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Effects of Orange Peel Biochar and *Cipangopaludina chinensis* Shell Powder on Soil Organic Carbon Transformation in Citrus Orchards

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Abstract: In view of the continuous decline in organic carbon content in citrus orchard soil, to explore the effects of biochar and farmland waste on the transformation of organic carbon in citrus orchard soil. In this study, the soil of a citrus orchard in Yangshuo County, Guilin, Guangxi, China, was collected. The citrus peel and the *Cipangopaludina chinensis* shell were used as raw materials, the citrus peel was used to prepare biochar, and the *Cipangopaludina chinensis* shell was powdered. The materials were added to the soil in different proportions. A 30-day indoor incubation soil was conducted to investigate the effects of adding different proportions of citrus peel biochar and *Cipangopaludina chinensis* shell powder on the transformation of organic carbon in citrus orchard soil. Compared with the control group, the addition of 4% orange peel biochar, 2% orange peel biochar + 2% *Cipangopaludina chinensis* shell powder, 2.6% orange peel residue biochar + 1.3% *Cipangopaludina chinensis* shell powder, and 3% orange peel biochar + 1% *Cipangopaludina chinensis* shell powder increased soil organic carbon by 22.49%, 20.06%, 19.81%, and 21.35%, respectively. Compared with the control, 2.6% orange peel biochar + 1.3% *Cipangopaludina chinensis* shell powder had the best effect on the improvement of soil organic carbon components, and microbial biomass carbon (MBC), dissolved organic carbon (DOC) and readily oxidized organic carbon (ROC) increased by 19.81%, 64.88%, 67.81%, and 19.44%, respectively. Different proportions of orange peel residue biochar and *Cipangopaludina chinensis* shell powder were applied to the soil of the citrus orchard to effectively increase the soil organic carbon component content and enzyme activities. This study provides a theoretical basis for the carbon sequestration mechanism of citrus orchard soil using different proportions of orange peel residue biochar and *Cipangopaludina chinensis* shell powder.

Keywords: citrus orchards; soil organic carbon; enzyme activities; citrus peel charcoal; *Cipangopaludina chinensis* shell powder



Citation: Hu, L.; Qin, R.; Zhou, L.; Deng, H.; Li, K.; He, X. Effects of Orange Peel Biochar and *Cipangopaludina chinensis* Shell Powder on Soil Organic Carbon Transformation in Citrus Orchards. *Agronomy* **2023**, *13*, 1801. <https://doi.org/10.3390/agronomy13071801>

Academic Editor: Andrea Baglieri

Received: 22 May 2023

Revised: 18 June 2023

Accepted: 19 June 2023

Published: 6 July 2023



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1. Introduction

The content of soil organic carbon is the most critical parameter in soil fertility, which can affect the physical, chemical, and biological transformation process of soil, and represents the most important carbon pool of the earth [1,2]. The slight change in soil organic carbon content will cause a change in CO₂ concentration in the atmosphere [3]. Organic carbon mineralization is one of the main reasons for the change in CO₂ concentration, and it is a key biochemical process in soil [4]. Therefore, how to increase the content of soil organic carbon and reduce the mineralization of soil organic carbon is the primary problem in solving the low quality and fertility of orchard soil. The change of organic carbon in

soil is affected by many factors, such as temperature, water content, soil properties, and soil enzyme [5]. Soil enzyme is an important driving force for the transformation of the carbon pool in the soil ecosystem, which is secreted by microorganisms, animals, and plants [6]. It can catalyze the degradation of organic matter and reflect the activity of soil microorganisms. It is an index commonly used to measure short-term changes in soil function [7].

Biochar is a high-carbon material obtained by biomass pyrolysis under anaerobic conditions [8]. Due to the rich organic carbon, high stability, high alkalinity, and rich pore structure of biochar [9], its addition to soil can increase soil organic carbon content [10] and stimulate soil microbial activity [9]. For example, Demisie et al. [11] applied oak and bamboo biochar to soil, which could increase soil organic carbon and enzyme activities and improve soil fertility by accumulating and immobilizing C. Lu et al. [12] had shown that adding biochar to soil could effectively reduce the decomposition of soil organic carbon, which was an effective measure to increase the effect of soil carbon sequestration.

After processing and eating, a large amount of *Cipangopaludina chinensis* shell waste is produced, resulting in a waste of resources. *Cipangopaludina chinensis* shells contain a large amount of calcium carbonate and chitin, and others contain a large amount of calcium carbonate substances, which have been shown to promote soil C sequestration and enrich bacterial diversity. Li et al. [13] found that free calcium carbonate could affect microbial activity and the decomposition rate of soil organic matter, thus changing the soil organic carbon pool. Samy [14] reported that natural lime materials significantly increased soil organic matter and enzyme activities. Chitin can provide carbon and nitrogen sources for microbial reproduction and growth in soil [15]. Russell [16] found that adding exogenous chitin to the soil can increase soil respiration and soil carbon content. Cai et al. [17] found that changes in chitin played an important role in the soil nitrogen cycle and soil organic carbon accumulation. These studies indicate that the *Cipangopaludina chinensis* shell powder as a natural lime material has great potential in the study of soil carbon sequestration.

The production of citrus fruits in China ranks first in the world, and a large amount of citrus peel waste is produced in the process of citrus production and processing [18]. Most of the citrus peel waste in China is still mainly discarded, which increases the burden on enterprises and the environment [19]. There is a large amount of organic matter in citrus peel. The organic waste is prepared into biochar, and then the biochar is put into the soil as an additional carbon source to increase the organic carbon content in the soil. Sial et al. [20] found that orange peel biochar had high fixed carbon content and low ash content and increased soil organic matter and enzyme activities during incubation. The feasibility of using orange peel waste to prepare biochar in soil was confirmed. However, in the current study, there is a lack of discussion on the effect of a single application of *Cipangopaludina chinensis* shell and mixed application of orange peel biochar and *Cipangopaludina chinensis* shell on soil carbon fixation. Therefore, in this paper, citrus peel biochar and *Cipangopaludina chinensis* shell powder were added to the soil to study the effects of different proportions of citrus peel biochar and *Cipangopaludina chinensis* shell powder on the transformation of organic carbon and enzyme activities in the soil and explore its change mechanism.

2. Materials and Methods

2.1. Experimental Design

The test soil was selected from the citrus orchard (24°47'33" N, 110°23'41" E) in the citrus industry demonstration area of Yangshuo County, Guilin City, Guangxi Zhuang Autonomous Region, China, with an altitude of 450 m. The area belongs to a subtropical monsoon climate, with an average annual temperature of 17 °C–25 °C and an average annual precipitation of 1538.9 mm. Daily discarded citrus peels were washed and dried and then burned in a muffle furnace (Kusite K-XR1200-20, China) at 500 °C for 2 h to prepare citrus peel biochar. The *Cipangopaludina chinensis* shell powder comes from daily kitchen waste. The *Cipangopaludina chinensis* shell is washed, dried, and crushed. The prepared

biochar and *Cipangopaludina chinensis* shell powder were passed through a 60-mesh sieve. The basic properties are shown in Table 1:

Table 1. Basic properties of test materials.

Type	pH	SOC (g·kg ^{−1})	CEC (cmol·kg ^{−1})	AK (mg·kg ^{−1})
Soil	3.73 ± 0.02	2 ± 0.05	4.89 ± 0.06	58.2 ± 0.31
Orange peel biochar	9.6 ± 0.02	3.31 ± 0.07	30.96 ± 0.14	404.9 ± 0.24
<i>Cipangopaludina chinensis</i> shell powder	8.53 ± 0.04	0.46 ± 0.001	440.3 ± 0.22	18.3 ± 0.12

Note: SOC, soil organic carbon; CEC, cation exchange capacity; AK, available K.

