

Article

Soil Organic Carbon Sequestration under Long-Term Chemical and Manure Fertilization in a Cinnamon Soil, Northern China

Yun Xiang ^{1,2}, Man Cheng ^{2,*}, Yongli Wen ² and Frédéric Darboux ³

¹ College of Resources and Environment, Shanxi Agricultural University, Jinzhong 030801, China; xiangyun@sxau.edu.cn

² Institute of Loess Plateau, Shanxi University, Taiyuan 030006, China; ylw@sxu.edu.cn

³ Université Grenoble Alpes, INRAE, ETNA, F-38402 St-Martin-d'Hères, France; frederic.darboux@inrae.fr

* Correspondence: chengman@sxu.edu.cn

Abstract: To mitigate climate change and improve food security, it is essential to understand how fertilizer strategies impact the dynamics of soil organic carbon and its fractions. The soil organic carbon (SOC), light fraction organic carbon (LFOC), and particulate organic carbon (POC) were investigated every five years in a corn (*Zea mays* L.) cropping system with chemical fertilization and manuring over twenty-four years (1992–2016) in a semiarid area of northern China. There were four treatments with chemical fertilizer (i.e., N1P1, N2P2, N3P3, N4P4), three treatments with chemical fertilizer plus manure (i.e., N2P1M1, N3P2M3, N4P2M2), and one treatment with manure alone (i.e., M6), and an unfertilized treatment (control). The carbon sequestration rate (C_{SR}) and efficiency (C_{SE}) of SOC, POC, and LFOC were identified. The results revealed that the fertilization treatments (N2P2, N3P3, N2P1M1, N3P2M3, N4P2M2, and M6) promoted SOC sequestration, with a sequestration rate of $0.19\text{--}1.29\text{ Mg ha}^{-1}\text{ y}^{-1}$. The excess application of chemical fertilizer caused a reduction in POC, whereas the application of NP, NPM or manure resulted in greater POC sequestration in soil, with a carbon sequestration rate of $0.04\text{--}0.24\text{ Mg ha}^{-1}\text{ y}^{-1}$. The LFOC stocks were $1.43\text{--}2.24\text{ Mg ha}^{-1}$ under the NP treatments, $2.47\text{--}6.68\text{ Mg ha}^{-1}$ under the NPM treatments and 8.12 Mg ha^{-1} under the M treatment; these stocks were all higher than that of the control treatment. Different fertilization strategies affected the pools of SOC with different sequestration rates. We found the carbon sequestration rates of SOC and LFOC were logarithmically correlated with the annual carbon input. When the annual C input is approximately $1.39\text{ Mg ha}^{-1}\text{ y}^{-1}$, the SOC level will be maintained; when the annual C input is higher than $0.8\text{ Mg ha}^{-1}\text{ y}^{-1}$, the LFOC level increases. This study describes the relationship between carbon inputs and the SOC(LFOC) sequestration rates under continuous fertilization in arid cropland. The results further evidence that the long-term fertilization of NPM and M increases the potential for SOC sequestration and quantifies the amount of exogenous carbon input required for soil organic matter enhancement.

Keywords: long-term fertilization experiment; particulate organic carbon; light fraction organic carbon; carbon sequestration rate



Citation: Xiang, Y.; Cheng, M.; Wen, Y.; Darboux, F. Soil Organic Carbon Sequestration under Long-Term Chemical and Manure Fertilization in a Cinnamon Soil, Northern China. *Sustainability* **2022**, *14*, 5109. <https://doi.org/10.3390/su14095109>

Academic Editors: Federica Raganati and Paola Ammendola

Received: 8 March 2022

Accepted: 21 April 2022

Published: 23 April 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Soil carbon (C) sequestration, the fixation of long-lived C pools in cropland soils, is a win-win strategy that augments food production and improves soil quality [1]. Soil organic carbon (SOC) is usually considered as an vital factor controlling soil physical, chemical and biological properties. The SOC content is a key factor in determining crop yields. Increased soil organic carbon typically benefits crop production through the provision of an energy source for microbial nutrient cycling and improved soil physical and chemical properties [2]. It has been determined that if the SOC content increases by 1 g kg^{-1} , crop yield increases by 10~20% [3,4]. An increasing number of researchers have suggested that agricultural soil has the potential to mitigate the increase in atmospheric greenhouse gases [5]. Smith

et al. [6] reported that agricultural soil could have the potential to sequester approximately 5500–6000 Mg CO₂-eq. yr^{−1} by 2030. At present, based on the double pressure of the food crisis and global warming, there is an urgent need to increase organic carbon sequestration in agricultural soils while ensuring yield.

The optimum SOC of cropland soils can be managed through agronomic measures and fertilizer application including mineral fertilization, conservation tillage, livestock management, and land use change [7]. Fertilization is an important determinant of SOC quantity in croplands since it can affect the equilibrium between primary C input and C decomposition [8]. It has been suggested that fertilization programs help sequester atmospheric CO₂ into soil by increasing plant growth and thus subsequently increase the SOC accumulation [9]. The application of manure is a management practice that can both improve the soil nutrient status and increase the SOC levels. The impact of fertilization on SOC stocks has been well documented, but the results have varied due to many factors, such as soil types, cropping systems, residue management and climate [4,10,11]. However, the relationship between carbon input and carbon sequestration under different fertilization is not clear. In addition, the complex process of soil carbon sequestration can only be studied in long-term fertilization experiments, as it takes a long time for soil C pools to balance. More studies on the effects of long-term fertilization on SOC dynamics and SOC sequestration rates would help us to fully understand C sequestration efficiency in agricultural soils.

The labile constituents of soil organic carbon are primarily responsible for the initial rapid rate of C mineralization and hence greatly influence nutrient cycles in soil [12]. Soil light fraction organic carbon (LFOC) and particulate organic carbon (POC), which are determined by physical fractionation techniques, have been studied frequently [13,14]. The light fraction organic carbon is considered a labile, fast or rapid turnover pool in SOC models [15]. Generally, particulate organic carbon (labile, >53 µm) consists of partially decomposed plant materials and byproducts of decomposition, which are unattached to mineral particles and vulnerable to disturbance [16]. Haynes [17] reported the proportions of POC and LFOC in SOC were 20–45% and 2–18%, respectively, in agricultural soils. Gosling et al. [18] indicated that POC and LFOC were strongly influenced by factors related to the recent history of organic matter addition. Other researchers also found that larger physically organic carbon (LFOC and POC) pools resulted from more C input from fertilization practices [13,19]. Quantifying the size of physically uncomplexed soil organic carbon is crucial for the understanding of the SOC storage. The responses of POC and LFOC to different C inputs could show more clearly how soil C sequestration responds to long-term fertilization at the micro-scale.

A long-term fertilizer experiment on a corn cropping system was set up in 1992 in northern China. It constitutes useful study material for carbon sequestration under long-term chemical and manure fertilization. The objectives of this study were (1) to monitor the changes in the contents of SOC, POC and LFOC under continuous corn cropping with different fertilization practices, (2) to study the impacts of different carbon inputs on the stocks of SOC, POC, LFOC with different fertilization practices, and (3) to identify the relationship between carbon inputs and the carbon sequestration rate under long-term fertilization.

2. Materials and Methods

2.1. Experimental Sites

A national long-term cinnamon soil fertility experiment was established in an artificial pasture in October 1992 in Shouyang County, Shanxi Province, China (113°06′3″ E, 37°58′23″ N, altitude of 1130 m above sea level), with one corn crop per year (April–September). The long-term experiment was included in the “National long-term soil fertility experiment network in arable land of China” in 2015. The study region experiences a dry-winter temperate climate, with a mean annual rainfall of 501 mm, an annual potential evaporation of 1600–1800 mm, and an annual sunshine duration of 2860 h. Approximately

70% of rainfall is concentrated in June–September. The annual temperature is 7.4 °C, the accumulated temperature above 10 °C is 3400 °C, the frost-free period is approximately 130 d, and the aridity index is 1.3. The soil is characterized as an Alfisol [20] developed from Malan loess. The underground water table is below 10 m deep.

2.2. Experimental Design and Treatments

This study is a part of the typical long-term fertilizer experiment in Northern China. An orthogonal design was adopted with three factors, nitrogen (N), phosphorus (P), and manure (M), in the whole fertilizer experiment. The whole experimental station included 18 fertilization treatments. We selected nine treatments to monitor the influence of the long-term application of manure and chemical fertilizers on SOC, LFOC and POC in this study. There were four treatments with chemical fertilizer (N1P1, N2P2, N3P3, N4P4), three treatments with chemical fertilizer plus manure (N2P1M1, N3P2M3, N4P2M2), one treatment with manure alone (M6), and an unfertilized control treatment (control). The treatments were arranged randomly in relatively large plots (6.66 m × 10 m), but without replication. N1, N2, N3 and N4 are 60, 120, 180 and 240 kg N ha^{−1}; P1, P2, P3 and P4 mean 37.5, 75, 112.5 and 150 kg P₂O₅ ha^{−1} and M1, M2, M3 and M6 mean 22,500, 45,000, 67,500 and 135,000 kg ha^{−1}. Table 1 shows the amount of fertilizer applied in the treatments. Urea (46% N) for N, calcium superphosphate (14% P₂O₅) for P and fresh cow dung for manure were used. Based on an analysis over 24 years, the applied manure contained 700 g kg^{−1} moisture, 404 g kg^{−1} C, 4.97 g kg^{−1} N, 1.46 g kg^{−1} P₂O₅ and 34.3 g kg^{−1} K₂O on an oven-dry weight basis.

