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# Effects of Biochar on the Net Greenhouse Gas Emissions under Continuous Flooding and Water-Saving Irrigation Conditions in Paddy Soils

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**Abstract:** In this study, we investigated the greenhouse gas emission under different application of biochar in the conditions of continuous flooding and water-saving irrigation in paddy fields, whereas, plant and soil carbon sequestration were considered in the calculation of net greenhouse gas emissions. The emission rates of methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), and nitrous oxide (N<sub>2</sub>O) gases were simultaneously monitored once every 7–10 days using the closed-chamber method. As a whole, the net greenhouse gas emission in the water-saving irrigation was more than that of the continuous flooding irrigation conditions. Compared with the water-saving irrigation, the continuous flooding irrigation significantly increased the CH<sub>4</sub> in the control (CK) and chemical fertilizer treatments (NPK). The CO<sub>2</sub> emissions increased in each treatment of the water-saving irrigation condition, especially in the chemical fertilizer treatments (NPK<sub>FW</sub>). Similarly, the soil N<sub>2</sub>O emission was very sensitive to the water-saving irrigation condition. An interesting finding is that the biochar application in soils cut down the soil N<sub>2</sub>O emission more significantly than NPK<sub>FW</sub> in the water-saving irrigation condition while the effect of biochar increased under the continuous flooding irrigation condition.

**Keywords:** biochar; water-saving irrigation; net greenhouse gas emissions; paddy soil

## 1. Introduction

Global warming is among the most urgent global issues nowadays [1]. The Intergovernmental Panel on Climate Change (IPCC) pointed out that carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and nitrous oxide (N<sub>2</sub>O) are the major greenhouse gases (GHGs) in the current global climate change process [2]. Globally, agriculture was recognized as a source of considerable greenhouse gas (GHG) emissions, contributing approximately 51% and 58% of the anthropogenic CH<sub>4</sub> and N<sub>2</sub>O emissions, respectively [3]. Rice (*Oryza sativa* L.), one of the world's most important food crops and the staple food for more than 50% of the world's population [4] was considered one of the major CH<sub>4</sub> sources [5]. Approximately 154 million ha worldwide are dedicated to rice cultivation and the world demand for rice will increase by more than 20% over the next 20 years [6]. Therefore, it is quite imperative to find a way to reduce the GHG emissions in rice paddy soils.

Biochar can reduce greenhouse gas emissions [7,8] and increase the carbon storage [9–12]. Biochar is defined as charred organic matter produced by pyrolysis. It has multiple uses in agriculture and is eventually applied as a soil amendment [13,14]. The carbon sequestration and GHG emission reduction effects of biochar on farmland soils come from its high chemical stability and biological stability [15].

Numerous studies have explored the GHG emission influences of biochar on the soil [9,16–18]. However, the impacts of biochar application on the soil's GHG emissions have not yet been clarified.

The application of biochar has shown to increase the soil aeration, promote CH<sub>4</sub> oxidation, and reduce its emission [19]. Feng et al. [20] found that paddy CH<sub>4</sub> emissions significantly decreased under biochar amendments, while it did not result from the inhibition of the methanogenic archaeal growth. On the other hand, Knoblauch et al. [21] reported that applying biochar increased the total amount of CH<sub>4</sub> emission by 1.6 times during a 96-day rice growing season due to the labile components of biochar that were predominant sources of methanogenic substrates. It was further found that biochar had no significant effect on soil respiration under different soil types, crop types, and different biochar types based on the data of several biochar field trials in China [16]. However, Zheng et al. [22] reported that a mixture of nitrogen fertilizer and biochar could promote soil CO<sub>2</sub> emissions. Apparently, the results of Sagrilo et al. [17] showed a statistically significant increase (by 28%) in the CO<sub>2</sub> emissions from biochar-amended soils due to the possible interactions between biochar and the soil's native organic carbon (SOC) which may have accelerated the loss of SOC, thus, reducing biochar's C sequestration potential. Furthermore, Yanai et al. [23] found that N<sub>2</sub>O emissions increased the intense sensitivity to soil moisture and the addition of biochar significantly stimulated the N<sub>2</sub>O emissions from soil rewetted at 83% of water-filled pore space (WFPS) compared to soil without charcoal addition. Contrarily, Cayuela et al. [18] found that biochar reduced the soil N<sub>2</sub>O emissions by 54% in the laboratory setting and in field studies.

