Effects of Applying Different Organic Materials on Grain Yield and Soil Fertility in a Double-Season Rice Cropping System

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Abstract: Double-cropping rice cultivation reduces soil fertility, and the extensive use of chemical fertilizers has harmful effects on both the environment and grain yield. The application of organic materials could be used as a practical strategy to maintain soil fertility and improve grain yield in a double-season rice cropping system. For this purpose, field experiments with six growing seasons over three years, from 2016 to 2018, were conducted to assess the effects of five organic materials (biochar, Chinese milk vetch, rice straw, rapeseed cake fertilizer, and manure) on the grain yield and soil fertility, aiming to save about 25% of the chemical nitrogen (N) fertilizer required for all rice growing stages. The result showed that, compared with CK (the most common dose of fertilizer in this study region; 100% chemical fertilizer without organic fertilizer), the grain yield and soil fertility of double-cropped rice were increased after applying organic fertilizers for three consecutive years. Specifically, the CRC treatment (Chinese milk vetch (10.77 t ha\(^{-1}\) in fresh)/rice straw (26.51 t ha\(^{-1}\) in fresh) + 75% chemical fertilizer) showed significantly higher rates of effective panicles (4.65–10.92%) and annual grain yield (8.00–8.82%). The total N, total phosphorus (P), total potassium (K), alkaline N, and available P content in the CRC soil were significantly increased by 11.85%, 12.22%, 15.08%, 23.32%, and 41.04%, respectively, relative to CK. The decomposition of the applied Chinese milk vetch and rice straw combined with 75% chemical fertilizer resulted in more soil humus (9.50 g kg\(^{-1}\)), humic acid (3.19 g kg\(^{-1}\)), fulvic acid (3.26 g kg\(^{-1}\)), and active organic carbon (5.78 g kg\(^{-1}\)) and a significantly higher carbon pool management index (13.5%), as well as significantly higher soil urease activity (18.10%) and acid phosphatase activity (17.64%). Therefore, in this study, Chinese milk vetch (10.77 t ha\(^{-1}\) in fresh)/rice straw (26.51 t ha\(^{-1}\) fresh) in the early rice season/rice straw (26.51 t ha\(^{-1}\) fresh) in the late rice season + 75% chemical fertilizer treatment was the optimal dose for the double-season rice cropping system. It resulted in higher rice yields and has the potential to be used for more sustainable soil fertility.

Keywords: organic materials; double-season rice cropping system; grain yield; soil fertility

1. Introduction

Rice feeds 65% of China’s population. China has an annual rice-sown area of about 30 million hectares and an annual yield of more than 200 million tons [1]. In 2021, China’s double-cropping rice area was about 9.47 million hectares, a decrease of 0.32 million hectares compared with 2020 [2]. Double-cropping rice production is crucial to global and national food security, but long-term chemical fertilizer application has led to soil acidification and fertility decline in Southern China, which is not conducive to long-term high and stable yields of double-cropped rice. It is necessary to improve soil fertility by applying soil amendments to maintain high rice quality and grain yield.

Numerous studies have shown that the application of organic materials as fertilizers could improve soil fertility and increase the grain yield. The combined application of organic materials and chemical fertilizers has a better effect on the rice growth, grain yield,
soil organic matter content, soil total nitrogen, available phosphorus, and available potassium content than either chemical fertilizer or organic fertilizer alone [3]. The application of organic materials significantly increases the soil pH, organic matter, alkaline nitrogen, available phosphorus, and potassium content. In addition, the application of organic materials reduces the soil bulk density, increases the number of soil microbial groups, improves the rice growth habitat, increases effective rice panicles, and increases rice dry matter accumulation, thus increasing the grain yield [4]. Meanwhile, it has been reported that the uptake of nitrogen, phosphorus, and potassium in the aboveground parts of rice, as well as the grain yield, is significantly increased following the application of organic materials [5]. In addition, applying organic materials could increase the seed-setting rate; harvest index of rice; and productivity of nitrogen, phosphorus, and potassium [6]. To date, most studies have focused on the effect of a single organic material on soil improvement, and there are few comparative studies on improving soil by replacing chemical fertilizers with different organic materials.

Many organic materials could be used to improve soil fertility and increase the rice yield, and combined applications of different organic materials with chemical fertilizers could lead to different effects on grain yield and soil fertility. Thus, a field experiment over six consecutive rice seasons from 2016 to 2018 was conducted to assess the dry matter accumulation, grain yield, changes in soil nutrients, and soil carbon pools. Five common organic materials in this study region were involved, namely biochar, Chinese milk vetch, rice straw, rapeseed cake, and manure. The objective of this study was to explore the potential effects of these treatments on rice growth characteristics and soil fertility. The fertilization heterogeneity of different organic materials was compared and studied. The effects of different organic materials (i.e., biochar, Chinese milk vetch, manure, rice straw, and rape seed cake), which were applied in both early- and late-season rice, on the season’s grain yield and soil fertility were clarified, and it was proven that the combined application of organic and inorganic fertilizers (i.e., replacing some inorganic fertilizer with organic fertilizer) was beneficial to maintain a continuous high grain yield and soil fertility in a double-season rice cropping system.

2. Materials and Methods

2.1. Trial Design

2.1.1. Trial Materials and Locations

The experiments were conducted in the growing seasons from 2016 to 2018 in Yanxi Town, Liuyang, Hunan Province, which is a typical double-cropping rice area. The soil type was loam soil, and the total N, total P, and total K contents of the soil were 1.09 g kg\(^{-1}\), 0.60 g kg\(^{-1}\), and 9.53 g kg\(^{-1}\), respectively. The contents of alkaline N, available P, and available K were 115.00 mg kg\(^{-1}\), 42.08 mg kg\(^{-1}\), and 72.75 mg kg\(^{-1}\), respectively. The soil organic matter content was 27.95 g kg\(^{-1}\), and the pH was 5.63. The rice varieties were Zhongzao 39 in the early rice season and Taiyou 390 in the late rice season. The biochar, which was purchased from Hunan Zhengheng Agricultural Technology Co., Ltd. (Changsha, China), was pyrolyzed at 500 °C, 9.53 pH. The manure was a commercial fertilizer, which was purchased from Xingyue Agricultural Technology Co., Ltd. (Yongkang, China). The rape seed cake, which was purchased from Hunan Loudi Tianzhuiyuan Oil Press. The main nutrients (dry basis) of different organic materials are listed in Table 1.

