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Effects of Two Types of Straw Biochar on the Mineralization of Soil Organic Carbon in Farmland

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Abstract: To investigate the effects of biochar on soil carbon composition and transformation, the effects of 1%, 2%, and 5% mass ratios of banana and cassava straw biochar on carbon dioxide release, total organic carbon (TOC), soluble organic carbon (SOC), and enzyme activity in soil were studied in incubation experiments at a constant temperature in the laboratory. The results showed that the cumulative CO₂ emissions from cassava straw were 15.82 (1% addition ratio) and 28.14 µg·kg⁻¹ (2%), which were lower than those from banana straw, i.e., 46.77 (1%) and 59.26 µg·kg⁻¹ (2%). After culture, the total organic carbon contents of cassava straw were 8.55 (5%), 5.27 (2%), and 3.98 µg·kg⁻¹ (1%), which were higher than those of banana straw, i.e., 6.31 (5%), 4.23 (2%), and 3.16 µg·kg⁻¹ (1%). The organic carbon mineralization rate in each treatment showed a trend of increasing first, then decreasing, and finally stabilizing. There was a very significant positive correlation between catalase and urease activity in soil with cassava straw biochar and between catalase activity and SOC mineralization with banana straw biochar. It plays an important role in the transformation and decomposition of organic carbon. These results show that the application of biomass carbon can significantly improve the organic carbon content and enzyme activity of farmland soil, increase the cumulative mineralization amount and mineralization rate of SOC, and thus increase the carbon sequestration capacity of soil.

Keywords: biochar; soil enzymes; organic carbon; straw; mineralization; first-order kinetic equation

1. Introduction

The link between the sharp change in global climate and the gradual increase in greenhouse gases, which is mainly manifested by global warming, is clear at a glance. The Paris Agreement signed by 195 countries in 2016 set the global temperature increase within 2 degrees Celsius as its main target and strives to limit the increase to 1.5 degrees Celsius [1]. China is a traditional agricultural country, and its farmland soil is an important source of greenhouse gas emissions. Due to the influence of human activities, its annual total greenhouse gas (GHG) emissions have reached 5.1~6.1 Pg CO₂-eq

(CO₂ equivalent) (1 Pg = 10¹⁵ g), accounting for 10~12% of the total global greenhouse gas emissions. Therefore, reducing greenhouse gases in farmland soil is of great significance to mitigate global temperature rise [2].

The organic matter content and basic fertility of most soils in China are relatively low, and straw returning to the field is a common soil fertilization method in the early stage of rural China [3]. China is a country rich in straw resources [4]. Straw, as an agricultural residue, is rich in nutrients. However, in agricultural systems, the direct application of straw to the soil will increase the content of soil organic carbon, promote microbial decomposition and produce greenhouse gases such as CO₂, CH₄, N₂O, etc. [5], resulting in the loss of soil nutrients and serious greenhouse effects. To improve the utilization efficiency of straw, crop straw can be converted into biochar. It has been reported that straw biochar can significantly increase the content of soil organic matter and maintain soil quality [6], and the application of straw-derived biochar was reported to enhance carbon sequestration in paddy soils [7]. Soil organic carbon mineralization is an important carbon source for CO₂ emissions, and organic carbon fixation is of great significance to the CO₂ sink [8]. SOC not only provides mineral nutrients for plant growth, but also provides energy for microbial degradation of organic matter. Some studies have shown that biochar can interact with the original soil organic matter after application to the soil, changing the mineralization rate of soil organic matter and thus affecting the release of CO₂ [9]. Biochar with a developed pore structure and large specific surface area can adsorb and encapsulate soil organic matter to reduce the mineralization of organic matter and carbon emissions [10], and the adsorption of CO₂ by biochar will also reduce carbon flux with the atmosphere [11]. This shows that biochar, as a carbon sequestration and emission reduction material, has the potential to be applied to soil over a long period.

Biochar, a carbon-rich solid with a molecular structure that consists of a high number of aromatic rings and porous characteristics, remains carbonized after biomass pyrolysis under anaerobic conditions [12]. Carbon-rich solids have higher thermal stability and stronger adsorption performance than common organic materials. Biochar is considered a soil remediation material to improve soil structure, maintain soil moisture, sequester carbon, and reduce GHG emissions [13,14]. Some studies have shown that the application of biochar to soil improves soil quality, thus increasing crop yield [15]. The carbon sequestration capacity of biochar prepared from *Miscanthus* modified by potassium acetate was 45% higher than that of untreated control [16]. Compared with the non-application of biochar, the application of biochar resulted in an average increase of 15% and 16% in soil CH₄ and CO₂ emissions, and an average decrease of 38% in N₂O emissions [17]. The physical and chemical properties of biochar determine the changes in soil properties. Some experimental results show that the yield and characteristics of biochar mainly depend on its pyrolysis temperature and raw materials [18,19].