2.2. Experimental Design

2.2.1. Soil Incubation Setting

As shown in Table 2 of the experimental design, there were 8 treatments in the experiment, and each treatment was repeated three times. The visible plant residues and gravels were carefully removed from the soil, and the soil was sieved by a 1 mm sieve after natural air drying. 2 kg of soil was added to the blank treatment and 1.92 kg of soil was added to the other treatments in 2 L open mouth wide mouth bottles. Before the experiment, each soil was pre-incubated in an incubator at 25 °C for 7 days under the condition of maintaining 60% water holding capacity by adding distilled water, and then biochar and *cipangopaludina chinensis* shell were added in proportion and fully mixed for incubation test. On the 1st, 3rd, 5th, 10th, 15th, 20th, and 30th day of the experiment, 150 g of soil was taken for analysis.

Table 2. Test treatment settings.

Addition Amount	Sample Identification
control	CK
4% Orange peel biochar	g4k0
4% <i>Cipangopaludina chinensis</i> shell powder	g0k4
2% Orange peel biochar + 2% <i>Cipangopaludina chinensis</i> shell powder	g2k2
1.3% Orange peel biochar + 2.6% <i>Cipangopaludina chinensis</i> shell powder	g1k2
2.6% Orange peel biochar + 1.3% <i>Cipangopaludina chinensis</i> shell powder	g2k1
1% Orange peel biochar + 3% <i>Cipangopaludina chinensis</i> shell powder	g1k3
3% Orange peel biochar + 1% <i>Cipangopaludina chinensis</i> shell powder	g3k1

2.2.2. Soil Mineralization Test Setting

50 g of soil was added to the blank treatment, and 48 g of soil was added to the other treatments in 500 mL incubation bottles. Before the experiment, each soil was pre-incubated in an incubator at 25 °C for 7 days under the condition of maintaining 60% water holding capacity by adding distilled water, and then biochar and *cipangopaludina chinensis* shell were added in proportion and fully mixed. Then, a 10 mL beaker containing 10 mL of 0.2 mol L^{−1} NaOH absorption solution was placed in a 500 mL incubation bottle. The incubation bottle was sealed and incubated at a 25 °C constant temperature incubator. The beaker was taken out on the 1st, 3rd, 5th, 10th, 15th, 20th, and 30th days, and the CO₂ release amount of each soil was determined by BaCl₂-HCl titration. After each measurement, the NaOH absorption solution was replaced, and soil moisture was supplemented by the weighing method.

2.3. Determination Indicators and Methods

The basic properties of soil, orange peel biochar, and *Cipangopaludina chinensis* shell powder were analyzed by soil agrochemical analysis [21]. The pH of the soil was determined by the pH meter method (water-soil ratio 2.5:1). The cation exchange capacity (CEC) was determined by the barium chloride-sulfuric acid forced exchange method. The

available-K (AK) in soil was extracted by ammonium acetate and determined by atomic absorption spectrometer (Perkin-Elmer Perkin Elmer AA8). The total organic carbon (SOC) of soil was determined by the potassium dichromate concentrated sulfuric acid volumetric method.

Soil organic carbon mineralization was determined by static alkali absorption method [22], soil urease activity was determined by indophenol blue colorimetry [23], soil catalase activity was determined by potassium permanganate titration [24], and soil sucrase activity was determined by the 3,5-dinitrosalicylic acid colorimetric method [25]. Soil readily oxidizable organic carbon (ROC) was determined by the potassium permanganate oxidation method [26], soil microbial biomass carbon (MBC) was determined by the fumigation extraction method (FE method), total organic carbon analyzer (Germany Jena MultiN/C3100) was used to determine [27], and soil water-soluble organic carbon (DOC) was extracted with pure water and determined by TOC analyzer [28].

2.4. Data Processing

The analysis data were processed by Excel 2016, and the data were compared by SPSS25 software. The data chart was drawn by origin2021.

3. Results

3.1. Effects of Adding Different Proportions of Orange Peel Biochar and *Cipangopaludina chinensis* Shell Powder on Soil pH, Soil Cation Exchange Capacity, and Available-K

The results of soil pH changes with time in different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder are shown in Figure 1. The addition of orange peel biochar and *Cipangopaludina chinensis* shell powder increased the pH value of the soil. The increase in soil pH value by *Cipangopaludina chinensis* shell powder was more than that of biochar. All treatments had the highest soil pH value on the 10th day and then decreased. The pH of the control and g4k0 decreased at the end of the experiment compared with the beginning, and the pH of the other groups increased at the end of the experiment compared with the beginning. The pH value of g3k1 was the highest in the first 10 days of the experiment, and the pH value of g2k2 was the highest after 15 days. At the end of the incubation, the pH values of g2k2, g2k1, and g1k2 were the highest, 7.95, 7.85, and 7.82, respectively.

The effects of different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil CEC over time are shown in Figure 2. Soil cation exchange capacity increased with time. Compared with the control, all treatments increased the soil cation exchange capacity, among which g4k0, g0k4, and g1k2 increased the most, which were 93.44 coml kg^{-1} , 91.58 $\text{coml} \cdot \text{kg}^{-1}$, and 107.21 $\text{coml} \cdot \text{kg}^{-1}$, respectively.

The effects of different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil AK are shown in Figure 3. As the proportion of orange peel biochar increases, soil AK increases. The citrus peel biochar just added to the soil significantly increased the content of AK in the soil, decreased sharply on the 5th day, tended to be stable, and increased again on the 15th day. The content of AK in the soil of the same treatment was lower than that at the beginning. The treatment group with high content of *Cipangopaludina chinensis* shell powder added to the soil showed an upward trend from day 5 to day 15, which was opposite to the change of orange peel biochar, indicating that *Cipangopaludina chinensis* shell powder had a reducing effect on soil AK. Orange peel residue biochar promoted the formation of soil AK, and its promotion was greater than the inhibitory effect of *Cipangopaludina chinensis* shell powder on soil AK. At the end of incubation, the contents of soil AK in treatments g4k0, g2k1, and g3k1 were the highest, which were 502.9 mg kg^{-1} , 464.3 mg kg^{-1} , and 441.7 mg kg^{-1} , respectively.

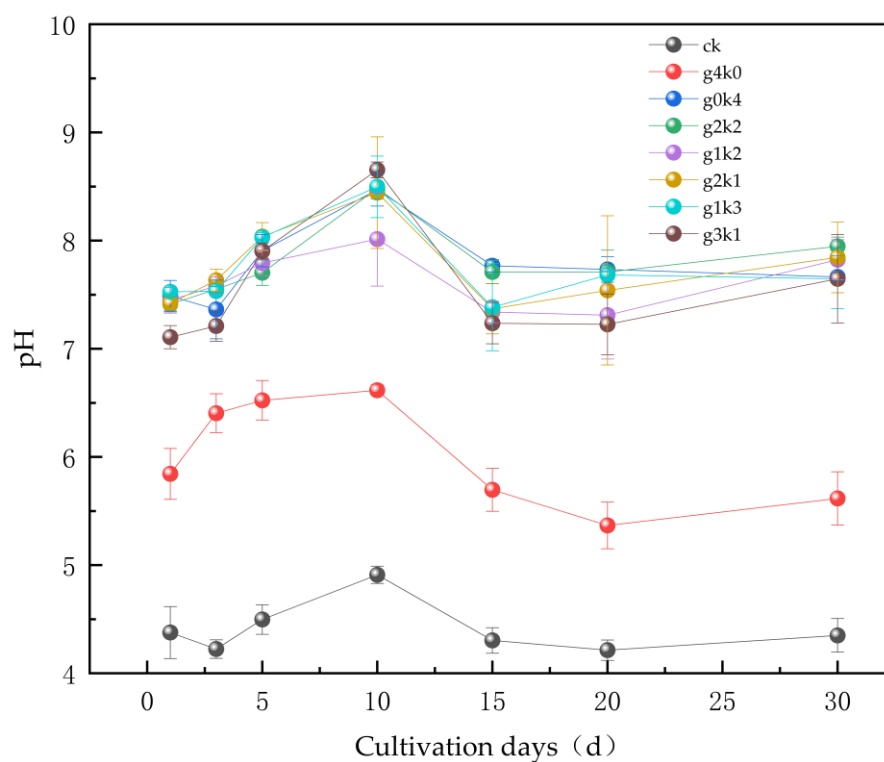


Figure 1. Effects of different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil pH.