As mentioned above, soil types, geographical conditions, crop types, biochar, and chemical fertilizer application can affect GHG emission by influencing microbial activities and through the changes in soil properties [20–23]. However, few studies have focused on the impacts of biochar on the net greenhouse gas emissions under different irrigation conditions in situ paddy soils.

The water resources per capita in China was only 2200 m<sup>3</sup>, one-quarter of the world's average, and rice was the major water consumer, consuming 70.4% of the total agricultural water consumption of the country [24]. In addition to the development of water-saving and drought-resistance rice varieties [25], water-saving irrigation is another effective and important factor to be considered for future water demands [26]. Sánchez et al. [27] found that the mid- and long-term implementation of sprinkler irrigation could be considered as potential, productive, and sustainable rice cropping system under Mediterranean conditions. Thus, it is essential to study the effect of water-saving irrigation conditions on net greenhouse gas (GHG) emissions since paddy water management is a promising option for CH<sub>4</sub> mitigation [28–30]. The mid-season drainage and multiple drainages are considered to be highly effective in mitigating methane efflux [30]. We hypothesized that the effects of biochar amendments on GHG emissions can be due to the different irrigation conditions but these effects have hardly been studied in paddy soils.

Therefore, the objective of this study was to investigate the impacts of two irrigation conditions on GHG emissions when the soil is added with biochar. Compared to the effects of water irrigation and biochar management measures on greenhouse gas emissions in paddy fields, we explored better water irrigation and fertilizer management measures that can mitigate the net GHG emissions. In this study, we used purple paddy soil because it is fertile and generally distributed in the Southwest of China.

## 2. Materials and Methods

### 2.1. Site Description

The pot experiments were conducted from March 2017 to September 2017 at the experimental greenhouse of Southwest University (E106°24' N29°48', 242 m above sea level) located in the Beibei District in Chongqing in southwestern China. The greenhouse has a subtropical monsoon humid climate with a mean annual air temperature of 18.3 °C and an average annual precipitation of 1100 mm. The soil type belonged to the Cambic Stagnic Anthrosols, named calcareous purple soil is also classified as Orthic Entisols (Chinese taxonomy) or Regosols (FAO taxonomy). The soil was developed from the parent material of gray-brown purple sand shale from the Mesozoic Jurassic Shaxi Temple group. Before the start of the experiment, the soil properties in the top 20 cm were as follows: the soil bulk

density was  $1.37 \text{ g cm}^{-3}$ , the pH was 7.86, the organic carbon was  $13.9 \text{ g kg}^{-1}$ , the alkaline nitrogen was  $121.52 \text{ mg kg}^{-1}$ , the available phosphorus (Olsen-P) was  $64.2 \text{ mg kg}^{-1}$ , and the available potassium ( $\text{NH}_4\text{OAc-K}$ ) was  $208.6 \text{ mg kg}^{-1}$ .

## 2.2. Experimental Design

There were two irrigation conditions: (1) continuous flooding irrigation: no fertilizer ( $\text{CK}_F$ ), conventional fertilization ( $\text{NPK}_F$ ), and  $40 \text{ Mg ha}^{-1}$  of biochar in combination with chemical fertilizer ( $\text{BC}_F$ ); (2) water-saving irrigation: no fertilizer ( $\text{CK}_{FW}$ ), conventional fertilization ( $\text{NPK}_{FW}$ ), and  $40 \text{ Mg ha}^{-1}$  of biochar in combination with chemical fertilizer ( $\text{BC}_{FW}$ ). The experimental pot was made of PVC with a diameter of 24.4 cm and height of 23 cm. Six kilograms of dry soil was put into each pot. Each treatment had six replicates. In the flooded treatment the rice was kept flooded during the whole growing period; and in the water-saving irrigation treatment, the rice was kept flooded and wet intermittently during the whole growing period.