Phosphorus is important for plant metabolic substances such as nucleotides, nucleic acids, and enzymes, as well as for energy transfer. In the soil, phosphorus is a rather immobile element, which bonds with common soil constituents such as calcium (Ca), aluminium (Al), and iron (Fe) [20]. The utilization of phosphorus is an important mechanism in organic carbon mineralization. The addition of phosphorus will improve soil fertility and enzyme activity, thus promoting carbon mineralization. In highly weathered and humid tropical regions, phosphorus is the most important limiting factor for microbial activity. Some studies have found that phosphorus has a direct impact on microbial activities, and the addition of phosphorus increases the number of microbial communities [21]. Studies have shown that if the carbon source is effective, the initial rate of microbial respiration will be significantly limited by phosphorus [22]. Soil enzymes play a key role in the process of soil biochemical reactions, affecting the decomposition and cycling of soil nutrients and soil carbon [23,24]. The effect of biochar addition on soil enzyme activity is affected by many factors, including different types of biochar, the interaction between enzymes and biochar, and the soil environment [24,25]. A large number of studies that examined the effect of biochar on soil enzyme activity showed that biochar pH, specific surface area, pyrolysis conditions, soil pH, temperature, and microorganisms could significantly change

the soil enzyme activity [26–28]. There are few reports on the effects of banana straw and cassava straw biochar on soil enzyme activity and C mineralization.

Therefore, the specific purposes of this study are (1) to analyze whether the application of biochar affects soil organic carbon, soil enzyme activity, and soil phosphorus and (2) to explore the mechanism through which biochar produced from banana and cassava straw affects soil carbon mineralization.

2. Materials and Methods

2.1. Soil and Biochar

In April 2019, the serpentine five-point method was used to collect 0–20 cm soil from farmland corn fields in Liuzhou City, Guangxi Zhuang Autonomous Region, China. The organic matter content and basic fertility of the soil are both low. The area belongs to a mid-subtropical monsoon climate with warm and humid conditions throughout the year, an average annual temperature of 17.8 °C, and annual precipitation of 189.9 mm. During soil collection, material on the soil surface was removed first, and then the collected soil was evenly mixed and transported to the laboratory in snakeskin bags for natural air drying. In the process of air drying, plant foliage, root systems, stones, etc., in the soil were removed, and the soil was broken into small clods of approximately 1 cm along the fissures. After the soil samples were air dried and mixed evenly, they were ground through a 60-mesh stainless steel sieve and bagged, and the basic characteristics of the soil were analyzed. As shown in Table 1, the test soil was acidic.

Table 1. Basic physical and chemical properties of soil.

pH	Ec (us·cm ^{−1})	Olsen-P (mg·kg ^{−1})	TOC (g·kg ^{−1})	CEC (cmol·kg ^{−1})
5.56 ± 0.01	40.50 ± 3.17	8.71 ± 0.16	5.31 ± 0.01	38.46 ± 0.25

Using banana straw and cassava straw as raw materials, biochar was prepared by slow pyrolysis in a box-type resistance furnace (model: 4–10 company: Shanghai Dongxing Building Materials Test Equipment Co., Ltd. No.689 Qishen Road, Minhang District, Shanghai) under the condition of 500 °C, 2 h, and oxygen restriction.

Banana straw and cassava straw were obtained from Wulidian Flower and Bird Market in Guilin City, Guangxi. They were naturally dried for two weeks, further dried at 70 °C, and crushed by a crusher through a 60-mesh screen.

2.2. Experimental Design

The experimental design included seven treatments: soil only, soil + 1% banana biochar, soil + 2% banana biochar, soil + 5% banana biochar, soil + 1% cassava biochar, soil + 2% cassava biochar, and soil + 5% cassava biochar, referred to as CK, 1% BSB, 2% BSB, 1% CSB, 2% CSB, and 5% CSB, respectively. All treatments were performed in triplicate.

Test Scheme: A total of 500 g of soil was placed in a 1 L white polyethylene bottle and biochar was added according to the different treatments, i.e., soil only, soil + 1% banana biochar, soil + 2% banana biochar, soil + 5% banana biochar, soil + 1% cassava biochar, soil + 2% cassava biochar, and soil + 5% cassava biochar. After the soil and biochar were mixed evenly, deionized water was added to maintain the field water holding capacity at 40–60%, and water was added by the weighing method. The soil samples were placed in a constant temperature incubator at 25 °C, and the culture period was set at 35 days. Samples were taken and analyzed on the 7th, 14th, 21st, 28th, and 35th days. Another batch of soil samples with the same conditions was set up, with a soil weight of 50 g. A 10 mL beaker filled with a certain concentration of sodium hydroxide solution (0.1 mol·L^{−1}) was placed in a white polyethylene bottle, and carbon dioxide emissions were analyzed on days 1, 3, 5, 7, 10, 15, 20, 25, and 30.

2.3. Soil Chemical Properties and Enzyme Activity Assays and Biochar Characterization by FTIR

Total organic carbon (TOC) in the soil was determined by potassium dichromate oxidation spectrophotometry [29]. The pH [30] value was determined by a pH meter at a ratio of soil to water of 1:2.5. Soil was extracted by deionized water, and soluble organic carbon (DOC) [31] was determined by a TOC analyzer after centrifugation. Available phosphorus was determined by NaHCO_3 extraction-molybdenum antimony colorimetry [29]. Catalase activity [32] was determined by potassium permanganate titration. Its calculation formula is as follows:

$$\text{Catalase activity (mLK MnO}_4\text{/gdrysoil)} = V/dwt \quad (1)$$

Urease activity [32] was determined by indophenol blue colorimetry and was expressed as the amount of urea converted into $\text{NH}_3\text{-N}$ per gram of soil per hour. Its calculation formula is as follows:

$$\text{Urease activity [mgNH}_4^+ - \text{N/(100gdrysoil}\cdot\text{3h)}] = (C \times V \times 10) \times 10/dwt \quad (2)$$

Each treatment was repeated three times, and no substrate (urea) and no soil treatment controls were set up. Soil CO_2 emissions were measured by the alkali absorption method. The KBr tableting method was used to characterize the samples by FTIR. FTIR adsorption spectra were recorded from wavelengths 4000 to 400 cm^{-1} , and the resolution was 0.09 cm^{-1} (Bruker Tensor 27, Ettlingen, Germany). A small amount of biochar samples passed through the 100-mesh sieve were mixed with KBr for FTIR analysis.