Table 1. The annual inputs of chemical fertilizer and manure in each treatment.

Treatments	Chemical Fertilizer		Manure (kg ha ^{−1})
	Urea (kg N ha ^{−1})	Calcium Superphosphate (kg P ₂ O ₅ ha ^{−1})	
Control	0	0	0
N1P1	60	37.5	0
N2P2	120	75	0
N3P3	180	112.5	0
N4P4	240	150	0
N2P1M1	120	37.5	22,500
N3P2M3	180	75	67,500
N4P2M2	240	75	45,000
M6	0	0	135,000

Note: N1, N2, N3, N4 is 60, 120, 180, 240 kg N ha^{−1}, P1, P2, P3, P4 is 37.5, 75, 112.5, 150 kg P₂O₅ ha^{−1}, and M1, M2, M3, M6 means 22,500, 45,000, 67,500, 135,000 kg ha^{−1}, respectively.

From 1992 to 2016, corn was sown with a planting density of 66,000 plants ha^{−1} at a depth of 6 cm to 8 cm by hand in mid-April every year. The plots were tilled twice with tractor-drawn disk plows to a depth of 15 cm before sowing the corn. There was no irrigation in the plots all the year around. The field management measures were the same in all the treatments. Corn was harvested manually in the first week of October using sickles, and straw was removed from the field. Mineral fertilizers and manure were spread in the last week of October every year, and then the field was plowed to a depth of 30–35 cm. From December to March of the next year, the soil was not disturbed.

2.3. Soil Samples and Analysis

For the initial soil sample (1992), soil pH, bulk density, porosity, texture, organic carbon, total nitrogen, total phosphorus, available nitrogen and available phosphorus were determined (Table 2). In 1996, 2001, 2006, 2011 and 2016, soil samples were obtained at 0–20 cm depth in the second week of October after the corn harvest. To collect representative samples, a total of 15 soil cores were collected using a 2.5-cm diameter auger from each treatment plot, and five random samples were mixed as one composite sample. Three

soil samples were collected for the laboratory experiment by mixing three soil cores from each subplot. In 2016, complementary soil samples were obtained at a depth of 20–40 cm to calculate the soil carbon stocks and their relationship with carbon input. The soil samples were air-dried and ground. One part of the samples was passed through a 2-mm sieve for the estimation of particulate organic carbon and light fraction organic carbon, and the other part was passed through a 0.149-mm sieve for SOC content analysis. The bulk density was determined using a ring of 100 cm³ and calculated by dividing the weight of dried soil by the volume of the core in the meantime [21]. The porosity was calculated by soil bulk density and the specific gravity value. The texture was measured by a hydrometer method [22]. The soil organic carbon (SOC) was determined by potassium dichromate (K₂Cr₂O₇) titration [23], total nitrogen (TN) by the Kjeldahl method [22], total phosphorus by the molybdenum antimony resistance colorimetric method [22], available nitrogen by the alkali solution diffusion method [22], and available phosphorus by the sodium bicarbonate extraction molybdenum antimony resistance colorimetric method [24].

Table 2. Soil physiochemical properties of the 0–20 cm soil layer in the experimental site.

Time	Treatments	pH	Bulk Density (g cm ⁻³)	Porosity (%)	Clay (%)	Soil Organic Carbon (g kg ⁻¹)	Total Nitrogen (g kg ⁻¹)	Total Phosphorus (g kg ⁻¹)	Available Nitrogen (mg kg ⁻¹)	Available Phosphorus (mg kg ⁻¹)
1992	Initial	8.40 ± 0.03 ^b	1.21 ± 0.03 ^b	54.40 ± 0.06	19.25 ± 0.45 ^a	13.80 ± 0.03 ^c	1.05 ± 0.02 ^c	0.76 ± 0.02 ^e	117.69 ± 0.41 ^c	4.84 ± 0.29 ^g
2016	Control	8.65 ± 0.03 ^a	1.33 ± 0.01 ^a	nd	17.21 ± 0.12 ^b	9.82 ± 0.04 ^e	0.83 ± 0.01 ^d	0.70 ± 0.01 ^e	62.76 ± 0.02 ^f	4.56 ± 0.05 ^g
	N1P1	8.49 ± 0.04 ^b	1.27 ± 0.02 ^a	nd	16.24 ± 0.09 ^b	9.80 ± 0.07 ^e	1.02 ± 0.12 ^c	0.61 ± 0.01 ^f	62.48 ± 2.03 ^f	10.06 ± 0.04 ^f
	N2P2	8.42 ± 0.01 ^b	1.26 ± 0.06 ^a	nd	20.63 ± 0.37 ^a	10.52 ± 0.10 ^d	1.28 ± 0.01 ^c	0.80 ± 0.02 ^d	70.90 ± 1.08 ^e	22.29 ± 0.02 ^e
	N3P3	8.47 ± 0.05 ^b	1.34 ± 0.02 ^a	nd	14.80 ± 0.25 ^c	10.26 ± 0.02 ^d	1.29 ± 0.03 ^c	0.83 ± 0.01 ^d	84.81 ± 0.03 ^d	33.60 ± 0.08 ^e
	N4P4	8.49 ± 0.02 ^b	1.32 ± 0.04 ^a	nd	18.52 ± 0.06 ^b	9.65 ± 0.05 ^e	1.36 ± 0.02 ^c	1.25 ± 0.02 ^b	100.95 ± 8.06 ^c	43.99 ± 0.03 ^d
	N2P1M1	8.38 ± 0.03 ^b	1.20 ± 0.01 ^b	nd	17.55 ± 0.13 ^b	14.57 ± 0.09 ^c	1.34 ± 0.01 ^c	0.83 ± 0.01 ^d	85.05 ± 0.05 ^d	24.74 ± 0.04 ^e
	N3P2M3	8.16 ± 0.05 ^c	1.22 ± 0.01 ^b	nd	16.51 ± 0.21 ^b	17.88 ± 0.27 ^b	2.17 ± 0.04 ^a	1.24 ± 0.02 ^b	126.23 ± 0.12 ^b	170.51 ± 0.09 ^b
	N4P2M2	8.30 ± 0.08 ^b	1.16 ± 0.04 ^b	nd	16.83 ± 0.17 ^b	14.65 ± 0.84 ^c	1.93 ± 0.03 ^b	0.95 ± 0.02 ^c	101.66 ± 0.09 ^c	86.97 ± 0.10 ^c
	M6	7.82 ± 0.02 ^d	1.16 ± 0.03 ^b	nd	12.66 ± 0.04 ^d	25.11 ± 0.34 ^a	2.69 ± 0.05 ^a	1.48 ± 0.03 ^a	150.80 ± 0.13 ^a	211.24 ± 0.12 ^a

Note: nd = no data; different lowercase letters indicate significant differences in soil properties under different treatments at $p < 0.05$; data are means ± standard error, $n = 9$.

Soil POC was measured following the procedure of Cambardella and Elliott [25]. Portions (10 g) of air-dried soil were dispersed in 30 mL of sodium hexametaphosphate, (Na)₆(PO₃)₆ (5 g L⁻¹), with shaking on a reciprocating shaker for 18 h. The resulting soil suspension was poured over a 53-μm screen under a flow of distilled water to ensure separation. All material remaining on the screen was washed into a dry dish, oven-dried at 60 °C for 48 h, and ground to determine the C content. The soil light fraction organic carbon was measured using a method from Janzen [26]. Portions (10 g) of air-dried soil were each placed in a centrifuge tube with 20 mL NaI solution (specific gravity ca. 1.7 g cm⁻³). The tubes were shaken on a reciprocating shaker for 60 min, and then centrifuged at 1000 × g for 15 min. The floating material was poured into a vacuum filter unit with a 45 μm millipore filter, and the material retained by the millipore paper was washed with 0.01 M CaCl₂ and distilled water, dried at 60 °C for 48 h, weighed and analyzed for C content.

For a given soil layer, the stocks (Mg ha⁻¹) of SOC, POC and LFOC were calculated as follows:

$$C_{\text{stocks}} = C \times \text{BD} \times H \times 0.1 \quad (1)$$

where C is the content (g kg⁻¹) of SOC, POC or LFOC; BD is the bulk density (g cm⁻³); H is the soil layer thickness (cm) and 0.1 is a unit conversion factor. The C_{stocks} of the 0–40 cm soil layer were calculated as the sum of the C_{stocks} of the 0–20 cm and 20–40 cm soil layers.

