Predicting changes in soil organic carbon after a low dosage and one-time addition of biochar blended with manure and nitrogen fertilizer

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Modeling plays an important role in predicting the long-term effects of biochar on soil organic carbon dynamics. The objective of our study was to apply the Century model to assess changes in temporal soil organic carbon in soil amended with manure and nitrogen fertilizer (MN), with manure and biochar (MB) or with manure, nitrogen fertilizer and biochar (MNB). We determined that, after 115 years, soil organic carbon stocks could not reach a steady state (equilibrium) or pre-cultivation levels, regardless of amendment type. Our results showed that a biennial input of manure and nitrogen fertilizer (MN) led to a 84% increase in soil organic carbon compared to a 79% (MNB) and 70% (MB) increase when amendments contained biochar. However, the quantity of organic matter input from crop residues and amendments was sufficient to increase the active fraction, with a turnover time of months to years, by 86%. In fact, carbon associated with the slow fraction, with a turnover time of 20 to 50 years, was the key driver for soil organic carbon accumulation in all amendment types. Although the passive fraction is the most stable form of carbon in the soil, with a turnover time of 400 to 100 years, once manure and biochar were added to the soil, this fraction increased up to 32%. Our results provided further insight into the ability of Century to accurately predict changes in soil organic carbon stocks when a combination of manure, nitrogen fertilizer or biochar were added to soil. Century predicted soil organic carbon stocks within -1% to +9% of measured values. However, further fine-tuning of the model is required since biochar undergoes chemical transformations (e.g., ageing) and changes soil physical parameters (e.g., bulk density) that can not be currently accounted for in the Century model. Addressing these limitations of Century will also help to increase the relationship between measured and predicted values.

1 Introduction

Over the last 200 years, land conversion followed by intensive agricultural practices was the primary agent for drastic losses of soil organic carbon (1). For example, land conversion from undisturbed ecosystems to managed agroecosystems depleted soil organic carbon stocks by 30% to 50% within five decades in temperate environments (2). Due to the decline in soil organic carbon stocks, coupled with soil erosion and declining soil fertility, sustainable approaches to agricultural management (e.g., conservation agriculture) emerged (3). To date, conservation agriculture has helped to improve soil structure, microbial diversity and biomass, water infiltration and storage, and plant nutrient availability due to greater soil organic matter retention (3). Thus, increased levels of soil organic matter are the driving force associated with improved soil properties under conservation agriculture (4).

Sandhu et al. (5) suggested that biochar, a carbon rich material produced by the pyrolysis (thermochemical conversion) of biomass, could also be used as an organic amendment to help ameliorate degraded soils. This is because biochar influences soil chemical and physical properties that encourage microbial activity (6). To date, most studies took place in tropical agroecosystems (7). This is because biochar raises soil pH, which improves soil microbial activity, and consequently increases soil fertility (7). Since soils in the temperate zone are inherently more fertile than tropical soils, the effect of biochar on soil physicochemical and biological properties and its ability to improve soil productivity remains inconclusive (8). However, Lévesque et al. (8) concluded that in temperate agroecosystems a broader view of biochar, moving beyond soil and crop productivity, may be preferable due to its potential to sequester carbon. Although biochar properties can vary widely depending on the type of feedstock and pyrolysis conditions, its aromatic structure causes it to be exceptionally recalcitrant, resisting chemical and biological degradation, making it stable in soil for hundreds of years (9). Thus, biochar has received attention from numerous researchers as a potential pathway for carbon sequestration and climate change mitigation (5).

To date, the majority of studies (>60%) evaluated the impact of biochar on soil using high application rates ranging from 1000 g m^{-2} to 3000 g m^{-2} (10). High biochar application rates were based on research that suggested more than 1000 g m^{-2} are required to observe a positive impact on temperate soil physicochemical properties (9). However, it is currently difficult to obtain a sufficient supply of high-quality biochar for large-scale agricultural applications (11). Additionally, Oelbermann et al. (11) suggested that high application rates are not economically feasible due to a shortage of high-quality biochar. In a systematic review of more than 25 meta-analyses on the use of biochar in agriculture, Schmidt et al. (12) observed a shift in the approach to biochar research in agriculture. They found that a handful of studies incorporated a low application rate of biochar in combination with other amendments including manure, mineral fertilizers, or other waste products (e.g., biosolids). These studies, however, focused on how a low biochar dosage affected soil properties and crop productivity (13–16), its impact on climate change resilience (17), with minimal information on its carbon sequestration potential (18).

Because of the extended time frame required to evaluate changes in soil organic carbon stocks, process-based models are a powerful approach to understand the drivers of long-term soil organic carbon dynamics and provide an opportunity to identify if biochar addition to agricultural soil causes carbon accumulation or loss (19). The Century model is one of the most widely used biogeochemical models due to its ability to predict soil organic carbon changes in diverse environments ranging from forests and grasslands to agricultural soil (20). But biochar modeling remains limited (21), including the outcome on changes in soil organic carbon with low biochar application rates (22). Furthermore, incorporating measured data from field studies with biochar into models is missing (23), and existing studies evaluated long-term biochar mineralization based on data collected from laboratory or short-term field studies (21). The objective of our study was to use the Century model to evaluate long-term changes in soil organic carbon stocks in soil amended with a low biochar application rate when blended with manure, and (or) nitrogen fertilizer. We also evaluated changes in the associated active, slow, and passive carbon fractions, and determined the relationship between measured and predicted values.