| Organic Materials          | Carbon (g kg\(^{-1}\)) | Total N (g kg\(^{-1}\)) | Total P (g kg\(^{-1}\)) | Total K (g kg\(^{-1}\)) | C/N     |
|---------------------------|-------------------------|--------------------------|--------------------------|--------------------------|---------|
| Biochar                   | 660.95                  | 1.39                     | 2.33                     | 3.04                     | 475.80  |
| Chinese milk vetch        | 402.4                   | 34.82                    | 3.93                     | 27.78                    | 11.56   |
| Rapeseed cake fertilizer  | 245.82                  | 52.96                    | 12.86                    | 13.85                    | 4.64    |
| Manure                    | 428.21                  | 21.33                    | 15.95                    | 27.23                    | 20.08   |
| Rice straw                | 443.38                  | 10.88                    | 1.35                     | 19.7                     | 40.75   |
2.1.2. Experiment Design

Five treatments were set up: BC (biochar + 75% chemical fertilizer), CRC (Chinese milk vetch (early rice season)/rice straw (late rice season) + 75% chemical fertilizer), RC (rapeseed cake + 75% chemical fertilizer), MC (manure + 75% chemical fertilizer), and CK (the most common dose of fertilizer in this study region; 100% chemical fertilizer without organic fertilizer). The N applied was set to 150 kg ha\(^{-1}\), and organic materials replaced 25% of the N applied in each organic material treatment. All organic materials were used as a base fertilizer that was spread into the plot evenly about two weeks before transplanting in the early rice season and three days before transplanting in the late rice season. The usage of biochar, Chinese milk vetch (fresh), rice straw (fresh), rape seed cake, and manure was 26.98 t ha\(^{-1}\), 10.77 t ha\(^{-1}\), 26.51 t ha\(^{-1}\), 0.72 t ha\(^{-1}\), and 1.76 t ha\(^{-1}\), respectively. The N applied was set at a ratio of 5:3:2 (base fertilizer: tillering fertilizer: panicle fertilizer) for each season. The base chemical N fertilizer was a compound fertilizer (N:P\(_2\)O\(_5\):K\(_2\)O; 15:15:15), and the topdressing chemical N fertilizer was urea (N: 46%). For all the treatments, the fertilizers P and K were 75 kg ha\(^{-1}\) and 150 kg ha\(^{-1}\), respectively. The P fertilizer was calcium superphosphate (P\(_2\)O\(_5\); 12%), and the K fertilizer was potassium chloride (K\(_2\)O; 60%). All the P was applied as the base fertilizer each season. The K was used at a rate of 6:4 at the transplanting and heading stages. All the treatments had the same timetable for fertilizer application in the same season.

In 2016–2018, early-season rice seeds were sown from 20 March to 23 March and transplanted from 20 April to 26 April; late-season rice seeds were sown from 18 June to 27 June and transplanted from 16 July to 25 July. All rice straws were moved out of the plot. The area of each planted plot was 220 m\(^2\), and each experiment was conducted in triplicate. Each plot was blocked by plastic-covered benches to prevent the exchange of water and fertilizers between different treatments. Separated water inlets and outlets were constructed at each planted plot. Other field management practices were consistent with local practices in a double-season rice cropping system, including weed, pest, and disease control.

2.2. Measurement Items and Methods

2.2.1. Grain Yield

At maturity, 3 m\(^2\) of rice plants for each treatment were harvested in each growing season during 2016–2018 to determine the rice yield, and the moisture content of all grains was adjusted to 13.50%. A total of 50 hills per sample were sampled to count the effective tillers per hill, and 10 hills with average effective tillers were used to test the weight of filled and empty grains. The weight of a 1000 grains per sample was measured in 3 replications, and then, we converted the weight to the number of filled and empty grains. We dried the filled and empty grains at 70 °C to a constant weight and then computed the number of spikelet per panicle, seed-setting rate, and 1000-grain weight.

2.2.2. Dry Matter Accumulation

Samples of each treatment were taken in three replicates at the tillering stage, the booting stage, the full heading stage, the mid-filling stage, and the mature stage. According to the number of average effective tillers, 10 representative hills were selected from each plot. The plants aboveground were dried at 105 °C for 30 min and then dried to a constant weight at 70 °C to test the dry matter weight.

2.2.3. Soil Nutrient Determination

The five-point sampling method was used to take the full-layer soil at the mature stage. The soil total nutrient content, available nutrient content, and soil enzyme activity were determined after air drying, grinding, and sieving. The soil was digested with H\(_2\)SO\(_4\)-H\(_2\)O\(_2\), and the total N and total P were determined by a flow analyzer [7], while the total K was determined by a flame spectrophotometer [8]. The soil organic matter (SOM) was determined by a potassium dichromate external heating method [9], and the active
organic carbon (AOC) in the soil was determined by the potassium permanganate oxidation method [10]. The alkaline nitrogen was determined by the alkali diffusion method, the available phosphorus was determined by the molybdenum–antimony anti-colorimetric method, and the available potassium was determined by an ammonium acetate extraction flame photometer [11].

2.2.4. Soil Enzyme Activity Determination

Soil urease and soil acid phosphatase activities were measured by the colorimetric method [12].

2.2.5. Carbon Pool Management Index (CPMI)

In 2018, the soil samples were collected at the mature stage in the late rice season to determine the soil total organic carbon content by the potassium dichromate external heating method [9], and the soil active organic carbon content was measured by the potassium permanganate oxidation method [10]. The calculation formula of CPMI is as follows:

\[
\text{Steady-state carbon} = \text{total organic carbon} - \text{active organic carbon} \tag{1}
\]

\[
\text{Carbon pool index (CPI)} = \frac{\text{field soil organic carbon}}{\text{reference field soil organic carbon}} \tag{2}
\]

\[
\text{Carbon pool activity (CPA)} = \frac{\text{active carbon}}{\text{steady-state carbon}} \tag{3}
\]

\[
\text{Carbon pool activity index (CPAI)} = \frac{\text{carbon pool activity of farmland}}{\text{carbon pool activity of reference soil}} \tag{4}
\]

\[
\text{Carbon pool management index (CPMI)} = \text{carbon pool index} \times \text{carbon pool activity index} \times 100 \tag{5}
\]