The carbon sequestration rate C_{SR} (Mg ha⁻¹ y⁻¹) and the carbon sequestration efficiency C_{SE} (%) of SOC, POC and LFOC were calculated as follows:

$$\Delta C_{\text{stocks}} = C_{\text{stocks-t}} - C_{\text{stocks-c}} \quad (2)$$

$$C_{\text{SR}} = \Delta C_{\text{stocks}}/n \quad (3)$$

$$C_{\text{SE}} = \Delta C_{\text{stocks}}/(C_{\text{input-t}} - C_{\text{input-c}}), \quad (4)$$

where $C_{\text{stocks-t}}$ and $C_{\text{stocks-c}}$ are the C stocks (Mg ha^{-1}) of the treatment and the control, respectively, in 2016, ΔC_{stocks} (Mg ha^{-1}) is the difference in C stocks between the fertilization and the control treatments in 2016, and n is the fertilization duration (i.e., 24 years from 1992 to 2016), and $C_{\text{input-t}}$ and $C_{\text{input-c}}$ are the carbon input of the fertilization and the control treatments during the period of fertilizer application, respectively.

The C_{input} (Mg ha^{-1}) of each treatment was calculated as:

$$C_{\text{input}} = [((Y_g + Y_s) \times R \times D_r + Y_s \times R_s) \times (1 - W_c) \times C_{\text{crop}} + M_c \times (1 - W_m) \times A_m] / 1000, \quad (5)$$

where Y_g (kg ha^{-1}) is the grain yield, Y_s (kg ha^{-1}) is the straw yield, R is the percentage of C from photosynthesis, considered equal to 26% [27], D_r is the average percentage of corn roots in the 0–40 cm soil depth, equal to 85.1% according to [28], R_s is the percentage of the corn stubble (3%, mean value measured over 24 years), W_c and C_{crop} are the corn water content and carbon content [28], respectively, M_c is the average carbon content of the manure (g kg^{-1}), W_m is the water content of the manure, A_m is the fresh weight of the manure (kg ha^{-1}) and 1000 is a unit conversion factor.

2.4. Statistical Analysis

SPSS 18.0 statistical software (SPSS Inc., Chicago, IL, USA) and Excel 2007 were used for the statistical analysis. A linear regression model was used to determine the relationships between SOC content and fertilization time. The differences in POC, LFOC, C_{SR} and C_{SE} among different fertilization treatments were tested using a one-way analysis of variance (ANOVA). The treatment means were compared at $p < 0.05$ using the Tukey method for all parameters.

3. Results

3.1. Changes in Soil Organic Carbon Content under Different Fertilization Treatments

The changes in SOC content under the different fertilization treatments are shown in Figure 1. SOC in the 0–20 cm soil layer decreased with time under the chemical fertilization treatments (N1P1, N2P2, N3P3, and N4P4) and the no-fertilization (control) treatment. Moreover, the extent of the decrease was slightly higher in the N1P1 treatment (with a decreasing rate of $0.21 \text{ g kg}^{-1} \text{ y}^{-1}$) than in the other NP treatments ($0.17\text{--}0.19 \text{ g kg}^{-1} \text{ y}^{-1}$). The SOC content under the NPM and M treatments did not show any clear trend. The SOC content under the N2P1M1, N3P2M3, and N4P2M2 treatments was $9.45\text{--}14.00 \text{ g kg}^{-1}$, $12.53\text{--}17.31 \text{ g kg}^{-1}$, and $13.81\text{--}14.65 \text{ g kg}^{-1}$, respectively. The SOC content under the M6 treatment varied from 13.81 g kg^{-1} to 25.69 g kg^{-1} . In 2016, the SOC content under the N2P1M1, N3P2M3, N4P2M2 and M6 treatments was 2.77 g kg^{-1} , 6.14 g kg^{-1} , 4.83 g kg^{-1} , and 15.87 g kg^{-1} higher than that of the control treatment.

3.2. Changes in Soil Particulate Organic Carbon Content under Different Fertilization Treatments

For the control, the content of soil POC of the 0–20 cm soil layer varied from 1.80 g kg^{-1} to 2.91 g kg^{-1} (Table 3). During the fertilization period, the soil POC content under the N1P1, N2P2 and N3P3 treatments did not show a clear trend, while the POC of the N4P4 treatment decreased continually with time (Table 3). From 1992 to 2016, the soil POC content of the N1P1, N2P2, N3P3 and N4P4 treatments decreased by 0.60 g kg^{-1} , 0.76 g kg^{-1} , 1.16 g kg^{-1} and 1.35 g kg^{-1} , respectively. After 24 years of fertilization, the soil POC content was significantly higher in the N1P1 and N2P2 treatments than in the control, while it was significantly lower in the N3P3 and N4P4 treatments than in the control. The soil POC content under the N2P1M1, N3P2M3 and N4P2M2 treatments decreased from 1992 to 2001 and then increased from 2001 to 2016. In 2016, the soil POC content under the NPM treatments was approximately 1.7 times that of the control. The POC content under the M6 treatment always had the highest value and increased with time. Overall, the soil POC content showed different trends under different fertilization treatments. The long-term application of high amounts of N and P alone led to a decrease in POC content, whereas the application of manure resulted in an increase in soil POC content.

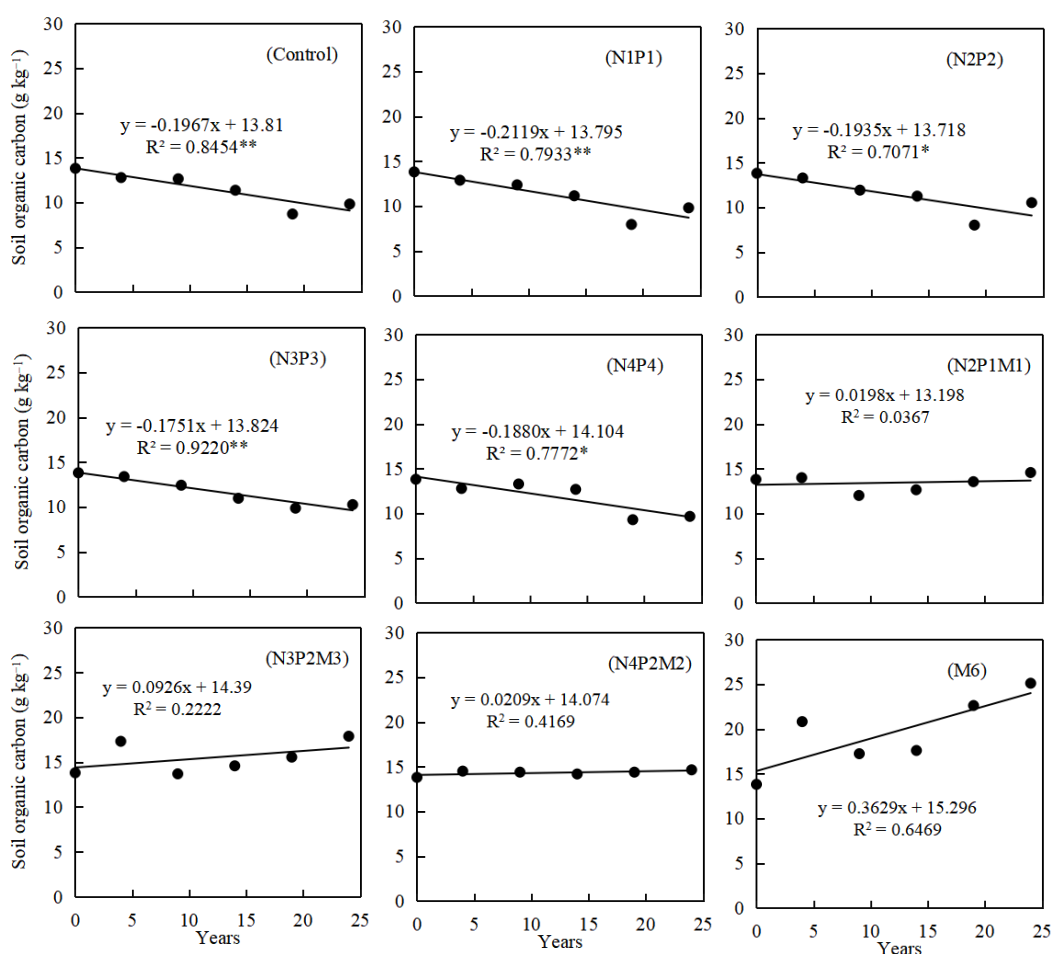


Figure 1. The changes of soil organic carbon content in 0–20 cm soil layer with time under different fertilization treatments. * and ** indicate the regressions in the figure were statistical at the 0.05 level and 0.01 level, respectively.

Table 3. Soil particulate organic carbon content of 0–20 cm soil layer with time under different fertilization treatments.