2.4. Calculation Method

The formula [33] for CO_2 emissions is as follows:

$$\text{CO}_2(\text{mL}\cdot\text{kg}^{-1}) = \{[(V_0 - V) \times c \times 0.022 \times (22.4/44) \times 1000] \times 2 \times 1000\}/m \quad (3)$$

where V_0 is the volume of standard hydrochloric acid consumed during blank titration, V is the volume of standard hydrochloric acid consumed during sample titration, c is the concentration of standard hydrochloric acid, 0.022 is the molar mass of carbon dioxide ($1/2\text{ CO}_2$), $M(1/2\text{ CO}_2) = 0.022\text{ g/mmol}$, and 22.4/44 is the number of milliliters per gram of CO_2 under standard conditions.

CO_2 release rate ($\text{mg/kg}\cdot\text{d}^{-1}$) = amount of organic carbon mineralized/ Δt ; Δt is the culture interval (d).

Cumulative soil CO_2 emissions were calculated as the total CO_2 emissions from the first day of culture to the day of measurement.

The first-order kinetic equation was applied to fit soil carbon mineralization under different culture conditions:

$$C_t = C_0(1 - e^{-kt}) \quad (4)$$

In the formula, C_t is the cumulative mineralization amount at culture time t (d), C_0 is the potential soil carbon mineralization ($\text{mg}\cdot\text{kg}^{-1}$); k is the rate constant of soil carbon mineralization, d^{-1} , and t is the culture time, d.

2.5. Statistical Analyses

The average value and standard deviation were calculated using the standard method in Excel 2016. One-way ANOVA was used to study the effects of biochar treatment on soil organic carbon, available phosphorus, and enzyme activities. The Duncan multiple-range test was used for post-test. All statistical tests were carried out using SPSS 24.0, and the mapping was completed using Origin 9.1 mapping software.

3. Results

3.1. FTIR of Biochar

The functional groups of straw biochar were characterized by infrared spectroscopy. As shown in Figure 1, the two samples had similar functional group structures. Due to the stretching of aliphatic C-H and O-H, their strength decreased, and aromatic C-H formed bands. After pyrolysis, aliphatic O-H peaks disappeared due to dehydration, decomposition, and conversion of functional groups. The peak value of the aromatic C=C skeleton vibration of the CSB sample biochar was more obvious than that of the BSB sample.

Figure 1. FTIR Spectra of BSB and CSB.

3.2. Soil Total Organic C, pH, Available P, Dissolved Organic C

The addition of banana biochar and cassava biochar significantly increased the pH value of the soil (Table 2), and the pH value increased with the increase in the proportion of biochar. The pH value in response to 1% banana biochar decreased first and then increased with culture time, and the pH value increased by 2.28 units compared with that of CK. The pH value in response to 2% banana biochar increased with culture time and was 4.13 units higher than that of CK. The pH value in response to banana biochar added at 5% increased with culture time and was 5.05 units higher than that of CK. The pH value in response to cassava biochar increased by 1.01 units (1%), by 1.78 units (2%), and by 2.35 units (5%) compared with CK. The pH value of cassava biochar first increased and then decreased. The change in pH in response to banana straw biochar was higher than that in response to cassava straw biochar.

Table 2. Effect of biochar on soil pH.

	7	14	21	28	35
CK	5.61 ± 0.11D	5.52 ± 0.18D	5.65 ± 0.16D	5.32 ± 0.39D	5.01 ± 0.07D
1%BSB	7.20 ± 0.05C	6.22 ± 0.14C	6.71 ± 0.08C	7.61 ± 0.09C	7.29 ± 0.14C
2%BSB	8.46 ± 0.05B	6.87 ± 0.18B	8.48 ± 0.30B	9.06 ± 0.04B	9.14 ± 0.12B
5%BSB	9.85 ± 0.03A	8.13 ± 0.17A	10.11 ± 0.02A	10.17 ± 0.01A	10.06 ± 0.01A
1%CSB	6.34 ± 0.05C	7.26 ± 0.11C	6.50 ± 0.48B	6.16 ± 0.15C	6.02 ± 0.03B
2%CSB	6.86 ± 0.02B	8.36 ± 0.27B	6.21 ± 0.67B	6.89 ± 0.74B	6.79 ± 0.41A
5%CSB	8.15 ± 0.14A	9.44 ± 0.02A	7.64 ± 0.10A	7.59 ± 0.28A	7.36 ± 0.63A

Note: The mean value ± standard deviation of soil pH in different time ($n = 3$), the same letter indicates that the effect of biochar addition on soil is not significant ($\alpha = 0.05$).