2.2.6. Soil Humus Carbon Fraction Determination

At the mature stage of late-season rice during the growing season in 2018, a five-point sampling method was used to determine the soil humus composition after air drying and sieving. The humus composition was extracted by the humus composition modification method [9,13]. The extractant was a mixture of 0.1 mol L\(^{-1}\) sodium pyrophosphate and 0.1 mol L\(^{-1}\) sodium hydroxide (pH = 13). The carbon content of humus (HE) and humic acid (HA) was determined by the potassium dichromate oxidation method, and the carbon content of fulvic acid (FA) was obtained by the difference subtraction method—that is, the carbon content of FA = the carbon content of HE - the carbon content of HA. PQ = the carbon content of HA/carbon content of HE. The HA sample was extracted and purified by the IHSS method. The air-dried soil sample was extracted using a 0.1 mol L\(^{-1}\) NaOH solution, and the extract was acidified to pH 1.5 using HCl to obtain a crude HA. After that, the HA dry sample was obtained via centrifugation, electrodialysis, rotary evaporation, and lyophilization, as described in [14].

2.3. Statistical Analysis

Each sample was analyzed in triplicate. The data were evaluated by one-way analysis of variance (ANOVA) in SPSS v25.0 (SPSS, Inc., Chicago, IL, USA). For separate means, the Duncan multiple range test was used. Significance was accepted at \(p \leq 0.05\).

3. Results

3.1. Grain Yield and Dry Matter Accumulation

3.1.1. Grain Yield

Applying organic materials to a field increased the effective panicles and grain yield of double-season cropping rice in the growing seasons of 2016–2018 (Table 2). However, these materials have different effects on the spikelet per panicle, 1000-grain weight, and seed-setting rate. Compared with CK, in the early rice seasons of 2016–2018, the effective panicles of BC and CRC were both increased significantly, while the seasonal effective
panicles were increased by 10.92% and 4.65% on average, respectively. In the late rice season of 2016–2018, BC significantly increased the effective panicles. BC and CRC increased the effective panicles by 8.00% and 8.82%, respectively. In addition, the grain yield of both BC and CRC were significantly increased. The seasonal grain yields of BC and CRC were increased by averages of 15.79% and 16.87% in the early rice season and by averages of 16.32% and 13.75% in the late rice season, respectively. BC and CRC increased the annual grain yield by 16.06% and 15.28%, respectively. CRC increased the grain yield more than BC in the early rice seasons in 2017 and 2018.

Table 2. Grain yields under different organic material treatments in 2016–2018.

| Year | Season       | Treatment | Effective Panicles \(\times 10^4\) ha\(^{-1}\) | Spikelet per Panicle | 1000-Grain Weight (g) | Seed-Setting Rate (%) | Grain Yield (t ha\(^{-1}\)) |
|------|--------------|-----------|-----------------------------------------------|---------------------|----------------------|-----------------------|---------------------------|
| 2016 | Early-season rice | BC        | 358.85 a                                      | 113.41 a            | 25.99 ab             | 81.11 a               | 8.07 a                    |
|      |              | CRC       | 350.78 a                                      | 109.01 a            | 25.39 b              | 83.33 a               | 7.72 b                    |
|      |              | RC        | 338.69 ab                                     | 114.92 a            | 26.24 ab             | 81.13 a               | 7.84 b                    |
|      |              | MC        | 346.75 ab                                     | 113.76 a            | 25.33 b              | 81.52 a               | 7.77 b                    |
|      |              | CK        | 318.53 b                                      | 110.62 a            | 26.52 a              | 82.22 a               | 7.16 c                    |
|      | Late-season rice | BC       | 348.88 a                                      | 125.82 a            | 25.25 a              | 72.01 b               | 7.87 a                    |
|      |              | CRC       | 368.48 a                                      | 113.29 c            | 25.33 a              | 73.12 b               | 7.65 a                    |
|      |              | RC        | 358.09 a                                      | 117.75 b            | 25.40 a              | 72.22 b               | 7.45 ab                   |
|      |              | MC        | 342.22 a                                      | 112.40 c            | 25.08 a              | 78.89 a               | 7.35 ab                   |
|      |              | CRC       | 321.44 b                                      | 110.20 c            | 25.22 a              | 76.09 c               | 6.66 b                    |
| 2017 | Early-season rice | BC        | 377.60 a                                      | 106.78 c            | 25.62 b              | 73.20 ab              | 6.87 a                    |
|      |              | CRC       | 332.84 b                                      | 109.91 b            | 26.36 a              | 82.81 a               | 7.12 a                    |
|      |              | RC        | 339.21 b                                      | 110.03 b            | 25.52 b              | 78.00 a               | 6.4 ab                    |
|      |              | MC        | 339.23 b                                      | 116.78 a            | 25.33 b              | 70.81 b               | 6.29 ab                   |
|      |              | CK        | 320.00 c                                      | 110.80 b            | 24.86 c              | 78.00 a               | 6.09 b                    |
|      | Late-season rice | BC       | 387.37 a                                      | 112.84 ab           | 26.18 a              | 74.02 b               | 8.06 a                    |
|      |              | CRC       | 362.11 b                                      | 112.42 ab           | 26.28 a              | 78.00 a               | 7.93 a                    |
|      |              | RC        | 362.11 b                                      | 119.27 a            | 25.67 a              | 74.00 b               | 7.58 ab                   |
|      |              | MC        | 378.95 ab                                     | 109.86 b            | 25.66 a              | 72.45 b               | 7.23 b                    |
|      |              | CRC       | 355.71 b                                      | 118.42 a            | 24.97 b              | 72.03 b               | 6.92 b                    |
| 2018 | Early-season rice | BC        | 345.97 a                                      | 106.30 a            | 25.83 a              | 82.45 a               | 7.64 a                    |
|      |              | CRC       | 337.66 a                                      | 111.65 a            | 25.65 a              | 83.71 a               | 7.95 a                    |
|      |              | RC        | 345.45 a                                      | 105.12 a            | 25.89 a              | 79.24 a               | 6.92 b                    |
|      |              | MC        | 348.11 a                                      | 109.19 a            | 25.58 a              | 75.95 a               | 6.43 b                    |
|      |              | CK        | 311.69 b                                      | 109.16 a            | 25.60 a              | 77.66 a               | 6.25 b                    |
|      | Late-season rice | BC       | 345.41 b                                      | 116.21 a            | 26.01 ab             | 80.00 ab              | 7.59 a                    |
|      |              | CRC       | 359.29 a                                      | 113.20 a            | 26.52 a              | 77.34 b               | 7.42 a                    |
|      |              | RC        | 360.12 a                                      | 106.00 b            | 25.57 a              | 81.21 a               | 7.25 ab                   |
|      |              | MC        | 335.78 bc                                     | 116.65 a            | 25.94 ab             | 79.38 ab              | 7.00 b                    |
|      |              | CK        | 324.37 c                                      | 105.41 b            | 26.09 ab             | 76.41 b               | 6.64 c                    |

All treatments were compared in the same season of the same year, different letters within a column represent significant differences at \(p < 0.05\).

