Heliyon 7 (2022) e08709

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

CellPress

Land use and site effects on the distribution of carbon in some humic soil profiles of KwaZulu-Natal, South Africa



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HIGHLIGHTS

• Humic soils have been converted from native vegetation to cropland and pasture.

• Land use does not affect overall organic carbon stock (0-100 cm) in humic soils.

• Organic carbon distribution in the profile is affected by soil texture.

• Iron and aluminium are more important than land use or site for stabilising carbon.

ARTICLE INFO

Keywords: Extractable aluminium and iron Humic soil Subsoil texture Soil organic carbon and stocks

ABSTRACT

Land use effects on the stocks of soil organic carbon (SOC) are generally based on the topsoil. Although subsoil horizons have lower concentrations, they contain a significant amount of SOC which may be more strongly protected than that in the topsoil layers. Analysis of SOC storage must therefore include the whole profile in respect of climate change mitigation. Humic soils in South Africa have high organic C in the A horizon, while the amount of C stocks through the whole profile depth is unknown. This study was conducted at six sites in KwaZulu-Natal Province to determine the effect of land use and site factors on C stocks, texture, pH and extractable aluminium (Al) and iron (Fe) concentrations and their vertical distribution to 100 cm in soils with thick (>45 cm) and thin (<45 cm) humic A horizons. The land use at some sites had been changed from grassland to maize and cultivated pasture and at others from forest to sugarcane farming. Cultivation with field crops reduced the organic C, mainly in the upper 20 cm (from 110 to 22 g C kg⁻¹), with limited effect in deeper layers. The soils with thick humic A horizons and finer texture which had more of the C stocks in the 0–20 cm depth. Although cultivation reduced the soil C stocks in the surface layers, land use did not significantly affect the overall C stock (0–100 cm) at all sites. The high contents of extractable Fe (up to 340 mg kg⁻¹) and Al (up to 3700 mg kg⁻¹) stabilised the soil C and were more important than the effects of either land use or other site factors.

1. Introduction

Soil organic carbon (SOC) storage could regulate climate change through mitigation of emission of greenhouse gases, especially CO₂ (Lai et al., 2016). Under natural conditions, SOC may be protected in soil aggregates for long periods of time (Six et al., 1998). However, cultivation encourages decomposition of soil organic matter (SOM), loss of CO₂, and reduction of SOC (Lal, 2004; Edmondson et al., 2014). Most studies that have measured organic C have concentrated on the topsoil emphasising soil fertility (Rumpel and Kögel-Knabner, 2011), with fewer on the deeper layers (Eswaran et al., 1993; Batjes, 1996; Jobbagy and Jackson,

2000; Kögel-Knabner and Amelung, 2021). Although the SOC concentration is usually higher in the topsoil, the larger soil volume of many subsoils (even at low C concentrations) could translate to a greater C stock in those layers, with significant implications for soil C storage capacity and climate change mitigation.

The ability of soil profiles to store C varies with properties such as clay content, soil structure and nutrient content (Homann et al., 1995; Grüneberg et al., 2014). Generally, soils with high clay content have a higher concentration of SOC because of enhanced soil aggregation and organic matter protection by clay minerals (Mills and Fey, 2004; Miles et al., 2008; Saiz et al., 2012). Formation of organo-mineral complexes with

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https://doi.org/10.1016/j.heliyon.2021.e08709

Received 1 September 2021; Received in revised form 24 November 2021; Accepted 30 December 2021

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different species of aluminium (Al) and iron (Fe) is also important, especially in well-drained tropical and sub-tropical soils (Van De Vreken et al., 2016). These factors could affect the distribution of SOC within a soil profile. In addition to internal soil properties, external factors such as climate, land use and land management also affect the amount of SOC (Touré et al., 2013).

Humic soils of South Africa have unique topsoil characteristics of high organic C (>18 g kg⁻¹) and oxides of Al and Fe, and low base status (Soil Classification Working Group, 1991, 2018). Their good internal drainage, water retention and low capability for compaction make them highly productive (Fey, 2010). The variety of parent materials (e.g., sandstone, dolerite and shale) and climatic conditions (varying rainfall) under which they have formed has resulted in variations in their physicochemical properties and the profile distribution of SOC and stocks.

These soils have some similar characteristics to Andosols, although they formed under very different conditions. As in Andosols, the formation of Al-organic matter and Fe-organic matter complexes (Sakai et al., 2010) is thought to be a major mechanism of SOC stabilisation in humic soils. Characteristically, their clay mineralogy is dominated by kaolinite and oxides of Fe and Al resulting in strong micro-aggregation and high physical stability (Fey, 2010). The protection of organic C in micro-aggregates and through organo-mineral complexes could affect the profile distribution of SOC. The strong weathering undergone by these soils and their differences in particle size distribution (due to differences in parent material) suggest that micro-aggregation and formation of organo-mineral complexes could be affected by site characteristics with a resulting effect on concentrations and stocks of SOC in the profile. In addition, SOC concentrations and stocks could be affected by land use.

The amount of C in the topsoil of humic soils is generally known because the concentration is a fundamental soil classification criterion (Soil Classification Working Group, 1991, 2018). However, the amount of C stocks through the whole profile depth, which can be greater than 100 cm, is not known.

The good physical properties of humic soils have resulted in the conversion of large areas of land from either natural forest or grassland to commercial forests, cultivated pastures and crops including vegetables, sugarcane and maize. Land use change from natural vegetation to arable crops and pasture affects many soil processes and can result in significant changes to SOC (Yimer et al., 2008). Conversion of natural grasslands to croplands can shift the equilibrium between C inputs by the vegetation and outputs through organic matter decomposition (Lehmann and Kleber, 2015) with resultant decline in soil C stocks. Some wattle plantations on humic soils have been converted to sugarcane production and the effects of such land use change on SOC stocks are not understood. Management practices associated with cultivation, such as tillage and application of fertilisers and lime, encourage microbial decomposition of SOM which may result in changes in soil pH and alter the ability of the soil to retain C (Osher et al., 2003).

Considering the high concentration of SOC in humic soils, it is not clear whether such decomposition of organic matter will have significant effects on SOC concentration and stocks in the profile. The effects of cultivation, fertiliser application and liming on distribution of SOC in the soil profile need to be understood in relation to mitigation of climate change through soil storage of C.