During the whole culture process, the available phosphorus content in the soil treated with different proportions of the two types of straw biochar increased with the increase in the proportion of biochar (Figure 2), and the available phosphorus content was the highest on the 35th day. From the first week to the end of the culture period, the available phosphorus content in the 1% BSB, 2% BSB, and 5% BSB treatments increased by 40.75~58.07%, 111.22~146.83%, and 346.30~483.31%, respectively, compared with CK ($p < 0.05$). In the third week, the increase in the available phosphorus content in the 1% BSB, 2% BSB, and 5% BSB treatments was 58.07%, 146.83%, and 440.98%, respectively. On the 35th day of culture, the increase in available phosphorus in the soil to which banana straw biochar was added was 52.42% (1%), 120.53% (2%), and 346.30% (5%), which indicated that the promotion effect of banana straw biochar on the available phosphorus content decreased slowly but changed slightly, and the available phosphorus content could be increased to a large extent as well as continuously. Compared with other treatments, the available phosphorus content in the soil treated with 5% CSB fluctuated greatly, indicating that the addition of a high proportion of biochar was beneficial for the accumulation and transport of available phosphorus in the soil. Compared with the control, the available phosphorus content in the soil treated with 1% CSB, 2% CSB, and 5% CSB significantly increased by 94.30%, 180.16%, and 528.13%, respectively. The increase in the soil available phosphorus content ranked as follows: 5% BSB > 2% BSB > 1% BSB, 5% CSB > 2% CSB > 1% CSB. The cassava straw biochar had a greater ability than the banana straw biochar to improve the available phosphorus content.

Figure 2. Cont.

Figure 2. Content of available phosphorus and total organic carbon and soluble organic carbon in soil after application of two kinds of straw biochar: (a) banana biochar application and (b) cassava biochar application. Duncan multiple-range test shows that there is significant difference between different letters at the same time ($p = 0.05$).

With respect to total soil organic carbon, the total soil organic carbon content under different biochar ratios increased to different degrees during the culture period, i.e., 5% BSB > 2% BSB > 1% BSB > CK, 5% CSB > 2% CSB > 1% CSB > CK. The total soil organic carbon content of the CSB biochar treatment was higher than that of the BSB treatment. Compared with CK, the total soil organic carbon content of the BSB treatment increased by 32.94~57.99% (1%), 71.42~93.15% (2%), and 170.98~220.09% (5%) ($p < 0.05$). The increase range of 5% BSB was the largest, which indicated that the effect of increasing total organic carbon was greater with a higher proportion of biochar, and each biochar treatment had a stable promotion effect on the total organic carbon content. The total organic carbon content of soil treated with CSB reached the maximum value in the second week of culture; the values in CK, 1% CSB, 2% CSB, and 5% CSB were 2.31, 4.10, 5.54, and 9.03 $\text{g}\cdot\text{kg}^{-1}$, respectively. In the third week of culture, the total organic carbon of soil treated with biochar gradually increased to a stable level with the advancement of time, and the ranges were 61.13~77.55%, 114.79~139.91%, and 209.58~300.16%. The difference between low, medium, and high concentrations was extremely significant. Based on the change trend of the total organic carbon content after biochar addition, the promotion effect of the two types of biochar was cassava straw biochar > banana straw biochar.

As shown in Figure 2, the soil soluble organic carbon showed an opposite trend in response to banana and cassava straw biochar application. In response to banana straw biochar, the content of soil soluble organic carbon decreased first and then increased with an increase in the application ratio, and the soluble organic carbon content was the lowest when 2% BSB was applied. In response to cassava straw biochar, the soil soluble organic carbon content decreased significantly with an increasing application ratio, and the content was the lowest when 5% CSB was applied. Compared with CK, the soluble organic carbon content of 5% BSB increased 1.69 times in the fifth week of culture, from 34.61 $\text{mg}\cdot\text{kg}^{-1}$ to 58.45 $\text{mg}\cdot\text{kg}^{-1}$, and the soluble organic carbon content of 5% CSB decreased 2.28 times, from 34.61 $\text{mg}\cdot\text{kg}^{-1}$ to 15.16 $\text{mg}\cdot\text{kg}^{-1}$. During the culture period, the DOC content in the soil treated with 5% BSB was significantly higher than that of the control and showed a significant upward trend, with an increase range of 14.93~68.92%. During the culture period, the DOC content in the 1% BSB and 2% BSB treatments began to decline after seven days, reaching a low value on day 14, and then increased to a high value on 28 days and 21 days, respectively. The DOC content of the medium and low concentration treatments was significantly lower than that of the control, and the effect of the medium concentration treatment was the greatest. With respect to cassava straw biochar, the DOC

content of the 1% CSB, 2% CSB, and 5% CSB treatments fluctuated greatly. Although the DOC content of the 1% CSB treatment was 4.06% higher than that of the CK treatment on the 35th day, on the whole, compared with that of the control treatment, the DOC content of the 1% CSB, 2% CSB, and 5% CSB treatments decreased by 6.66~29.68%, 7.28~52.55%, and 53.45~83.71%, respectively, i.e., the higher the biochar concentration, the lower the DOC content. The response rate of soil to banana straw and cassava straw biochar was very fast, and the soil DOC content decreased greatly in response to the two types of biochar. The degree of decrease of the soil DOC content was 2% BSB > 1% BSB > 5% BSB, 5% CSB > 2% CSB > 1% CSB. The effect of the two types of biochar on the soluble organic carbon content was cassava straw biochar > banana straw biochar.

