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Effect of Biochar Amendment on Methane Emissions from Paddy Field under Water-Saving Irrigation

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Abstract: Biochar has been proposed as a new countermeasure to mitigate climate change because of its potential in inhibiting greenhouse gas emissions from farmlands. A field experiment was conducted in Taihu Lake region in China to assess the effects of rice-straw biochar amendment on methane (CH$_4$) emissions from paddy fields under water-saving irrigation using three treatments, namely, control with no amendment (C0), 20 t ha$^{-1}$ (C20), and 40 t ha$^{-1}$ rice-straw biochar amendments (C40). Results showed that biochar application significantly decreased CH$_4$ emissions by 29.7% and 15.6% at C20 and C40 biochar addition level, respectively. C20 significantly increased soil dissolved organic carbon, total nitrogen, and NH$_4^+$-N by 79.5, 24.5, and 47.7%, respectively, and decreased NO$_3^-$-N by 30.4% compared with C0. On the other hand, no significant difference was observed in soil pH and soil organic carbon in all treatments. C20 and C40 significantly increased and decreased soil oxidation-reduction potential, respectively. Compared with C0, rice yield and irrigation water productivity significantly increased by 24.0% and 33.4% and 36.3% and 42.5% for C20 and C40, respectively. Thus, rice-straw biochar amendment and water-saving irrigation technology can inhibit CH$_4$ emissions while increasing rice yield and irrigation water productivity. The effects of increasing rice yield and irrigation water productivity were more remarkable for C40, but C20 was more effective in mitigating CH$_4$ emission.

Keywords: biochar; water-saving irrigation; methane emission; rice yield

1. Introduction

Global warming, which is caused by greenhouse gases, is a serious concern for human society. Methane (CH$_4$) is an important greenhouse gas features with 28 times global warming potential than carbon dioxide with a unit mass at a 100 year scale (IPCC, 2013). The pre-industrial atmospheric concentration of CH$_4$ reached 0.715 ppmv and currently measures 1.774 ppmv and maintains a 0.6% increase in speed annually [1,2]. Studies have shown that CH$_4$ emitted from soil accounts for 15% to 30% of the total emissions every year [3]. Paddy field is an important source of CH$_4$ and contributes to 12% of the total annual emission from soil [4,5]. China is a primary rice producer that accounts for 22% of rice area and 34% of rice production of the world [6]. Therefore, studies should specifically evaluate CH$_4$ emissions from Chinese paddy fields and propose effective mitigation measures via farm management.

Biochar is a C-rich solid material produced with high temperature and limited oxygen using organic matter [7]. Initial studies have shown that incorporating biochar in soil can alter soil properties and features the potential to enhance crop productivity and reduce greenhouse gas
emissions [8–10]. Zhang et al. [11] noticed that biochar addition increased soil organic carbon, C/N, and NH$_4^+$-N and decreased soil bulk density and NO$_3^-$-N. Randolph et al. [12] discovered that incorporation of biochar in soil increased soil pH and improved water retention, electrical conductivity, aggregate stability, and micronutrient contents. Akhtar et al. [13] observed that biochar addition increased soil moisture contents; furthermore, the quality and yield of tomato improved with biochar amendment. Sun et al. [10] registered that mean rice yield increased by 947 kg ha$^{-1}$ after incorporating biochar into paddy fields. Several studies have reported that biochar addition suppressed CH$_4$ emissions [14–16]. Feng et al. [17] discovered that methanotrophic proteobacterial abundances increased and methanogenic:methanotrophic abundances significantly decreased with biochar amendments, similar to the report by Xu et al. [18]. Wang et al. [19] noted that CH$_4$ emission decreased along with increasing soil oxidation—reduction potential (Eh). In a case study, Qin et al [20] discovered a significant negative relationship between CH$_4$ emission and soil dissolved organic carbon (DOC). Pratiwi and Shinogi [14] indicated that soil properties, such as increased saturated hydraulic conductivity and macroporosity, which cause CH$_4$ mitigation, improved with biochar application. In addition, decreased CH$_4$ emission may be related to N speciation. Xu et al. [18] reported that NO$_3^-$-N content was positively correlated with methanogenic gene abundance. Wang et al. [21] explained that biochar increased NH$_4^+$-N content and CH$_4$ oxidation. However, contradictory results were observed in other literature [22–24]. Wang et al. [25] registered that incorporation of biochar into soil increased CH$_4$ emissions because of increased potential substrates for methanogens. Research results also indicated that biochar causes no significant effect on CH$_4$ emissions [26,27]. The different materials, production conditions, addition rates of biochar and soil texture, and farm management are the main causes for these divergent results [26,28]. Therefore, experiments must be conducted to reveal the effects of the addition of diverse biochars on CH$_4$ emissions in different regions.