There have been no studies carried out on the effect of land use change on C stocks and other physicochemical properties, including their vertical distribution, in humic soils of South Africa. This study was therefore undertaken to investigate the effects of land use and site factors on C stocks, texture, pH and extractable Al and Fe and their vertical distribution in some humic soils with thick (>45 cm) and thin (<45 cm) humic A horizons. Knowing the amounts and distribution of SOC stocks and other physicochemical properties of humic soils under different site characteristics, as affected by land use, is essential to understand the determinants of SOC storage in the soils and in making management decisions to minimise CO_2 emissions.

2. Materials and methods

2.1. Study sites and soil sampling

Soils were sampled at six sites (Table 1) under different land uses on commercial farms in KwaZulu-Natal Province, South Africa (Figure 1).

The soils from Cedara and Karkloof had a thin humic A horizon. The soils at both sites were derived from dolerite parent material and classified as Inanda form (Soil Classification Working Group, 2018); Umbric Rhodic Ferralsol (IUSS Working Group WRB, 2014). The Underberg soil also had a thin humic A horizon but was derived from Ecca shale and classified as Magwa form; Umbric Xanthic Ferralsol. The soils from Eston and Eshowe (Magwa form) and Wartburg (Inanda form) were derived from Natal Group sandstone parent material and all had a thick humic A horizon.

At Cedara and Karkloof the land use had been changed from uncultivated grassland to maize (*Zea mays*) and cultivated pasture. At Underberg all lands had been cultivated and so the pasture land use was compared to that under maize. At Eston and Wartburg (both commercial wattle (*Paraserianthes lophantha*)) and Eshowe (natural forest), large portions of the land had been converted to cultivation of sugarcane (*Saccharum officinarum*). A summary of the land use and management practices at the study sites is presented in Table 2.

Soil samples were collected from pits at three sampling points per land use per site at 0-5, 5-10, 10-15, 15-20, 20-30, 30-40, 40-50, 50-60, 60-80, and 80-100 cm depths. All the samples were air-dried, crushed and sieved to pass a 2-mm mesh before laboratory analysis.

2.2. Soil analysis

2.2.1. Total carbon concentration and stocks

Total C was analysed in triplicate using a LECO Trumac CNS Auto-Analyser version 1.1x (LECO Corporation, 3000 Lakeview Ave, ST. Joseph, MI, USA). The humic soils are naturally strongly weathered and acidic and so the measured total C represents organic C. Soil C stocks (Mg ha⁻¹) were calculated using Eq. (1) (Ellert and Bettany, 1995). The C stock in each sampled layer depth of the soil profiles was also expressed as a percentage of the total C stock.

where: X is the content of soil C (g kg⁻¹); BD is the bulk density (kg m⁻³) of the sampled layer (measured using undisturbed core samples taken in triplicate from each layer at each sampling site; results not shown); layer depth is the soil depth (m); 10000 is the conversion factor for m⁻² to ha⁻¹; 0.001 is the conversion factor for kg to Mg.

2.2.2. Iron and aluminium

Iron and Al were extracted in duplicate using the Mehlich 3 method (Mehlich, 1984). The soil (4 g) was suspended in 40 ml of the extractant ($0.2 \text{ M CH}_3\text{COOH} + 0.25 \text{ M NH}_4\text{NO}_3 + 0.015 \text{ M NH}_4\text{F} + 0.013 \text{ M HNO}_3 + 0.001 \text{ M EDTA}$) and shaken on an end-over-end shaker at 180 rpm for 5 min, and then centrifuged at 3500 rpm for 10 min. The extracts were analysed for Fe and Al by inductively coupled plasma atomic emission spectroscopy (Varian 720-ES ICP-AES).

2.2.3. Soil pH

Soil pH was measured in duplicate at a 1:2.5 soil: 1.0 M KCl solution ratio (van Reeuwijk, 2002) by immersing the electrode of a Hanna pH micro-processer meter (Model 211) into the supernatant liquid after the suspension had been allowed to stand for 30 min.

2.2.4. Particle size distribution

Particle size distribution was determined in duplicate by the pipette method (Gee and Bauder, 1986) after removal of organic matter with hydrogen peroxide (van Reeuwijk, 2002). Clay and silt were determined

Table 1. Geographic coordinates, elevation and climate of the study sites.

Study site	Coordinates	Elevation (m)	Average maximum temperature (°C)	Average minimum temperature (°C)	Average annual rainfall (mm)
Eston	29°37'S; 30°23'E	928	24.2	12.4	805
Eshowe	28°52'S; 31°25'E	555	26.7	15.4	1113
Wartburg	29°28'S; 30°37'E	933	24.5	11.1	798
Cedara	29°32'S; 30°17'E	1118	25.0	14.1	874
Karkloof	29°37'S; 30°28'E	1155	24.1	10.8	1150
Underberg	29°28'S; 30°37'E	1596	19.0	6.6	800



Figure 1. Location of the study sites in KwaZulu-Natal Province, South Africa.

after dispersion with Calgon (sodium hexametaphosphate and sodium bicarbonate) through sedimentation and sand was determined by dry sieving. The textural class was determined from the textural triangle (Soil Classification Working Group, 1991).

2.3. Statistical analysis

All data for each sampled depth layer were subjected to one-way analysis of variance (ANOVA), using the site-land use combination as the only factor. Multiple comparisons with the Tukey-Kramer test were performed to determine differences among means for all parameters at p < 0.05. The relationships between soil properties and SOC were analysed by Pearson's correlation coefficient for 0–30 cm, 30–60, 60–100 and 0–100 cm depths across all land uses and sites. The analyses were performed using GenStat 18th edition (VSN International, 2015). The model developed by Ros (2015) was tested for its effectiveness in estimating SOC stocks in the different humic soils, and compared to measured values.

3. Results

3.1. Soil carbon

Soil C declined with depth and the humic A horizons had more C than the underlying B horizons. There was >18 g kg⁻¹ C to a depth of 20 cm at

Cedara, 40 cm at Karkloof, 50 cm at Eston and Underberg, 60 cm at Wartburg and 100 cm at Eshowe (Table 3).