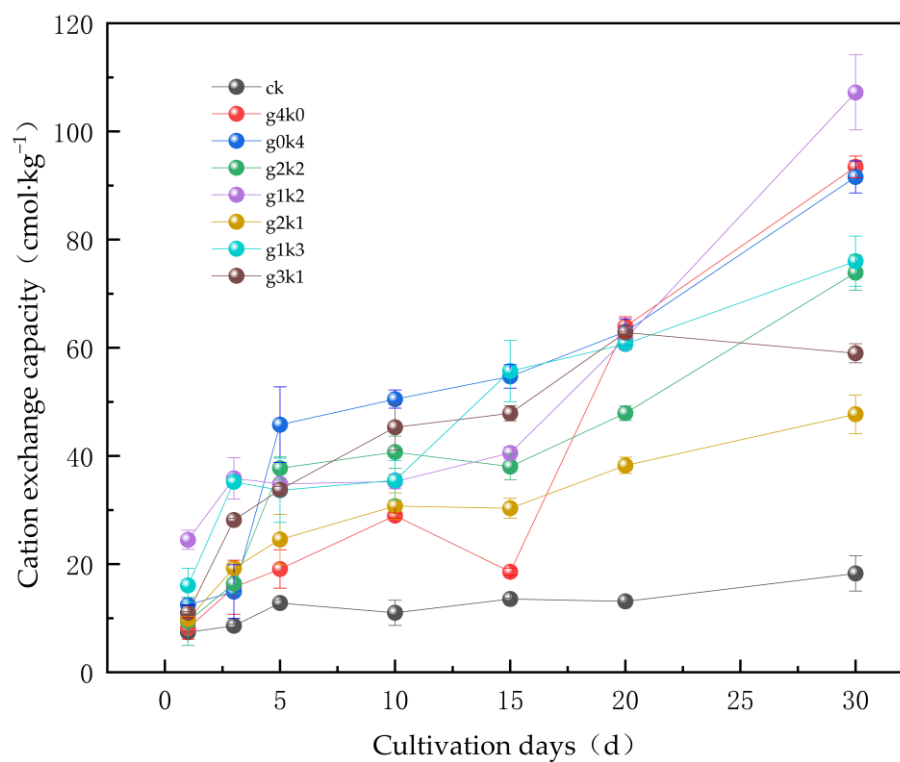


Figure 2. Effects of different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil CEC.

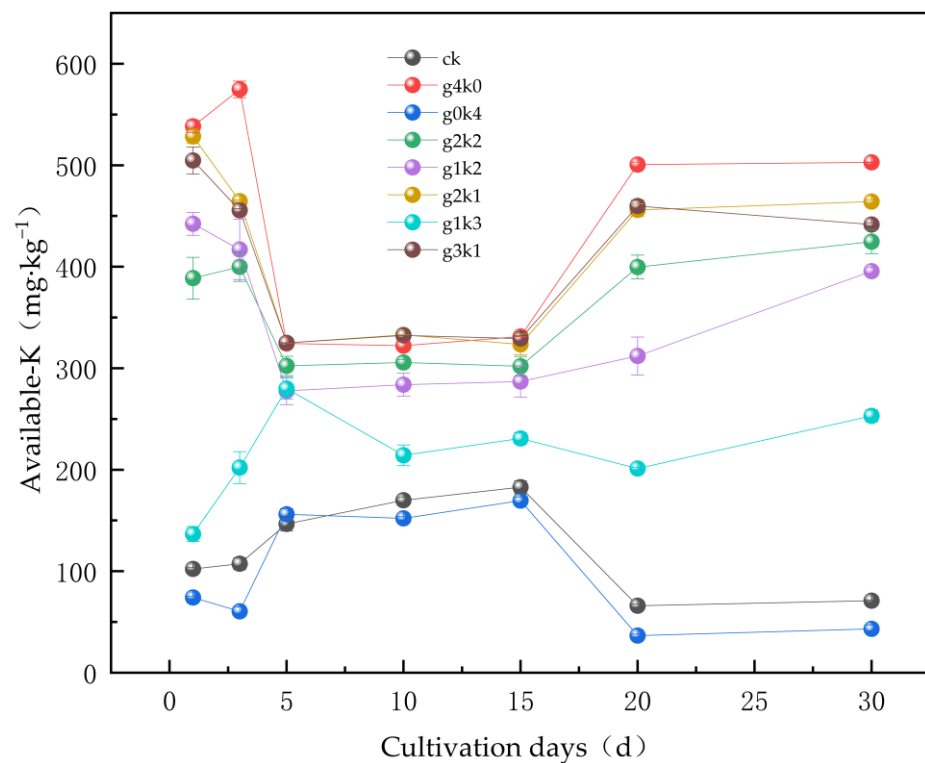


Figure 3. Effects of different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil available-K.

3.2. Effects of Adding Different Proportions of Orange Peel Biochar and *Cipangopaludina chinensis* Shell Powder on Soil Carbon Sequestration

According to Figure 4, the results show that the mineralization rate on the 5th day was about 30% of that on the first day, and the mineralization rate on the 10th day was about 20% of that on the first day. From the beginning of incubation to the 10th day of incubation, the mineralization rate was the highest at the beginning and then decreased rapidly. The duration of this stage was short, but the amount of mineralization was large, and the duration of the next 20 days was long, and the amount of mineralization was small. Compared with the control group, all treatment groups had a promoting effect on soil mineralization within 30 days. At the end of the incubation, g2k1 increased the least, increasing by 17.38% of the control group, followed by g3k1 and g4k0, and g0k4 increased the most, increasing by 44.56% of the control group. With the increase in the proportion of *Cipangopaludina chinensis* shell powder, the soil mineralization rate increased. As shown in Figure 5, the cumulative emissions of soil CO₂ showed that the addition of biochar and *Cipangopaludina chinensis* shell powder significantly increased the cumulative emissions of soil CO₂ in the soil, among which ck < g2k1 < g3k1 < g4k0 < g1k2 < g2k2 < g1k3 < g0k4, indicating that the combination of high-content biochar and low-content *Cipangopaludina chinensis* shell powder can reduce the CO₂ emissions caused by a single application of orange peel biochar and *Cipangopaludina chinensis* shell powder.

