 b	106.6 ab	119.8 a
GRf	1.37 abc	1.27 bcd	1.01 b	1.01 b	138.3 a	126.3 a
UAL	1.41 ab	1.27 bcd	0.94 b	1.13 ab	132.8 a	140.9 a
PA	1.56 a	1.44 ab	0.81 b	0.91 b	126.2 a	114.6 ab

Note. CLf—fertilised crop cultivation; CLunf—non-fertilised crop cultivation; GRunf—non-fertilised cut grassland cultivation; GRf—fertilised cut grassland cultivation; UAL—uncultivated abandoned land; PA—pine afforested field. Letters indicate differences ($p < 0.05$) between land use in the 0–15 and 15–25 cm layers.

The CPI values showed that in Arenosol soils, slightly higher SOC sequestration occurred in the upper 0–15 cm layer except for in CL unf and GR unf. Among all investigated land uses, higher CPI (1.56, $p < 0.05$) was found in PA soil and UAL, and GR was significantly higher than CL. In terms of SOC accumulation, UAL and GRf land uses were equivalent, although, in the latter, green biomass was used for feed production and was removed from the field. Without the use of GR mineral fertilisers, the ability of herbaceous plants to accumulate SOC was significantly reduced. The lowest ($p < 0.05$) CPI was found in the CLunf soil.

To assess the qualitative changes in SOC, LI is often calculated, which reflects the changes in soluble organic compounds due to changes in land-use type. The differences between the variants were determined only in the upper layer. Significantly higher LI values were found in CLunf (0–15 cm) and UAL (15–25 cm), whereas the lowest values were found in PA and UAL (0–15 cm), and the LI in cultivated grassland was similar. The same LI (0.90–1.13) in the 15–25 cm layer was present in all variants, which shows that less labile organic compounds are formed in them. The effect of land use on the value of the LI between 0–15 and 15–25 cm depths was insignificant ($p > 0.05$), except for CLunf. Statistically lower LI values in deeper layers were observed in this study.

The CMI reflects differences in the formation of SOC and labile humic substances in the soil. CMI in the upper layer ranged from 105 to 138, although no statistical difference was found; however, relative to CLf, the GRf, UAL, and PA ecosystems were restored more intensively, and CLunf (15–25 cm) was restored more slowly. Larger differences were found at deeper depths, where labile C accumulation was restored in the UAL, GR, and PA, and in the CLunf (15–25 cm) it was lost.

4. Discussion

The promotion of organic carbon accumulation in low fertility Arenosol soil aims to prevent its degradation, increase environmental sustainability, and reduce CO₂ emissions, which influence the climate warming processes. The main source of organic matter in the soil is plant biomass [1,33–35], therefore, to optimise the use of Arenosol soil, farmers often abandon traditional agricultural practices (arable land use) and replace it with grassland or tree plantations [11,36].

Data from this experiment confirmed that SOC accumulation in Arenosol soils is faster in forest (PA) soils, which is associated with tree litter and belowground tree root biomass. SOC content was higher by 55.8% in the 0–15 cm layer and 42.4% in the 15–25 cm layer ($p < 0.05$) than in CLf. An analogous effect of forests on SOC sequestration has been described by scientists from various countries [2,11,12,37,38]. The conversion of CL to grassland was less efficient than that of CL to PA but also significantly increased soil SOC. When assessing the influence of grassland use on SOC accumulation, it is important to note that SOC accumulation occurs in a similar way in UAL and GRf soils, although their use of aboveground biomass differs. The entire plant biomass grown during the vegetation period remains on the soil surface and becomes a source of organic matter during mineralisation in the UAL. In GRf, the aboveground parts of the plants are used for fodder production, and only grass residues and roots participate in the synthesis of new humic substances. Ref. [39] stated that the increase in SOC sequestration in a fertilised grassland cannot be explained by an increase in root biomass or aboveground residues, but rather is linked to a narrower C:N ratio in such soil, which may have caused increased microbial C use efficiency, positively affecting SOC storage. Without the use of fertilisers in GR land use, grass biomass grows poorly and the SOC accumulation rate in the soil slows down and equals that of CLf. The positive effect of mineral fertilisers on SOC accumulation in grassy land use has also been confirmed in other scientific publications [40,41].

Researchers [2] conducted a long-term study in which sandy soil was fertilised with NPK fertilisers and summarised that the values of SOC, non-labile carbon, humic substances, and humic acids increased by 58%, 61%, 22%, and 24%, respectively, compared to the control treatment in the 41-year experiment with NPK. Significant differences in CPI values were determined between NPK and CaNPK. From the perspective of sustainable agriculture, relying solely on mineral fertilisers without incorporating manure into soil management is not the proper direction.