Water resources per capita in China is less than a quarter of that of the world, and agriculture used water faces notable challenges. As a major user, reducing the amount of irrigation water in paddy fields bears strategic significance in easing water-using pressure. Under these circumstances, rice water-saving irrigation technology has been promoted in large areas. Previous literature has revealed that rice water-saving irrigation significantly decreases CH$_4$ emissions [29–31], which mainly results from changes in the physicochemical properties of soil [32]. Incorporating biochar into soil can also alter pH, C/N dynamics, and other soil properties [33–35]. Thus, the combination of water-saving irrigation technology and addition of biochar influences soil environment and CH$_4$ emissions. However, relevant studies are barely accessible. In the present study, a field experiment was conducted to reveal the effects of rice-straw biochar on CH$_4$ emissions from a paddy field under water-saving irrigation in Taihu Lake region in China. This study aimed to (1) show the effects of biochar on CH$_4$ emissions from paddy field under water-saving irrigation and to (2) test whether biochar addition increases rice yield and irrigation water productivity of paddy fields under water-saving irrigation.

2. Materials and Methods

2.1. Experiment Site and Design

The experiment was conducted at State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering of Hohai University, Kunshan Experiment station (34°63′21″ N, 121°05′22″ E), located in Eastern Taihu Lake region, China. The study area is a part of subtropical monsoon climate zone in Southeast China, with a mean annual air temperature, precipitation, evaporation, and sunshine duration of 15.5 °C, 1097.1 mm, 1365.9 mm, and 2085.9 h, respectively, and frost-free period of 234 days year$^{-1}$. The locals are accustomed to rice-wheat rotation. Soil in the experimental site is classified as Hydragric Anthrosol. The basic properties of this soil classification are as follows: organic matter of 21.71 g kg$^{-1}$ for the top 0–18 cm layer, total nitrogen (TN) of 1.79 g kg$^{-1}$, total phosphorus of 1.4 g kg$^{-1}$, total potassium of 20.86 g kg$^{-1}$, pH (H$_2$O) of 7.4, and soil bulk density of 1.32 g cm$^{-3}$ for the 0–30 cm layer.
The experiment was conducted with a lysimeter and each plot features an area of 5 m² (2.5 × 2 m) (Figure 1a). Three treatments—namely, 0 (C0), 20 (C20), and 40 t ha⁻¹ (C40) rice-straw biochar addition—were applied in triplicates. The rice-straw biochar used in the experiment provided by Zhejiang Biochar Engineering Technology Research Center and produced at a heating rate of 15 °C min⁻¹ and highest treatment temperature of 600 °C and sustained in a muffle oven under N₂ atmosphere for 2 h. The main properties of biochar are listed in Table 1. Biochar was evenly spread in the plots manually and incorporated into soil (approximately 20 cm) using the shovel and hoe at 1 day prior to transplantation of rice. Controlled irrigation was adopted for paddy field water regime. Under this practice, controlled irrigation was maintained with 5–25 mm of water layer only in the re-greening stage. For other stages, irrigation was applied to maintain soil moisture, and standing water was avoided, except during periods of pesticide and fertilizer applications, with the combination of soil moisture for root layer accounting for 60% to 80% of saturated soil moisture content as irrigation control indicator (Table 2). Base fertilizer was applied to the soil 1 day prior to rice transplantation, and the same fertilizer was used among the three treatments (Table 3). In the experiment, Suxiangjing rice variety was used. Plant and row spacings were set at 13 and 25 cm with three or four rice seedlings per hill, respectively.