3.3. Soil Enzyme Activity

As shown in Figure 3, the soil catalase activity was the highest in response to the 5% straw biochar treatments, followed by the 2% treatments, the 1% treatments, and the CK treatment. There were significant differences among the different BSB treatments in different periods. The catalase activity of the 5% BSB biochar treatment was the highest in the third week of culture, $40.17 \text{ mL} \cdot \text{g}^{-1}$, and the catalase activity of the 2% BSB biochar treatment was the highest in the fifth week of culture, $43.73 \text{ mL} \cdot \text{g}^{-1}$. CK, 1% CSB, 2% CSB, and 5% CSB showed significant differences at different stages. The catalase activity in the 5% CSB and 2% CSB treatments reached the highest level in the third week of culture, $33.30 \text{ mL} \cdot \text{g}^{-1}$ and $27.67 \text{ mL} \cdot \text{g}^{-1}$, respectively. Throughout the whole culture period, the trend of the catalase activity in different treatments was similar.

Figure 3. Content of soil catalase and urease after application of two kinds of straw biochar; BSB is banana biochar and CSB is cassava biochar. Duncan multiple-range test shows that there is significant difference between different letters at the same time ($p = 0.05$).

As shown in Figure 3, the soil urease activity in the different straw biochar treatments was obviously different. The urease activity ranked as 2% BSB > 1% BSB > CK > 5% BSB with respect to the banana straw biochar, compared with 5% CSB > 2% CSB $\approx$ 1% CSB $\approx$ CK with respect to the cassava straw biochar treatment. There was a significant difference in the urease content among the different proportions of banana straw biochar in the first week of culture. In the third week of culture, there was no significant difference in the urease content between the 5% BSB treatment and the CK treatment. Urease activity in the 2% BSB and 1% BSB treatments was significantly higher than that in the CK treatment, i.e., by 134.99% and 108.47%, respectively. In the fourth week of culture, there was no significant difference in the soil urease content between the 1% BSB and 2% BSB treatments. The urease activity in the 2% BSB and 1% BSB treatments was significantly higher than that in CK, i.e., by 109.29% and 118.60%, respectively. There was no significant difference between the CK, 1% CSB, and 2% CSB treatments during the whole culture period. Except for the third week of culture, there was no significant difference between the CK, 1% CSB, and 2% CSB treatments. The urease activity of the 5% CSB treatment increased by 184.33% compared with CK.

3.4. Soil Carbon Mineralization

During the 35-day culture period, the change trend of cumulative soil carbon mineralization in the two different biochar treatments was roughly similar (Figure 4) and gradually increased over time. The cumulative soil carbon mineralization in the 1% CSB treatment increased slowly after 0–10 days of culture and tended to be stable in the later period. The cumulative soil carbon mineralization in the 2% CSB treatment increased slowly in the first 15 days and tended to be stable in the later period. At the end of the culture period, the cumulative carbon mineralization in the BSB treatment was 11.41–52.57 $\mu\text{g}\cdot\text{g}^{-1}$ and that in the CSB treatment was 11.41–35.03 $\mu\text{g}\cdot\text{g}^{-1}$. During the whole culture process, the cumulative carbon mineralization in soil treated with different proportions of biochar was significantly higher than that of CK, and after the fifth week of culture, the cumulative carbon dioxide emissions from soil treated with BSB were in the order of 2% BSB > 1% BSB > 5% BSB. The cumulative carbon dioxide emissions from soil treated with CSB were in the order of 5% CSB > 2% CSB > 1% CSB. Compared with CK, the cumulative mineralization of soil carbon in the 1% BSB, 2% BSB, and 5% BSB treatments increased by 72.63%, 78.40%, and 71.66%, respectively. The cumulative mineralization of soil carbon in the 1% CSB, 2% CSB, and 5% CSB treatments increased by 19.09%, 54.51%, and 71.19%, respectively.

Figure 4. Cont.

Figure 4. Cumulative emission of soil carbon dioxide and mineralization rate after application of two straw biochar: BSB is banana biochar and CSB is cassava biochar.

As seen in Table 3, the first-order kinetic equation accurately simulated the mineralization dynamics of soil organic carbon during the 30-day culture period. In general, the mineralization potential (C_p) of soil treated with different proportions of biochar was obviously different. The range of soil treated with BSB biochar was $12.617\sim 67.918\ \mu\text{g}\cdot\text{g}^{-1}$ and that of soil treated with CSB biochar was $12.617\sim 42.318\ \mu\text{g}\cdot\text{g}^{-1}$. It can be seen that the mineralization potential of soil increased with the increase in the proportion of biochar. However, the rate constant (k) of soil carbon mineralization showed an opposite trend. The k value of soil treated with BSB biochar varied from 0.128 to $0.036\ \text{d}^{-1}$, while that of soil treated with CSB biochar varied from 0.128 to $0.132\ \text{d}^{-1}$, which is consistent with the trend of the soil carbon mineralization rate in Figure 4. Compared with CK, the mineralizable potential of the 1% BSB, 2% BSB, 5% BSB, 1% CSB, 2% CSB, and 5% CSB treatments increased by 72.758%, 79.383%, 81.423%, 6.686%, 52.835%, and 70.185%, respectively.

Table 3. Kinetic parameters of soil carbon mineralization treated by two straw biochar.