3.1.2. Dry Matter Accumulation

Compared with CK, the application of organic materials in the early rice season increased the dry matter accumulation, except during the tillering stage (Table 3). The application of organic materials in the late rice season increased the dry matter accumulation at all growing stages. At the mature stage in 2016, BC increased the dry matter accumulation by 12.39% and 14.76% in the early and late seasons, respectively, compared with CK. In the growing seasons in 2017, BC increased the dry matter accumulation by 11.21% and 11.71%, respectively, whereas it was increased by 26.80% and 21.46% with BC in the growing seasons in 2018.

Compared with CK, in 2016, CRC increased the dry matter by 7.77% and 12.39% at the mature stage in the early and late seasons, respectively. The dry matter under CRC was increased by 17.53% and 9.67% in 2017, respectively, while CRC increased the dry matter by 26.96% and 20.57% in 2018.
Table 3. Dry matter accumulation under different organic material treatments in 2016–2018 (t ha\(^{-1}\)).

| Year  | Season       | Treatment | Tillering Stage | Booting Stage | Full Heading Stage | Mid-Filling Stage | Mature Stage |
|-------|--------------|-----------|-----------------|---------------|--------------------|------------------|--------------|
| 2016  | Early-season | BC        | 1.22 a          | 6.92 b        | 10.53 a            | 12.68 a          | 15.33 a      |
|       |              | CRC       | 1.07 b          | 7.00 b        | 10.39 a            | 12.56 a          | 14.70 b      |
|       |              | RC        | 1.16 ab         | 7.57 a        | 10.22 ab           | 12.31 a          | 15.65 a      |
|       |              | MC        | 1.14 ab         | 6.65 c        | 10.16 ab           | 12.38 a          | 15.13 a      |
|       |              | CK        | 1.25 a          | 6.36 c        | 9.68 b             | 11.78 b          | 13.64 c      |
|       | Late-season  | BC        | 2.50 a          | 7.56 a        | 10.99 a            | 12.52 a          | 14.54 a      |
|       |              | CRC       | 2.27 b          | 7.62 a        | 11.05 a            | 12.38 a          | 14.24 a      |
|       |              | RC        | 2.03 bc         | 7.02 b        | 10.49 b            | 12.31 a          | 14.20 a      |
|       |              | MC        | 2.08 bc         | 6.95 b        | 10.51 b            | 11.25 b          | 14.08 ab     |
|       |              | CK        | 1.83 c          | 6.34 c        | 9.47 c             | 11.06 b          | 12.67 b      |
| 2017  | Early-season | BC        | 1.29 a          | 7.22 a        | 9.44 b             | 12.24 a          | 13.89 b      |
|       |              | CRC       | 1.07 b          | 7.44 a        | 9.97 a             | 12.40 a          | 14.68 a      |
|       |              | RC        | 1.29 a          | 6.82 b        | 9.19 b             | 12.09 ab         | 13.43 b      |
|       |              | MC        | 1.28 a          | 6.52 bc       | 9.30 b             | 11.24 b          | 12.99 c      |
|       |              | CK        | 1.23 a          | 6.24 c        | 8.56 c             | 11.07 b          | 12.49 d      |
|       | Late-season  | BC        | 1.64 b          | 7.42 a        | 11.34 a            | 13.44 a          | 15.36 a      |
|       |              | CRC       | 1.58 b          | 7.21 a        | 10.96 b            | 13.42 a          | 15.08 a      |
|       |              | RC        | 1.75 a          | 7.27 a        | 11.26 a            | 12.68 b          | 14.91 a      |
|       |              | MC        | 1.57 b          | 6.98 b        | 11.02 b            | 12.58 b          | 14.58 ab     |
|       |              | CK        | 1.49 c          | 6.89 b        | 10.33 c            | 12.08 c          | 13.75 b      |
| 2018  | Early-season | BC        | 1.47 a          | 6.39 a        | 8.09 a             | 12.06 a          | 15.33 a      |
|       |              | CRC       | 1.38 a          | 5.89 ab       | 7.08 b             | 11.48 ab         | 15.35 a      |
|       |              | RC        | 1.39 a          | 5.40 b        | 8.75 a             | 11.53 ab         | 14.33 ab     |
|       |              | MC        | 1.50 a          | 5.46 b        | 8.18 a             | 11.21 ab         | 13.10 ab     |
|       |              | CK        | 1.44 a          | 5.16 b        | 7.09 b             | 10.72 b          | 12.09 b      |
|       | Late-season  | BC        | 1.90 a          | 7.56 a        | 9.48 b             | 12.70 a          | 14.94 a      |
|       |              | CRC       | 1.76 ab         | 6.74 ab       | 10.32 a            | 12.02 ab         | 14.83 a      |
|       |              | RC        | 1.79 ab         | 7.14 a        | 9.07 b             | 12.85 a          | 14.74 a      |
|       |              | MC        | 1.96 a          | 6.17 b        | 9.33 b             | 12.22 ab         | 14.38 ab     |
|       |              | CK        | 1.52 b          | 5.45 c        | 8.43 b             | 11.26 b          | 12.30 b      |

All treatments were compared in the same season of the same year, different letters within a column represent significant differences at \( p < 0.05 \).

3.2. Soil Fertility under Different Organic Material Treatments

3.2.1. Soil alkaline N

The application of organic materials increased the soil alkaline nitrogen content in all six rice cropping seasons, and there was a significant increase in the late rice season over the three consecutive years (Table 4). The average soil alkaline content of CK was 114.38 mg kg\(^{-1}\) in the early rice season over the three years. Compared with CK, the average soil alkaline nitrogen contents of BC, CRC, RC, and MC were increased by 18.49%, 15.98%, 6.07%, and 9.14%, respectively.