At each site, soils under field crops had less C in the 0–5 cm depth than when uncultivated (p < 0.05). At 5–10 cm, soils under field crops had lower C than uncultivated soils only at the Eston, Cedara and Karkloof sites, with no significant differences between land uses in layers below 10 cm (Table 3). Soil C under pasture was similar to grassland for all layers at the sites where both land uses occurred. On the other hand, soils under field crops had lower C than pasture only in the 0–5 cm depth at Karkloof.

The soils under field crops had no significant differences in C between sites at most depths. Cultivated soils from Eshowe had higher C at depths below 40 cm than at Cedara, Karkloof and Underberg under pasture. The soil from Cedara had less C than that from Karkloof at 0–5 and 15–20 cm, and Underberg in the top 20 cm. The grassland soil at Cedara and forest soil at Eshowe had significantly lower C than the forest soil at Eston at 5–10 cm (Table 3).

3.2. Soil carbon stocks

Land use did not affect the overall C stock (0–100 cm) at all sites, while site effects were significant (Table 4). The cultivated soils at Eshowe and Wartburg had higher total stock than at Cedara at 0–100 cm. Pasture soils at 0–100 cm at all sites had similar C stocks. The forest soil at

Table 2. Land use and management at the study sites.

Land use Description of land	d use and management
Eston and Wartburg	
Sugarcane (cultivated)	Formerly this land was under commercial wattle (<i>Paraserianthes lophantha</i>) forestry but is now planted to sugarcane (<i>Saccharum officinarum</i>). Fertilisers (NPK) are applied regularly. Dolomitic lime is applied to some fields to reduce soil acid saturation to 20 %, hence lime rates vary from 1 to 10 t ha ⁻¹ . There is no irrigation and 10 t ha ⁻¹ of chicken litter is applied before planting. The cane is burned before harvesting and the trash and residues are removed. Kale (<i>Brassica oleracea</i> var. <i>sabellica</i>) is usually planted as a rotation crop before re-planting sugarcane at Wartburg.
Forest (uncultivated)	The area has wattle trees (Paraserianthes lophantha) with no lime, fertilisers or irrigation used. Forest litter is left to accumulate on the soil surface.
Eshowe	
Sugarcane (cultivated)	The area is planted to sugarcane, with 130, 20, and 140 kg ha ⁻¹ of N, P and K, respectively, applied regularly. Dolomitic lime is also applied at 1 to 10 t ha ⁻¹ to reduce soil acid saturation to 20 % once every 10 years. There is no irrigation. Sunn hemp (<i>Crotalaria juncea</i>) or oats (<i>Avena sativa</i>) are usually planted as a rotation crop before re-planting sugarcane. The cane is burned before harvesting and the trash and residues are removed.
Forest (uncultivated)	The area has indigenous trees with no lime, fertilisers or irrigation used. Forest litter is left to accumulate on the soil surface.
Cedara	
Maize (cultivated)	Maize (<i>Zea mays</i>) is rotated with wheat (<i>Triticum aestivum</i>) during the winter (dry season). Fertilisers are applied every year at about 120 kg N ha ^{-1} , 20 kg P ha ^{-1} and 40 kg K ha ^{-1} while lime is applied once every 3 years based on acid saturation. Organic matter inputs include excreta of grazing cows during the winter. The area has been ploughed and conservation tillage was introduced 3 years before sampling. There is no irrigation.
Pasture (cultivated)	<i>Eragrostis curvula</i> is grown, cut and baled for cattle feed when mature, and is also grazed. Fertilisers are applied annually at 300, 10, and 200 kg ha ^{-1} , for N, P and K respectively, with no liming or irrigation. Organic matter inputs include excreta of grazing cows. No-till has been practised for 16 years.
Grassland (uncultivated)	The area has Kikuyu grass (Pennisetum clandestinum), with no fertiliser, lime, irrigation or tillage. The grass is burned.
Karkloof	
Maize (cultivated)	Maize is rotated with winter wheat, and the area has been under conservation tillage for 10 years before sampling. Fertilisers are applied every year at about 150 kg N ha ⁻¹ , 14 kg P ha ⁻¹ and 50 kg K ha ⁻¹ while lime is applied based on acid saturation. Organic matter inputs include excreta of grazing cows during the winter season. There is no irrigation.
Pasture (cultivated)	Ryegrass (<i>Lolium perenne</i>) and clover (<i>Trifolium</i> spp) are grown for grazing dairy cattle. The area has been under no-till for more than 10 years. Annually about 350 kg N ha ^{-1} as urea, 60 kg P ha ^{-1} , 80 kg K ha ^{-1} and lime are applied. Irrigation is applied with a centre pivot, while organic matter inputs are through excreta of grazing animals.
Grassland (uncultivated)	The area has Kikuyu grass. There is no application of fertilisers or lime and no irrigation or tillage. The grass is burned.
Underberg	
Maize (cultivated)	The area is used for maize and rotated with wheat during the winter season. Soil preparation involves the use of subsoiling, tillage and grading. Fertilisers are applied every year at about 120 kg N ha ⁻¹ , 20 kg P ha ⁻¹ and 40 kg K ha ⁻¹ while lime is applied based on acid saturation. Organic matter inputs included excreta of grazing cows during the winter There is no irrigation.
Pasture (cultivated)	Ryegrass has been grown for 10 years, and clover was recently planted (3 years). Lime at 1 t ha^{-1} and 365 kg N ha^{-1} as urea are applied annually after replanting. Physically, the formation of grazing course for the plant is used for incident of grazing course for the plant is used for incident of grazing course.

Wartburg had higher stock than the grassland soils at Karkloof and Cedara at 0–100 cm. The cultivated soil from Eshowe had higher C stock than those from Cedara, Karkloof and Underberg at 40–60 cm (Table 4). When expressed as a percentage of profile C stock, the soils from Eshowe and Wartburg had a lower proportion of the C stock in the 0–20 cm depth and higher in the 20–100 cm depth when compared with Cedara, Karkloof and Underberg. The pasture soil from Cedara had a lower C stock than those at Karkloof and Underberg only at 0–20 cm, with no differences between the sites when expressed as a percentage of profile C stock (Table 4).

Uncultivated soils from Eston and Karkloof at 0–20 cm had a higher C stock and as a percentage of profile C stock than other sites. Eshowe and Wartburg soils had higher C stocks in the 60–100 and 20–100 cm depths when compared to soils from Cedara, Karkloof, Underberg and Eston.