2 Methods

2.1 Field site description and management

The field site was located on a commercial poultry-cash crop farm in Bayfield, Ontario, Canada (43°34'45.8"N, 81°39'52.2"W). The area was located 183 m above sea level with a 1.5% slope. Weather data (30-year mean) was obtained from a nearby weather station located in Dashwood (43°20'48.8"N, 81°38'07.6"W), Ontario with a mean annual temperature of 8.3°C and an average annual precipitation of 858 mm (Figure 1). The soil was classified as a uniform calcareous Grey-Brown Luvisol with a sandy loam texture. In the years before biochar addition (prior to May 2016), commercial farming practices of the study site included an annual rotation of maize (*Zea mays* L.) and soybean (*Glycine max* Merr. L.). Poultry manure, based on switchgrass bedding (*Panicum virgatum* L.), was added in April at 600 g m^{-2} and topped off with nitrogen fertilizer at 135 kg N ha^{-1} in the years when maize was produced
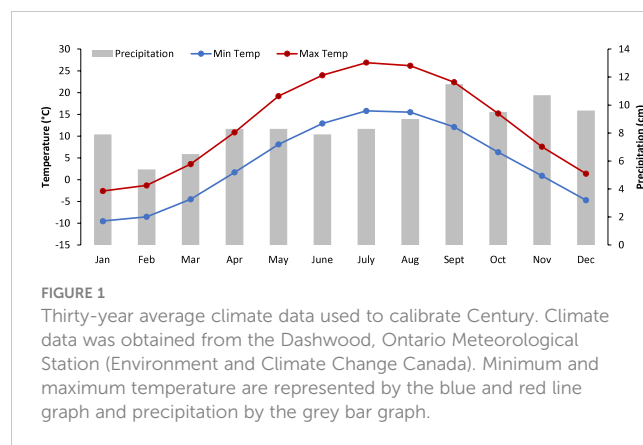

FIGURE 1

Thirty-year average climate data used to calibrate Century. Climate data was obtained from the Dashwood, Ontario Meteorological Station (Environment and Climate Change Canada). Minimum and maximum temperature are represented by the blue and red line graph and precipitation by the grey bar graph.

(Table 1). The soil was cultivated in April of each field season using a disc harrow (0-20 cm) and weeds were controlled with N-phosphonomethyl glycine (Glyphosate).

The field experiment was established in May 2016 and included 600 g m^{-2} poultry manure + 13.5 g N m^{-2} fertilizer (MN); 300 g m^{-2} poultry manure + 300 g m^{-2} biochar (MB); and 300 g m^{-2} poultry manure, 13.5 g N m^{-2} fertilizer + 300 g m^{-2} biochar (MNB). The experimental design was a randomized design, and each treatment was replicated three times. The plot size for each treatment replicate was 10 m x 10 m, with a 3 m border between plots. Biochar was added using a drop spreader and incorporated into the soil using a Salford RTS vertical tillage unit to ensure uniform distribution of the biochar. Commercial farm management operations, including herbicide additions and fertilizer application rates, used standard agronomic practices for this region of southwestern Ontario, Canada. The field study was conducted over three growing seasons, beginning in May 2016 with a maize crop and biochar addition, a soybean crop in 2017 and a maize crop in 2018. Biochar was added to the respective treatment replicates only in 2016, whereas manure and nitrogen fertilizer were added biennially when maize was produced. No soil amendments were added during the years soybeans were produced. The biochar was provided by Titan Carbon Smart Technologies (Saskatoon, Saskatchewan, Canada). The feedstock of the biochar was a 1:1 mix of pine (*Pinus* spp.) and spruce (*Picea* spp.) (Table 1). Biochar was produced using slow pyrolysis (550°C, 15 min).

2.2 In field data collection

Prior to the initiation of the study, five soil samples (0-20 cm) were collected in April 2016 from each treatment replicate to determine baseline values. Further soil samples were collected from each treatment replicate after crop harvest in October 2016, 2017, and 2018. Fresh soil was used to quantify pH using a 1:1 soil and ultrapure water mixture using a BioKit AB15B (Houston, TX, USA) pH meter (24). The remaining soil was air dried and sieved to 2 mm. Carbonates were removed by washing 2 g of soil with 50 mL of 0.5 M HCl (25). The soil-acid solution was shaken three times over 24 h on a reciprocating shaker at 200 rpm (Heidolpj Unimax 1010 DT, Schwabach, Germany). Following a settling period of 30 min, the acid was removed using a pipette and discarded (25). The acid treated soil was washed by adding 50 mL ultrapure water and shaking the soil at 200 rpm for 15 minutes, after which the water was removed with a pipette and discarded (25). The washing procedure was repeated daily for four days after which the soil was dried at 30°C for two days, ground in a ball mill (Retsch® ZM1, Haan, Germany) and analyzed for soil organic carbon and total nitrogen using a Costech 4010 (Valencia, USA) elemental analyzer.

2.3 Century parameterization

Century is a site-specific model based on the interactions between climate, crops, and soil. Parameterization of the model

TABLE 1 Physicochemical characteristics of the manure and biochar applied to soil in southern Ontario, Canada.

	Biochar Properties	Manure Properties
Origin	Pine & Spruce (50:50)	Poultry, switchgrass bedding
Pyrolysis temperature (°C)	550	
Oxygen (g kg^{-1})	59.6	
Ash (g kg^{-1})	30.7	
Moisture wet (%)	0.3	
Moisture dry (%)	0.3	34.1
Bulk density (g cm^{-3})	0.14	0.41
Surface area (m^2 g^{-1})	265	
Pore volume (cm^3 g^{-1})	0.10	
Saturation capacity wet (%)	51	
Saturation capacity dry (%)	105	
Hydrophobicity index (%)	9	
Particle size distribution (%)		
<0.50 mm	1.0	
0.50–1.00 mm	0.6	
1.00–2.00 mm	13.0	
2.00–2.80 mm	12.6	
2.80–4.75 mm	35.7	
>4.75 mm	37.1	
EC (μS cm^{-1})	150	77
pH	7.2	7.9
C (g kg^{-1})	800	307
N (g kg^{-1})	1.5	34
C/N	533	9
H/C	0.037	
NH$_4^+$N (mg kg^{-1})		3,369
P (mg kg^{-1})	303	8,730
K (mg kg^{-1})	3,003	18,600
Ca (mg kg^{-1})	6,795	14,200
Mg (mg kg^{-1})	2,302	4,700
Mn (mg kg^{-1})	118	357
S (mg kg^{-1})	266	3,555
Na (μg g^{-1})	891	3,700
Al (mg kg^{-1})	591	1
B (μg g^{-1})	5.35	20.5
Cu (μg g^{-1})	8.57	175