In the late rice season over three years, the average soil alkaline content of CK was 108.40 mg kg\(^{-1}\). Compared with CK, the average soil alkaline nitrogen contents of BC, CRC, RC, and MC increased by 16.30%, 18.78%, 12.74%, and 12.53%, respectively.

3.2.2. Soil Available P

Over three consecutive years, the application of organic material showed that it had no effects on the accumulation of soil available phosphorus year by year (Table 4). However, it increased the soil available phosphorus content each year when compared with CK. For example, in the late rice season of 2018, the soil available phosphorus contents of BC, CRC, RC, and MC were increased by 16.52 mg kg\(^{-1}\), 18.15 mg kg\(^{-1}\), 14.07 mg kg\(^{-1}\),
and 12.24 mg kg\(^{-1}\), respectively. In addition, BC and CRC significantly increased the soil available phosphorus content in all six rice seasons over three years. The soil available phosphorus of BC and CRC was increased by 11.43 mg kg\(^{-1}\) and 12.91 mg kg\(^{-1}\) in the early rice season of 2016, respectively, and by 7.81 mg kg\(^{-1}\) and 10.19 mg kg\(^{-1}\) in the late rice season of 2016. The soil available phosphorus of BC and CRC was increased by 21.98 mg kg\(^{-1}\) and 24.31 mg kg\(^{-1}\) in the early rice season of 2017, respectively, and by 17.56 mg kg\(^{-1}\) and 23.34 mg kg\(^{-1}\) in the late rice season of 2017. The soil available phosphorus of BC and CRC was increased by 21.33 mg kg\(^{-1}\) and 24.88 mg kg\(^{-1}\) in the early rice season of 2018, respectively, and by 16.52 mg kg\(^{-1}\) and 18.15 mg kg\(^{-1}\) in the late rice season of 2018.

### Table 4. Soil alkaline N, available P, and available K under different organic material treatments (mg kg\(^{-1}\)).

| Year | Season       | Treatment | Alkaline N | Available P | Available K |
|------|--------------|-----------|------------|-------------|-------------|
| 2016 | Early-season rice | BC  | 134.24 a | 55.22 a | 108.42 b |
|      |               | CRC      | 123.68 b | 56.70 a | 105.16 b |
|      |               | RC       | 119.49 b | 52.99 a | 116.30 a |
|      |               | MC       | 120.53 b | 51.33 a | 105.40 b |
|      |               | CK       | 116.81 b | 43.79 b | 97.86 c  |
|      | Late-season rice | BC  | 122.50 a | 50.05 a | 107.06 a |
|      |               | CRC      | 125.57 a | 52.43 a | 105.38 a |
|      |               | RC       | 116.20 b | 49.76 a | 108.75 a |
|      |               | MC       | 122.12 a | 47.73 ab | 99.45 b  |
|      |               | CK       | 109.36 c  | 42.24 b  | 95.99 c  |
| 2017 | Early-season rice | BC  | 136.88 a | 64.03 a | 107.25 b |
|      |               | CRC      | 135.45 a | 66.36 a | 105.75 b |
|      |               | RC       | 126.28 b | 59.38 ab | 115.60 a |
|      |               | MC       | 131.86 a | 61.74 ab | 112.50 a |
|      |               | CK       | 118.82 c  | 42.05 b  | 103.95 b |
|      | Late-season rice | BC  | 124.16 a | 61.25 b  | 101.58 a |
|      |               | CRC      | 127.32 a | 67.03 a  | 97.77 b  |
|      |               | RC       | 122.82 a | 60.96 b  | 111.84 a |
|      |               | MC       | 120.91 a | 59.12 b  | 109.00 a |
|      |               | CK       | 107.69 b | 43.69 c  | 94.15 b  |
| 2018 | Early-season rice | BC  | 135.46 a | 64.58 ab | 116.55 bc |
|      |               | CRC      | 138.85 a | 68.13 a  | 109.88 c |
|      |               | RC       | 118.20 b | 63.70 ab | 123.22 b |
|      |               | MC       | 122.12 b | 60.65 b  | 148.57 a |
|      |               | CK       | 107.51 c  | 43.25 c  | 96.53 d  |
|      | Late-season rice | BC  | 131.56 a | 60.74 a  | 105.56 bc |
|      |               | CRC      | 133.38 a | 62.37 a  | 102.31 bc |
|      |               | RC       | 127.61 b | 58.29 a  | 110.32 b |
|      |               | MC       | 122.92 b | 56.46 a  | 120.91 a |
|      |               | CK       | 108.16 c  | 44.22 b  | 99.20 c  |

All treatments were compared in the same season of the same year, different letters within a column represent significant differences at \(p < 0.05\).

#### 3.2.3. Soil Available K

Compared with CK, the application of organic materials increased the soil available potassium content (Table 4). In 2016, except for CRC, the soil available potassium content in the early rice season was higher than in the late rice season. In 2017 and 2018, the soil available potassium contents in the early rice season were higher than those in the late rice season, except for CK. In 2016, BC and RC increased the available potassium by 10.79% and 18.84% in the early rice season and by 11.53% and 13.29% in the late rice season, respectively. In 2017, BC and RC increased the available potassium by 3.17% and 11.21% in the early rice season and by 7.89% and 18.79% in the late rice season. In 2018, BC and RC increased...
the available potassium by 20.74% and 27.65% in the early rice season and by 6.41% and 11.21% in the late rice season.

3.2.4. Soil Total N, Total P, Total K, and SOM

Compared with CK, the application of organic materials increased the soil total nitrogen content of BC, CRC, RC, and MC by 0.10–0.11 g kg$^{-1}$, 0.12–0.13 g kg$^{-1}$, 0.09–0.12 g kg$^{-1}$, and 0.08–0.09 g kg$^{-1}$, respectively (Table 5). Additionally, the soil total phosphorus content of the BC, CRC, RC, and MC were increased by 0.05–0.07 g kg$^{-1}$, 0.06–0.08 g kg$^{-1}$, 0.07–0.09 g kg$^{-1}$, and 0.05–0.08 g kg$^{-1}$, respectively. The soil total potassium content of BC, CRC, RC, and MC were increased by 1.00–1.17 g kg$^{-1}$, 1.14–1.44 g kg$^{-1}$, 0.63–0.66 g kg$^{-1}$, and 0.81–0.85 g kg$^{-1}$, respectively. CRC had better effects on the soil total N, P, and K than the other treatments in this study. The SOM content of BC and CRC were increased significantly by 14.92% and 10.75%, respectively. In general, among the four organic material treatments, BC was better able to increase the SOM content than the other treatments.