As SOC content increased, more mobile organic compounds were formed in the Arenosol soil. Depending on the type of land use, the amount of MHSs was 29.9–35.8% of the SOC. More favourable conditions for their synthesis were created in PA soil and, compared to CLf, their amount increased by 92.2% in the 0–15 cm layer and 61.1% in the 15–25 cm layer ($p < 0.05$). As with SOC, in GRf and UAL soils, these substances were lower than in PA, but still significantly higher than in CLf. Increasing the amount of mobile humic substances has both positive and negative effects. On the one hand, they mineralise faster and replenish the supply of nutritional elements in the soil; on the other hand, CO₂ emissions become more active during decomposition [42]. Land-use changes also influenced the synthesis of MHAs and MFAs. More favourable conditions for MHA formation were found in PA and GRf soils, whereas significantly higher MFA content was found in CLunf. Mineral fertilisers promote the formation of more valuable MHAs in the CL and GR. According to [43], N addition can alter the physical and chemical properties of soil, which can affect soil enzyme activity, microbial biomass, quality indices, and the

composition distribution of HAs and FAs. However, it should be noted that Ref. [44] reported contrasting results. According to this study, the long-term application of mineral fertilisers (NPK) without organic matter input can accelerate humus mineralisation and soil quality degradation (lower SOC and HS content and predominance of FA).

SOC fractions, such as mobile fractions, POXC, and WEOC, reflect the direct changes in SOM pools and are more sensitive to land-use and management changes than SOC [4,5,23,26]. Therefore, POXC and WEOC indicators are often used to assess changes in SOC quality due to land-use change [20,45,46]; however, some argue [47] that carbon oxidised by KMnO_4 is not a reliable measure of labile C and should be referred to as POCX when used as a parameter for characterising soil C. Ref. [6] presented similar views on POXC evaluation. This study did not establish relationships between POXC and other pools and suggested that POXC encompasses a different nature of SOC while providing complementary information on the biogeochemical stability of SOC.

After analysing POXC, we found that the conversion of arable land use (CLf) to other land uses increased the formation of active C in the soil by an average of 1.3–35.5%. A significant increase in this C fraction ($p < 0.05$) was found in GRf and UAL soils. Ref. [11] found (in a study of pine plantation in sandy soil), a negative correlation between POXC and clay or clay plus silt contents, in which the clay content increase with depth is followed by a decrease in measured POXC concentration. The amount of POXC correlates with pH because soil pH exerts a direct effect on enzyme activity and influences the soil microbial community structure and soil nutrient availability. In contrast, our research showed a weak correlation with pH. Improved soil health and a more suitable environment for microorganisms were demonstrated by the distribution of POXC content. More suitable ecosystem conditions due to the amount of biomass and moisture regime microorganisms (GRf, UAL, and PA) in the deeper layer were still observed in GRunf [48,49]. Similar results on the influence of land use on POXC have been published in [49]. The findings of the latter study revealed that POXC predominantly accumulates in forest soil compared to grassland and arable soils, making the latter more conducive to long-term SOC storage than forest soils. The high amount of labile SOC in forest topsoils poses a risk of considerable SOC loss caused by wildfires, mechanical disturbances, or increasing temperatures. The different assessments of the influence of land use on the amount of POXC in the soil by scientists from different countries show that this question requires additional research and a deeper causality analysis.

The WEOC indicator was also used to evaluate changes in SOC quality after CL conversion to other land-use types. WEOC content in Arenosol soil was small and constituted only 1.26–1.63% of SOC in the 0–15 cm layer and 1.40–1.67% of SOC in the 15–25 cm layer. The formation of WEOC was significantly influenced by grassland use (GRf, UAL) and PA, which accumulate many organic residues on the soil surface. These compounds increased in the entire 0–25 cm layer compared to CLf. An analogous influence of forests on the amount of WEOC in soil has also been found in other soils [50]. The data from our experiment correspond to the conclusions of [51,52], the authors of which, after summarising various publications on dissolved organic matter (DOM) and water-extractable organic matter (WEOM) research data, summarised that most studies indicate that DOM/WEOM concentration decreases in the order of forest floor > grassland Ah > arable Ah, whereas soluble organo-metal complexes are more abundant in forest than agricultural soils.