(Continued)

TABLE 1 Continued

	Biochar Properties	Manure Properties
Fe (μg g^{-1})	3,623	299
Zn (μg g^{-1})	91.35	281

can be achieved by modifying climate, soil chemical, physical and biological characteristics, and agroecosystem management practices. Plant production is a sub-model in century that stimulates aboveground and belowground biomass productivity of forests, grasslands, savannas, or crops [26]. The soil organic matter sub-model predicts changes in soil active, slow, and passive carbon fractions based on microbial decomposition of crop residues and resultant microbial products that are the foundation in the formation of humus [20]. Of the total soil organic matter pool, approximately 2% to 4% is composed of the active fraction that includes soil microbes and microbial products with a turnover time of several months to a few years [27]. The slow fraction composes 45% to 65% of the total soil organic matter pool with a turnover time of 20 to 50 years and includes resistant plant material acquired from stabilized soil microbial products and structural plant material [27]. The passive fraction contains 30% to 40% of the total soil

organic matter pool and is represented by chemically and physically protected mineral associated organic material [20]. Soil texture controls the extent to which the decomposed compounds are stabilized [26]. The Century model was originally developed to determine changes in soil organic carbon stocks for grassland ecosystems [26], but the model can also simulate changes in temperate and tropical environments that include various land management systems ranging from row cropping to complex agroecosystems [28, 29]. To date, Century is one of the most widely used models because of its ability to simulate changes in soil organic carbon in diverse environments [20].

We used version 4.0 of the Century model to simulate changes in soil organic carbon and its associated fractions (0-20 cm) after a low dosage and one-time addition of biochar. The model was initiated for >10,000 years under a mixed deciduous-coniferous forest which is native to this region of southwestern Ontario, Canada to estimate equilibrium in plant productivity and soil organic carbon levels i.e., when soil organic carbon stabilizes and there are no further changes with time. After equilibrium was attained the first year of simulation began in 1882 with grass/hay for livestock production (Table 2). Monthly average maximum and minimum temperature and monthly total precipitation (30-year average) were obtained from a nearby Environment and Climate Change Canada meteorological station managed in Dashwood, Ontario (Figure 1). After initializing soil organic carbon levels,

TABLE 2 Scheduling of agricultural management practices in Century based on actual historical events that occurred at the field site in Ontario, Canada.

Year	Management Practice
-10,000 to 1880	**Forest** Mixed deciduous-coniferous forest (MIX) with >10,000 years of simulation to estimate equilibrium soil organic carbon levels and plant productivity. Growth from April to August.
1881	**Forest Harvest** Crops: mixed deciduous-coniferous forest (MIX) Harvest: tree removal by clear cut (CC) in October
1882 to 1945	**Grass/Hay for Livestock production** Crop seeding and production: grass 100% cool season (GCD) seeded in April Cultivation: plough (P) in April (establishment phase only) Fertilizer: straw manure (M) applied annually in April Harvest: hay (H) in August
1946 to 1965	**Annual Cereal Grain Rotation** Crop seeding and production: annual grain rotation of medium harvest wheat (WMED) and oats (OAT) with seeding in April Cultivation: plough (P) in April (annually) Fertilizer: straw manure (M) applied annually in April Harvest: grain only (G) in July for both crops
1966 to 2015	**Annual Corn-Soybean Rotation** Crop seeding and production: medium harvest corn (CHI) seeded in April and rotated annually with soybean (SYBN) seeded in May Cultivation: cultivator (C) in April (annually) Fertilizer: 13.5 g N m^{-2} for corn and 1 g N m^{-2} for soybeans Harvest: grain only (G) in October for corn and September for soybeans

2016 to 2130	**Annual Corn-Soybean Rotation with Biochar**
	Crop seeding and production: high harvest corn (CHI) seeded in April rotated annually with soybean (SYBN) seeded in May
	Cultivation: cultivator (C) in April (annually)
	Harvest: grain only (G) in October for corn and September for soybeans
	Fertilizer (FERT) and organic matter (OMAD) addition:
	    MN amendment: 184 g C m^{-2} manure + 13.5 g N m^{-2}. Added only in years corn is produced.
	    MB amendment: 91 g C m^{-2} manure + 240 g C m^{-2} biochar. Biochar added in 2016 only.
	    MNB amendment: 13.5 g N m^{-2} + 91 g C m^{-2} manure + 240 g C m^{-2} biochar. Biochar added in 2016 only.

land management events were scheduled according to actual historical events prior to the addition of biochar in 2016 (Table 2). Soil properties prior to the addition of biochar (Table 3) were obtained from Jiang (30). The proportion of soil organic carbon initial values for the active fraction was 3%, 65% for the slow fraction and 32% for the passive fraction (31). The OMAD.100 file was changed and reflected the addition of 184 g C m^{-2} manure for MN, or 91 g C m^{-2} manure + 240 g C m^{-2} biochar for MB and MNB (Table 4). The C/N ratio of the manure and biochar were also adjusted accordingly (Table 4). An additional file in FERT.100 was created to reflect the addition of 13.5 g m^{-2} nitrogen fertilizer to MN and MNB. Crop parameters for maize and soybeans were modified to accommodate regional crop production values (Table 4). Default values set by Century were used for atmospheric nitrogen deposition and nitrogen fixation rates. All other parameters used in this simulation were provided by Century and modified parameters are listed in Table 4. We used a monthly time-step for simulation output to align predicted values with their corresponding month of soil sampling in the field.