Different Treatments	Fitting Parameter		
	$C_p/\mu\text{g}\cdot\text{g}^{-1}$	k/d^{-1}	R^2
CK	12.617 ± 0.253	0.128 ± 0.007	0.99
1% BSB	46.314 ± 1.487	0.119 ± 0.010	0.98
2% BSB	61.197 ± 1.138	0.100 ± 0.004	0.99
5% BSB	67.918 ± 5.624	0.036 ± 0.004	0.99
1% CSB	13.521 ± 0.549	0.462 ± 0.097	0.79
2% CSB	26.751 ± 1.048	0.150 ± 0.018	0.96
5%CSB	42.318 ± 2.167	0.132 ± 0.019	0.94

Note: BSB is banana straw biochar, CSB is cassava straw biochar, C_p represents soil carbon mineralization potential, and k represents soil carbon mineralization rate constant.

The dynamic trend of the carbon dioxide mineralization rate in soil treated with the two types of straw biochar was basically the same. Overall, the CO_2 emission rate of each treatment during the whole culture period can be roughly divided into three stages: the soil CO_2 emission rate decreased rapidly until day 5, decreased slowly from 5–10 days, and gradually reached a stable state from 10–30 days, and then the CO_2 emission rate of each treatment approached zero.

The carbon sequestration capacity of biochar can be compared by analyzing the ratio of soil CO_2 emissions to total soil organic carbon in a certain period of time [34]. The higher the ratio, the weaker the carbon sequestration capacity, and vice versa. By comparing the ratio of CO_2 emissions and soil TOC content in the middle stage of culture with different biochar and concentration treatments, the carbon sequestration capacity of each treatment during the whole culture period can be roughly analyzed. As shown in Table 4, the ratio of the treatments was ranked as follows: 1% BSB > CK >

2% BSB > 2% CSB > 1% CSB > 5% CSB > 5% BSB. The carbon fixation capacity of banana straw biochar was ranked as 5% BSB > 2% BSB > CK > 1% BSB, and the carbon fixation capacity of cassava straw was ranked as 5% CSB > 1% CSB > 2% CSB > CK.

Table 4. Ratio of CO₂ emission and TOC of two straw biochar in medium culture stage.

	CO ₂ Emissions (μg/g)	TOC Content (g/kg)	CO ₂ /TOC (%)
CK	0.42	1.12	0.16
1%BSB	3.13	1.95	0.22
2%BSB	5.33	2.47	0.14
5%BSB	5.68	3.95	0.03
1%CSB	0.55	2.10	0.07
2%CSB	1.86	2.80	0.08
5%CSB	3.37	4.39	0.04

3.5. Correlation Analysis between Soil Organic Carbon, Soil Enzymes, and Soil Physical and Chemical Properties

As shown in Table 5, in the soil treated with banana straw biochar, available phosphorus was significantly positively correlated with pH, organic carbon, and soluble organic carbon and was significantly negatively correlated with catalase and urease activities. pH was significantly positively correlated with total organic carbon and soluble organic carbon and was significantly negatively correlated with catalase. Catalase had a highly significant negative correlation with organic carbon and a significant negative correlation with soluble organic carbon. Urease was negatively correlated with organic carbon and soluble organic carbon. Organic carbon and soluble organic carbon were significantly positively correlated.

Table 5. Correlation of physical and chemical properties, organic carbon, and enzyme activities of soil treated with two kinds of straw biochar.

5						
Banana Straw Biochar						
Indicators	Olsen-P	pH	Catalase	Urease	SOC	DOC
Olsen-P	1	0.868 **	−0.864 **	−0.477 **	0.955 **	0.635 **
pH		1	−0.926 **	−0.139	0.855 **	0.301 *
Catalase			1	0.113	−0.859 **	−0.289 *
Urease				1	−0.377 **	−0.734 **
SOC					1	0.492 **
DOC						1
6						
Cassava Straw Biochar						
Indicators	Olsen-P	pH	Catalase	Urease	SOC	DOC
Olsen-P	1	0.772 **	−0.806 **	0.807 **	0.936 **	−0.821 **
pH		1	−0.497 **	0.430 **	0.888 **	−0.811 **
Catalase			1	−0.719 **	−0.732 **	0.637 **
Urease				1	0.688 **	−0.624 **
SOC					1	−0.842 **
DOC						1

Note: ** at the level of 0.01 (double tails), the correlation is extremely significant; * at the 0.05 level (double tails), the correlation was significant.

As seen from Table 6 in the soil with cassava straw biochar, available phosphorus had a very significant positive correlation with pH, urease, and organic carbon and a very significant negative correlation with catalase and soluble organic carbon. pH was positively correlated with urease and organic carbon and negatively correlated with catalase and soluble organic carbon. Catalase had a very

significant positive correlation with soluble organic carbon and a very significant negative correlation with urease and organic carbon. Urease had a very significant positive correlation with organic carbon and a very significant negative correlation with soluble organic carbon. Organic carbon and soluble organic carbon were significantly negatively correlated with each other.

Table 6. Correlation between Soil CO₂ Emission and Enzyme Activity.

	Banana Straw Biochar			Cassava Straw Biochar		
	Urease	Catalase	CO ₂ Emissions	Urease	Catalase	CO ₂ Emissions
CO ₂ emissions	0.442	0.515 *	1	0.751 **	0.732 **	1
Catalase	0.113	1		−0.719 **	1	
Urease	1			1		

Note: * at the level of 0.05 (double tails), the correlation is significant; ** at level 0.01 (double tails), the correlation is extremely significant.

As seen from Table 6, soil catalase and CO₂ emissions were significantly positively correlated in the banana straw biochar treatment, and soil CO₂ emissions under the cassava straw biochar treatment were extremely significantly positively correlated with urease and catalase.