Treatment \ Year	Soil Particulate Organic Carbon (g kg ⁻¹)					
	1992	1996	2001	2006	2011	2016
Control	2.91 ± 0.11 ^a	2.38 ± 0.05 ^{Bb}	1.80 ± 0.10 ^{Dd}	2.05 ± 0.06 ^{Cc}	2.00 ± 0.05 ^{Cc}	1.87 ± 0.01 ^{Ed}
N1P1	2.91 ± 0.11 ^a	2.39 ± 0.01 ^{Bb}	1.80 ± 0.08 ^{Dc}	2.37 ± 0.08 ^{Bb}	2.06 ± 0.05 ^{Cc}	2.31 ± 0.03 ^{Db}
N2P2	2.91 ± 0.11 ^a	2.64 ± 0.07 ^{ABab}	1.83 ± 0.03 ^{Dc}	2.26 ± 0.07 ^{Bb}	2.25 ± 0.12 ^{Cb}	2.15 ± 0.02 ^{Db}
N3P3	2.91 ± 0.11 ^a	2.07 ± 0.12 ^{Cb}	1.89 ± 0.05 ^{Dc}	2.16 ± 0.08 ^{Bb}	2.13 ± 0.04 ^{Cb}	1.75 ± 0.01 ^{Fc}
N4P4	2.91 ± 0.11 ^a	2.52 ± 0.12 ^{ABab}	2.16 ± 0.10 ^{Cb}	2.03 ± 0.02 ^{Cbc}	1.87 ± 0.05 ^{Cc}	1.56 ± 0.01 ^{Fd}
N2P1M1	2.91 ± 0.11 ^a	2.59 ± 0.01 ^{ABb}	2.20 ± 0.04 ^{Cc}	2.75 ± 0.14 ^{Bab}	2.94 ± 0.10 ^{Ba}	3.08 ± 0.28 ^{Ca}
N3P2M3	2.91 ± 0.11 ^a	2.90 ± 0.16 ^{Aa}	2.73 ± 0.07 ^{Ba}	3.06 ± 0.08 ^{ABa}	3.14 ± 0.03 ^{ABa}	3.30 ± 0.01 ^{Ba}
N4P2M2	2.91 ± 0.11 ^a	2.03 ± 0.05 ^{Cc}	2.66 ± 0.01 ^{Bb}	3.03 ± 0.10 ^{ABa}	3.02 ± 0.11 ^{ABa}	2.98 ± 0.01 ^{Ca}
M6	2.91 ± 0.11 ^a	3.18 ± 0.10 ^{Aa}	3.09 ± 0.04 ^{Aa}	3.36 ± 0.08 ^{Aa}	3.52 ± 0.19 ^{Aa}	3.65 ± 0.01 ^{Aa}

Note: Different capital letters indicate significant differences in soil POC under different fertilization treatments for a given year at $p < 0.05$; different lowercase letters indicate significant differences in soil POC for a given treatment among the various years at $p < 0.05$; data are means ± standard error, $n = 9$.

3.3. Changes in the Soil Light Fraction Organic Carbon Content under Different Fertilization Treatments

The content of soil LFOC in the 0–20 cm soil layer varied from 0.67 g kg⁻¹ to 3.78 g kg⁻¹ (Table 4). For the control, the LFOC content was basically the same in the first ten years and

decreased by 1.10 g kg^{-1} from 2001 to 2016. In the N1P1 and N2P2 treatments, the LFOC content did not show a clear trend. In the N3P3 and N4P4 treatments, the soil LFOC content remained constant from 1992 to 2001, was the lowest in 2006, and increased by 0.83 g kg^{-1} and 1.13 g kg^{-1} , respectively, from 2006 to 2016. The LFOC content of the NPM treatments increased from 1992 to 2001, decreased from 2001 to 2011 and then increased from 2011 to 2016. The content of LFOC was always the highest in the M6 treatment ($2.14\text{--}3.78 \text{ g kg}^{-1}$). In 2016, the LFOC content of the 0–20 cm soil layer for the NP, NPM and M6 treatments was 1.1–2.2, 1.6–3.0 and 3.6 times that of the control plot, respectively, while the LFOC content of the 20–40 cm soil layer under the N1P1, NPM and M6 treatments was significantly higher than that of the control plot (Table 5).

Table 4. Soil light organic fraction carbon content of 0–20 cm soil layer with time under different fertilization treatments.

Year	Light Fraction Organic Carbon (g kg ⁻¹)					
Treatment	1992	1996	2001	2006	2011	2016
Control	2.14 ± 0.04 ^a	2.01 ± 0.02 ^{Ba}	2.20 ± 0.05 ^{Ba}	1.13 ± 0.01 ^{Db}	0.92 ± 0.01 ^{Db}	1.06 ± 0.10 ^{Eb}
N1P1	2.14 ± 0.04 ^a	1.75 ± 0.02 ^{Cb}	2.05 ± 0.04 ^{Ba}	1.43 ± 0.02 ^{Cb}	0.74 ± 0.01 ^{Dc}	1.52 ± 0.05 ^{Db}
N2P2	2.14 ± 0.04 ^a	1.62 ± 0.04 ^{Cb}	2.13 ± 0.01 ^{Ba}	0.72 ± 0.01 ^{Ec}	1.06 ± 0.06 ^{Cbc}	1.49 ± 0.07 ^{Db}
N3P3	2.14 ± 0.04 ^a	1.93 ± 0.09 ^{Ca}	2.18 ± 0.01 ^{Ba}	0.67 ± 0.02 ^{Ec}	0.79 ± 0.02 ^{Dc}	1.50 ± 0.01 ^{Db}
N4P4	2.14 ± 0.04 ^a	2.21 ± 0.09 ^{ABa}	2.34 ± 0.06 ^{ABa}	1.16 ± 0.04 ^{Dc}	1.46 ± 0.01 ^{Bb}	2.29 ± 0.12 ^{Ca}
N2P1M1	2.14 ± 0.04 ^b	2.51 ± 0.02 ^{Aa}	2.70 ± 0.04 ^{Aa}	1.41 ± 0.08 ^{Cd}	1.36 ± 0.04 ^{Bd}	1.68 ± 0.04 ^{Dc}
N3P2M3	2.14 ± 0.04 ^{bc}	2.41 ± 0.13 ^{Ab}	2.76 ± 0.02 ^{Ab}	2.08 ± 0.02 ^{ABc}	1.62 ± 0.03 ^{ABd}	3.22 ± 0.11 ^{Ba}
N4P2M2	2.14 ± 0.04 ^c	2.06 ± 0.02 ^{Bc}	2.40 ± 0.04 ^{ABb}	1.86 ± 0.04 ^{Bd}	1.49 ± 0.05 ^{Be}	2.98 ± 0.12 ^{BCa}
M6	2.14 ± 0.04 ^c	2.77 ± 0.07 ^{Ab}	2.62 ± 0.01 ^{Ab}	2.78 ± 0.02 ^{Ab}	2.80 ± 0.13 ^{Ab}	3.78 ± 0.36 ^{Aa}

Note: Different capital letters indicate significant differences in soil LFOC under different fertilization treatments for a given year at $p < 0.05$; different lowercase letters indicate significant differences in soil LFOC for a given treatment among the various years at $p < 0.05$; data are means $\pm$ standard error, $n = 9$.

Table 5. The content of SOC, POC, LFOC in 0–20 cm and 20–40 cm layer under different fertilization treatments in 2016.

Treatment	SOC		POC		LFOC	
	0–20 cm	20–40 cm	0–20 cm	20–40 cm	0–20 cm	20–40 cm
Control	9.82 ± 0.04^{Ea}	8.90 ± 0.05^{Db}	1.87 ± 0.01^{Ea}	0.89 ± 0.01^{Eb}	1.06 ± 0.10^{Ea}	0.97 ± 0.01^{Da}
N1P1	9.80 ± 0.07^{Ea}	6.57 ± 0.02^{Eb}	2.31 ± 0.03^{Da}	0.91 ± 0.03^{Eb}	1.52 ± 0.05^{Da}	1.27 ± 0.04^{Cb}
N2P2	10.52 ± 0.10^{Da}	8.98 ± 0.05^{Db}	2.15 ± 0.02^{Da}	1.93 ± 0.05^{Bb}	1.49 ± 0.07^{Da}	1.01 ± 0.01^{Db}
N3P3	10.26 ± 0.02^{Da}	9.37 ± 0.09^{CDb}	1.75 ± 0.01^{Fa}	1.17 ± 0.04^{Db}	1.50 ± 0.01^{Da}	0.98 ± 0.02^{Db}
N4P4	9.65 ± 0.05^{Ea}	6.57 ± 0.02^{Eb}	1.56 ± 0.01^{Fa}	0.93 ± 0.02^{Eb}	2.29 ± 0.12^{Ca}	0.62 ± 0.02^{Eb}
N2P1M1	14.57 ± 0.09^{Ca}	12.07 ± 0.17^{Bb}	3.08 ± 0.08^{Ca}	1.48 ± 0.03^{Cb}	1.68 ± 0.04^{Da}	1.29 ± 0.03^{Cb}
N3P2M3	17.88 ± 0.27^{Ba}	12.74 ± 0.09^{Bb}	3.30 ± 0.01^{Ba}	2.06 ± 0.02^{Bb}	3.22 ± 0.11^{Ba}	1.79 ± 0.02^{Bb}
N4P2M2	14.65 ± 0.04^{Ca}	10.03 ± 0.29^{Cb}	2.98 ± 0.01^{Ca}	1.64 ± 0.01^{Cb}	2.98 ± 0.12^{BCa}	1.34 ± 0.01^{Cb}
M6	25.11 ± 0.34^{Aa}	13.62 ± 0.20^{Ab}	3.65 ± 0.01^{Aa}	2.37 ± 0.06^{Ab}	3.78 ± 0.36^{Aa}	2.87 ± 0.03^{Ab}

Note: SOC = soil organic carbon, POC = particulate organic carbon, LFOC = light fraction organic carbon; different capital letters indicate significant differences in soil organic carbon or carbon fractions under fertilization treatments for a given year at $p < 0.05$; different lowercase letters indicate significant differences in soil LFOC among the different soil layers for a given treatment at $p < 0.05$; data are means $\pm$ standard error, $n = 9$.