2.4 Statistical analysis

Measured field data were compared with predicted data using the regression function in SPSS version 28 (33). The following metrics were used to determine the strength of the relationship between measured and predicted values: correlation coefficient (r), coefficient of determination (r^2), adjusted r^2, root mean squared deviation (RMSD), root mean squared error (RMSE), the mean difference (M) between measured and predicted values of soil organic carbon, the coefficient of residual mass (CRM) to determine if the model over- or under estimated values of soil organic carbon, and modeling efficiency (EF) which compares predicted values to the average measured values (34, 35). The threshold probability level for determining goodness of fit was P < 0.05.

TABLE 3 Soil physicochemical characteristics (0-20 cm) prior to adding manure and biochar in 2016 at the field site in southern Ontario, Canada (adapted from 30).

	MN	MB	MNB
Sand (g kg^{-1})	60	60	60
Silt (g kg^{-1})	22	22	22
Clay (g kg^{-1})	18	18	18
pH	7.14	7.15	7.18
Soil organic carbon (g kg^{-1})	10.9	11.2	11.2
Soil total nitrogen (g kg^{-1})	1.40	1.20	1.20
Bulk density (g cm^{-3})	1.27	1.27	1.26
Soil organic carbon (g C m^{-2})	2,774	2,853	2,836
Soil total nitrogen (g N m^{-2})	3.81	2.79	2.88
C/N	7.3	10.2	9.8

3 Results

The introduction of grass and hay forage for livestock production between 1882 and 1945 caused soil organic carbon stocks to decline. In fact, the soil organic carbon stock decreased by 12% when mixed deciduous-coniferous forest was converted to grass and hay forage production in 1882. Soil organic carbon stocks further declined by 16% during the annual cereal grain rotation (1946 to 1965) and declined by another 23% during the annual corn-soybean rotation between 1966 and 2015 (Figure 2). Soil organic carbon stocks began to recover in 2016 with the addition of manure or manure blended with biochar and (or) nitrogen fertilizer. However, 115 years, pre-1881 soil organic carbon stock that accumulated under a mixed deciduous-coniferous forest were not reached regardless of amendment type added (Figure 2).

When sustainable agroecosystem management practices began in 2016, the Century predicted an 84% increase, after 115 years, in soil organic carbon when 600 g m^{-2} manure was blended with nitrogen fertilizer (MN). But when manure was cutback to 300 g m^{-2} and blended with 300 g m^{-2} biochar (MB), the soil organic carbon stock increased only by 70%. However, when 300 g m^{-2} of manure was blended with biochar (300 g m^{-2}) and nitrogen fertilizer (MNB), the soil organic carbon stock increased by 79% (Figure 2).

When manure or manure blended with biochar and (or) nitrogen fertilizer and added to the soil starting in 2016, all carbon fractions increased (Figure 3). For example, the active and slow fractions showed the greatest increase in soil organic carbon. An increase in the active fraction ranged from 68% to 86% and increase in the slow fraction ranged from 78% to 88%. For both active and slow fractions, the MN amendment type always had the greatest increase followed by the MNB and MB amendment types. Although the passive fraction is the most stable form of carbon in the soil, the addition of manure with nitrogen fertilizer (MN) led to a 32% increase in this fraction. Likewise, the presence of biochar in MB and MNB led to a 12% and 23% increase, respectively, in the passive fraction.

Model performance was very good to good with a strong relationship between measured field data and predicted values for soil organic carbon stocks in MN and MB, with P-values ranging from 0.005 to 0.017 (Table 5). Model performance for MNB was poor and did not show a significant relationship (P=0.341) between measured and predicted values. The near zero values for the coefficient of residual mass (CRM) for all amendment types indicated a lack of bias in the distribution of the predicted values with respect to the measured values. Century overestimated soil organic carbon stocks in MN by 9% and by 4% in MNB but underestimated by 1% for MB (Figure 4). However, overall model performance was good since EF values were close to 1.0, indicating a near perfect fit.

4 Discussion

4.1 Soil organic carbon stock predictions

We found that land conversion from mixed deciduous-coniferous forest to grass and hay production for livestock forage,

TABLE 4 Century parameters measured or modified during model calibration for soil amended with manure + N fertilizer (MN), manure + biochar (MB), and manure, N fertilizer + biochar (MNB) in southern Ontario, Canada.