Figure 1. (a) The plan of the single lysimeter and static chamber; (b) the profile of lysimeter and static chamber.
Table 1. Main properties of the biochar used in the experiment.

| Biochar            | pH  | C Content/% | Total N/% | Total P/% | Total K/% | CEC/cmol kg⁻¹ | Special Surface Area/m² g⁻¹ | Total Pure Volume/cm³ g⁻¹ |
|--------------------|-----|-------------|-----------|-----------|-----------|----------------|----------------------------|----------------------------|
| Rice straw biochar | 10.1| 42.6        | 0.75      | 0.15      | 1.06      | 44.8          | 81.9                      | 0.08                       |

Table 2. Controlled thresholds in different stages for controlled irrigation.

| Limit Regreening Stage | Tillering Stage | Jointing and Booting Stage | Heading and Flowering Stage | Milk Stage | Ripening Stage |
|------------------------|-----------------|--------------------------|----------------------------|------------|---------------|
| Upper limit            | Initial         | Middle                   | Late                       |            |               |
| Lower limit            | 25 mm           | 100%θ₁₁               | 100%θ₂₁          | 100%θ₂₂    | 100%θ₂₃       |
| Observed root zone depth (cm) | 5 mm | 70%θ₁₁          | 65%θ₂₁          | 75%θ₂₂    | 80%θ₂₃       |
|                        | -               | 0-20                    | 0-20                      | 0-30       | 0-40          |

θ₁₁, θ₂₁, and θ₂₂ represents average volumetric soil moisture for the 0-20, 0-30, and 0-40 cm layers, respectively.

Table 3. Experimental fertilization practice (kg ha⁻¹).

| Treatment | Base Fertilization | Tiller Fertilization | Panicle Fertilization |
|-----------|--------------------|----------------------|-----------------------|
|           | N (CF + Urea)      | P₂O₅                 | K₂O                   | Biochar (t ha⁻¹) | N (Urea) | N (Urea) |
| C₀        | 153.6              | 63                   | 89.25                 | 0              | 69.6     | 69.6     |
| C₂₀       | 153.6              | 63                   | 89.25                 | 20             | 69.6     | 69.6     |
| C₄₀       | 153.6              | 63                   | 89.25                 | 40             | 69.6     | 69.6     |

Base, tiller, and panicle fertilization occurred on 28 June, 16 July, and 11 August, respectively. CF: compound fertilizer. C₀, C₂₀, and C₄₀ indicates 0, 20, and 40 t ha⁻¹ rice-straw biochar addition.

2.2. Gas Sampling and Analysis

Gas samples were collected with the static chamber in situ [29] (Figure 1b). The static chambers were made of polyvinyl chloride (PVC), 5 mm thick, and featured a cross-sectional area of 0.25 m² (50 × 50 cm) and height of 60 cm for two separate parts (bottom and top layers). A sink at the top of the bottom layer was used for sealing and story-adding in the later growth stages of rice. The chamber was covered by aluminum foil to reduce temperature variations caused by solar radiation in the chamber during the sampling period. The bases for the PVC chambers were installed in all plots before rice transplantation and retained there until rice harvest. Gas was collected using a 60 mL syringe connected with a rubber tube, which was inserted into the chamber from flank. The first gas sample was collected two days after rice transplantation with a collecting interval of five days, and the interval was increased to a week after September. The gas samples were collected at the second, fourth, sixth, and eighth day after fertilizer application. Four gas samples from each chamber were collected at 10 min interval from 10 a.m. to 11 a.m. of each sampling day. Gas samples were stored and transported in Tedlar airbag, and CH₄ concentrations were analyzed by using a gas chromatograph (Agilent 7890A, Agilent Science and Technology Ltd., PaloAlto, CA, USA). CH₄ flux was calculated according to the following equation, and cumulative emissions for the rice season were calculated through interpolation–integration

\[ F = \rho \cdot h \cdot \frac{273}{273 + T} \cdot \frac{dC}{dt} \]  

where \( F \) refers to the gas emission flux (mg m⁻² h⁻¹); \( \rho \) represents the CH₄ density at standard state (0.714 kg m⁻³); \( h \) corresponds to the height of the chamber above the water surface (m); \( T \) is the mean air temperature inside the chamber during sampling (°C); \( dC/dt \) denotes the CH₄ mixing ratio concentration (mg m⁻³ h⁻¹), which depends on the fitting line slope of four gas sample densities and corresponding sampling times (0, 10, 20, and 30 min) of each group.
2.3. Yield Measurement, Soil Sampling, and Analysis

Rice yield was estimated by harvesting the plants per unit area of each plot manually. Three hills of rice plants were selected randomly in each plot to determine the filled grain number, setting percentage, thousand kernel weight (TKW), and panicle number.