Table 5. The total N, P, K, and SOM under different organic material treatments in 2018 (g kg$^{-1}$).

| Treatment | Total N | Total P | Total K | SOM  |
|-----------|---------|---------|---------|------|
|           | Early-Season Rice | Late-Season Rice | Early-Season Rice | Late-Season Rice | Early-Season Rice | Late-Season Rice | Late-Season Rice |
| BC        | 1.19 a | 1.19 a | 0.66 a | 0.67 a | 10.52 a | 10.72 a | 36.89 a |
| CRC       | 1.21 a | 1.21 a | 0.67 a | 0.68 a | 10.66 a | 10.99 a | 35.55 a |
| RC        | 1.18 a | 1.20 a | 0.68 a | 0.69 a | 10.15 a | 10.21 ab | 32.17 b |
| MC        | 1.17 a | 1.17 a | 0.66 a | 0.68 a | 10.33 a | 10.40 ab | 32.55 ab |
| CK        | 1.09 b | 1.08 b | 0.61 b | 0.60 b | 9.52 b | 9.55 b | 32.10 b |

Different letters within a column represent significant differences at $p < 0.05$.

3.2.5. Soil Carbon Pools

After three years of the application of organic materials, the total organic carbon (TOC) content, active organic carbon (AOC) content, carbon pool index (CPI), and carbon pool management index (CPMI) of the soil were higher than those of CK (Table 6). In terms of the TOC content, BC > CRC > MC > RC > CK, and in terms of the (AOC) content, CRC > BC > MC > RC > CK. The TOC content was significantly increased by BC (21.63%) and CRC (10.62%). BC, CRC, and MC significantly increased the AOC content by 11.69%, 12.67%, and 11.50%, respectively. BC and CRC significantly increased the CPI by 21.00% and 11.00%, respectively. CRC and MC significantly improved the soil CPMI by 13.50% and 16.28%, respectively.

Table 6. Soil carbon pools under different organic material treatments in 2018.

| Treatment | AOC (g kg$^{-1}$) | TOC (g kg$^{-1}$) | CPA | CPAI | CPI | CPMI |
|-----------|-------------------|------------------|-----|------|-----|------|
| BC        | 5.73 a            | 22.56 a          | 0.34 b | 0.90 b | 1.21 a | 108.53 b |
| CRC       | 5.78 a            | 20.62 a          | 0.39 a | 1.03 a | 1.11 a | 113.50 a |
| RC        | 5.55 ab           | 18.86 b          | 0.42 a | 1.10 b | 1.01 b | 110.83 ab |
| MC        | 5.72 a            | 18.87 b          | 0.44 a | 1.15 a | 1.01 b | 116.28 a |
| CK        | 5.13 b            | 18.64 b          | 0.38 a | 1.00 b | 1.00 b | 100.00 b |

Different letters within a column represent significant differences at $p < 0.05$.

3.2.6. Soil Humus

Compared with the CK, the application of organic materials increased the content of humic acid (HA), fulvic acid (FA), humin (HM), and PQ in the soil (Table 7). BC increased the HA, HM, and HA/FA by 0.91 g kg$^{-1}$, 3.45 g kg$^{-1}$, and 0.33 g kg$^{-1}$, respectively. CRC increased the FA by 0.17 g kg$^{-1}$. The differences in HA and HM between BC and CK were extremely significant. The differences in FA between the five treatments was not significant. The differences in PQ between CK and the other treatments were significant.
Table 7. Soil humus under different organic material treatments in 2018 (g kg\(^{-1}\)).

| Treatment | HA    | FA    | HM    | HA/FA | PQ %  |
|-----------|-------|-------|-------|-------|-------|
| BC        | 3.70 a| 3.10 a| 12.21 a| 1.23 a| 19.85 a|
| CRC       | 3.19 b| 3.26 a| 9.50 b | 0.98 ab| 19.98 a|
| RC        | 3.00 b| 3.25 a| 8.80 c | 0.94 ab| 19.93 a|
| MC        | 3.10 b| 3.11 a| 9.24 b | 0.99 ab| 20.06 a|
| CK        | 2.79 c| 3.09 a| 8.76 c | 0.90 b | 18.97 b|

Different letters within a column represent significant differences at \( p < 0.05 \).

3.2.7. Soil Enzyme Activity

The application of organic materials increased the soil urease activity in different years and different rice seasons (Table 8). In the growing seasons in 2016, CRC increased the soil urease activity by 31.19% and 44.03% in the early and late rice seasons, respectively. In 2017, CRC and RC had a better effect on improving the soil urease activity in both the early and late seasons. In 2018, CRC increased the soil urease activity by 18.34% and 18.10% in the early and late rice seasons, respectively. There were great effects of CRC on improving the soil urease activity in the 2018 growing season. In summary, in three years, CRC had the highest efficiency and best effects on improving the soil urease activity.

Table 8. Soil enzyme activity under different organic material treatments.