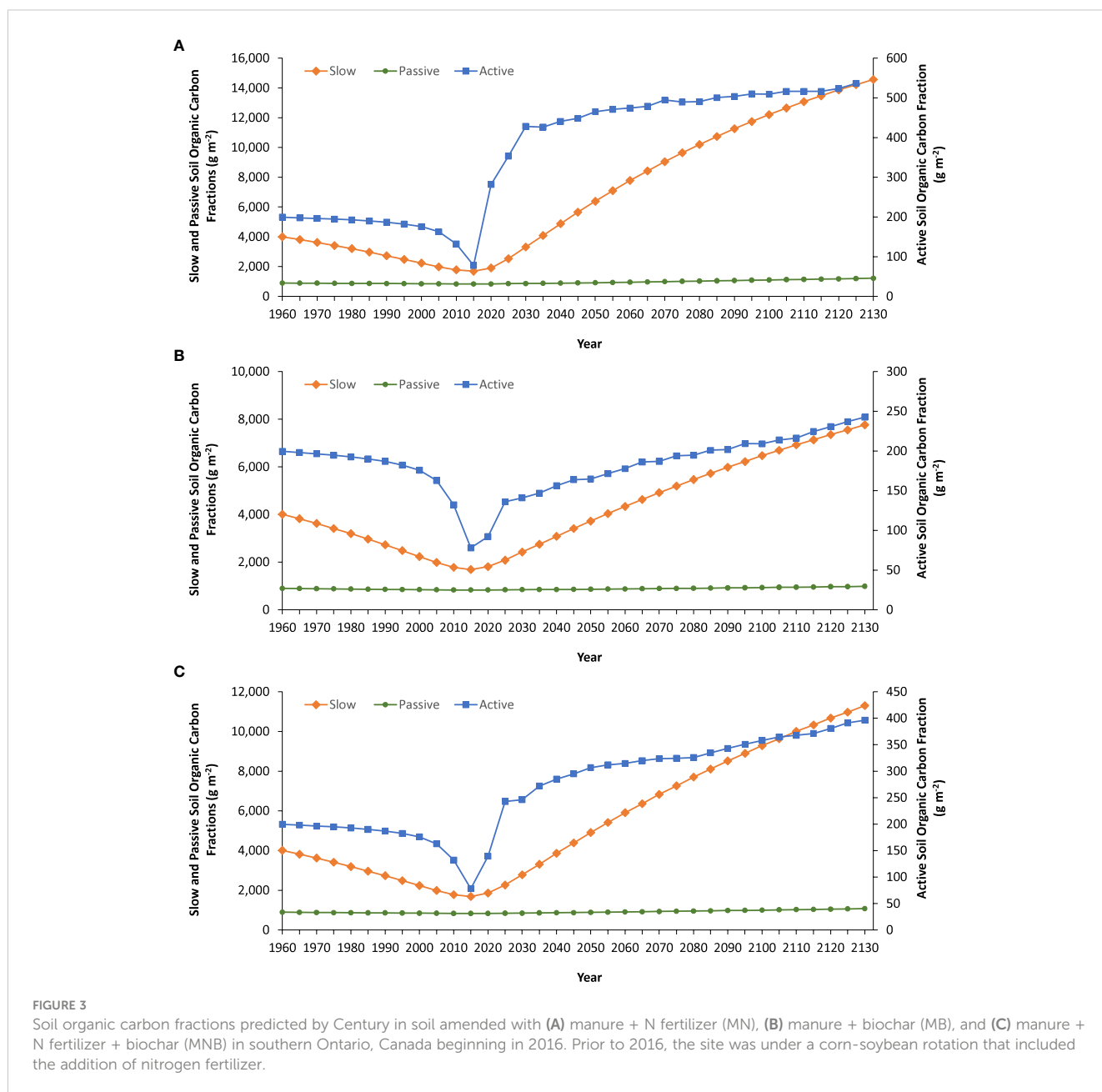| Parameter	Description	Code	Value
Site	Number of soil layers	nlayer	8
	Number of soil layers in the top level	nlaypg	5
	Fraction of excess water lost by drainage	drain	0.5
	Soil pH	pH	7.16
	Bulk density (g cm^{-3})	bulkd	1.27
	Initial value for unlabelled carbon in surface organic matter with fast turnover (%)	Som1ci(1,1)	0.08
	Initial value for unlabeled carbon in soil organic matter with fast turnover (%)	som1ci(2,1)	3
	Initial value for unlabeled carbon in soil organic matter with slow turnover (%)	som2ci(1)	65
	Initial value for unlabeled carbon in soil organic matter with passive turnover (%)	som3ci(1)	32
Fixed	Maximum surface structural decomposition rate	dec1(1)	1.5
	Maximum soil structural decomposition rate	dec1(2)	1.5
	Maximum surface metabolic decomposition rate	dec2(1)	10
	Maximum soil metabolic decomposition rate	dec2(2)	10
	Maximum decomposition rate of surface organic matter with active turnover	dec3(1)	4
	Maximum decomposition rate of soil organic matter with active turnover	dec3(2)	4
	Maximum decomposition rate of soil organic matter with slow turnover	dec4	0.0013
	Maximum decomposition rate of soil organic matter with passive turnover	dec5	0.05
	Maximum C/N ratio for material entering the slow pool	varat2(1,1)	20
	Maximum C/N ratio for material entering the passive pool	varat3(1,1)	8
	Fraction per month of gross mineralization which is volatilized	vlossg	0.01
Organic matter addition	Grams of carbon added with the addition of organic matter (g m^{-2})	astgc	186 (MN); 333 (MB); 333 (MNB)
	Lignin fraction of organic matter	astlig	0.16
	C/N ratio of added organic matter	astrec(1)	9 manure; 170 biochar
Crop	Initial fraction of carbon allocated to roots	frtc(1)	0.25
	Final fraction of carbon allocated to roots	frtc(2)	0.25
	Potential aboveground monthly production for crops (g m^{-2})	prdx(1)	650 (corn); 300 (soybean)
	Planting month reduction factor to limit seedling growth	pltmrf	0.5
	Value of aglivc at full canopy cover	fulcan	150
	Optimum temperature for production	ppdf(1)	26
Cultivation	Cultivation factor for SOM1 decomposition [plowing (P) and cultivator (C)]	clteff(1)	1.5
	Cultivation factor for SOM2 decomposition [plowing (P) and cultivator (C)]	clteff(2)	1.5
	Cultivation factor for SOM3 decomposition [plowing (P) and cultivator (C)]	clteff(3)	1.5
	Cultivation factor for soil structural material decomposition [plowing (P) and cultivator (C)]	cleeff(4)	1.5
Harvest	Fraction of aboveground live which will not be affected by harvest operation	Aglrem	0.005
	Fraction of the remaining residue that will be left standing	remwsd	1.0
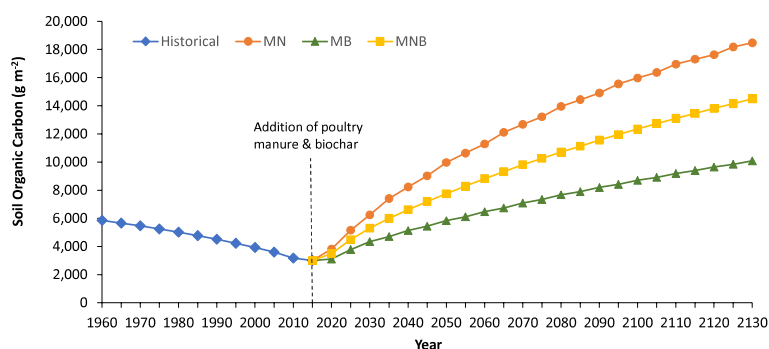
FIGURE 2
Soil organic carbon predicted by Century in soil amended with manure + N fertilizer (MN), manure + biochar (MB), and manure + N fertilizer + biochar (MNB) in southern Ontario, Canada beginning in 2016 (dashed vertical line). Prior to 2016, the site was under a corn-soybean rotation that included the addition of nitrogen fertilizer (c.f., Table 2 for historical management practices).