The percentage of the profile C stock in the 0–20 cm depth ranged from 25 to 50 % and in the 20–100 cm depth from 42 to 75 % for Eston, Eshowe and Wartburg. At Cedara, Karkloof and Underberg, the proportion of profile C stock in the 0–20 cm depth ranged from 35 to 58 % and from 42 to 65 % in the 20–100 cm depth (Table 4).

3.3. Extractable iron

At 0–5 and 5–10 cm, the cropped soils had significantly lower extractable Fe than uncultivated and pasture soils at all sites except Eshowe (0–5 cm), while there were no differences at 15–20 cm except at Wartburg and Underberg (Table 5). Below 20 cm, there were no differences as a function of land use, except at Karkloof at all depths, Wartburg at 60–80 and 80–100 cm where cultivated soils had lower extractable Fe than uncultivated, and Eston at 40–50 and 80–100 cm where the cultivated soil had higher extractable Fe.

Cultivated soils were significantly different in extractable Fe between sites in the top 10 cm, with Eston having the highest, followed by Underberg and Eshowe, with Wartburg, Karkloof and Cedara having the least (Table 5). The cultivated soil from Eston had higher Fe than all other sites at most depths from 10 to 60 cm. Below 60 cm those at Wartburg, Cedara and Karkloof had lower Fe than at Underberg, Eshowe and Eston.

The pasture soil from Underberg had significantly higher extractable Fe than those at Cedara and Karkloof at 0–5, 40–50, 60–80 and 80–100 cm (Table5). There were significant differences between sites in extractable Fe in the uncultivated soils (grassland and forest), with Eshowe < Cedara = Wartburg < Karkloof < Underberg = Eston at 0–5 cm (Table 5). At 5–10 cm, extractable Fe at Cedara was the lowest of all the sites. Most sites were similar below 10 cm. The humic A horizons had more extractable Fe than the underlying B horizons (Table 5).

3.4. Extractable aluminium

At Karkloof and Underberg there was no difference between land uses in extractable Al at most depths except at 20–30 and 30–40 cm at Underberg where soil under maize was higher than under pasture (Table 6). There were also no land use differences in the top 30 cm of the Eston soils, while the soil under sugarcane had higher extractable Al than under forest below 30 cm. At Eshowe, soil under sugarcane had lower Al at all depths except 0–5 cm. The cultivated soil (under maize) at Cedara generally had lower Al than the other land uses at most depths.

The cultivated soils from Eshowe and Eston had significantly higher Al concentrations than the other sites at most depths (Table 6). Cultivated soils at Eston below 60 cm and Eshowe below 80 cm had higher extractable Al than the others. Pasture soils were in the order Cedara > Karkloof > Underberg at most depths, except 10–15, 30–40, 40–50 and 80–100 cm where Cedara = Karkloof. Uncultivated soils at Cedara and Wartburg (grassland and forest) had higher extractable Al than the other sites in the top 10 cm. Below 10 cm, uncultivated soils from Wartburg

Table 3. Concentration of soil carbon ($g kg^{-1}$) under different land uses at the six sites at each sampled depth (n = 42).

Site	Land use	0–5	5–10	10–15	15–20	20–30	30–40	40–50	50–60	60–80	80–100
						(cm)					
Eston	Sugarcane	40 ^{abc}	38 ^{abc}	28 ^a	23 ^a	22 ^{abc}	26 ^{ab}	26 ^{abcd}	18 ^{abc}	15 ^{abcd}	10 ^{abc}
	Forest	88 ^{fgh}	110 ^g	52 ^{abc}	33 ^{abc}	24 ^{abc}	20 ^{ab}	18 ^{abcd}	12 ^{ab}	12 ^{abcd}	4 ^a
Eshowe	Sugarcane	49 ^{abcd}	43 ^{abcd}	43 ^{abc}	41 ^{abc}	39 ^{abcd}	38 ^b	33 ^d	30 ^c	22 ^{de}	21 ^{de}
	Forest	72 ^{defg}	49 ^{bcd}	41 ^{abc}	35 ^{abc}	30 ^{abcd}	28 ^{ab}	27 ^{bcd}	27 ^c	21 ^{cde}	18 ^{cde}
Wartburg	Sugarcane	33 ^{ab}	31 ^{ab}	24 ^a	30 ^{ab}	29 ^{abcd}	26 ^{ab}	24 ^{abcd}	22 ^{bc}	17 ^{bcde}	14 ^{bcd}
	Forest	76 ^{defg}	54 ^{bcdef}	46 ^{abc}	44 ^{bc}	40 ^{bcd}	37 ^b	33 ^{cd}	30 ^c	29 ^e	24 ^e
Cedara	Maize	24 ^a	23 ^a	22 ^a	22 ^a	14 ^a	11 ^a	10^{ab}	8 ^a	6 ^{ab}	3 ^a
	Pasture	51 ^{abcd}	43 ^{abcd}	25 ^a	26 ^{ab}	24 ^{abc}	15 ^{ab}	9 ^{ab}	6 ^a	4 ^a	3 ^a
	Grassland	63 ^{cdef}	57 ^{cdef}	30 ^{ab}	23 ^a	19 ^{ab}	18 ^{ab}	14 ^{abc}	13 ^{ab}	10^{abcd}	6 ^{ab}
Karkloof	Maize	57 ^{bcde}	52 ^{bcde}	37 ^{abc}	28 ^{ab}	34 ^{abcd}	20^{ab}	12^{ab}	10^{ab}	8 ^{abc}	7 ^{ab}
	Pasture	108 ^h	64 ^{def}	50 ^{abc}	51 ^{cd}	46 ^{cd}	24 ^{ab}	8 ^a	6 ^a	3 ^a	0.9 ^a
	Grassland	97 ^{gh}	78 ^f	71 ^c	52 ^{cd}	45 ^{cd}	32 ^{ab}	23 ^{abcd}	12^{ab}	5 ^{ab}	0.6 ^a
Underberg	Maize	60 ^{bcdef}	52 ^{bcde}	46 ^{abc}	35 ^{abc}	32 ^{abcd}	27 ^{ab}	21^{abcd}	12 ^{ab}	8 ^{abc}	6 ^{ab}
	Pasture	85 ^{efgh}	76 ^{ef}	64 ^{bc}	66 ^d	51 ^{ab}	32 ^{ab}	19 ^{abcd}	13 ^{ab}	11 ^{abcd}	3 ^a

Values followed by different letters in a column are statistically different for each site-land use treatment per depth at p = 0.05; Humic A horizon = bold font; B horizon = normal font.