4. Discussion

4.1. CO₂ Emissions

Biochar can seriously affect soil carbon dioxide emissions [35]. Ameloot et al. [36], reported, biochar was prepared from willow wood (*Salix dasyclados*) and swine manure digestion material at 350 and 700 °C, respectively; when the four treatments of blank, DS350, DS700, WS350, and WS700 were applied to agricultural soil, the C mineralization in all treatments increased rapidly in the early stage, and then the CO₂ emission continued to increase at a much slower rate, which is similar to our results. This may be due to the rapid degradation of unstable or volatile components in the soil and the slow degradation of stable components in the soil. Moreover, soil rewetting will also lead to active microbial activities and increased C mineralization [37]. Indicators such as biochar properties, soil types, and interactions between biochar and soil also play an important role in the process of organic carbon mineralization [31]. During the incubation period, there was no significant difference in cumulative CO₂ emissions between the control group and 1% CSB, which indicated that the degree of mineralization of biochar may have been very small, which may be related to the concentration of biochar added. In a biochar-modified system, the mineralization rate of biochar (1% CSB) had little effect on CO₂ emissions [24], and the cumulative CO₂ emissions of 1% CSB were significantly lower than those of 2% CSB and 5% CSB ($p < 0.05$). However, the cumulative emissions of 5% BSB were significantly lower than those of 1% BSB and 2% BSB, which is most likely related to the different functional groups on the surface of the biochar materials. The mineralization rate of the two types of biochar applied at different proportions was higher in the initial stage (0–5 days), which is probably due to the rapid decomposition of the internal components of the biochar [38]. Our results show that the mineralization rate of organic carbon in the 1% CSB biochar treatment was slightly lower than that in the control treatment. During the whole incubation period, the mineralization rate of organic carbon in the 5% BSB biochar treatment was in a stable state after a rapid decline. The mineralization rate of organic carbon in the 5% BSB biochar treatment was lower than that in the 5% CSB treatment, which indicates that BSB biochar was more stable than CSB, and the ratio of CO₂/TOC was 5% BSB < 5% CSB. Generally, the degradation of unstable C in biochar occurs easily and rapidly, while the degradation of refractory C is difficult and slow [39].

4.2. Impacts on Soil Nutrients after Different Straw Biochar Applications

Carbon is an important nutrient that determines rice growth and productivity. Biochar is obtained by pyrolysis at high temperature and contains high amounts of stable C. However, the mechanism by which biochar affects organic carbon is complex. Biochar can enhance soil carbon sequestration and reduce carbon dioxide emissions. This study found that compared with the treatment without biochar, the application of banana straw and cassava straw biochar had a significant effect on organic carbon. Different straw biochar applications can increase the content of soil organic carbon. The content of soil organic carbon is directly proportional to the amount of biochar applied. The higher the amount of biochar applied, the higher the content of organic carbon, which is consistent with the conclusion of [40]. The increase in the organic carbon content may be due to the high organic carbon content in biochar [29]. The CSB treatment increased the organic carbon content more significantly than the BSB treatment.

The ability of soil to store and supply phosphorus can be reflected by the available phosphorus content, and available phosphorus in soil is also an index of the soil phosphorus level [29]. The results of this experiment showed that the addition of banana straw biochar and cassava straw biochar significantly increased the available phosphorus content and effectively improved the acidity of soil over a long period. Banana straw biochar had a stronger ability to increase soil pH, and its ability to increase the soil available phosphorus content was slightly weaker than that of cassava straw biochar. Overall, banana straw biochar improved the physical and chemical properties of the soil. In terms of time, pH and the available phosphorus content responded quickly to biochar, and biochar can greatly increase the soil pH and available phosphorus content in a short time. From the concentration point of view, the pH value and available phosphorus content of the soil were significantly positively correlated with the amount of biochar added, i.e., the more biochar applied, the greater the improvement in the soil physical and chemical properties, which is consistent with the research results of [41]. After biochar application, the pH value of the soil increased significantly compared with that of the CK. The pH value of the BSB treatment biochar increased by 2.61~5.05 units and that of the CSB treatment increased by 1.99~3.92 units. These results are consistent with previous research [30]. The analysis of variance results reported by them showed that the pH value of the biochar treatment increased significantly by 0.2~0.3 units compared with the control. The reason for the large change in soil pH may be that biochar is generally alkaline, and basic ions such as calcium and magnesium will be released and exchanged after entering the soil. The concentrations of hydrogen and aluminum plasma in the soil decrease, increasing the pH [42]. After biochar is applied to the soil, the available phosphorus content in the soil continuously increases. On the one hand, the biochar slowly releases its own phosphorus ions into the soil; on the other hand, the rich functional groups on the surface of the biochar can adsorb mineral element ions in the soil, hindering the absorption of phosphorus ions and decreasing the loss of soil nutrients and phosphorus [43]. In addition, this experiment showed that the pH of the soil with the two types of biochar had a very significant positive correlation with the available phosphorus content. It may be that after the biochar was applied to the acidic soil, the pH of the biochar decreased, dissolving and releasing its own mineral elements and releasing phosphorus ions [44].