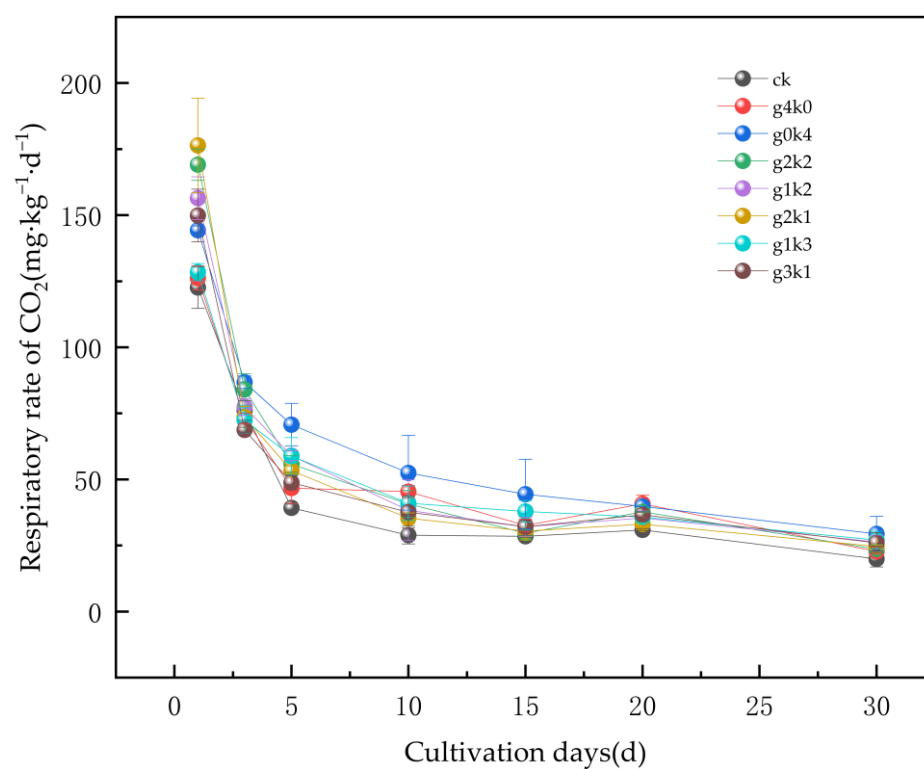


Figure 4. Effects of different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil CO₂ rate.

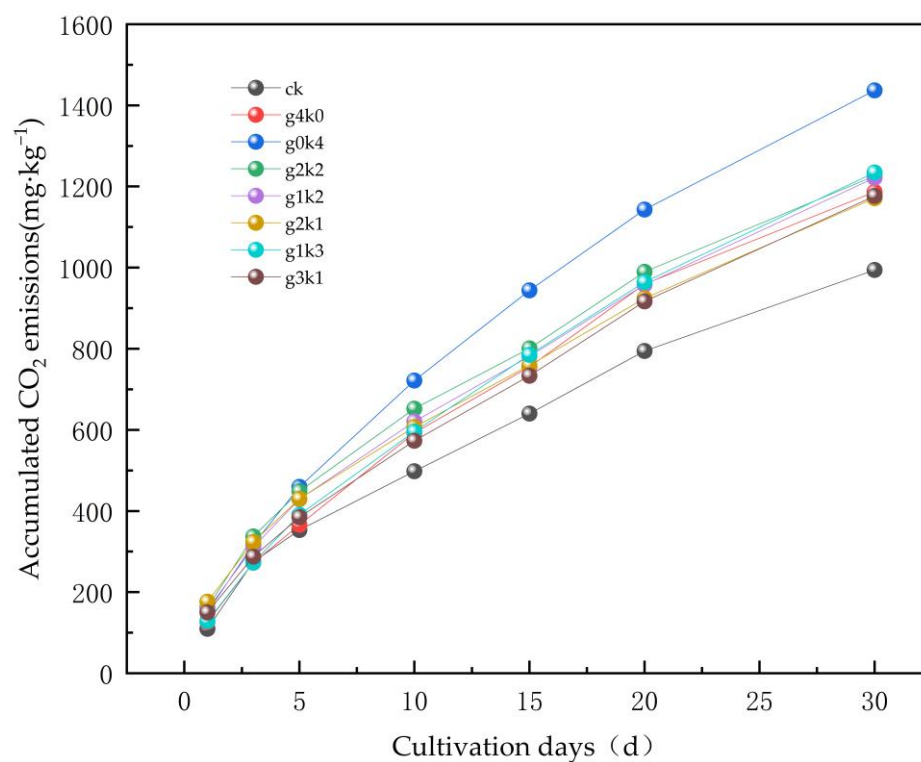


Figure 5. Effects of different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil CO₂ cumulative emissions.

As shown in Figure 6, the addition of orange peel biochar and *Cipangopaludina chinensis* shell powder significantly increased the SOC content in the soil. At the end of incubation,

compared with the control group, the organic carbon of each treatment increased by 0.14 g kg^{-1} to 0.58 g kg^{-1} , and the SOC increased with the increase in orange peel biochar content. During the whole incubation process, the change of SOC showed a trend of increasing first and then decreasing. At the end of the incubation, except for g2k2, the SOC decreased compared with the beginning. The addition of orange peel biochar and *Cipangopaludina chinensis* shell powder alleviated the decrease in SOC during the incubation process. The mitigation effect of orange peel biochar was better than that of *Cipangopaludina chinensis* shell powder. The change of MBC is shown in Figure 7, and the changing trend with time. The MBC reached the highest on the 5th day and showed a downward trend from the 10th day to the 20th day. At this stage, the microbial biomass carbon of most treatments was lower than that of the control, indicating that in the whole incubation soil, the addition of orange peel biochar and *Cipangopaludina chinensis* shell powder first promoted the MBC, then began to enter the inhibition stage, and then increased the MBC content. On the 30th day of the experiment, the MBC of each treatment was higher than that of the control, of which g2k2 increased the most, about 2.5 times of the control.

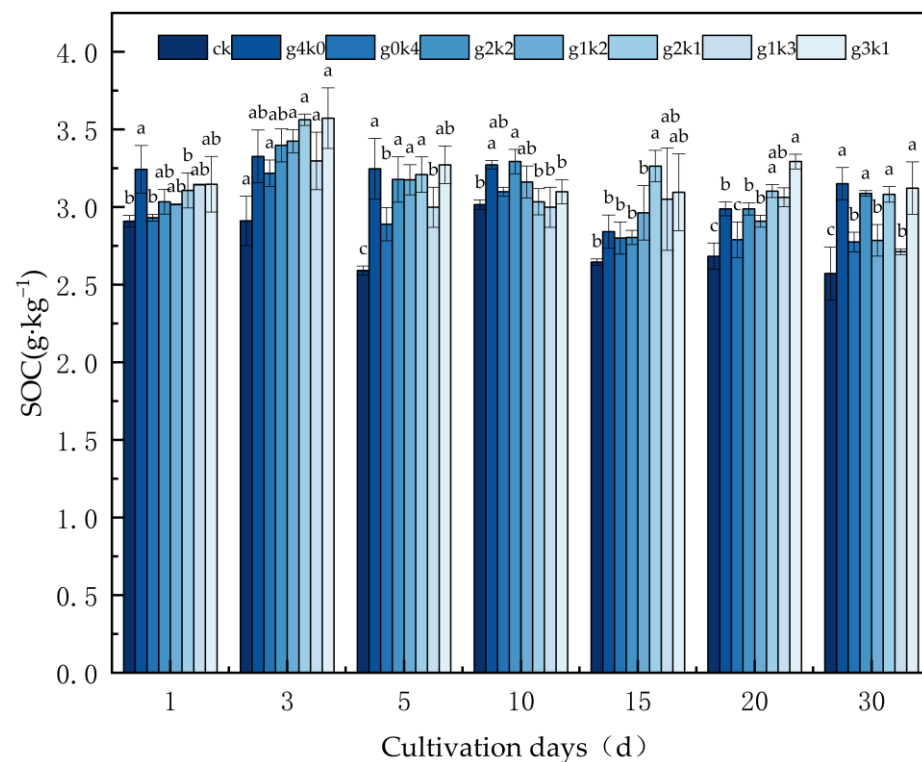


Figure 6. Effects of different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil organic carbon (SOC). Different lowercase letters in each soil layer represent significant differences at the $p < 0.05$ level.