| Year | Season          | Treatment | Soil Urease Activity (mg d\(^{-1}\) g\(^{-1}\)) | Soil Acid Phosphates Activity (µmol d\(^{-1}\) g\(^{-1}\)) |
|------|-----------------|-----------|-----------------------------------------------|--------------------------------------------------|
|      |                 |           |                                               |                                                  |
| 2016 | Early-season rice | BC       | 1.25 b                                        | 23.76 b                                          |
|      |                  | CRC      | 1.43 a                                        | 24.50 a                                          |
|      |                  | RC       | 1.28 b                                        | 23.13 b                                          |
|      |                  | MC       | 1.39 a                                        | 22.28 c                                          |
|      |                  | CK       | 1.06 c                                        | 21.57 d                                          |
|      | Late-season rice | BC       | 1.24 b                                        | 21.88 bc                                         |
|      |                  | CRC      | 1.57 a                                        | 25.43 a                                          |
|      |                  | RC       | 1.22 b                                        | 23.54 b                                          |
|      |                  | MC       | 1.18 c                                        | 24.89 ab                                         |
|      |                  | CK       | 1.03 c                                        | 20.45 c                                          |
| 2017 | Early-season rice | BC       | 1.27 b                                        | 22.52 b                                          |
|      |                  | CRC      | 1.47 a                                        | 23.43 a                                          |
|      |                  | RC       | 1.39 a                                        | 24.09 a                                          |
|      |                  | MC       | 1.24 b                                        | 23.13 a                                          |
|      |                  | CK       | 1.11 b                                        | 21.10 c                                          |
|      | Late-season rice | BC       | 1.22 b                                        | 22.74 ab                                         |
|      |                  | CRC      | 1.38 a                                        | 23.48 a                                          |
|      |                  | RC       | 1.31 a                                        | 23.12 a                                          |
|      |                  | MC       | 1.30 a                                        | 22.67 ab                                         |
|      |                  | CK       | 1.14 b                                        | 18.53 b                                          |
| 2018 | Early-season rice | BC       | 1.18 a                                        | 22.23 b                                          |
|      |                  | CRC      | 1.29 a                                        | 23.12 ab                                         |
|      |                  | RC       | 1.22 a                                        | 24.37 a                                          |
|      |                  | MC       | 1.23 a                                        | 23.73 a                                          |
|      |                  | CK       | 1.09 b                                        | 20.86 c                                          |
|      | Late-season rice | BC       | 1.19 b                                        | 21.56 b                                          |
|      |                  | CRC      | 1.37 a                                        | 23.21 a                                          |
|      |                  | RC       | 1.25 b                                        | 23.58 a                                          |
|      |                  | MC       | 1.25 b                                        | 22.88 ab                                         |
|      |                  | CK       | 1.16 b                                        | 19.73 c                                          |

All treatments were compared in the same season of the same year, different letters within a column represent significant differences at \( p < 0.05 \).

In 2016, CRC, RC, and MC significantly increased the soil acid phosphatase activity in both the early and late rice seasons. CRC increased the soil acid phosphate by 13.58% and 24.35% in the early and late rice seasons of 2016, while it increased the soil acid phosphate
by 11.04% and 26.71% in the early and late seasons of 2017, respectively, and increased the soil phosphate by 10.83% and 17.64% in 2018. All four organic material treatments significantly increased the soil acid phosphatase activity in 2018, while RC had the highest soil acid phosphatase activity, with an increase of 24.77% and 16.83% in the early and late rice seasons, respectively. In general, the application of organic materials increased the soil acid phosphatase activity in six rice seasons over three years. CRC and RC had better effects on the soil acid phosphatase activity than BC and MC.

4. Discussion

4.1. Effects of Different Organic Materials on Grain Yield

Fertilization is an important technology in crop production, which could significantly improve the grain yield per unit area, and the combined application of organic and inorganic fertilizers is an effective cultivation measure to gain sustainable high rice yields [15]. Returning organic materials to the field could increase the rice leaf area index, improve the photosynthetic capacity of rice functional leaves [16], prolong the photosynthetic time of rice leaves, and promote dry matter accumulation [17]. High dry matter accumulation is the basis of high yields, which is very important for rice yield increase. According to the results in Tables 2 and 3, the four organic material treatments improved rice dry matter accumulation and the grain yield. The reason why organic material application increased the crop yield might be that it improved the yield constituent factors, mainly manifested as increasing the rice effective panicle number, spikelet number per panicle, and seed-setting rate. In addition, it was reported that the combined application of Chinese milk vetch + chemical fertilizer significantly increased the effective panicles and seed-setting rate of double-cropping rice [18], which was consistent with our experimental results, because organic materials brought a lot of nutrients to the soil for rice after its decomposition. However, other studies showed that, with an increase in the dose of green manure, the effective panicles decreased significantly, while spikelet per panicle and the seed-setting rate increased [19]. This might be because, in the decomposing process of green manure, a large number of microorganisms competed with rice for nitrogen. Therefore, the rice tiller initiation was inhibited, and the backward-shift of the fertilizer response promoted the panicle initiation and dry matter accumulation at the filling stage. Consequently, the seed-setting rate and spikelet number per panicle were increased.

From the second year of the experiment, CRC gained a higher annual grain yield than BC. The possible reason is that biochar is produced by the pyrolysis of rice husks at high temperature, and as a result, its main nutrients exist as available nutrients that can be rapidly absorbed and utilized by crops [20]. As an organic fertilizer, the fertilizer efficiency of Chinese milk vetch was delayed by the process of decomposition, so its fertilization effect was slower than that of biochar. However, after one year of nutrient accumulation, the fertilizer efficiency of Chinese milk vetch had a greater effect on the rice yield than that of the biochar treatment. Therefore, it is important to pay more attention to the nitrogen supply in the early stage of rice growth, and it is also very important to adopt cultivation measures such as exposing paddy fields to sunshine in a timely manner to control inefficient tillers and secure a good grain yield.

4.2. Effects of Different Organic Materials on Soil Fertility

The application of organic materials increased the soil nutrient accumulation. In the present study, the application of organic fertilizer improved the soil nutrient content. On the one hand, organic materials can provide nutrients for plant growth after their own decomposition; on the other hand, absorption was enhanced by the organic matter in the soil colloids produced by the decomposition of organic materials, reducing the loss and leaching of chemical nutrients in the soil [21]. Different organic fertilizers have different effects on soil nutrient accumulation due to having different elemental contents [16]. The available nutrients were the nutrients that could be used by rice directly, which plays a crucial role in increasing the grain yield.
In this study, after six rice cropping seasons in three consecutive years, the soil alkaline nitrogen contents in the four organic material treatments were significantly higher than that in CK. Moreover, the soil total nitrogen and alkali-hydrolyzed nitrogen contents in CRC were higher than those in RC and MC, but the soil urease activity in the CRC treatment was lower than that in RC and MC. The reason might be that, on the one hand, many pores were generated, and the specific surface area was increased in the biochar preparation process. Thus, biochar had a great adsorption effect on ions and colloids and could fix nitrogen nutrients in the soil [16]. Since biochar adsorption was mainly physical, its soil urease activity was low. The nutrients released from rapeseed cake and manure were due to the reactions of microorganisms and soil enzymes [22], so the biochemical reactions in the soil were intense; therefore, the soil urease activity was higher than that of the biochar treatment. Although the decomposition of rapeseed cake and manure could also produce organic matter and soil aggregates, which could adsorb and fix soil nutrients, compared with the amount of biochar, this process takes a long time, and the soil aggregates amount is small, so the adsorption effect is basically negligible [23].