Table 4. Soil carbon stocks (Mg ha^{-1}) (and percentage) in different layers of the soil profiles under different land uses at the six sites (n = 42).

Site	Land use	Depth (cm)									
		0–20	20–40	40–60	60–100	20–100	0–100				
Eston	Sugarcane	80 ^{abc} (32 ^{AB})*	58 ^{ab} (23 ^A)	55 ^{bcde} (22 ^D)	57 ^{ab} (23 ^{CDE})	170 ^{abcd} (68 ^{DE})	250 ^{abcd}				
	Forest	146 ^{ef} (50 ^{DE})	65 ^{ab} (22 ^A)	40 ^{abcd} (14 ^{ABCD})	40 ^{ab} (14 ^{ABCD})	145 ^{ab} (50 ^{AB})	291 ^{bcde}				
Eshowe	Sugarcane	96 ^{abcd} (25 ^A)	83 ^{ab} (22 ^A)	71 ^{de} (19 ^{CD})	127 ^d (34 ^E)	281 ^{de} (75 ^E)	377 ^{de}				
	Forest	103 ^{bcd} (28 ^A)	79 ^{ab} (22 ^A)	73 ^{de} (20 ^D)	110 ^{cd} (30 ^E)	262 ^{cde} (72 ^E)	365 ^{cde}				
Wartburg	Sugarcane	77 ^{ab} (27 ^A)	73 ^{ab} (25 ^A)	63 ^{cde} (22 ^D)	76 ^{bc} (26 ^{DE})	212 ^{bcde} (73 ^E)	289 ^{bcde}				
	Forest	103 ^{bcd} (26 ^A)	89 ^b (22 ^A)	77 ^e (19 ^{CD})	130 ^d (33 ^E)	296 ^e (74 ^E)	399 ^e				
Cedara	Maize	56 ^a (43 ^{CDE})	31 ^a (24 ^A)	22 ^{ab} (17 ^{BCD})	21 ^a (16 ^{BCD})	74 ^a (57 ^{BDC})	130 ^a				
	Pasture	88 ^{abcd} (48 ^{CDE})	58 ^{ab} (32 ^A)	18 ^a (10 ^{AB})	18 ^a (10 ^{ABC})	94 ^a (52 ^{ABC})	182 ^{ab}				
	Grassland	72 ^{ab} (35 ^{ABC})	50 ^{ab} (25 ^A)	35 ^{abc} (17 ^{BCD})	46 ^{ab} (23 ^{CDE})	131 ^{ab} (65 ^{CDE})	203 ^{ab}				
Karkloof	Maize	112 ^{bcde} (42 ^{BCD})	78 ^{ab} (30 ^A)	31 ^{abc} (12 ^{ABC})	42 ^{ab} (16 ^{BCD})	151 ^{abc} (57 ^{BCD})	263 ^{abcd}				
	Pasture	159 ^f (58 ^E)	86 ^b (31 ^A)	20 ^a (7 ^A)	10 ^a (4 ^A)	116 ^{ab} (42 ^A)	275 ^{bcde}				
	Grassland	118 ^{cde} (49 ^{CDE})	69 ^{ab} (29 ^A)	39 ^{abcd} (16 ^{BCD})	14 ^a (6 ^{AB})	122 ^{ab} (51 ^{ABC})	240 ^{abc}				
Underberg	Maize	95 ^{abcd} (43 ^{BCD})	58 ^{ab} (26 ^A)	37 ^{abc} (17 ^{BCD})	32 ^{ab} (14 ^{ABCD})	127 ^{ab} (57 ^{BCD})	222 ^{ab}				
	Pasture	126 ^{def} (43 ^{BCD})	87 ^b (30 ^A)	40 ^{abcd} (14 ^{ABCD})	38 ^{ab} (13 ^{ABCD})	165 ^{abc} (57 ^{BCD})	291 ^{bcde}				

^{*} Lower-case superscripts in a column are for comparisons of C stocks in Mg ha⁻¹ and the upper-case superscripts in a column are for comparisons of C stocks as a percentage of profile C stock for each site-land use treatment per layer at p = 0.05.

and Eshowe had higher Al concentrations than those from other sites at most depths (Table 6). There was no difference in the concentration of extractable Al between the humic A horizons and the underlying B horizons.

3.5. Soil pH

All the soils were acidic with most samples having a pH of < 5.0. The exceptions were at 80–100 cm under grassland at Cedara (pH = 5.2) and below 20 cm at Karkloof under maize where the pH increased with depth from 5.1 to 6.1 (results not shown). There were no land use effects at most of the sites except Karkloof at all depths and Eston at 5–10, 10–15 and 15–20 cm where the cultivated soil had higher pH than uncultivated and pasture soils.

3.6. Soil texture

Soils from Eston were sandy clay loams (21-37 % clay; 15-28 % silt; 47-55 % sand), while at Eshowe the soil under forest was sandy clay loam throughout the profile (21-30 % clay; 13-28 % silt; 48-56 % sand)

and clay loam (0–5 and 10–15 cm) and loam under sugarcane (19–28 % clay; 27–38 % silt; 41–59 % sand). At Wartburg the soil under sugarcane was mainly a clay loam (27–41 % clay; 16–30 % silt; 34–46 % sand) and that under forest a clay (33–52 % clay; 19–37 % silt; 28–34 % sand). All the soils at Cedara and that under maize at Karkloof had a clay texture at all depths (47–66 % clay; 19–45 % silt; 7–22 % sand). The other soils at Karkloof were mainly silty clay at all depths of the profile (39–57 % clay; 37–53 % silt; 4–16 % sand). The soils at Underberg were mainly silty clay loam (36–44 % clay; 42–52 % silt; 11–16 % sand) to 40 cm and silty clay in deeper layers, irrespective of land use.

3.7. Relationship between carbon and other soil properties across all land uses at the six sites

Soil C was significantly positively correlated with extractable Fe at all depths and with percent silt in the 0–30 cm layer (Table 7). Soil C was negatively correlated with pH in the 30–60 cm layer, with clay below 30 cm and with silt below 60 cm depth (Table 7). The correlation of SOC was positive with sand below 30 cm and with extractable Al below 60 cm (Table 7).