3.4. The Responses of SOC, POC and LFOC Stocks to Different Amounts of C Input

After 24 years of fertilization, the total carbon input varied from 20.5 Mg ha^{-1} to 435.6 Mg ha^{-1} (Table 6). Except for the N1P1 and N4P4 treatments, the change in SOC stocks (ΔC_{stocks}) of other treatments was positive, from 4.66 Mg ha^{-1} to 31.00 Mg ha^{-1} , with a sequestration rate of $0.19 \text{ Mg ha}^{-1} \text{ y}^{-1}$ to $1.29 \text{ Mg ha}^{-1} \text{ y}^{-1}$. The sequestration rates of SOC stocks under the M and NPM treatments followed the order $M6 > N3P2M3 > N2P1M1 > N4P2M2$ and were significantly higher than those under the NP treatments. Except in the N4P4 treatment, the changes in POC stocks were positive, from 0.86 Mg ha^{-1}

to 5.21 Mg ha^{-1} . The sequestration rate of POC increased in this order: $\text{N4P4} < \text{N1P1} \approx \text{N3P3} < \text{N2P2} \approx \text{N4P2M2} < \text{N2P1M1} \approx \text{N3P2M3} \approx \text{M6}$. The changes in LFOC stocks under the M6, N4P2M2 and N3P2M3 treatments were $>5.0 \text{ Mg ha}^{-1}$, significantly higher than those in the other treatments, while the changes in LFOC stocks were significantly higher under the N2P1M1 and N4P4 treatments (approximately 2.30 Mg ha^{-1}) than under the N1P1, N2P2 and N3P3 treatments (approximately 1.54 Mg ha^{-1}). Accordingly, the sequestration rates of LFOC under the M6 and N3P2M3 treatments were the highest, followed by those of the N4P4, N2P1M1 and N4P2M2 treatments, while those of the N1P1, N2P2 and N3P3 treatments were the lowest (approximately $0.06 \text{ Mg ha}^{-1} \text{ y}^{-1}$).

Table 6. The change, carbon sequestration rate and carbon sequestration efficiency of soil organic carbon (SOC), particulate organic carbon (POC) and light organic fraction carbon (LFOC) stocks in 0–40 cm soil layer after 24 years' fertilization.

Treatment	Total C Input (Mg ha^{-1})	ΔC_{stocks} (Mg ha^{-1})			C_{SR} ($\text{Mg ha}^{-1} \text{ y}^{-1}$)			C_{SE} (%)		
		SOC	POC	LFOC	SOC	POC	LFOC	SOC	POC	LFOC
Control	$20.54 \pm 0.04^{\text{F}}$									
N1P1	$33.08 \pm 0.96^{\text{E}}$	$-5.02 \pm 0.10^{\text{F}}$	$1.21 \pm 0.01^{\text{D}}$	$1.75 \pm 0.07^{\text{E}}$	$-0.21 \pm 0.01^{\text{F}}$	$0.05 \pm 0.01^{\text{C}}$	$0.07 \pm 0.01^{\text{D}}$	$-40.0 \pm 0.01^{\text{F}}$	$9.63 \pm 0.01^{\text{B}}$	$13.95 \pm 0.01^{\text{B}}$
N2P2	$36.22 \pm 0.36^{\text{E}}$	$4.66 \pm 0.17^{\text{E}}$	$3.76 \pm 0.07^{\text{C}}$	$1.45 \pm 0.09^{\text{E}}$	$0.19 \pm 0.01^{\text{E}}$	$0.16 \pm 0.01^{\text{B}}$	$0.06 \pm 0.01^{\text{D}}$	$29.73 \pm 0.01^{\text{B}}$	$24.00 \pm 0.01^{\text{A}}$	$9.22 \pm 0.01^{\text{C}}$
N3P3	$36.02 \pm 0.70^{\text{E}}$	$5.27 \pm 0.13^{\text{E}}$	$0.86 \pm 0.08^{\text{E}}$	$1.43 \pm 0.04^{\text{E}}$	$0.22 \pm 0.01^{\text{E}}$	$0.04 \pm 0.01^{\text{C}}$	$0.06 \pm 0.01^{\text{D}}$	$34.05 \pm 0.01^{\text{A}}$	$5.56 \pm 0.01^{\text{C}}$	$9.21 \pm 0.01^{\text{C}}$
N4P4	$35.32 \pm 0.65^{\text{E}}$	$-4.71 \pm 0.08^{\text{F}}$	$-0.42 \pm 0.06^{\text{F}}$	$2.24 \pm 0.18^{\text{D}}$	$-0.20 \pm 0.01^{\text{F}}$	$-0.02 \pm 0.01^{\text{D}}$	$0.09 \pm 0.01^{\text{CD}}$	$-31.84 \pm 0.01^{\text{F}}$	$-2.82 \pm 0.01^{\text{F}}$	$15.18 \pm 0.02^{\text{A}}$
N2P1M1	$106.53 \pm 1.53^{\text{D}}$	$21.08 \pm 0.32^{\text{C}}$	$4.74 \pm 0.03^{\text{B}}$	$2.47 \pm 0.09^{\text{D}}$	$0.88 \pm 0.02^{\text{C}}$	$0.20 \pm 0.01^{\text{A}}$	$0.10 \pm 0.01^{\text{C}}$	$24.51 \pm 0.01^{\text{C}}$	$5.51 \pm 0.01^{\text{C}}$	$2.87 \pm 0.01^{\text{E}}$
N3P2M3	$237.32 \pm 1.67^{\text{B}}$	$26.24 \pm 0.39^{\text{B}}$	$5.84 \pm 0.03^{\text{A}}$	$6.68 \pm 0.13^{\text{B}}$	$1.09 \pm 0.02^{\text{B}}$	$0.24 \pm 0.01^{\text{A}}$	$0.28 \pm 0.01^{\text{A}}$	$12.11 \pm 0.01^{\text{D}}$	$2.69 \pm 0.01^{\text{D}}$	$3.08 \pm 0.01^{\text{D}}$
N4P2M2	$174.45 \pm 2.70^{\text{C}}$	$17.43 \pm 0.36^{\text{D}}$	$4.09 \pm 0.02^{\text{B}}$	$5.07 \pm 0.13^{\text{C}}$	$0.73 \pm 0.02^{\text{D}}$	$0.17 \pm 0.01^{\text{B}}$	$0.21 \pm 0.01^{\text{B}}$	$11.32 \pm 0.01^{\text{D}}$	$2.66 \pm 0.01^{\text{D}}$	$3.29 \pm 0.01^{\text{D}}$
M6	$435.59 \pm 3.36^{\text{A}}$	$31.00 \pm 0.53^{\text{A}}$	$5.21 \pm 0.06^{\text{A}}$	$8.12 \pm 0.39^{\text{A}}$	$1.29 \pm 0.03^{\text{A}}$	$0.22 \pm 0.01^{\text{A}}$	$0.34 \pm 0.02^{\text{A}}$	$7.47 \pm 0.01^{\text{E}}$	$1.26 \pm 0.01^{\text{E}}$	$1.96 \pm 0.01^{\text{F}}$

Note: ΔC_{stocks} means the change in C stocks; C_{SR} means carbon sequestration rate; C_{SE} means carbon sequestration efficiency; different capital letters indicate significant differences in the change, carbon sequestration rate and carbon sequestration efficiency of soil organic carbon or carbon fractions under fertilization treatments for a given year at $p < 0.05$; data are means $\pm$ standard error, $n = 9$.

Apart from the N1P1 and N4P4 treatments, the carbon sequestration efficiency (C_{SE}) of SOC was positive, from 7.5% to 34.0%. The C_{SE} of POC varied from 1.3% to 24.0% in the fertilization treatments, with the exception of that in the N4P4 treatment. The C_{SE} of LFOC with 24-year fertilization was between 2.0% and 15.2%. The relationship of the annual carbon input to the carbon sequestration rate was simulated by a logarithmic equation (Figure 2). The soil organic carbon sequestration rates of SOC and LFOC were logarithmically correlated with the annual carbon input from the corn cropping system ($p < 0.01$). The C_{SR} of POC was not correlated with the annual carbon input ($p > 0.05$). Through the logarithmic equation, we calculated that when the annual C input is approximately $1.4 \text{ Mg ha}^{-1} \text{ y}^{-1}$, the C_{SR} is zero, i.e., the soil organic carbon level is maintained. The LFOC level will increase when the annual C input is greater than $0.8 \text{ Mg ha}^{-1} \text{ y}^{-1}$.