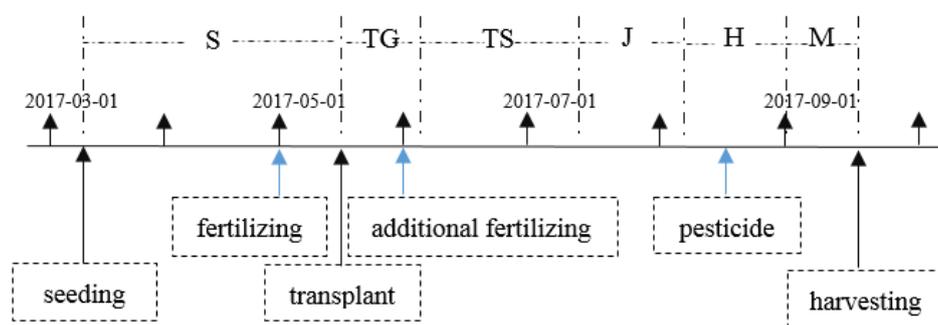
The biochar was produced from rape straw via pyrolysis at temperatures of  $500 \text{ }^\circ\text{C}$  with a residence time of about 2 h. All the biochar used in the experiments was bought from Sichuan Jiusheng Agricultural Company. The organic carbon content of the biochar was  $6.3 \text{ g kg}^{-1}$ , the content of nitrogen was  $4.4 \text{ g kg}^{-1}$ , the content of phosphorus was  $1.0 \text{ g kg}^{-1}$ , the content of potassium was  $10.5 \text{ g kg}^{-1}$ , and the pH was 8.9. Chemical fertilizer inputs were kept in each treatment except the CK treatment. The amount of fertilizer applied in  $\text{BC}_F$  and  $\text{BC}_{FW}$  was calculated by the following (Table 1):

$$\text{Amount of fertilizer} = (\text{the contents of nitrogen, phosphorus, and potassium in the treated fertilizer} - \text{the contents of nitrogen, phosphorus, and potassium in the treated fertilizer in biochar}) / \text{mass fraction of fertilizer.} \quad (1)$$

**Table 1.** The amount of fertilizer applied in different treatments/ $\text{g}\cdot\text{pot}^{-1}$ .

Treatment	ID	Urea		Superphosphate	Potassium Chloride	Biochar
		60%	40%			
Control	$\text{CK}_F, \text{CK}_{FW}$	0	0	0	0	0
Fertilizer only	$\text{NPK}_F, \text{NPK}_{FW}$	1.56	1.04	6.00	1.60	0
$40 \text{ Mg ha}^{-1}$ biochar and fertilizer	$\text{BC}_F, \text{BC}_{FW}$	0.96	0.64	5.14	0.26	106.68

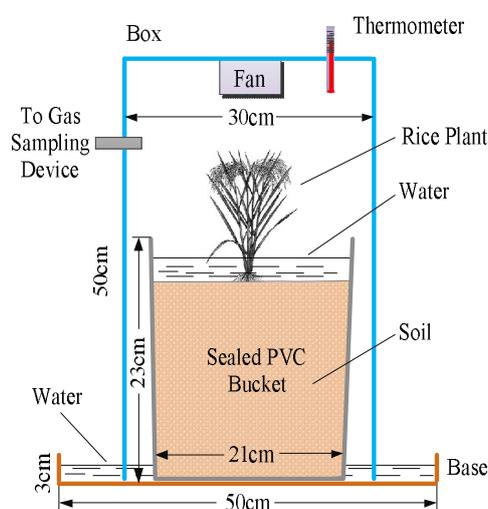
The variety of rice was “Yi Xiangyou 2115”, which is the general rice in Southwest China and the planting area in Chongqing occupies about 40% of the total rice area. The rice was seeded on 10th March 2017, transplanted on 14th May and two strains of rice were planted within each pot. After germination, the pots were fertilized at rates equivalent to  $150 \text{ kg N ha}^{-1}$  urea,  $75 \text{ kg P ha}^{-1}$  calcium superphosphate, and  $90 \text{ kg K ha}^{-1}$  potassium chloride, which was according to the habits of the local farmers, with  $0.2 \text{ g}$  of nitrogenous fertilizer,  $0.12 \text{ g}\cdot\text{kg}^{-1}$  of  $\text{P}_2\text{O}_5$  and  $0.16 \text{ g kg}^{-1}$  of  $\text{K}_2\text{O}$  in each kilo of dry soil. On 1st May, all the calcium superphosphates and potassium chlorides and 60% of urea were mixed with the biochar and soil. The rest (40%) of the urea was dissolved in water and applied to the soil surface on 1st June. On 15th August 2017, a pesticide was applied to the rice leaf and on 14th September 2017, the rice was harvested (Figure 1).