According to the change of ROC in Figure 8, the content of soil readily oxidizable organic carbon decreased by 1.62% to 18.47% with the increase in the proportion of *Cipangopaludina chinensis* shell powder incubation compared with the control. The content of ROC in soil increased by 1.62% to 11.99%, and g2k1 increased the most. The application of *Cipangopaludina chinensis* shell powder in the soil is not conducive to the increase in ROC content, while orange peel biochar has a promoting effect on ROC. Throughout the entire experimental process, the ROC was the lowest on the 10th day and the highest on the 15th day. Except for g2k1, all other treatments showed a decrease in ROC at the end compared to the beginning.

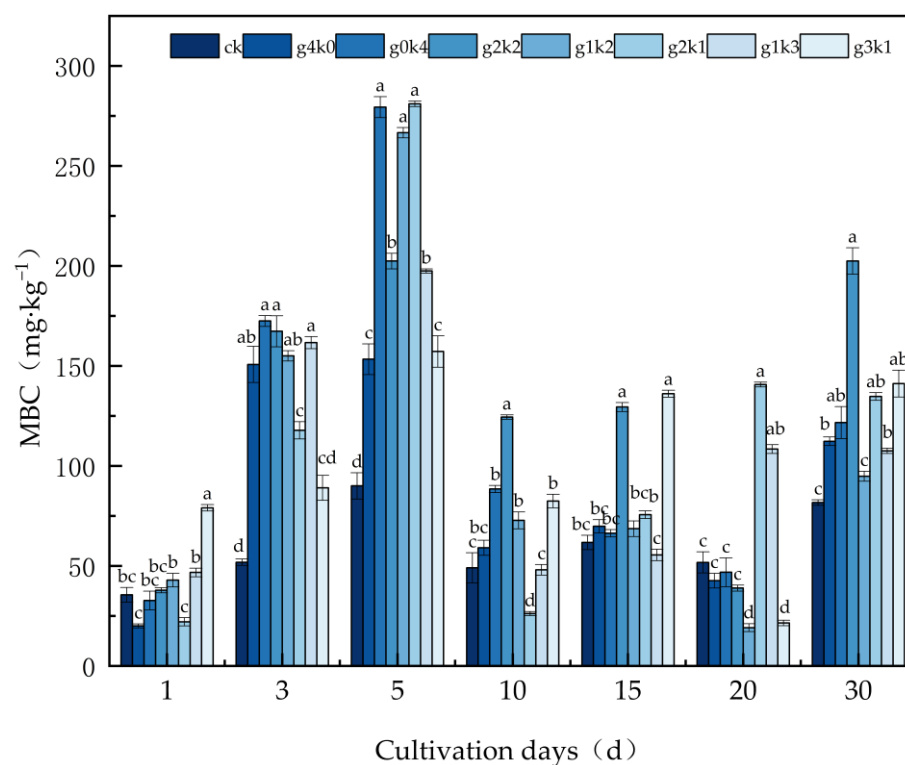


Figure 7. Effects of different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil microbial biomass carbon (MBC). Different lowercase letters in each soil layer represent significant differences at the $p < 0.05$ level.

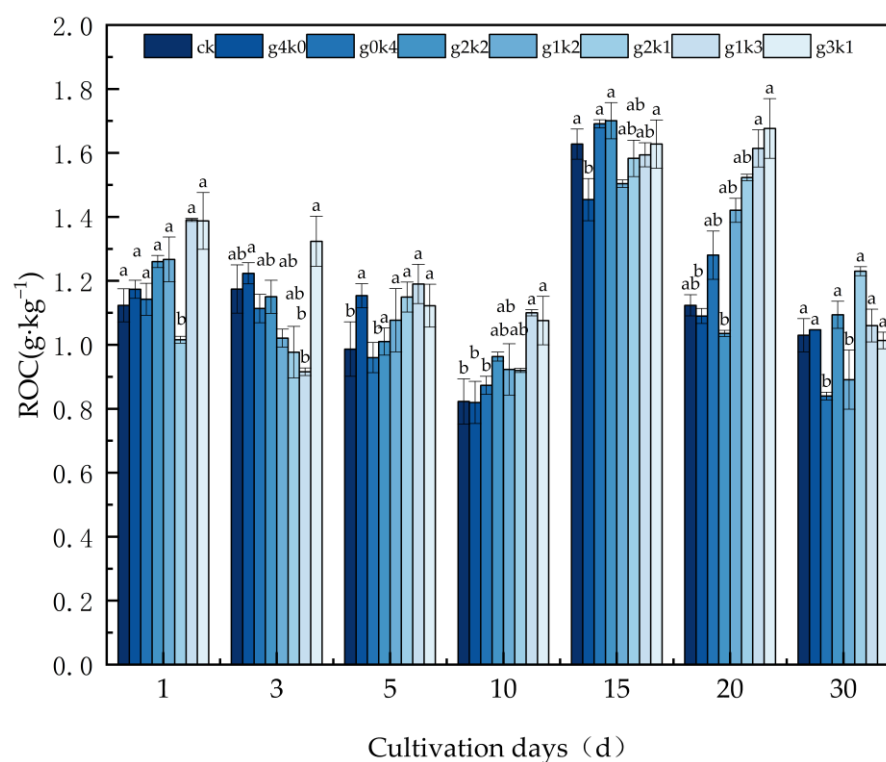


Figure 8. Effects of different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil readily oxidized organic carbon (ROC). Different lowercase letters in each soil layer represent significant differences at the $p < 0.05$ level.

As shown in Figure 9, compared with the control, all treatments increased DOC by 9.17% to 50.24%, with the highest increase in the g2k1 treatment. On the 3rd day, the DOC of each treatment significantly decreased, and the content of DOC reached its peak on the 10th day for g0k4 and g2k2, while the content of DOC reached its peak on the 15th day for other treatments. The content of DOC in g0k4 treated from the 15th to the 20th day of incubation was lower than that in the control group. The promotional effect of orange peel biochar on DOC is higher than that of *Cipangopaludina chinensis* shell powder. By the end of incubation, the DOC content of each treatment and control group increased by 9.17% to 67.81%, with g2k1 increasing the most and g1k2 the least compared to the control group.