At the beginning of straw returning, the microbial activity was intense, and microorganisms competed for nitrogen with the late-season rice. However, there was a nitrogen residue of Chinese milk vetch from the early season, which can provide nitrogen for rice in this stage. In the late growing stage of rice, the consumption of nitrogen by microorganisms gradually decreased; on the other hand, the nitrogen in the straw was released into the soil, so that the nitrogen content in the soil was increased. Meanwhile, after straw decomposition, the carbon required for microbial reproduction was reduced, resulting in a large amount of microbial deaths, and nitrogen from microorganisms was released into the soil, which increased the nitrogen content of the soil.

In addition, some studies have shown that the available nitrogen content in soil was decreased after applying biochar to a field [24], which is contrary to the results in this experiment. The reason might be due to the different soil conditions of the two experiments. In this experiment, paddy soil had a higher soil moisture, and the contact area between soil ions, organic matter colloids, and biochar was wider and more sufficient, so soil nitrogen was more easily adsorbed and fixed by biochar [25]. Therefore, after three years of experiments, the total nitrogen content in soil showed an increase.

Soil humus is the main part of soil organic colloids, which can regulate soil fertility, structure, and properties. Organic material application could improve the soil humus content and optimize its structure [26]. HA is the most active component in humus, which can be chelated with microelements to develop organic salts and be reserved in soil [27]. Additionally, it plays an important role in transporting nutrients and water for rice plants. Stable polymers can be produced by combining HA with soil clay particles to improve the physical stability of the soil structure. This promotes crop growth and improves soil fertility [28]. An increase in HA always causes an improvement in soil humification. The study shows that, compared with CK, the combined application of organic and inorganic fertilizer could increase the soil HA/FA ratio and significantly increase the soil HA content, which indicates that the application of organic materials could significantly increase the soil humus content, improve the soil maturation degree, and promote the transformation of the soil fertility status in a more appropriate direction [29]. The increase of PQ in soil also indicated that, after organic materials were added, the humus degree in soil was improved, and the soil fertilizer retention ability was increased. Among the four organic material treatments, BC gained the highest HA and HM contents. This might result from the powerful adsorption capacity of biochar, which helped reduce the loss of soil nutrients, including soil humus [30].

The soil organic carbon content and soil CPMI are usually used to characterize soil fertility changes. The soil organic carbon might not change along with the agronomic management immediately, while soil CPMI could characterize the soil organic matter changes caused by soil managements and then reflect the decline or renewal of the soil fertility [31]. According to Table 5, the application of organic materials increased the TOC
and AOC contents and the CPI and CPMI, but the effects of different organic materials on the soil were different [32]. Compared with the application of 100% chemical fertilizers, the combined application of Chinese milk vetch + chemical fertilizers could significantly increase the TOC, CPMI, and AOC, which indicates that the decomposition of Chinese milk vetch helped renew the soil carbon pool and improve the soil quality. Compared with other organic materials, the labile carbon pool of straw mainly includes organic acids, polysaccharides, and amino acids, which could be preferentially decomposed by microorganisms. Additionally, sufficient carbon sources and nutrients could stimulate the microbial activity, increase the microbial quantity, promote the decomposition of organic materials [33], and accumulate soil AOC. Compared with rapeseed cake and manure treatment, Chinese milk vetch straw + chemical fertilizers treatment had the highest AOC in this study. Other studies found that the effects of different organic materials on the active components of organic matter from high to low were pig manure, biochar, and straws [34], which were different from our results (Table 6). The possible reason was that the soil backgrounds of the two experiments were different. The soil moisture content in paddy fields is higher, the contact area of organic materials and soil is greater, the microbial activities in the soil are more intense and rapid, and the enzymatic reactions are more abundant. However, more detailed reasons need to be further explored and verified.

The enzyme activity in soil reflects the decomposition intensity and the resynthesis intensity of organic matter, which could be used as the basis for soil fertility evaluations [35], and it is widely reported that organic material application could improve the enzyme activity, which is consistent with the results of this paper [36]. In this study, the soil urease activity and soil acid phosphatase activity were significantly improved under CRC. Both the soil urease activity and soil acid phosphatase of BC were the lowest among the four organic material treatments. Raw materials of biochar lose lots of nutrients after pyrolysis, and the residual components are mainly inorganic, so, compared to the three other organic materials, biochar lacks substrates for enzymatic reactions, while the enzyme activity of CRC, RC, and MC increased the enzymatic reactions. The developed hole structure and prodigious surface area of biochar could adsorb and encapsulate the soil organic matter and inorganic salt ions and reduce the loss of nutrients such as nitrogen and phosphorus in soil [37]. The soil urease and phosphatase activities of BC were lower than those of MC, but the total nitrogen and phosphorus contents of BC were higher than those of MC over three consecutive years.

5. Conclusions

The application of five organic materials with chemical fertilizers helps us not only to gain a high rice yield but also to attain a more sustainable paddy field for the double-season rice cropping system. Additionally, more nitrogen, phosphorus, and carbon were released in the soil after the decomposition of organic materials, which supplied more available nutrients to the growing rice. CRC (Chinese milk vetch + 75% chemical fertilizer) gained a higher soil AOC content and CPMI than the other treatments, which showed improved soil fertility. The high HA, FA, and HM contents and PQ of CRC also led to a better habitat for rice. Therefore, CRC gained the highest annual grain yield (15.05 t ha\(^{-1}\) in 2017 and 15.35 t ha\(^{-1}\) in 2018) in the last two years of the field experiments mainly by producing a higher yield in the early season rice with more effective panicles and more spikelet per panicle. In summary, CRC was the optimal treatment in terms of both the high rice yield and sustainability.

Author Contributions: Conceptualization, N.T. and Z.Y.; investigation, J.Y., B.L., C.F., S.L., C.L. and G.M.; writing—original draft preparation, J.Y.; writing—review and editing, M.S.S., N.T., Z.Y. and J.Y.; and supervision, N.T. and Z.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Public Welfare (Agriculture)-Scientific Research Project, grant number 201503123-05, and the National Key R&D Program of China (2018YFD0301005).
Data Availability Statement: Not applicable.

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

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