Three topsoil (0–20 cm) samples were randomly collected in each plot after harvest using auger boring. Any visible plant residues and gravels were removed manually. The samples were placed in sealed plastic bag and kept in the refrigerator for further analysis (within a week). Fresh soil samples were analyzed for DOC. The remaining soil samples were air-dried and passed through a 2 mm sieve partly (to analyze soil pH, NH$_4^+$-N, and NO$_3^-$-N), 0.15 mm sieve partly (to analyze soil organic matter, soil organic carbon (SOC), total phosphorus (TP), and total potassium (TK)), and a 0.25 mm sieve (for TN analyses) [36]. Soil pH was measured on a 1:2.5 (soil/water) ratio with a compound electrode (Chuandi Instrument Ltd., Nanjing, China). Soil organic matter, SOC, and DOC were analyzed by using the potassium bichromate method [36,37]. The contents of NO$_3^-$-N and NH$_4^+$-N were analyzed by using the copper-chrome reduction-diazo coupling and indophenol blue colorimetric method, and soil TN was measured using Kjeldahl procedure [36]. TP and TK of soil were measured using sodium carbonate and sodium hydroxide alkali fusion method, respectively [36]. Soil bulk density was measured using the cutting ring method [36].

2.4. Other Measurements

Soil Eh was measured using a portable potentiometer (Chuandi instrument Ltd., Nanjing, China) although the detector was buried in the field. Soil moisture was recorded automatically (half an hour at a time) by HOBO soil water content automatic measurement system (Onset Company, Bourne, MA, USA). The water layer was recorded at 8 a.m. using vertical rulers, which were pre-embedded in the field. The amount of irrigation water was calculated on the basis of the difference in water meter before and after irrigation.

2.5. Statistical Analysis

Statistical data analysis was carried out using the statistical software SPSS 20.0. Significant differences in CH$_4$ fluxes and emissions, rice yield, amount of irrigation water, and soil indexes indicating the effects of biochar amendment were tested by Duncan’s multiple range test at 0.05 probability level.

3. Results

3.1. CH$_4$ Fluxes and Emissions

The patterns of CH$_4$ fluxes were similar among the three treatments (Figure 2). CH$_4$ emissions were evidently concentrated in the early stage of rice growth (days after transplantation (DAT) ≤ 39). CH$_4$ fluxes of C40 were higher than those of other treatments before the first emission peak. Afterward, CH$_4$ fluxes of C0 were higher than those of C20 and C40 until rice harvest. Several CH$_4$ flux peaks were observed with or without biochar amendment over the rice seasons, and the highest CH$_4$ flux was discovered in C0 22 DAT, with the value of 17.5 mg m$^{-2}$ h$^{-1}$. CH$_4$ emissions increased after five days of tiller and panicle fertilization practice. Paddy soil acted as a CH$_4$ sink 103 DAT for a short period; this finding may result from the steady decrease in soil water content due to natural drying management. The cumulative CH$_4$ emissions from initial rice transplantation to harvest of C0, C20, and C40 were 15.42, 10.84, and 13.01 g m$^{-2}$, respectively. Biochar amendment significantly decreased CH$_4$ emissions by 45.8 and 24.1 kg ha$^{-1}$ compared with non-amended soil (Figure 3).
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Figure 2. Dynamics of CH$_4$ fluxes (mean ± SD) under rice-straw biochar amendments. C0, C20, and C40 indicate the biochar addition rate of 0, 20, and 40 t ha$^{-1}$. The arrows indicate fertilization practice (base, tiller, and panicle fertilization in turn).

Figure 3. Cumulative CH$_4$ emissions over the rice season and rice yield of different treatments. Different letters indicate significant difference according to Duncan’s multiple range test ($p < 0.05$). C0, C20, and C40 indicate the biochar addition rates of 0, 20, and 40 t ha$^{-1}$, respectively.