Labile C compounds were washed out of the upper Ah horizon with precipitation and were one of the factors influencing its thickness [53,54]. Under Lithuanian climatic conditions, leaching of SOC in sandy loam soil averages approximately $20 \text{ kg C ha}^{-1} \text{ year}^{-1}$ [54]. Plant sources affect the load and composition of DOM leaching [55,56]. The authors of Ref. [57] suggest that leaf-derived DOC may contribute to the formation of an A horizon and even to the accumulation of soil organic carbon (SOC) in the B horizon during soil development, either by adsorption or microbial biomass incorporation. Studies with isotope C^{14} revealed that the dominant process maintaining the WEOC pool in the mineral soil appears to be the microbial release of water-soluble compounds from SOM [58]. According

to our research data, after changing CLf to other land uses, the thickness of the Ah horizon increased the most in PA, UAL, and GRf over 25 years—from 1.0 to 4.0 cm—while CLf and GRunf did not change significantly, and CLf decreased by 2.8 cm.

After performing a correlational analysis of Ah thickness and different forms of humus compounds, it was found that MFA content had a greater effect on its thickness ($r = 0.9396$); only a moderate dependence was found for MHS, MHA, POXC, and WEOC content. The same trend was found in pine plantation in sandy soil studies [11]: POXC decreased with depth. There are two explanations for this: First, the influence of rhizodeposition on processes that control SOC stabilisation and destabilisation may contribute to the increase in labile C pools in the subsoil. Second, the decline in microbial biomass and microbial activity with depth and the availability of mineral surfaces for the sorption of organic C compounds might create a selective preservation of labile C pools in deep soil layers.

After performing a CPI assessment, we confirmed the conclusions made by other scientists [1,4,23,45–47] for different land uses in that it was found that faster SOC accumulation occurs in natural ecosystems: PA, UAL, and GRf compared to CLf. The lability index (LI) shows that more labile compounds are formed in the CLunf and UAL agrosystems. According to the carbon management index, the most favourable C management methods were GRf, UAL, and PA, and the least suitable was CLunf.

5. Conclusions

The conversion of arable land to other types of land use changes the accumulation of OC and its qualitative composition, depending on the applied agrotechnical practices and the phytocenosis of the land use. The conversion of arable land use to pine plantation (PA) and herbaceous land use (GRf, UAL) promotes the accumulation of SOC in Arenosol soils, and at the same time, MHS synthesis in the soil increases. Most MHSs are formed in PA, with slightly less in GRf and UAL than in CLf. The decreasing order of MHS content in different land use types in the 0–15 cm layer was PA > GRf, UAL > CLf, CLunf, and GRunf. Mineral fertilisers used in CL and GR promoted MHS formation in the soil, but the differences were not significant in all cases. The amount of MHSs increased in both the 0–15 and 15–25 cm layers. Different land-use vegetation and applied agrotechnical practices had unequal influences on the formation of MHAs and MFAs, which is reflected by changes in the ratio of these substances in different land uses. More suitable conditions for the formation of MHAs were found in PA, Grunf, and GRf soils, where a higher ratio of MHA/MFA was found, compared to other land uses. More MFA compounds were formed in the CLunf soil. In grassland soil uses (GR, UAL) and PA, compared to CLf, the amounts of POXC were significantly ($p < 0.05$) higher: in the 0–15 cm layer, they were 24.1–35.5%, and in the 15–25 cm layer, they were 25.4–39.5%. The sequence of land use according to changes in POXC amounts in the 0–15 cm layer was GRf, UAL, and PA > GRunf, CLf, and CLunf. The accumulation of WEOC compounds followed the same trend as that of POXC. WEOC was found significantly more in soil used for grassland (in the 0–15 cm layer, 7.4–71.1%, and in the 15–25 cm layer, 12.4–40%) compared to CLf, except for GRunf. The amount of WEOC in decreasing order of land use was GRf, UAL, and PA > CLunf, CLf, and GRunf. The change in Ah horizon thickness after the conversion of arable land use to other land uses was most dependent on the amount of MFAs ($r = 0.9396$) and had a weak correlation ($r = 0.6329$) with the amount of POXC in the soil. The decreasing order of the CPI index of different land uses was PA > UAL, GRf, >GRunf > CLunf, which confirms that faster OC accumulation in Arenosol soils occurred in PA and soil used for grass (GRf and UAL). The variation in CLI values (GRf, UAL, and PA > GRunf and CLunf) shows that in PA, UAL, and GRf land uses, relatively more mobile OM forms are formed, which maintains the OC balance in the soil. According to the CPI, it was found that the highest amounts of SOC were in the GRf, UAL, and PA agroecosystems compared to CLf. The lability index (LI) showed that more labile compounds were formed in agroecosystems CLunf and GR. According to the carbon management index, we can say that the most favourable ways of managing SOC are UAL, PA, and GRf, and the most unfavourable is

CLunf. More detailed follow-up studies are required before a confirmed conclusion can be reached. This study extends our understanding of labile compound changes in the soil during conversion.

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