and subsequent conversion to row crop production led to a rapid decline in soil organic carbon stocks and associated carbon fractions. Such a decline in soil organic carbon stocks upon land conversion to agriculture have been observed on a global scale (36), and losses will likely be heightened in the future due to a changing climate (37) since warming enhances microbial activity and the transformation of soil organic carbon (1). Additionally, agriculture also causes a fundamental disruption in the soil's steady state due to a drastic reduction in the quantity and quality of organic matter returned to the soil that leads to a depletion of soil organic carbon stocks (39, 40). For example, crop residue removal has increased from 0.5 Pg C y^{-1} to 1.6 Pg C y^{-1} between 1910 and 2005 due to heightened demands for food, fibre, and fuel (39, 41). Furthermore, Li et al. (42) determined that a 25% reduction in organic matter input caused a 1.6% decrease in soil organic carbon. In fact, we found an 51% decrease in soil organic carbon over 113 years, representing the time from initiation of agriculture in 1881 to 2015. Our results corroborate with those of Powlson et al. (43) who reviewed data from multiple long-term experiments in temperate and tropical agroecosystems. They determined that soil organic carbon stocks declined between 38% and 67% compared to pre-cultivation levels (43). Although our study showed a considerable increase (84%) in soil organic carbon stocks over 115 years once manure and (or) biochar were added, we found that pre-cultivation soil organic carbon stocks were not reached. Similarly, Powlson et al. (43) found that increases in soil organic carbon levels ranged from 60% to 70% of pre-cultivation values once conservation practices were initiated. But they concluded that soil organic carbon stocks will likely never approach pre-cultivation levels (43). This is because the rate of soil organic carbon loss and accumulation is influenced by land management practices including the quantity and quality of residue returned to the soil and the type and frequency of tillage (39, 44). Furthermore, there is an upper limit of carbon storage that depends on the soil's inherent soil organic carbon level which is closely tied to soil texture (45). However, we also found that after 115 years of manure and (or) biochar addition, soil organic carbon equilibrium was not reached. This was likely due to an inherently low soil organic carbon level in the coarse textured soil (60% sand, 22% silt, 18% clay) used in our

study. This suggested that soil amended with manure and (or) biochar has a greater carbon sequestration potential if the soil texture is coarse, since silt and clay content control the upper level (saturation) of soil carbon sequestration (46).

Although carbon input in MB and MNB (331 g C m^{-2}) was almost double compared to that in MN (184 g C m^{-2}), soil organic carbon accumulation was greater in MN after 115 years. This was due to the biennial addition of manure (i.e., in the years when maize was produced) since Century was scheduled to mirror commercial farming practices that took place at the field site. Conversely, Century was scheduled, paralleling field site management practices, only by a one-time addition of biochar to MB and MNB. Therefore, over the 115-year simulation carbon input from manure was cumulative and contributed to the greater soil organic carbon stock in MN. We therefore recommend that a more frequent low dosage of biochar should be applied in future field studies that can further increase soil organic carbon stocks. For example, Dil and Oelbermann (22) used Century and determined that an annual addition of biochar at 200 g C m^{-2} increased soil organic carbon stock by 10,522 g m^{-2} over 150 years in a light textured soil. However, the study by Dil and Oelbermann (22) did not integrate field data into their simulation. Although there is a wide variation in the ability of manure to increase soil organic carbon stocks over the long-term (>5 years), a recent meta-analysis by Gross and Glaser (47) determined that manure increased soil organic carbon stocks, regardless of environmental conditions. For example, they found a 40% increase in soil organic carbon after 20 years in temperate agroecosystems (47). However, our results were comparable to those by Jenkinson and Rayner (48) who predicted changes in soil organic carbon over a 120-years using field data from long-term research sites in England. Furthermore, nitrogen availability becomes unrestricted when a legume is integrated into the rotation (49). The greater nitrogen availability from the legume decreases the mineralization of old carbon and leads to the accumulation of soil organic carbon (50). This could also explain the difference in soil organic carbon stocks in our study (e.g., MN) compared to Gross and Glaser (47), who did not include legumes in their meta-analysis.

Compared to the pre-2016 land management practice, amendments with biochar also increased soil organic carbon

FIGURE 3
Soil organic carbon fractions predicted by Century in soil amended with **(A)** manure + N fertilizer (MN), **(B)** manure + biochar (MB), and **(C)** manure + N fertilizer + biochar (MNB) in southern Ontario, Canada beginning in 2016. Prior to 2016, the site was under a corn-soybean rotation that included the addition of nitrogen fertilizer.

stocks, over the 115-year simulation, by ≥70%. This is because biochar, due to incomplete combustion, is the only plant-derived organic matter that as a higher intrinsic stability than other sources of organic matter (51). Although biochar is stable over the long-term, it is also affected by microbial degradation depending on the pyrolysis conditions under which it was produced (52). For example, a high pyrolysis temperature, carbon to nitrogen ratio and a pH >8.1 caused an increase in soil organic carbon (52). However, biochar produced with a low pyrolysis temperature and narrow carbon to nitrogen ratio, like that used in our study, is more readily available to the microbial community (52). This could also explain the lower soil organic carbon stock predicted by Century in our study in MB and MNB compared to MN. Furthermore, the soil used in our study was sandy, which does not

provide a physical and chemical protection mechanism for the biochar, allowing the readily decomposable fractions to be more accessible to the microbial community (52).