Table 5. Concentration of extractable iron (mg kg⁻¹) under different land uses at the six sites at each sampled depth (n = 28).

Site	Land use	0–5	5–10	10–15	15–20	20–30	30–40	40–50	50–60	60–80	80–100
							- (cm) ———				
Eston	Sugarcane	254 ^f	224 ^{de}	263 ^{bc}	278 ^e	255 ^e	292 ^e	276 ^d	248 ^f	130 ^{de}	154 ^g
	Forest	340 ^g	296 ^f	304 ^c	259 ^{de}	252 ^e	198 ^{de}	182 ^c	179 ^{ef}	87 ^{cd}	61 ^{cde}
Eshowe	Sugarcane	174 ^{de}	159 ^c	135 ^{ab}	145 ^{abc}	149 ^{abcde}	134 ^{bcd}	152 ^{bc}	132 ^{bcde}	127^{de}	131 ^g
	Forest	114 ^{ab}	220 ^{de}	184 ^{bc}	174 ^{bcd}	121 ^{abcd}	146 ^{cd}	134 ^{bc}	156 ^{def}	127 ^{de}	128 ^g
Wartburg	Sugarcane	134 ^{bc}	127 ^b	75 ^a	76 ^a	66 ^{abcd}	58 ^{abc}	46 ^a	38 ^{abc}	17 ^a	6 ^a
	Forest	180 ^{de}	233 ^e	141 ^{ab}	194 ^{cde}	130 ^{abcde}	127 ^{abcd}	95 ^{ab}	63 ^{abcd}	79 ^{bc}	40 ^{bcde}
Cedara	Maize	93 ^a	94 ^a	97 ^a	88 ^{ab}	38 ^{ab}	18 ^a	14 ^a	6 ^a	10 ^a	16 ^{abc}
	Pasture	166 ^{cde}	163 ^c	109 ^a	105 ^{ab}	102 ^{abcd}	46 ^{abc}	34 ^a	28^{ab}	34 ^a	28 ^{bcd}
	Grassland	155 ^{cd}	147 ^{bc}	109 ^a	77 ^a	42 ^{abc}	27 ^{ab}	22^{a}	16 ^a	18 ^a	30 ^{bcde}
Karkloof	Maize	134 ^{bc}	102 ^a	107^a	103 ^{ab}	33 ^a	44 ^{abc}	39 ^a	44 ^{abc}	41 ^{ab}	53 ^{bcde}
	Pasture	$237^{\rm f}$	206 ^d	194 ^{abc}	175 ^{bcd}	174 ^{de}	64 ^{abc}	38 ^a	15 ^a	7 ^a	*
	Grassland	195 ^e	163 ^c	191 ^{abc}	148 ^{abc}	166 ^{bcde}	179 ^{de}	153 ^{bc}	136 ^{de}	90 ^{cd}	74 ^{def}
Underberg	Maize	169 ^{de}	154 ^c	136 ^{ab}	91 ^{ab}	148 ^{abcde}	102 ^{abcd}	161 ^{bc}	96 ^{abcde}	119 ^{cde}	109 ^{fg}
	Pasture	325 ^g	208^d	212 ^{abc}	201 ^{cde}	169 ^{cde}	141 ^{cd}	139 ^{bc}	74 ^{abcde}	140 ^e	75 ^{ef}

Values followed by different letters in a column are statistically different for each site-land use treatment per depth at p = 0.05; *below detection; Humic A horizon = bold font; B horizon = normal font.

4. Discussion

The higher organic C concentration in the upper soil layers and its decrease with depth at all sites were consistent with the main additions of organic matter to the soil surface. Organic C was significantly greater under forest, grassland and pasture, as expected, due to the lack of disturbance in these land uses compared to the cultivated soils. This might be due to protection within soil aggregates and their destruction through tillage that increases aeration and exposes the organic matter to microbial decomposition, reducing the C, especially in the surface layers. The C concentrations found in this study were similar to those of Ros (2015) who measured the amounts of C in some humic soils derived from dolerite and shale to 100 cm depth under farmlands, forestry plantations and grasslands in the Midlands region of KwaZulu-Natal.

The substantial amount of organic C in the 5–20 cm depth and less in deeper layers below 40 cm of uncultivated clay soils, compared to the loam soils, could be due to the eluviation of C in the coarser-textured soils. The high clay percentage in soils derived from dolerite (Cedara

and Karkloof) and shale (Underberg) could have caused restriction in the movement of C down the soil profile, while soils with higher sand contents at Eston and Eshowe had more soil C below the 40–50 cm depth (Burke et al., 1989; Miles et al., 2008; Preger et al., 2010; Carvalho et al., 2017). The movement of organic C in response to textural differences explains the C stocks that were lower as a proportion of the total in the 0–20 cm depth and higher in the 20–100 cm depth of soils from Eshowe and Wartburg than soils from Cedara, Karkloof and Underberg. However, there may also be fewer roots at depth in the finer-textured subsoils due to either poor penetration due to the clay content (Schneider and Don, 2019) or the lack of necessity for roots to extend into the subsoil for water or nutrients due to a greater amount of both in the upper layers (Zeng et al., 2006).

Although cultivation resulted in lower C concentrations in the 0–5 and 5–10 cm depths at most sites, effects on the soil C stocks were only significant at Eston in the 0–20 cm depth. The lower C in the upper layers did not result in a decline in the overall C stock. This could be due to the high soil C (from 110 to 22 g kg⁻¹) in the different layers within the 0–20

Table 6. Concentration of extractable aluminium (mg kg⁻¹) under different land uses at the six sites at each sampled depth (n = 28).