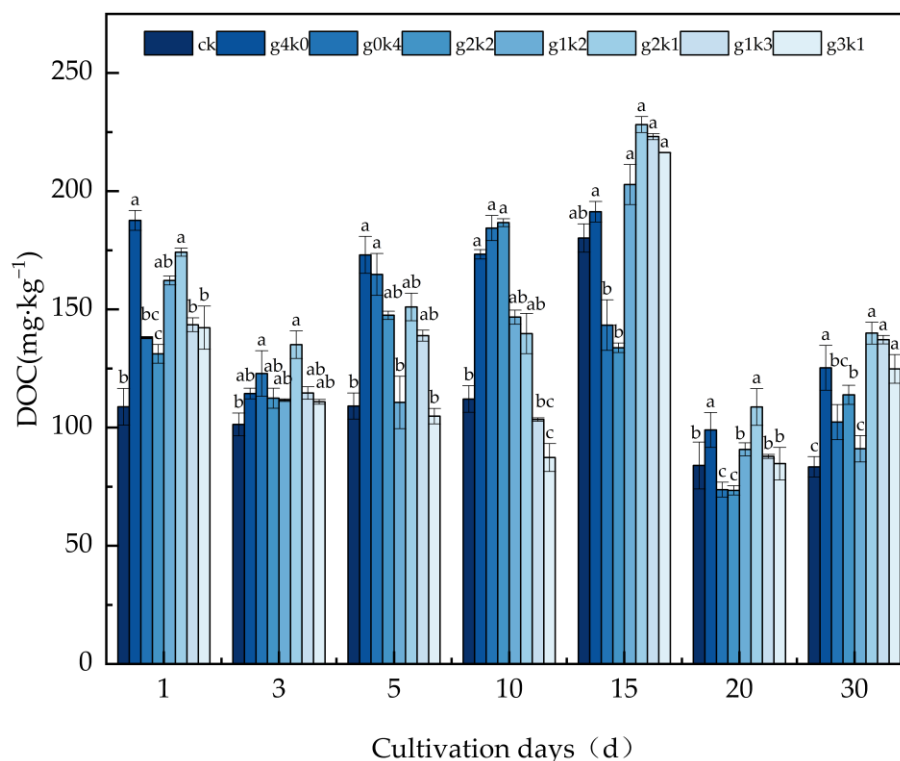


Figure 9. Effects of different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil dissolved organic carbon (DOC). Different lowercase letters in each soil layer represent significant differences at the $p < 0.05$ level.

3.3. Effects of Adding Different Proportions of Orange Peel Biochar and *Cipangopaludina chinensis* Shell Powder on Soil Enzyme Activities

From Figure 10, compared with the control, each treatment increased the soil catalase activity to different degrees in the early stage of incubation, and the improvement effect of *Cipangopaludina chinensis* shell powder was better. In the soil incubation, g2k2 increased the most, with an increase of 122.47%, and then decreased first, then increased, and then decreased. At the end of the incubation, each treatment increased the soil catalase activity, with an increase of 77.55% to 165.31%, with the highest g4k0 and the lowest g2k1. The catalase activity at the end of each treatment decreased compared with the beginning. According to the change of soil urease in Figure 11, compared with the control, each treatment increased soil urease activity to varying degrees. Except for g2k1, the other groups were the lowest on the 10th day. In the treatment, g1k3, g1k2, g2k1, and g3k1 gradually increased with time, and there was no obvious change in other treatment groups. At the end of incubation, the soil urease activities of g1k3, g1k2, g2k1, and g3k1 were the highest, which were $1.11 \text{ mg (g d)}^{-1}$, $1.10 \text{ mg (g d)}^{-1}$, $1.02 \text{ mg (g d)}^{-1}$, and $0.98 \text{ mg (g d)}^{-1}$, respectively, indicating that the promotion effect of a single application of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil urease was slightly worse than

that of compound application of orange peel biochar and *Cipangopaludina chinensis* shell powder. As shown in Figure 12, during the whole incubation process, the sucrase activity of each treatment did not change much in the first 15 days. From the 15th day to the 20th day, the soil sucrase activity began to increase significantly except for the control and decreased on the 30th day. In the early stage of incubation, the addition of orange peel biochar and *Cipangopaludina chinensis* shell powder increased the invertase activity of the soil, and g4k0 and g2k2 increased the most, which was 131.46% and 115.83% of the control. At the end of incubation, all treatments significantly increased soil sucrase activity, with g0k4 and g2k2 increasing the most, 9.27 mg (g h)^{−1} and 6.80 mg (g h)^{−1}, respectively.

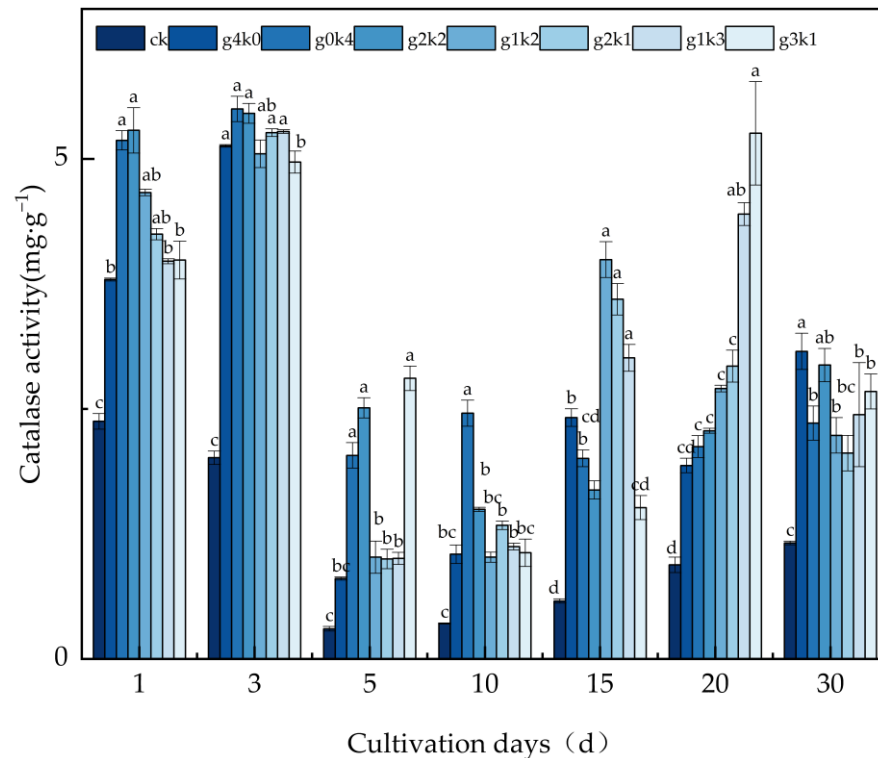


Figure 10. Effects of different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil catalase activity. Different lowercase letters in each soil layer represent significant differences at the $p < 0.05$ level.

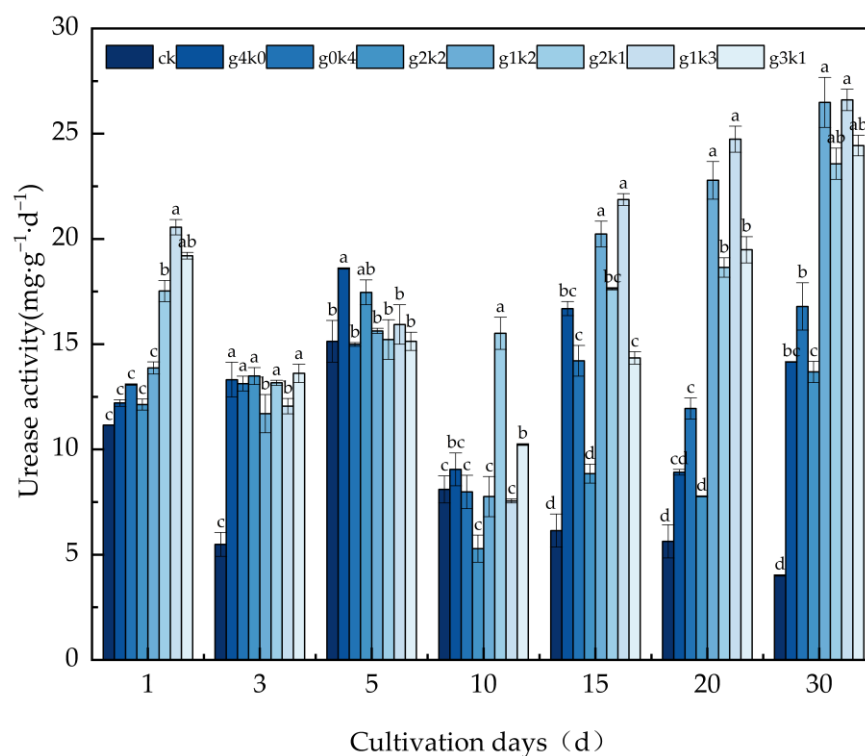


Figure 11. Effects of different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil urease activity. Different lowercase letters in each soil layer represent significant differences at the $p < 0.05$ level.