The greater accumulation of soil organic carbon in MNB, compared to MB, over the 115-year simulation was likely due to the presence of nitrogen fertilizer combined with manure and biochar. Previous studies showed that an effective way to promote efficient soil organic matter formation includes the input of a diverse source of organic materials (1). This is because diverse sources of organic matter (i.e., molecular diversity) causes an energy limitation on microbes, decreasing soil organic matter mineralization (53). Additionally, van Groenigen et al. (54) found that an increasing input of nitrogen leads to an accumulation of soil

TABLE 5 Statistical tests applied for agreement between measured and predicted values of soil organic carbon stocks in soil amended with manure + N fertilizer (MN), manure + biochar (MB), and manure + N fertilizer + biochar (MNB) in southern Ontario, Canada.

	MN	MB	MNB
n	3	3	3
r	0.999	0.999	0.859
r^2	0.999	0.999	0.739
Adjusted r^2	0.999	0.998	0.478
P	0.005	0.017	0.341
RMSD (g C m^{-2})	534	77	270
RMSE (g C m^{-2})	436	63	221
CRM (g C m^{-2})	-0.091	0.013	-0.044
M (g C m^{-2})	252	-36	127
EF (g C m^{-2})	0.984	0.999	0.996

n, number of samples (crop seasons); r, correlation coefficient; r2, coefficient of determination; RMSD, root mean squared deviation or standard deviation of the measured; RMSE, root mean squared error or standard error of the estimate; CRM, coefficient of residual mass [($\Sigma_{measured}$ - $\Sigma_{simulated}$)/$\Sigma_{measured}$]; M, mean difference between simulated and measured values of SOC; EF, model efficiency [1- ($\Sigma_{simulated}$ - $\Sigma_{measured}$)^2/($\Sigma_{measured}$ - $\bar{x}_{measured}$)^2. positive CRM, values indicate an underestimation of simulated results, whereas negative CRM values indicate an overestimation of simulated results.

organic carbon which, in our study, likely contributed to the greater soil organic carbon stock in MNB. In a 15-week mesocosm study, Ibrahim et al. (55) determined that biochar blended with fertilizer regulated carbon mineralization because more nitrogen substrates were available to the microbial community that depended on nitrogen. Although blending biochar with manure and a source of mineralizable nitrogen is contradictory with respect to potentially greater greenhouse gas emissions, results from a previous study at the same field site as our study showed no significant difference in CO_2 and N_2O emissions among amendment types (16). We also determined that model performance for MNB was poor, compared to MB, and it did not show a significant relationship between

FIGURE 4
Relationship between measured and predicted values of soil organic carbon in soil amended with manure + N fertilizer (MN; orange circles), manure + biochar (MB; green triangles), and manure + N fertilizer + biochar (MNB; yellow squares) in southern Ontario, Canada.

measured and predicted values. We recommend that more reliable simulation outcomes should be based on a greater number of data points (e.g., number of years) from field measurements to provide a more robust comparison with predicted values.

Soil organic carbon fractions decreased upon initiation of agricultural activities in 1882, with little change in the passive fraction. However, all three fractions increased after 2016, once manure and (or) biochar were added, where the greatest rise was observed in the active and slow fractions. This suggested that the active and slow carbon fractions were controlled by land-use change (i.e., change from the pre-cultivation forest ecosystem to cultivated agroecosystems) and different agroecosystem management practices (i.e., change from grass/hay production to cereal and maize crop rotations). Land conversion and changes in land-use management decreased primary production, soil nutrient status and the quantity and quality of organic matter returned to the soil compared to pre-cultivation levels (39). This likely led to the mineralization of old carbon sources, causing a decline in the various carbon fractions (56). However, a sufficient input of organic matter, and therefore an increase in each of the carbon fractions, occurred once manure and (or) biochar were applied to the soil. For example, Gross and Glaser (47) determined that soil with a low initial soil organic carbon stock will have a large response to the addition of organic matter and show no depletion with time. Also, the addition of organic matter increased nitrogen availability, which affected microbial growth and the mineralization of new carbon derived from the amendments (57). This suggested that carbon stabilization is controlled by the quantity and quality of the organic residues entering the soil ecosystem.

The greater accumulation of carbon in the active and slow fractions in MN, compared to MB and MNB, was due to the biennial addition of manure (47). However, the one-time addition of biochar, when blended with manure and nitrogen fertilizer (MNB), led to a similar accumulation of carbon in the active and slow fractions as MN. This suggested that biochar increased soil organic carbon stabilization within the organo-mineral fraction (60). Additionally, our results showed that the active and slow carbon fractions did not reach equilibrium during the 115-year simulation period. Gross and Glaser (47) suggested that soil carbon saturation not only depends on the properties of the soil and of the organic matter added to the soil, but also on the inherent soil organic carbon content. They found that soil with an inherently low soil organic carbon content requires a longer time to reach equilibrium compared to soil with an inherently high soil organic carbon content (47).