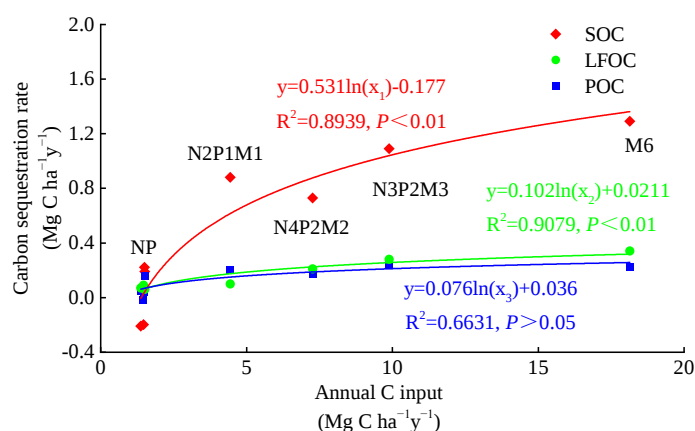


Figure 2. The correlation between annual C input and the sequestration rate of soil organic carbon (SOC), particulate organic carbon (POC), and light organic fraction carbon (LFOC).

4. Discussion

4.1. Effect of Long-Term Fertilization on Soil Organic Carbon

Soil organic carbon is a result of the balance between C inputs, in the form of crop residues and organic fertilizers, and soil carbon decomposition as mediated by soil microorganisms and the environment [2]. Our results showed that the long-term application of relatively low (60 kg N hm^{-2} plus $37.5 \text{ kg P}_2\text{O}_5 \text{ hm}^{-2}$) or high (240 kg N hm^{-2} plus $150 \text{ kg P}_2\text{O}_5 \text{ hm}^{-2}$) amounts of chemical fertilizer resulted in a decrease of $5.0 \text{ Mg ha}^{-1} \text{ C}$ compared to that in soil under the no-fertilizer treatment, with a carbon sequestration rate of $-0.20 \text{ Mg ha}^{-1} \text{ y}^{-1}$. Our results are not completely consistent with previous results. Urkurkar et al. [10] observed that the SOC content slightly increased with long-term mineral fertilization in a 16-year experiment. Dong et al. [11] and Yang et al. [4] showed that long-term inorganic fertilizer application can promote the accumulation of SOC. Chemical fertilization affects SOC mainly through the crop residues left in the field after harvest [29]. In the present study, most of the aboveground biomass was removed, and only 3% of the aboveground biomass residues (the stubble) were returned to the soil. Long-term chemical fertilization affected SOC by augmenting the C input from the crop residues (as Figure 3 shows). This implies that the carbon input from the N1P1 treatment and the N4P4 treatment, which was mainly from stubble, root biomass and rhizodeposition, was less than the carbon output of soil mineralization and other processes. Another important reason: we suspect low SOC levels are due in part to the positive priming of C that results from high background levels of available N [30], as shown in Table 2. There was lower C/N ratio and higher available N in the N4P4 treatment, compared to other NP treatments. Under the N4P4 treatment, a low soil C/N ratio and high available N is conducive to the mineralization of soil organic carbon [31]. A high N level resulted in more microbial activity and enhanced the mineralization of SOC [32]. Schimel and Weintraub (2003) also explained the C loss from soil respiration with high N availability as a consequence of saturated enzyme kinetics [33].

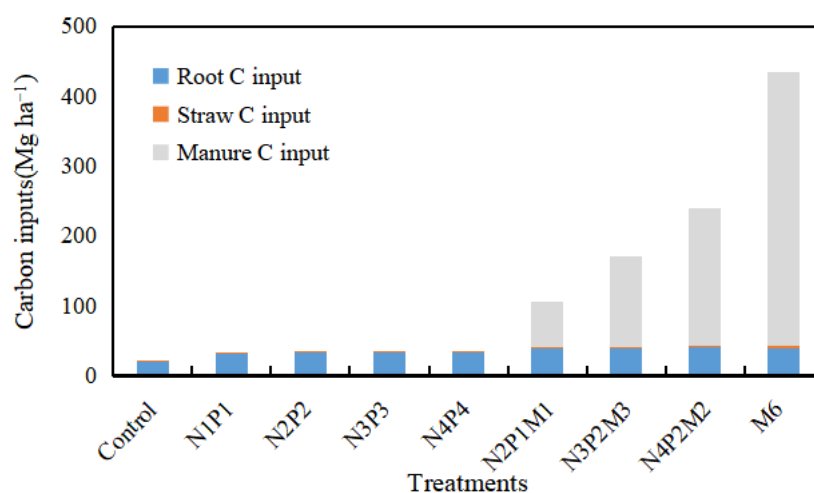


Figure 3. The cumulative carbon input of root, straw and manure under different treatments.

The combination of inorganic and organic fertilizers is usually considered the best way to enrich soil [34]. Our results also showed that under the NPM treatments and the M6 treatment, the changes in SOC stocks were from $17.4 \text{ Mg ha}^{-1} \text{ C}$ to $31.0 \text{ Mg ha}^{-1} \text{ C}$ higher than that in the no-fertilization treatment, and the carbon sequestration rate in these treatments varied from $0.73 \text{ Mg ha}^{-1} \text{ y}^{-1}$ to $1.29 \text{ Mg ha}^{-1} \text{ y}^{-1}$. Rudrappa et al. reported that the 0–45 cm soil profile accumulated carbon by $71.1\text{--}731 \text{ Mg ha}^{-1} \text{ y}^{-1}$ with the application of 100% NPK and farmyard manure in India [35]. Ghosh et al. [36] calculated that the carbon accumulation rate in NPK+FYM was $0.74 \text{ Mg C ha}^{-1} \text{ y}^{-1}$ higher than that in the control plot in the 0–90 cm soil layer after 44 years of fertilization in India. The

higher SOC sequestration potential was most likely due to the increased carbon inputs from manure C input with the application of manure (Figure 3). More importantly, manure is semi-decomposed organic matter, and the application of manure represented the organic matter with high content of refractory components such as lignin and polyphenols was inputted [37]. Manure application can effectively promote SOC sequestration in the long term corn system.

4.2. Effects of Long-Term Fertilization on Selected Soil Organic Carbon Fractions

Soil POC and LFOC are important C fractions, which are major sources of plant nutrients. Our results showed that the content of soil POC decreased in the first 10 years and increased in the last 15 years. After 24 years of fertilization, with the exception of the N4P4 treatment (0.42 Mg ha^{-1} lower), POC stocks in the 0–40 cm soil layer were $0.86\sim 3.76 \text{ Mg ha}^{-1}$ higher in the NP treatments, $4.09\sim 5.84 \text{ Mg ha}^{-1}$ higher in the NPM treatments, and 5.21 Mg ha^{-1} higher in the M6 treatment than in the control. This implied that a higher level of chemical fertilizer application caused a reduction in POC, whereas the application of relatively low amounts of NP ($<240 \text{ kg ha}^{-1}$ plus 150 kg ha^{-1}), NPM or manure resulted in higher POC in the soil. Yan et al. suggested that, compared to chemical fertilizers and straw, the application of manure was the most effective way to enhance soil POC in a paddy soil [38]. Whalen et al. [39] also suggested that significant quantities of C from organic manure are stored in the soil particulate fraction. Long-term manuring increased soil POC content, on the one hand, due to the manure enriching in nonpolar alkyl compounds of the calcium humate fraction [40,41], which directly contributed to POC. On the other hand, the reason for this is that the manure increased crop productivity, combined with the presence of more root biomass and exudates containing lignocellulose residues [42] and the greater biochemical recalcitrance [43], which indirectly contributed to POC. The application of excess chemical fertilizers probably decreased the POC content and stocks, partly due to the high available N and low C/N (as is mentioned above), and partly due to the destruction of the soil micro-aggregates [44], which were considered important aggregates providing physical protection for soil POC.

The soil light fraction is, approximately speaking, plant semi-decomposed residue, which contains carbohydrate constituents, lignin derivatives and aliphatic compounds [29] which are more sensitive to soil management measures and the cropping system than the total organic matter [45]. Our results revealed that the soil LFOC content, compared to that in the control treatment, increased by $1.43\sim 2.24 \text{ Mg ha}^{-1}$ in the NP treatments, by $2.47\sim 6.68 \text{ Mg ha}^{-1}$ in the NPM treatments and by 8.12 Mg ha^{-1} in the M treatment. Li et al. [13] reported that a long-term (24 year) double standard rate of organic manure fertilizer could enhance LFOC content, and a mineral fertilizer treatment had no significant effect on LFOC compared to that in the control treatment. Similar results have been reported by [46,47], who found that LFOC was the highest in the M treatment, because the manure could directly provide different organic carbon compounds which could contribute light fraction organic carbon. In addition, the manure could indirectly affect the LFOC by providing a C source for soil microorganisms and increasing macropores for microbial growth, which in turn accelerate the soil's biological activities to convert the manure C into LFOC (Moharana et al., 2020). With respect to the NP fertilization, more root biomass was considered the major immediate factor compared with no fertilization [9]. In a word, long term NP, NPM and M fertilization enhanced LFOC in cinnamon soil in northern China.