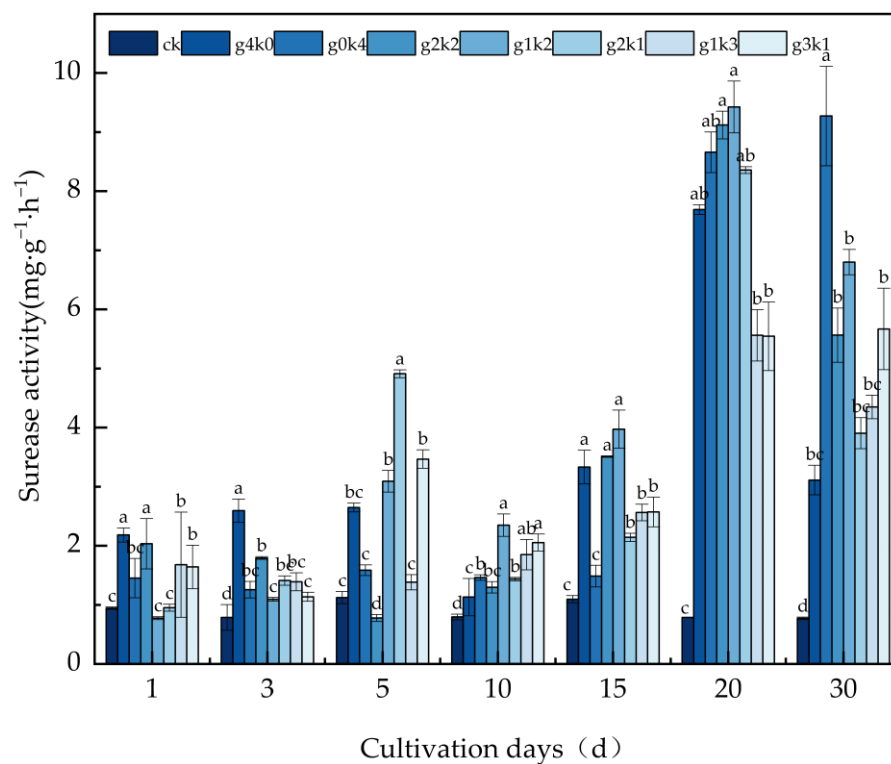


Figure 12. Effects of different proportions of orange peel biochar and *Cipangopaludina chinensis* shell powder on soil invertase. Different lowercase letters in each soil layer represent significant differences at the $p < 0.05$ level.

3.4. The Correlation of Soil Indexes in the Study

As shown in Table 3, soil pH was significantly positively correlated with soil urease and microbial biomass carbon ($p < 0.05$, the same as below), and the correlation coefficients were 0.34 and 0.32, respectively. Soil pH was very significantly positively correlated with CEC and SOC ($p < 0.01$, the same as below), and the correlation coefficient was 0.35 and 0.40, indicating that CEC, urease, microbial biomass carbon, and organic carbon content in soil could be regulated by changing soil pH. Soil CEC was very significantly positively correlated with soil sucrase, and the correlation coefficient was 0.62, indicating that CEC in soil was closely related to the change of soil sucrase activity. AK in soil was very significantly positively correlated with organic carbon in the soil. The correlation coefficient was 0.55 and significantly positively correlated with catalase and urease. The correlation coefficients were 0.32 and 0.31, respectively, indicating that the change of available potassium in soil could lead to the change of organic carbon content, catalase activity and urease activity in soil. There was a very significant positive correlation between soil organic carbon and catalase, and the correlation coefficient was 0.52. There was a very significant negative correlation between soil sucrase and water-soluble organic carbon, and the correlation coefficient was 0.40, indicating that the increase in sucrase activity in the soil would lead to the decrease in water-soluble organic carbon in the soil. There was a significant positive correlation between urease and easily oxidized organic carbon in the soil, and the correlation coefficient was 0.31. Soil urease was very positively correlated with microbial biomass carbon, and the correlation coefficient was 0.35, indicating that the change of active components in soil was closely related to the change of enzyme activities in soil.

Table 3. Correlation of various components in soil.

	CEC	AK	SOC	Sucrase	Catalase	Urease	DOC	ROC	MBC
pH	0.35 **	0.21	0.40 **	0.23	0.22	0.34 *	0.05	0.03	0.32 *
CEC		0.12	−0.11	0.62 **	−0.13	0.18	−0.19	−0.08	0.12
AK			0.55 **	0.14	0.32 *	0.31 *	0.08	0.02	0.04
SOC				−0.18	0.52 **	0.18	0.12	0.11	0.26
Sucrase					−0.04	0.22	−0.40 **	0.12	0.01
Catalase						0.20	0.04	0.20	0.07
Urease							0.13	0.31 *	0.35 **
DOC								0.25	0.01
ROC									−0.17

** Correlation is significant at the 0.01 level (two-tailed). * Correlation is significant at the 0.05 level (two-tailed). Note: CEC, cation exchange capacity; AK, available K; SOC, soil organic carbon; DOC, dissolved organic carbon; ROC, readily oxidized organic carbon; MBC, microbial biomass carbon.

4. Discussion

4.1. Effects of Adding Orange Peel Biochar and *Cipangopaludina chinensis* Shell Powder on Soil Basic Properties

Each treatment increased the soil pH value to varying degrees in this experiment. The surface of biochar has negatively charged phenolic groups, carboxyl groups, and hydroxyl groups, which can bind to H^+ ions in the soil, increasing soil pH [29]. The main reason for the increase in soil pH value caused by *Cipangopaludina chinensis* shell powder is that $CaCO_3$ in the *Cipangopaludina chinensis* shell dissolves into the soil, resulting in a large number of OH^- into the soil and increasing the pH value [30]. In this study, the pH value of biochar itself was higher than that of *Cipangopaludina chinensis* shell powder, and the pH value of biochar in each treatment was lower than that of *Cipangopaludina chinensis* shell powder. It may be due to the surface alkalinity of *Cipangopaludina chinensis* shell powder being higher than that of biochar, or biochar contains a large amount of organic matter, which is added to the soil to promote the decomposition of organic matter. This process may release organic acids [30,31]. In this study, each treatment could significantly increase the number of soil cations, and the number of cations in the soil increased with time. In

the correlation analysis, the soil pH value was positively correlated with the soil CEC. The increase in soil pH value resulted in the increase in the negative charge in the variable charge component, and the negative charge contained in the soil was the main determinant of soil CEC. Therefore, the soil CEC increased after adding biochar and *Cipangopaludina chinensis* shell powder [32]. *Cipangopaludina chinensis* shell powder provides a large amount of calcium, which can replace hydroxyl aluminum polymer (in some acidic soils, it will prevent permanent charge) and increase CEC in soil [33]. The addition of biochar to soil significantly increased soil AK by 2.5 to six times, and AK increased with the increase in biochar content. In this study, the AK in biochar was 40.49 mg kg^{-1} , and the AK in the original soil was 5.82 mg kg^{-1} . After the application of biochar, the maximum AK in the soil was 57.47 mg kg^{-1} , indicating that biochar could activate the AK content in the soil, and this changed with time. It shows that biochar can activate the content of AK in the soil, and this activation effect decreases with time [34]. The content of AK in *Cipangopaludina chinensis* shell powder was 1.83 mg kg^{-1} , which was the same as that of Zhao Lifang [35]. It was found that adding limestone significantly reduced the content of AK in the soil, and the content of AK decreased with the increase in limestone content in the soil.