3.2. Soil Properties

Table 4 presents the data on soil properties at the end of the experiment. Biochar amendments significantly increased soil DOC and TN concentration by 79.5% and 24.5%; and 141.9% and 25.3% for C20 and C40 biochar addition rates, respectively ($p < 0.05$). Incorporating 20 t ha$^{-1}$ biochar into soil significantly increased NH$_4^+$-N by 47.7% and decreased NO$_3^-$-N by 30.4% compared with that without biochar amendment ($p < 0.05$), whereas C40 slightly influenced NH$_4^+$-N and NO$_3^-$-N.
concentrations. The significant differences of NH$_4^+$-N and NO$_3^-$-N were only recorded between 20 t ha$^{-1}$ biochar amendment and non-amended soil. C20 increased soil Eh obviously whereas C40 yielded the opposite result. The data showed no remarkable biochar effect on soil pH and SOC. Compared with non-amended soil, biochar amendments slightly increased soil pH and SOC at the end of the experiment.

### 3.3. Rice Yield and Irrigation Water Productivity

The results showed that biochar amendments significantly increased rice yield and irrigation water productivity (Table 5, $p < 0.05$). Data showed that biochar addition increased filled grain number and setting percentage and caused no effect on TKW. In addition, rice panicle significantly increased by 48.0% and 50.3% following C20 and C40 biochar amendment, respectively, relative to no biochar amendment soil. Rice yield enhanced along with increasing amount of added biochar and increased by 1291 and 1950 kg ha$^{-1}$ following C20 and C40 biochar amendment, respectively, compared with C0. Although biochar amendments showed no significant effect on irrigation water, owing to the notable rice yield increase, irrigation water productivity significantly increased by 0.290 and 0.369 kg m$^{-1}$ at C20 and C40 biochar addition level, respectively, compared with that without biochar amendment.

#### Table 5. Filled grain number, setting percentage, thousand kernel weight, rice panicle, yield, irrigation water, and irrigation water productivity (mean ± standard deviation, $n = 3$) under rice-straw biochar amendments.

| Treatment | Filled Grain Number/Panicle | Setting Percentage/% | Thousand Kernel Weight/g | Panicle Number/m$^{-2}$ | Yield/kg ha$^{-1}$ | Irrigation Water/mm | Irrigation Water Productivity/kg m$^{-2}$ |
|-----------|----------------------------|----------------------|--------------------------|-------------------------|-------------------|---------------------|----------------------------------------|
| C0        | 64.2 ± 5.58$^b$            | 68.4 ± 3.2$^b$       | 23.9 ± 1.45$^a$          | 179 ± 7$^b$             | 5371 ± 584$^b$   | 619.0 ± 17.0$^a$   | 0.868 ± 0.070$^b$                      |
| C20       | 87.1 ± 8.70$^a$            | 78.3 ± 3.7$^b$       | 21.6 ± 2.14$^b$         | 265 ± 11$^a$            | 6662 ± 199$^a$   | 575.5 ± 58.5$^a$  | 1.158 ± 0.154$^a$                      |
| C40       | 85.4 ± 17.2$^b$            | 13.7 ± 10.2$^a$      | 23.3 ± 0.91$^a$         | 232 ± 18$^a$            | 7321 ± 943$^a$   | 592.0 ± 44.0$^a$  | 1.237 ± 0.236$^a$                      |

C0, C20, and C40 indicate the biochar addition rate of 0, 20, and 40 t ha$^{-1}$. Means ± SD in the same column with the different letter indicate significant difference according to Duncan’s multiple range test ($p < 0.05$).

### 4. Discussion

#### 4.1. Effect of Biochar Amendment on CH$_4$ Emissions

Results of the current study showed that incorporation of rice-straw biochar into paddy soil under water-saving irrigation suppressed CH$_4$ emissions, consistent with other previous reports [35,38,39]. A field experiment conducted by Liu et al. [40] indicated that CH$_4$ emission was significantly reduced by up to 40% with biochar amendment relative to non-amended treatment. In an outdoor pot experiment, Pratiwi and Shinogi [14] mixed rice husk biochar in the paddy soil and observed that total CH$_4$ emissions reduced by 45.2% and 54.9% at 2% and 4% biochar application rate, respectively. Biochar amendment may indirectly reduce CH$_4$ emissions by altering soil properties, such as soil pH, Eh, or other influencing factors.