4.3. How to Maintain or Enhance Soil Organic Carbon in Agricultural Soils

Numerous studies have shown that fertilizer or manure application can increase crop yields and soil organic matter and improve soil quality [48]. There is no doubt that the application of fertilizer can directly and indirectly affect carbon input. In these long-term fertilization systems, the C_{SR} of SOC, POC and LFOC was $-0.21\sim 1.29 \text{ Mg ha}^{-1} \text{ y}^{-1}$, $-0.02\sim 0.24 \text{ Mg ha}^{-1} \text{ y}^{-1}$, and $0.06\sim 0.34 \text{ Mg ha}^{-1} \text{ y}^{-1}$, respectively. This implied that different fertilization strategies can affect the pool of SOC with different sequestration

rates. We found higher carbon sequestration efficiency in the N2P2 and N3P3 treatments. This is consistent with Li et al. [13], who reported that control and mineral fertilization treatments had more efficient C sequestration from added C inputs. In addition, we showed a logarithmic relationship between the SOC/LFOC sequestration rate and the annual C input and calculated that if the annual C input were approximately $1.4 \text{ Mg ha}^{-1} \text{ y}^{-1}$, the SOC content would be maintained. If the annual C input were higher than $0.8 \text{ Mg ha}^{-1} \text{ y}^{-1}$, the LFOC content would increase. Zhang et al. [2] and Cai et al. [49] established the relationship between exogenous carbon input and soil carbon stocks in paddy fields. Cai et al. [40] also used the initial soil organic carbon storage to correct the relationship between exogenous carbon input and soil organic carbon storage, and reduced the error of soil organic carbon stocks predicted by exogenous carbon input. However, because of different soil types, climate, etc., more research needs to be carried out in other long-term fertilizer experiments, which then could help quantitatively predict the exogenous carbon input required for soil organic matter enhancement.

5. Conclusions

This study clearly indicated that 24-year applications of chemical fertilizer or manure significantly altered the dynamics of SOC, POC and LFOC. SOC content decreased over time under no fertilization by $0.17 \text{ g kg}^{-1} \text{ y}^{-1}$, decreased under NP fertilization by $0.18\text{--}0.21 \text{ g kg}^{-1} \text{ y}^{-1}$, increased under NPM fertilization by $0.02\text{--}0.09 \text{ g kg}^{-1} \text{ y}^{-1}$ and increased under M fertilization by $0.36 \text{ g kg}^{-1} \text{ y}^{-1}$. We found that a moderate amount of chemical fertilization (N2P2, N3P3), NPM fertilization and manure could promote SOC sequestration over that in the control, with a sequestration rates of $0.19\text{--}1.29 \text{ Mg ha}^{-1} \text{ y}^{-1}$. Excess chemical fertilizer caused a reduction in POC, whereas the application of NPM and manure resulted in higher POC sequestration in soil at rates of $0.04\text{--}0.24 \text{ Mg ha}^{-1} \text{ y}^{-1}$. The LFOC increased by $1.45\text{--}8.12 \text{ Mg ha}^{-1}$ ($0.06\text{--}0.34 \text{ Mg ha}^{-1} \text{ y}^{-1}$) under long-term fertilization. We explored the logarithmic relationship between the SOC/LFOC sequestration rate and the annual C input and calculated that when the annual C input is approximately $1.4 \text{ Mg ha}^{-1} \text{ y}^{-1}$, the SOC content will be maintained. When the annual C input is higher than $0.8 \text{ Mg ha}^{-1} \text{ y}^{-1}$, the LFOC content will increase. Thus, from the present study, we can conclude that the application of NPM fertilizer or manure increases the potential for SOC sequestration in a corn cropping system of northern China.

Author Contributions: Y.X. and M.C. conceived and designed the study. M.C. and F.D. wrote and edited the manuscript. Y.W. and Y.X. performed the experiments and analyzed the data. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by the National Natural Sciences Foundation of China (41807072, 41807025), Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi (2020L0037, 2020L0160), Foundation of the youth science and technology research in Shanxi province (201901D211131); the demonstration project of safe use technology of cultivated land from Shanxi Agricultural Ecological Environment Construction Station (QTZB-2021-F035) and the project of scientific and technological innovation of Shanxi Agricultural University(2020BQ16).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained in the article.

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

References

1. Lal, R. Soil carbon sequestration to mitigate climate change. *Geoderma* **2004**, *123*, 1–22. [\[CrossRef\]](#)
2. Zhang, W.J.; Liu, K.I.; Wang, J.Z.; Shao, X.F.; Xu, M.G.; Li, J.W.; Wang, X.J.; Murphy, D.V. Relative contribution of maize and external manure amendment to soil carbon sequestration in a long-term intensive maize cropping system. *Sci. Rep.* **2015**, *5*, 10791. [\[CrossRef\]](#) [\[PubMed\]](#)