Input from the various carbon sources such as manure or manure blended with biochar likely stimulated the microbial community to become more active, which may have preserved the active carbon pool despite disturbance from tillage. For example, Ouyang et al. (61) also found that the addition of manure counteracted the impact of tillage on the active soil organic carbon fraction in northeastern China. Lorenz and Lal (52) also determined that when biochar was added to a coarse-textured soil, it caused an increase in soil-specific surface area that enhanced soil nutrient cycling and microbial activity. Furthermore, our modeling results determined that carbon associated with the
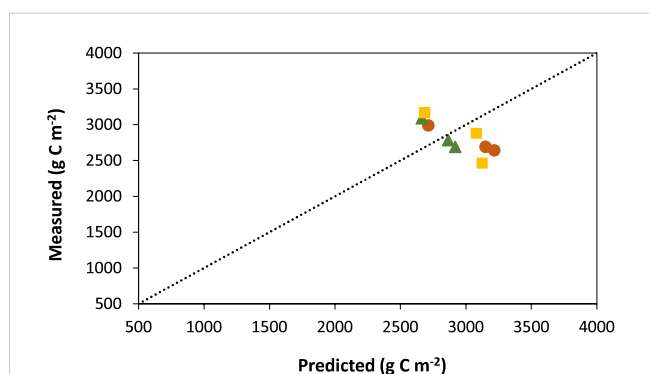
slow fraction was the key driver in soil organic carbon accumulation once manure and (or) biochar were added to the soil. We also found that the slow fraction resisted the impact of disturbance from cultivation with a disc harrow (0-20 cm depth) and soil organic carbon was maintained by input of manure and (or) biochar. This is because the slow fraction is physically protected and has a more chemically complex structure, which makes it more resistant to decomposition than the active fraction (20). Additionally, Carvalho-Leite et al. (62) determined that carbon accumulation in the slow fraction is related to the quantity carbon and nutrients added to the soil. Although Cong et al. (63) found that nitrogen fertilizer decreased carbon in the passive fraction, our simulation results showed a 29% increase in the passive fraction in MNB, compared to a 18% in crease in MN and MB. Pulcher et al. (21) suggested that biochar carbon may not be directly mineralized to CO_2 but may transfer to carbon pools with different degradation rates. This is because the biochar used in our study has a hydrogen-to-organic carbon ratio lower than 0.4, which is considered highly stable with carbon remaining in soil for more than 100 years (64). Accordingly, results from our study predicted that a one-time addition of manure blended with biochar and nitrogen fertilizer (MNB) can stabilize a greater proportion of the carbon in the passive fraction than when blending manure with nitrogen fertilizer (MN) or when bending manure with biochar (MB).

4.2 Model performance and limitations

Differences between measured and predicted values in our study ranged from +9% to -1.3% and was within range of other studies. For example, Alves Primo et al. (29) determined that Century over- and underestimated soil organic carbon stocks up to 15% in semiarid slash and burn and agroforestry systems in Brazil. Similarly, in temperate agroecosystems soil organic carbon stocks deviated between +10% to -15% between measured and predicted values (38, 65). However, our study was limited by the availability of only three years of field data for model validation. Discrepancies between measured and predicted values in our study were also due to Century's failure to accommodate changes in bulk density with increasing soil organic carbon stocks. Instead, Century assumes bulk density as a constant parameter throughout the simulation (58). With increasing soil organic carbon stocks, bulk density decreases with time, influencing the quantity of carbon sequestered (47). For example, Lorenz and Lal (52) noted that biochar could reduce soil bulk density by 3 to 31%. Various environmental factors including fluctuating moisture and temperature conditions, freeze-thaw events and microbial activity control the dissolution, oxidation and fragmentation of biochar that can change its physicochemical characteristics (59). For example, Wang et al. (32) found that soil minerals accumulated on the surface of the aged biochar and suggested that this improved soil physical stability which could lead to enhanced carbon sequestration. Therefore, the soil organic carbon stock in amendments with biochar may be an underestimation in our study since Century does not account for biochar ageing. However, it is also crucial to consider how soil physicochemical properties and soil amendments (e.g., manure, biochar) are affected by future climate change scenarios which could

affect long-term soil organic carbon stocks. For example, Jiang et al. (17) determined that short-term climate effects of elevated CO_2, warming or the combined effect of elevated CO_2 and warming did not influence biochar. But they found that climate effects influenced how carbon was accessed by the microbial community in amendments with manure and biochar (17). Furthermore, leaching and bioturbation cause the downward translocation and stabilization of biochar within the soil profile (52). However, translocation of carbon (i.e., biochar) to deeper soil horizons is not accounted for in Century since the model only predicts soil organic carbon stocks to a 20 cm depth.

5 Conclusion

We evaluated if soil amended with biochar is able to sequester a greater quantity of soil organic carbon over the long-term (115 years), compared to soil without biochar, using the Century soil organic matter model. After 115 years, none of the amendment types were able to reach pre-cultivation soil organic carbon stocks and none of the amendment types reached equilibrium. The lower input of organic matter from crop residues and amendments, compared to a mixed deciduous-coniferous forest likely contributed to the inability to reach pre-cultivation soil organic carbon stocks. This was likely due to the inherently low level of soil organic carbon of the soil used in our study which required a longer time to reach a steady state. We found that Century predicted the greatest increase in soil organic carbon when manure was blended with fertilizer compared to soil amended with biochar. Although carbon input in amendments containing biochar had more carbon, the low dosage and one-time addition of biochar caused the slower accumulation of soil organic carbon compared to the biennial addition of manure. We also determined a greater increase in soil organic carbon when biochar was blended with manure and nitrogen fertilizer likely due to a greater regulation of carbon mineralization since more nitrogen substrates were available to the microbial community. Thus, biochar blended with manure and nitrogen fertilizer may have a different effect on soil organic carbon compared to biochar blended with manure only. Carbon associated with the slow fraction was the key driver in soil organic carbon accumulation for all amendment types. Although Century was able to predict soil organic carbon stocks within ±9% of measured values, we recommend that fine tuning the model to address some of its current limitations with respect to biochar (i.e., bulk density, ageing, bioturbation), which will strengthen the relationship between measured and predicted values.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

MO contributed to conception and design of the field study. RJ and MM organized the database and performed the analysis of the

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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