Soluble organic carbon is mainly organic matter that can pass through 0.45 µm micropores and can be dissolved in water, acid, or alkali solution [45]. DOC can not only provide certain nutrients for soil, but also plays a certain role in soil nutrient cycling. In this study, a low concentration of banana straw biochar inhibited the DOC content, a high concentration significantly promoted the DOC content, and all concentrations of cassava straw biochar reduced the DOC content. The DOC content of each treatment decreased except for the high-concentration banana straw biochar treatment. Similar research results have been reported. For example, [46] conducted a field experiment and found that a low concentration of biochar had little effect on the soil DOC, while a high concentration significantly increased the soil DOC concentration. There was a significant negative correlation between the DOC content and catalase activity in the banana straw biochar treatment. According to the research results of the interaction and influence between enzyme activity and soil microbial activity [47], it is speculated

that the addition of a high concentration of banana straw biochar may change the soil environment in which microorganisms live, reduce the absorption of DOC by microorganisms, and lead to an increase in the DOC content. The 1% BSB, 2% BSB, 1% CSB, 2% CSB, and 5% CSB treatments all significantly reduced the soil DOC content, reduced the loss of soil DOC, and benefitted soil carbon sequestration. In summary, the addition of biochar increased the soil TOC content, reduced the leaching loss of soil DOC, and improved the soil fertility.

4.3. Effects of Different Types of Straw Biochar on Soil Enzyme Activity

Soil enzymes are a sensitive index of soil fertility, and changes in soil microorganisms disturbed by the external environment can be reflected by enzyme activity [47]. This study shows that, compared with CK, the two types of straw biochar treatments with different proportions significantly increased soil enzyme activity, which is similar to other research results [48]. The activity of catalase increased with the addition of the two kinds of biochar, which may be due to the adsorption performance of biochar and the easy storage of the porous structure of biochar, thus improving the activity of catalase [49]. There was no obvious regularity of soil enzyme activity in each treatment over time. The urease activity of the 5% BSB treatment was lower than that of the other treatments. The urease activity of the 5% CSB treatment was significantly higher than that of the other treatments, which may be because BSB biochar contains fewer nutrients that can be utilized by urease, and it is also possible that BSB inhibits enzymatic reactions by adsorbing the enzyme matrix, thus reducing enzyme activity [50]. With the change in the influence of biochar on enzyme activity over time, the BSB biochar treatment improved catalase activity more than the CSB treatment. During the whole culture period, the enzyme activities of each biochar treatment decreased, with great fluctuation. The catalase activity of the two biochar treatments was negatively correlated with available phosphorus and pH. The urease activity of CSB was positively correlated with pH and available phosphorus. The research results are different from those of a previous study [51], but other research [52] showed that during a 46-day experiment on the short-term effect of peanut straw biochar on waste orchard soil, the increase in the pH value significantly reduced urease activity, indicating that the addition of biochar continuously affects the soil environment, and the relationship between soil enzyme activity and soil physical and chemical properties is complex. The inhibition of soil enzyme activity by biochar may be because many charged particles carried on the surface of biochar can adsorb enzymes, thus reducing enzyme activity. Research shows that there are several factors that influence the adsorption of enzymes by biochar; one is pH. When the pH is higher than the isoelectric point of enzymes, biochar adsorbs more enzymes. Second, a larger biochar pore size and specific surface area are conducive to adsorption. The third factor is the type of enzyme. Different enzymes have different adsorption effects [53]. Therefore, the adsorption of enzymes by biochar may be the reason for the large change in the soil enzyme activity.

4.4. Effects of Soil Enzyme Activity on Soil Organic Carbon Mineralization

Catalase and urease play an important role in the transformation and decomposition of soil organic matter and are key participants in the soil carbon cycle [54]. Soil organic carbon mineralization is a biochemical reaction in which microorganisms promote the decomposition of organic compounds and release CO₂. Most of the enzymes in soil are also derived from soil microorganisms. As shown in Table 6, there was a significant positive correlation between soil catalase and CO₂ emissions in the banana straw biochar treatment. In the cassava straw biochar treatment, soil CO₂ emissions had a very significant positive correlation with urease and catalase. Previous studies have found that an increase in atmospheric CO₂ concentration can improve the growth and metabolic level of plants. As a result, the types and quantities of plant metabolic secretions change, thus indirectly affecting soil enzyme activity; moreover, the change of CO₂ concentration will cause the change of pH value, which will indirectly affect the activity of soil enzymes [55]. In this study, after 35 days of mineralization, the urease activity of soil treated with 5% BSB biochar was significantly lower than that treated with

5% CSB biochar, which may be related to different organic carbon components and different enzyme performance differences [56].

5. Conclusions

- (1) There were significant differences in catalase and urease activities among different treatments. Compared with the CK treatment, the soil enzyme activities in each treatment were higher. There was a very significant positive correlation between catalase and urease activities and soil organic carbon mineralization between the cassava straw biochar and banana straw biochar.
- (2) The cumulative CO₂ emission of cassava straw biochar with 1% and 2% addition ratios is lower than that of banana straw biochar, which indicates that cassava straw biochar has a more certain emission reduction effect than banana straw biochar. The content of organic carbon in each treatment was higher than CK (blank control), indicating that the two kinds of biomass char were beneficial to the promotion of organic carbon, and the content of organic carbon in cassava straw biochar was higher than that in banana straw biochar. The mineralization trend of soil organic carbon is basically the same when the two kinds of straw biochar are applied. The application of biochar increases the mineralization rate and accumulated mineralization amount of soil organic carbon. Different straw biochar has different effects on soil organic carbon mineralization. Banana straw biochar has a stronger mineralization effect on soil organic carbon than cassava straw biochar.

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