3. Xu, M.G.; Liang, G.Q.; Zhang, F.D. *The Evolution of Soil Fertility in China*; Agricultural Science and Technology Press: Beijing, China, 2006.
4. Yang, Z.C.; Zhao, N.; Huang, F.; Lv, Y.Z. Long-term effects of different organic and inorganic fertilizer treatments on soil organic carbon sequestration and crop yields on the North China Plain. *Soil Till. Res.* **2015**, *146*, 47–52. [\[CrossRef\]](#)
5. Young, L.M. Carbon sequestration in agriculture: The U.S. policy in context. *Am. J. Agric. Econ.* **2003**, *85*, 1164–1170. [\[CrossRef\]](#)
6. Smith, P.; Martino, D.; Cai, Z.; Gwary, D.; Janzen, H.; Kumar, P.; McCarl, B.; Ogle, S.; O'Mara, F.; Rice, C.; et al. Greenhouse gas mitigation in agriculture. *Philos. T. R. Soc. B.* **2008**, *363*, 789–813. [\[CrossRef\]](#)
7. Bhattacharyya, R.; Kundu, S.; Srivastva, A.K.; Gupta, H.S.; Prakash, V.; Bhatt, J.G. Long term fertilization effects on soil organic carbon pools in a sandy loam soil of Indian sub-Himalayas. *Plant Soil* **2011**, *341*, 109–124. [\[CrossRef\]](#)
8. Dou, X.; He, P.; Zhu, P.; Zhou, W. Soil organic carbon dynamics under long-term fertilization in a black soil of China: Evidence from stable C isotopes. *Sci. Rep.* **2016**, *6*, 21488. [\[CrossRef\]](#)
9. Purakayastha, T.J.; Rudrappa, L.; Singh, D.; Swarup, A.; Bhadraray, S. Long-term impact of fertilizers on soil organic carbon pools and sequestration rates in maize-wheat-cowpea cropping system. *Geoderma* **2008**, *144*, 370–378. [\[CrossRef\]](#)
10. Urkurkar, I.S.; Tiwari, A.; Chitale, S.; Bajpai, R.K. Influence of long-term use of inorganic and organic manures on soil fertility and sustainable productivity of rice (*Oryza sativa*) and wheat (*Triticum aestivum*) in Inceptisols. *Indian J. Agric. Sci.* **2010**, *80*, 208–212.
11. Dong, W.Y.; Zhang, X.Y.; Wang, H.M.; Dai, X.Q.; Sun, X.M.; Qiu, W.W.; Yang, F.T. Effect of different fertilizer application on the soil fertility of paddy soils in red soil region of Southern China. *PLoS ONE* **2012**, *7*, 1–9. [\[CrossRef\]](#)
12. Cheng, M.; An, S.S. Responses of soil nitrogen, phosphorous and organic matter to vegetation succession on the Loess Plateau of China. *J. Arid Land* **2015**, *7*, 216–223. [\[CrossRef\]](#)
13. Li, J.; Wen, Y.C.; Li, X.H.; Li, Y.T.; Yang, X.D.; Lin, Z.; Song, Z.Z.; Cooper, J.M.; Zhao, B.Q. Soil labile organic carbon fraction and soil organic carbon stocks as affected by long-term organic and mineral fertilization regimes in the North China. *Soil Till. Res.* **2018**, *175*, 281–290. [\[CrossRef\]](#)
14. Conrad, K.A.; Dalal, R.C.; Allen, D.C.; Fujinuma, R.; Menzies, N.W. A free light fraction carbon and nitrogen, a physically uncomplexed soil organic matter distribution within subtropical grass. *Soil Res.* **2018**, *56*, 820–828. [\[CrossRef\]](#)
15. Sequeira, C.H.; Alley, M.M.; Jones, B.P. Evaluation of potentially labile soil organic carbon and nitrogen fractionation procedures. *Soil Biol. Biochem.* **2011**, *43*, 438–444. [\[CrossRef\]](#)
16. Lavalley, J.M.; Soong, J.L.; Cotrufo, M.F. Conceptualizing soil organic matter into particulate and mineral-associated forms to address global change in the 21st century. *Global Change Biol.* **2020**, *26*, 261–273. [\[CrossRef\]](#)
17. Haynes, R.J. Labile organic matter fractions as central components of the quality of agricultural soils: An overview. *Adv. Agron.* **2005**, *85*, 221–268.
18. Gosling, P.; Parsons, N.; Bending, G.D. What are the primary factors controlling the light fraction and particulate soil organic matter content of agricultural soils? *Biol. Fert. Soils* **2013**, *49*, 1001–1014. [\[CrossRef\]](#)
19. Yang, X.Y.; Ren, W.D.; Sun, B.H.; Zhang, S.L. Effects of contrasting soil management regimes on total and labile soil organic carbon fractions in a loess soil in China. *Geoderma* **2012**, *177*, 49–56. [\[CrossRef\]](#)
20. Soil Survey Staff. *Key to Soil Taxonomy*, 11th ed.; U.S. Department of Agriculture: Washington, DC, USA, 2010.
21. Veihmeyer, F.J.; Hendrickson, A.H. Soil density and root penetration. *Soil Sci.* **1948**, *65*, 487–493. [\[CrossRef\]](#)
22. Bao, S.D. *Soil Agrochemical Analysis*; China Agricultural Press: Beijing, China, 2000; pp. 176–185.
23. Walkley, A.J.; Black, I.A. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Sci.* **1934**, *37*, 29–38. [\[CrossRef\]](#)
24. Qlsen, S.R.; Cole, C.; Watanabe, F.S.; Dean, L.A. *Estimation of Available Phosphorus in Soils by Extraction with Sodium Bicarbonate*; US Department of Agriculture: Washington, DC, USA, 1954.
25. Cambardella, A.A.; Elliott, E.T. Particulate soil organic matter changes across a grassland cultivation sequence. *Soil Sci. Soc. Am. J.* **1992**, *56*, 777–783. [\[CrossRef\]](#)
26. Janzen, H.H.; Campbell, C.A.; Brandt, S.A.; Lafond, G.P.; Townley-Smith, L. Light-fraction organic matter in soils from long-term crop rotation. *Soil Sci. Soc. Am. J.* **1992**, *56*, 1799–1806. [\[CrossRef\]](#)
27. Li, C.; Frolking, S.; Harriss, R. Modeling carbon biogeochemistry in agricultural soils. *Glob. Biogeochem. Cycles* **1994**, *8*, 237–254. [\[CrossRef\]](#)
28. Jiang, G.; Xu, M.; He, X.; Zhang, W.; Huang, S.; Yang, X.; Liu, H.; Peng, C.; Shirato, Y.; Iizumi, T.; et al. Soil organic carbon sequestration in upland soils of northern China under variable fertilizer management and climate change scenarios. *Glob. Biogeochem. Cycles* **2014**, *28*, 319–333. [\[CrossRef\]](#)
29. Gregorich, E.G.; Beare, M.H.; McKim, U.F.; Skjemstad, J.O. Chemical and biological characteristics of physically uncomplexed organic matter. *Soil Sci. Soc. Am. J.* **2006**, *70*, 975–985. [\[CrossRef\]](#)
30. Wander, M.M.; Yun, W.; Goldstein, W.A.; Aref, S.; Khan, S.A. Organic N and particulate organic matter fractions in organic and conventional farming systems with a history of manure application. *Plant Soil* **2007**, *291*, 311–321. [\[CrossRef\]](#)
31. Kuzyakov, Y.; Friedel, J.K.; Stahr, K. Review of mechanisms and quantification of priming effects. *Soil Biol. Biochem.* **2000**, *32*, 1485–1498. [\[CrossRef\]](#)
32. Li, P.Z.; Lin, X.X. Characteristics of organic materials decomposition in infertile red soils. *Acta Ecol. Sin.* **2002**, *22*, 1224–1230.
33. Schimel, J.P.; Weintraub, M.N. The implications of exoenzyme activity on microbial carbon and nitrogen limitation in soil: A theoretical model. *Soil Biol. Biochem.* **2003**, *35*, 549–563. [\[CrossRef\]](#)

34. Malthi, S.S.; Lemke, R.; Wang, Z.H.; Chhabra, B.S. Tillage, nitrogen and crop residue effects on crop yield, Onutrient uptake, soil quality, and greenhouse gas emissions. *Soil Till. Res.* **2006**, *90*, 171–183. [\[CrossRef\]](#)
35. Rudrappa, L.; Purakayasha, T.J.; Singh, D.; Bhadraray, S. Long-term manuring and fertilization effects on soil organic carbon pools in a Typic Haplustepts of semi-arid subtropical India. *Soil Till. Res.* **2006**, *88*, 180–192. [\[CrossRef\]](#)
36. Ghosh, A.; Bhattacharyya, R.; Meena, M.C.; Dwivedi, B.S.; Singh, G.; Agnihotri, R.; Sharma, C. Long-term fertilization effects on soil organic carbon sequestration in an Inceptisol. *Soil Till. Res.* **2018**, *177*, 134–144. [\[CrossRef\]](#)
37. Silver, W.L.; Miya, R.K. Global patterns in root decomposition: Comparisons of climate and litter quality effects. *Oecologia* **2001**, *3*, 407–419. [\[CrossRef\]](#) [\[PubMed\]](#)
38. Yan, D.; Wang, D.; Yang, L. Long-term effect of chemical fertilizer, straw, and manure on labile organic matter fractions in a paddy soil. *Biol. Fert. Soils* **2007**, *44*, 93–101. [\[CrossRef\]](#)
39. Whalen, J.K.; Hu, Q.; Liu, A. Compost applications increase water-stable aggregates in conventional and no-tillage systems. *Soil Sci. Soc. Am. J.* **2003**, *67*, 1842–1847. [\[CrossRef\]](#)
40. Mao, J.; Dan, C.O.; Fang, X.W.; He, Z.; Schmidt-Rohr, K. Influence of animal manure application on the chemical structures of soil organic matter as investigated by advanced solid-state NMR and FT-IR spectroscopy. *Geoderma* **2008**, *146*, 353–362. [\[CrossRef\]](#)
41. Duan, Y.H.; Yang, H.B.; Shi, T.H.; Zhang, W.J.; Xu, M.G.; Gao, S.D. Long-term manure application to improve soil macroaggregates and plant-available nitrogen in a Mollisol. *Soil Till. Res.* **2021**, *211*, 105035. [\[CrossRef\]](#)
42. Bhattacharyya, R.; Tuti, M.D.; Bisht, J.K.; Bhatt, J.C.; Gupta, H.S. Conservation tillage and fertilization impacts on soil aggregation and carbon pools in the Indian Himalayas under an irrigated rice-wheat rotation. *Soil Sci.* **2012**, *177*, 218–228. [\[CrossRef\]](#)
43. Puget, P.; Drinkwater, L.E. Short-term dynamics of root- and shoot-derived carbon from a leguminous green manure. *Soil Sci. Soc. Am. J.* **2001**, *65*, 771–779. [\[CrossRef\]](#)
44. Tuo, D.F.; Xu, M.X.; Li, Q.; Liu, S.H. Soil aggregate stability and associated structure affected by long-term fertilization for affected by long-term fertilization for a loessia soil on the Loess Plateau of China. *Pol. J. Environ. Stud.* **2017**, *26*, 827–835. [\[CrossRef\]](#)
45. Gregorich, E.G.; Ellert, B.H.; Carter, M.R.; Monreal, C.M. Towards a minimum data set to assess soil organic matter quality in agricultural soils. *Can. J. Soil Sci.* **1994**, *74*, 367–385. [\[CrossRef\]](#)
46. Zhang, Z.M.; Yan, J.; Han, X.Z.; Zou, W.X.; Chen, X.; Lu, X.C.; Feng, Y.T. Labile organic carbon fractions drive soil microbial communities after long-term fertilization. *Glob. Ecol. Conserv.* **2021**, *32*, e01867. [\[CrossRef\]](#)
47. Tong, X.G.; Xu, M.G.; Wang, X.J.; Zhang, W.J.; Cong, R.H. Long-term fertilization effects on organic carbon fractions in a red soil of China. *Catena* **2010**, *113*, 251–259. [\[CrossRef\]](#)
48. Blair, N.; Faulkner, R.D.; Till, A.R.; Korschens, M.; Schulz, E. Long-term management impacts on soil C, N and physical fertility: Part II: Bad Lauchstadt static and extreme FYM experiments. *Soil Till. Res.* **2006**, *91*, 39–47. [\[CrossRef\]](#)
49. Cai, A.D.; Xu, M.G.; Zhang, W.J.; Wang, B.R.; Cai, Z.J. Establishing and verification of the relationship between soil organic carbon storage and exogenous carbon input. *J. Plant Nutr. Fertil.* **2020**, *26*, 934–941.