Biochar may suppress CH$_4$ emissions by increasing soil pH while influencing microbial activities [27]. In the present study, soil pH totaled 7.12, 7.15, and 7.19 under C0, C20, and C40 treatments, respectively. Although an upturn was observed along with increasing biochar addition
rate, no significant difference was discovered among the three treatments in terms of different biochar amendment levels. Liu et al. [40] registered that biochar amendment increased soil pH and attributed this result to the reduction of CH₄ emission. Yang et al. [35] indicated that increased soil pH enhanced methanotroph activity and decreased CH₄ emissions with biochar amendment. Qin et al. [20] noted that CH₄ emission was negatively correlated with soil pH. Butnan et al. [26] indicated that increased pH may suppress methanogenic activity and result in decreased CH₄ emissions; this finding was affirmed by the study conducted by Xu, et al. [18], who discovered the significant negative correlation between soil pH and CH₄ production potential.

Soil Eh is an important index that reflects soil aeration. In the intensive emission period (DAT ≤ 39), CH₄ fluxes showed a significant negative correlation with soil Eh (Figure 4), agreeing with the result of field experiment carried out by Wang et al. [19] and Xu et al. [41]. Wang et al. [19] observed that CH₄ oxidation was significantly positively correlated with soil Eh. The improved soil aeration and increased oxygen content that followed the increase in soil Eh made soil conditions favorable for methanotrophs and decreased CH₄ emissions. In the current study, C20 biochar amendment increased soil Eh (DAT ≤ 39) and significantly decreased CH₄ emissions. The increased soil Eh may enhance methanotroph activity and CH₄ oxidation rate, which in turn reduces CH₄ emission.

Figure 4. Relationship between CH₄ fluxes and soil Eh of different treatments at DAT ≤ 39. DAT = day after transplantation. C0, C20, and C40 indicates the biochar addition rate of 0, 20, and 40 t ha⁻¹, respectively.

DOC concentration is a parameter of substrate availability for CH₄ production and affects CH₄ emissions [19]. Qin et al. [9] also outlined that DOC is a primary source of CH₄ production. Wang et al. [23] observed that incorporating biochar produced at 300 °C into soil increased CH₄ emissions and contributed this enhancement to the high soil DOC content. The current study showed that biochar application into soil at 600 °C significantly increased soil DOC concentration while decreasing cumulative CH₄ emissions in both addition levels relative to no-biochar amendment (Table 4). This phenomenon was contrary to the results in the aforementioned literature. Liu et al. [42]
reported that the content of stable carbon in biochar will increase with pyrolysis temperature. Therefore, although biochar addition increased soil DOC content in the experiment, stable carbon is hard to use by methanogenic bacteria. Previous studies revealed that biochar addition in Inceptisol slightly influenced methanogenic archaeal community compositions [17]. Therefore, increased soil DOC that follows biochar amendment shows inconsistencies in promoting CH$_4$ emissions. Qin et al. [20] found that CH$_4$ emission was negatively correlated with soil DOC content and soil organic matter, showing agreement with our results. The negative relationship between CH$_4$ emission and DOC illustrates the enhancement of re-oxidation capacity in the rhizosphere following biochar addition, which in turn, can decrease CH$_4$ emission; in addition, recalcitrance of biochar restricts the availability of DOC for methanogens, which may inhibit CH$_4$ production [20]. Therefore, in the current study, the availability restriction of DOC and absorption of CH$_4$ following biochar addition may result in the suppression of CH$_4$ emission.

In the present study, data showed that biochar amendments increased soil NH$_4^+$-N and decreased NO$_3^-$-N compared with that without biochar addition (Table 4). Xu et al. [18] discovered a significant positive correlation between NO$_3^-$-N and methanogenic gene abundance. Wang et al. [21] contributed the increase of NH$_4^+$-N to biochar absorption, which can reduce the competition between NH$_4^+$-N and methanotrophs and increase CH$_4$ oxidation. Xie [43] explored the effects of nitrogen on CH$_4$ oxidation and methanotrophs using paddy soil. The results showed that CH$_4$ oxidation rate was facilitated at high NH$_4^+$-N content in soil, which mainly resulted from alteration of methanotroph community. When NH$_4^+$-N content increased, azotification of the community was suspended, and CH$_4$ oxidation rate increased. Therefore, in the current study, high content of NH$_4^+$-N following biochar addition may increase CH$_4$ oxidation rate and in turn decrease CH$_4$ emissions. Further investigations are to gain insights into the underlying mechanisms of the effects of biochar addition on CH$_4$ emissions.