Site	Land use	0–5	5–10	10–15	15–20	20-30	30–40	40–50	50–60	60–80	80–100
						(cm))				
Eston	Sugarcane	1708 ^{cdef}	1657 ^{bcd}	1733 ^{de}	1859 ^c	1921 ^{de}	2411 ^d	2407 ^{ef}	3189 ^f	3196 ^{gh}	2730 ^g
	Forest	2200^{efgh}	1690 ^{bcd}	1313 ^{bcd}	1655 ^c	2230 ^e	1436 ^{bc}	1612 ^{cd}	1306 ^{abc}	2003 ^{de}	1433 ^{bcd}
Eshowe	Sugarcane	2610 ^{hi}	2457 ^{ef}	2341 ^f	2481 ^d	2121 ^e	1996 ^{cd}	3670 ^g	2674 ^{ef}	1506 ^{bcd}	2522 ^{fg}
	Forest	1848 ^{defg}	2092 ^{de}	3089 ^g	3307 ^e	3329 ^f	3173 ^e	3206 ^g	3140 ^f	2621 ^{fg}	3003 ^g
Wartburg	Sugarcane	1040 ^{abc}	1258 ^{ab}	1243 ^{abc}	1399 ^{bc}	1613 ^{cde}	1544 ^{bc}	1551 ^{bcd}	1389 ^{bc}	1520 ^{bcd}	1402 ^{bcd}
	Forest	2326 ^{fgh}	2530 ^{efg}	3315 ^g	3580 ^e	3695 ^f	3491 ^e	2974 ^{fg}	1267 ^{abc}	3407 ^h	3623 ^h
Cedara	Maize	715 ^a	955 ^a	875 ^{ab}	1062 ^{ab}	730 ^{ab}	844 ^{ab}	917 ^{abc}	1228^{abc}	1017 ^b	946 ^b
	Pasture	2394 ^{ghi}	2972 ^g	1807 ^e	2719 ^d	2120 ^e	2391 ^d	1514 ^{bcd}	2798 ^f	2400 ^{ef}	2071 ^{ef}
	Grassland	3019 ⁱ	2593 ^{fg}	1479 ^{cde}	1577 ^c	1386 ^{bcd}	1521 ^{bc}	1534 ^{bcd}	2329 ^{def}	1741 ^{cd}	1414 ^{bcd}
Karkloof	Maize	1576 ^{bcde}	1560 ^{bc}	1687 ^{cde}	1778 ^c	1728 ^{cde}	1735 ^{cd}	1818 ^{de}	1840 ^{cde}	1850 ^{cde}	1813 ^{de}
	Pasture	1476 ^{bcd}	1938 ^{cd}	1935 ^{ef}	1458 ^{bc}	1169 ^{bc}	1735 ^{cd}	1916 ^{de}	1637 ^{bcd}	1341 ^{bc}	1560 ^{cde}
	Grassland	1613 ^{bcde}	1714 ^{bcd}	1826 ^e	1904 ^c	1838 ^{cde}	1915 ^{cd}	2049 ^{de}	1840 ^{cde}	1918 ^{cde}	1076 ^{bc}
Underberg	Maize	1020 ^{ab}	852 ^a	868 ^{ab}	995 ^{ab}	1279 ^{bcd}	1544 ^{bc}	842 ^{ab}	775 ^{ab}	172 ^a	7 ^a
	Pasture	555 ^a	977 ^a	813 ^a	629 ^a	338 ^a	325 ^a	470 ^a	443 ^a	43 ^a	29 ^a

Values followed by different letters in a column are statistically different for each site-land use treatment per depth at p = 0.05; Humic A horizon = bold font; B horizon = normal font.

cm depth, such that the effects of C content in the upper 10 cm did not significantly affect the C stock of the 0-20 cm layer. The lowest C stocks were in the 60-100 cm depth, particularly in the higher clay content soils, under both cultivated and uncultivated land uses. The C stocks found in this study were higher than those reported by Ros (2015) of 13.7, 13.4 and 17.1 kg m⁻³ (equivalent to 137, 134 and 171 Mg ha⁻¹) for cultivated, grassland and forest soils, respectively, to a depth of 100 cm in humic soils from the same region. In addition, the C stocks in this study were higher than those of non-humic soils in studies that investigated subsoil C stocks to a depth of 100 cm (Kunlanit et al., 2019; Ramalho et al., 2020; Gentile et al., 2021). Kunlanit et al. (2019) found forest soils had higher stocks of SOC (115.0 Mg ha^{-1}) than under paddy rice (100 Mg ha^{-1}) and cassava (87 Mg ha^{-1}) and Ramalho et al. (2020) found C stocks under no-tillage and ryegrass grazing were 212.2 and 202.2 Mg C ha^{-1} , respectively, in the 0–100 cm depth. Gentile et al. (2021) found the mean cumulative C stock of kiwifruit orchards and pasture were 169 and 168 Mg C ha⁻¹, respectively, down to 200 cm. These results clearly show that humic soils have higher stored C to a depth of 100 cm than non-humic soils and mitigate CO2 emission with positive effects on soil quality and climate change.

The model developed by Ros (2015) for profile C stocks based on C concentrations in the topsoil either closely estimated (Cedara and Underberg) or overestimated (Karkloof) the volumetric C stocks in soils with a thin humic A but grossly underestimated those in soils with thick humic A horizons, irrespective of land use. For example, the estimated C stocks in the forest soils of Eston, Eshowe and Wartburg were equivalent to 249, 223 and 256 Mg ha⁻¹, while the measured values were 291, 365 and 399 Mg ha⁻¹, respectively (Table 3). This suggests that the model needs modification if it is to be useful for estimating C stocks in soils with thick humic A horizons.

Carbon concentrations >18 g kg⁻¹ were found below 50 cm, with more in the soils with thick humic A horizons. This suggests that thick humic soils can store more C at depth compared to thin humic soils. Although thin humic soils can store a substantial amount of C, depending on site and management practises (Thorburn et al., 2012), they are more prone to a decline because most of the C is in the surface layers which are most affected by a change in land use (Borchard et al., 2019).

Although the soils from Cedara, Underberg and Karkloof had thin humic A horizons while those at Eston, Eshowe, Wartburg had thick humic topsoils, these groups did not result in significant differences in the overall C stock to a depth of 100 cm. This could be explained by the distribution of the C between the topsoil and subsoil of the two groups (Kunlanit et al., 2019). The thin humic soils had more C in the topsoil and less in the subsoil while the reverse was the case for the thick humic soils. Carbon stored in the deeper layers of soil may persist for longer than that closer to the surface where there is more rapid decomposition of organic matter as a result of processes such as wetting and drying, warming and cooling, greater gas exchange (more O₂), and increased microbial activity (Fierer and Schimek, 2002). If long-term soil C storage is to be effective in assisting the mitigation of climate change the subsoil layers are of crucial

Table 7. Pearson's correlation coefficients of soil carbon and selected soil properties.