4.2. Effects of Adding Orange Peel Biochar and *Cipangopaludina chinensis* Shell Powder on Soil Organic Carbon Transformation

In this study, all treatments could promote soil mineralization, and the soil CO_2 emission rate increased with the increase in the content of *Cipangopaludina chinensis* shell powder in the soil, which was the same as the research conclusions of Zhang [22] and Ge [36]. Bertrand [37] found that calcium carbonate released CO_2 during soil incubation to increase the release of carbon in the soil, and 35% of the released carbon came from inorganic carbon, which increased the content of inorganic carbon and promoted soil respiration. Chitin in *Cipangopaludina chinensis* shell powder was added to the soil and rapidly decomposed and metabolized to provide nutrients for microorganisms in the soil to promote microbial respiration [14]. Orange peel biochar and *Cipangopaludina chinensis* shell powder are used as external carbon sources to promote the growth of soil microorganisms and decompose organic carbon in soil [38]. In this study, the addition of biochar and *Cipangopaludina chinensis* shell powder significantly increased soil organic carbon content, which was consistent with the research conclusions of Cross [39] and Zhao [35]. There was a significant positive correlation between soil pH and soil organic carbon content, indicating that soil organic carbon changes can be regulated by changing soil pH, mainly due to the positive or negative priming effect of pH on soil microbial activity [40]. The addition of orange peel biochar and *Cipangopaludina chinensis* shell powder significantly increased the content of MBC and DOC in the soil, orange peel biochar increased the content of ROC in the soil, and *Cipangopaludina chinensis* shell powder decreased the content of ROC in the soil, which was consistent with the results of Luo [41] and Li [40]. In the early stage of soil incubation, the biochar of orange peel residue and the powder of *Cipangopaludina chinensis* shell increased the MBC in the soil, and the pH value in the soil was positively correlated with MBC, indicating that the change of MBC was due to the increase in soil pH value caused by the addition of biochar and *Cipangopaludina chinensis* shell powder, which stimulated the reproduction of microorganisms in the soil, resulting in the increase of microbial biomass carbon in the soil [42], and also led to the increase in DOC content in the soil. The higher pH value of the *Cipangopaludina chinensis* shell powder can promote the life activities of microorganisms in the soil, and the organic carbon content of the orange peel residue biochar treatment was significantly higher than that of the *Cipangopaludina chinensis* shell powder treatment in the later stage of the incubation. Therefore, the soil MBC of the high proportion of orange peel residue biochar treatment (g2k1 and g3k1) was higher than that of the *Cipangopaludina chinensis* shell powder treatment (g1k3 and g1k2) in the later stage. In the g2k2 treatment, the soil pH value was the highest, and the organic carbon content was high, so the g2k2 soil microbial biomass carbon content was the highest. In this study, the content of DOC in soil treated with a high proportion of

orange peel residue biochar was higher than that in soil treated with a high proportion of *Cipangopaludina chinensis* shell powder. Under high pH conditions, some DOC was easily neutralized by other substances such as Ga and Mg in the soil, resulting in a decrease in soil DOC content [36].

4.3. Effects of Adding Different Proportions of Orange Peel Biochar and *Cipangopaludina chinensis* Shell Powder on Soil Enzyme Activities

The process of organic carbon change in the soil is an important microbial-mediated process. Soil microorganisms must catalyze the decomposition of soil organic matter by producing soil enzymes [12]. The activity of soil catalase can show the redox capacity of the soil, which is closely related to the conversion rate of soil organic matter [43]. Soil urease can act on the carbon-nitrogen bond in soil organic matter and hydrolyze ammonia or amino salt, carbon dioxide, and water. In high organic matter soil, urease activity is high [44]. Soil invertase activity can directly affect the stability of soil organic carbon and its storage in the environment by participating in the conversion of carbohydrates in the soil, providing sufficient energy for the growth and reproduction of soil organisms, and its activity changes can reflect the accumulation and decomposition of soil organic carbon [45]. In this study, the addition of different proportions of biochar and *Cipangopaludina chinensis* shell powder to the soil increased the activities of catalase, urease, and invertase in the soil to varying degrees, which was consistent with the results of Lu [46] and Song [47]. In the treatment, g4k0 and g2k2 had the highest increase in soil catalase activity, which may be because the application of biochar changed the physical structure of the soil and increased the soil water content, increasing catalase activity [48]. The soil urease activity in the treatment of adding *Cipangopaludina chinensis* shell powder was significantly higher than that in the treatment of a single biochar application. It is because the *Cipangopaludina chinensis* shell powder contains chitin, which provides a large amount of nitrogen source in the soil [49]. A large number of studies have shown that the higher the nitrogen content in the soil, the higher the soil urease activity [44]. Jiang et al. [50] added biochar to tea garden soil, which significantly increased soil sucrase activity, the same as the results of this study. He et al. [51] added exogenous calcium carbonate to brown soil for soil incubation soil, and the sucrase in the soil decreased. Contrary to the conclusion of this experimental study, it may be due to the addition of calcium carbonate to the *Cipangopaludina chinensis* shell powder. It also has chitin, which is an exogenous organic matter, that increases soil organic carbon and soil microbial activity, and soil sucrase activity depends on soil organic carbon [52].

5. Conclusions

Orange peel biochar was added to the soil to increase the content of organic carbon components and enzyme activities in the soil and promote organic carbon mineralization. The *Cipangopaludina chinensis* shell powder was added to the soil to increase SOC, MBC, DOC, urease activity, catalase activity, and sucrase activity in the soil, and decreased ROC and AK. The effect of *Cipangopaludina chinensis* shell powder on urease activity and sucrase activity in soil was better than that of orange peel residue biochar. Different proportions of orange peel residue biochar and *Cipangopaludina chinensis* shell powder had different effects on soil, and the treatment of g2k1 (2.6% orange peel residue biochar +1.3% *Cipangopaludina chinensis* shell powder) had the best effect on soil organic carbon components and enzyme activities. Compared with the control, the activities of SOC, MBC, DOC, ROC, catalase, urease, and sucrase in soil with 2.6% orange peel residue biochar +1.3% *Cipangopaludina chinensis* powder increased by 19.81%, 64.88%, 67.81%, 19.44%, 77.55%, 487.12%, and 406.62%. In this study, it was shown that both orange peel residue biochar and *Cipangopaludina chinensis* shell powder showed positive effects on soil. After compound application, the appropriate proportion promoted the conversion of organic carbon in soil compared with a single application. This study proves the

feasibility of adding orange peel and *Cipangopaludina chinensis* shell waste to orchard soil after treatment.

Author Contributions: L.H.: conceptualization and data curation. R.Q.: software, writing original draft preparation, and data curation. L.Z., H.D., and K.L.: data curation and supervision. X.H.: writing review, editing, and funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Guangxi Surface project, grant number [2022GXNS-FAA035555]. Guangxi Key Research and Development Program, grant number [AB22080097]. The Key Laboratory of Ecology of Rare and Endangered Species and Environmental Protection (Guangxi Normal University), Ministry of Education, China, grant number [ERESEP2022Z13].

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors without undue reservation.

Acknowledgments: We thank Yulong River Citrus Planting Core Demonstration Base in Yangshuo County, Guilin, for providing us with experimental materials.

Conflicts of Interest: The author declares no conflict of interest.

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