In the present study, total CH$_4$ emission over the rice season significantly decreased by 45.8 kg ha$^{-1}$ at C20 biochar addition rate, and this value was higher than the reduction following C40 biochar amendment (a decrease of 24.1 kg ha$^{-1}$). Qu et al. [3] observed that the decrease in CH$_4$ emission is lesser along with increasing amount of added biochar compared with non-amended soil. High-level C input may affect the community and activity of microorganisms, decrease CH$_4$ oxidation rate, and in turn increase CH$_4$ emissions. The content of NH$_4^+$-N in C20 was higher than that in C40, which can reduce the competition between NH$_4^+$-N and methanotrophic and increase CH$_4$ oxidation. The high content of NO$_3^-$-N in C40 implies higher methanogenic gene abundance, which may increase CH$_4$ emission compared with C20. The proper application amount of biochar should be determined before addition to the field.

### 4.2. Effect of Biochar Amendment on Rice Yield and Irrigation Water Productivity

In the present study, biochar amendments significantly enhanced rice yield regardless of the added amount. Similarly, Zhang et al. [44] registered that rice yield increased at both biochar addition levels regardless of N fertilization; according to Wang et al. [45], the dry weight of rice grain increased by 24.5, 47.3, and 63.7% at 4, 8, and 12% bamboo biochar addition rates, respectively.

Incorporation of biochar into soil can improve soil fertilization by increasing the availability of N, P, K, Ca, and Mg and increasing crop uptake of these soil nutrients [39,46]. Rice is an ammonia-preferred crop. In the present study, soil TN and NH$_4^+$-N concentrations increased following biochar amendment, which may partly result in the enhancement of rice yield. Randolph et al. [12] discovered that biochar amendment increased micronutrient content and water retention. As explained by Andrenelli et al. [47], enhancement of soil water retention may be related to pelletized biochar inherent retention capacity and rearrangement of soil aggregates with pellets. In a soil column experiment, Wang et al. [48] revealed that increased soil water retention resulted from the formation of biochar-soil double-layer structure due to biochar amendment. Infiltration of water constantly cumulated in the upper layer until soil water content reached the threshold value. Our results showed that irrigation water reduced at both biochar addition rates; this result may be related to the
improvement of soil water retention properties. With increased rice yield and reduced irrigation water, irrigation water productivity significantly increased by 0.290 and 0.369 kg m\(^{-3}\) at C20 and C40 biochar addition levels compared with the non-amended soil. Biochar amendments can increase rice yield and irrigation water productivity simultaneously.

5. Conclusions

The experiment was conducted in a paddy field to reveal the effects of rice-straw biochar on CH\(_4\) emissions, rice yield, and irrigation water productivity combined with water-saving irrigation technology. The results showed that biochar amendment significantly reduced CH\(_4\) emissions by 45.8 and 24.1 kg ha\(^{-1}\) at C20 and C40 addition rates over the rice season, respectively, and suppression was weaker along with increasing biochar addition level. Biochar addition caused no effect on the pH and SOC content of soil. C20 biochar addition significantly increased the DOC, TN, and NH\(_4^+\)-N concentration of the soil and mean soil Eh of DAT \(\leq\) 39 relative to non-amended soil. CH\(_4\) fluxes show a significant negative correlation with soil Eh in the intensive emission period (DAT \(\leq\) 39), and the significant reduction of CH\(_4\) emission that followed C20 biochar amendment may partly result from the increase in soil Eh. In the current study, the restriction on the availability of DOC and absorption of CH\(_4\) that followed biochar addition may result in suppression of CH\(_4\) emission. In addition, decreased CH\(_4\) emission may be relevant with increased content of NH\(_4^+\)-N and CH\(_4\) oxidation rate. Biochar amendment significantly increased rice yield and irrigation water productivity by 1291 kg ha\(^{-1}\) and 0.290 kg m\(^{-3}\) at C20 biochar addition rate, and by 1950 kg ha\(^{-1}\) and 0.369 kg m\(^{-3}\) at C40 biochar addition rate. The results suggest that C20 biochar addition effectively reduced CH\(_4\) emissions from paddy field under water-saving irrigation, whereas C40 addition rate more effectively enhanced rice yield and irrigation water productivity. Further investigations are still needed to clarify the underlying mechanisms of biochar effects on CH\(_4\) emissions.

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