Parameter	Depth (cm)									
	0-30 (n = 70)	30-60 (n = 42)	60-100 (n = 28)	0-100 (n = 140)						
Extractable Fe	0.49**	0.43**	0.42*	0.62**						
Extractable Al	0.01	0.15	0.68**	0.09						
рН	0.08	-0.41**	-0.05	-0.14						
Clay	-0.14	-0.39**	-0.36*	-0.13						
Silt	0.47**	-0.08	-0.49**	0.16						
Sand	-0.19	0.34*	0.59**	-0.01						

**Correlation is significant at $p \le 0.01$. *Correlation is significant at $p \le 0.05$. importance. The results from this study show that the thick humic soils are therefore of particular interest in this respect with their higher C contents deeper in the profile. Soils with high sand content store more C in the subsoil, where there is limited oxygen, while in clayey soils protection in micro-aggregates and formation of organo-mineral complexes could be a more important process.

The lack of an effect of land use on the C stocks in both thick and thin humic soils could be due to the high amount of C naturally present in these soils such that conversion to cultivation has had little effect (Gentile et al., 2021). The decline in SOM and thus loss of C that would be expected following conversion may have been counterbalanced by inputs from decomposing crop roots and shoot residues that play a vital role in the maintenance and accumulation of SOM (Mwafulirwa et al., 2019). Although there has been a loss of C from the cultivated soils compared to the uncultivated soils at each site in this study, this has been moderated by the use of land for either a long-term crop such as sugarcane (Carvalho et al., 2017) or the use of conservation agriculture methods such as no-till, crop rotation and cover crops that have allowed profile C stocks to remain high (Govaerts et al., 2009).

Stabilisation of C in humic soils is encouraged by their low pH and high concentrations of extractable Fe and Al (Rumpel and Kögel-Knabner, 2011; Neculman et al., 2013; Mora et al., 2014). The soils in this study had acidic pH that was not affected significantly by land use, particularly within sites, except at Eston and Karkloof. However, even at these two sites the highest pH values were only about 5.0 in the topsoil probably as a result of liming. These low pH values, together with low base cation content, will discourage microbial activity and thus allow C to remain in the soil (Mora et al., 2014).

The positive correlations between C and extractable Fe in the 0-100 cm and Al in the 60-100 cm depths suggest that Fe and Al might be assisting in sequestering soil C. The lack of correlation between Al and C in the topsoil, while the correlation was significantly positive in the subsoil, agreed with the findings of Dell'Olio et al. (2008), who also used Mehlich 3 to extract Al and Fe. The concentration of Mehlich 3 extractable Al was around 7 times higher in the topsoil and about 11 times higher in the subsoil, when compared to Fe, which could explain the significant correlation of Al with C in the subsoil (Dell'Olio et al., 2008). The soil C released by microbial activity as a result of conversion to cultivation is stabilised over the long term by forming strong chemical bonds on the surface of clay particles through interactions with Fe and Al oxides (Briedis et al., 2016). The orders of magnitude higher Al than Fe extracted with Mehlich 3 can be explained by the presence of fluoride (F) in the extractant which extracts Al but not Fe from amorphous oxides. Fernandez Marcos et al. (1998) showed that Al extractable by oxalate was strongly correlated with the Mehlich 3 extractable fraction. However, the correlation was not significant for Fe. The concentrations of Al (up to 3700 mg kg^{-1}) were generally higher and those of Fe (up to 340 mg kg^{-1}) generally lower than those observed by Fernandez Marcos et al. (1998) in Northwest Spain (Al: 24–2600; Fe:150–1500 mg kg⁻¹). The significant positive correlation between Mehlich 3 extractable Fe and C suggests that available Fe is important in the stabilisation of organic C in humic soils. Fernandez Marcos et al. (1998) reported a strong correlation of Mehlich 3 and the DTPA extractable Fe (available) fraction, and explained the relationship by the EDTA in the Mehlich 3 extractant. The presence of Al and Fe is therefore probably a more important factor controlling the fate of organic C in humic soils than the climatic conditions or the land use, both of which varied across the sites in this study while C stocks were largely unaffected. Although land use appeared to affect extractable Fe and Al, possibly due to organic matter that can complex with these cations, their concentration appeared to be more related to site factors, including the extent of weathering. Although there was no clear trend with rainfall, the loamy soils at Eston and Eshowe had higher extractable Fe and Al than the more clavey soils at Cedara, Underberg and Karkloof suggesting that greater aeration in the sandier soils could have increased the release of these cations (Van De Vreken et al., 2016).

5. Conclusion

This study found that cultivation reduced the organic C of humic soils, mainly in the upper 20 cm, with limited effect in deeper layers. Although cultivation reduced soil C stocks in the surface layers, the total C stock of the profile to 100 cm was not significantly affected when compared to uncultivated soils. The distribution of the C was such that soils from sites with dolerite and shale parent materials accumulated C close to the surface (thin humic A) while in those developed from sandstone (thick humic A) more C accumulated in deeper layers of the profiles. The C stocks ranged from 130-290 and 250–399 Mg ha^{-1} for soils with thin (clayey) and thick (sandy) humic A horizons, respectively. The soils with thick humic A horizons stored more C (up to 70 % of the total) in the deeper layers compared to those with thin humic A horizons which had more of the C stocks (up to 50 % of the total) in the 0–20 cm depth. The acidic nature of humic soils, both uncultivated and cultivated (despite additions of lime), together with their high contents of extractable Fe and Al, encourage stabilisation of the soil C and were more important than the effects of both land use and climate. The lack of negative effects of cultivation on C stocks in humic soils shows that they are highly effective in storing C regardless of land use. In order to maintain the high amounts of SOC and so assist in the long-term storage of C needed to assist the mitigation of climate change it is recommended that conservation agriculture methods such as no-till, crop rotation and cover crops be used for the management of humic soils.

Declarations

Author contribution statement

Ntwanano Moirah Malepfane: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Pardon Muchaonyerwa: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Jeffrey Charles Hughes; Rebecca Zengeni: Conceived and designed the experiments; Wrote the paper.

Funding statement

This work was supported by the National Research Foundation (Grant number: GUN93593).

Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Acknowledgements

We are grateful to the farmers and land owners for permitting us to collect soil samples from their properties. We thank the Soil Science technical staff for their assistance with laboratory analysis.

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