**Figure 1.** The growth and development of the crops and the management of the croplands. S, TG, TS, J, H, and M represent the seedling stage, the turning green stage, the tillering stage, the jointing stage, the heading stage, and the milk stage, respectively. In the continuous flooding irrigation condition, the rice was watered every two days in the seedling stage and the turning green stage and every day in the other stages in order to keep the soil continuously flooded. In the water-saving irrigation condition, the rice was watered every five days in the seedling stage and the turning green stage, two or three days in the tillering stage, the heading stage, and the early milk stage so that the soil can be intermittent flooded and wetted appropriately.

### 2.3. Gas Sampling and Analysis

A closed-chamber method [31–33] was used to estimate the  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$  emission fluxes. Rounded PVC chambers (50 cm in diameter and 3 cm in height) were placed permanently under the pots as pedestals. The experiment pots were placed over the pedestals. Opaque stainless steel chambers (30 cm  $\times$  30 cm surface area and 50 cm in height) covering the pots were also placed on the pedestals as the lid chambers to monitor the GHG emission rates. The extension connection boxes (surface area of 30 cm  $\times$  30 cm and a height of 50 cm or 100 cm) were used when the rice grew high enough and exceeded 50 cm in height. The extension connection box was placed between the pedestals and the top chambers and the water was sealed at the connection. The chamber was lined with reflective aluminum foil and covered with quilts outside it to maintain an ambient air temperature in the chamber headspace during the measurements. An electric fan (8 mm diameters) was installed inside and just below the top of the chamber to circulate the air and to ensure that the gas inside the chamber was well mixed during the sampling. One butyl rubber septum port was installed on the side of the chamber for gas sampling (Figure 2).



**Figure 2.** The schematic of the sampling device.

The gas measurements were conducted between 8:00 and 12:00 a.m. each week during the rice growing season. In the case of fertilization, the sampling frequency was increased—once every 2 days—lasting a week. The air gas samples were collected using 60-mL gas-tight syringes at 0, 10, 20, and 30 min after closing the chamber. JM 624 digital thermometers were used to measure the temperature in the chamber. Three gas samples in each replicate of each treatment were then brought back to the laboratory for analysis immediately. The concentrations of the three GHGs in the collected air samples were measured by gas chromatography (Agilent GC-7890A, USA). A flame ionization detector (FID), thermal conductivity detector (TCD), and a  $^{63}\text{Ni}$  electron capture detector (ECD) were used for quantifying the  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  concentrations, respectively.

The  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  emission rates were calculated from the increase in each gas concentration per unit surface area of the chamber for a specific time interval. The calibrating gases ( $\text{CH}_4$   $9.97 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ ,  $\text{CO}_2$   $808 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ , and  $\text{N}_2\text{O}$   $0.501 \times 10^{-6} \text{ mol}\cdot\text{mol}^{-1}$ ) were provided by the Chinese Academy of Metrology. A closed-chamber equation [5,34] was used to estimate the seasonal fluxes from each treatment:

$$F = \rho \times (V/A) \times (\Delta c/\Delta t) \times (273/T) \quad (2)$$

where  $F$  is flux of the  $\text{CH}_4$ ,  $\text{CO}_2$  ( $\text{mg m}^{-2} \text{ h}^{-1}$ ) or  $\text{N}_2\text{O}$  ( $\mu\text{g N}_2\text{O m}^{-2} \text{ h}^{-1}$ );  $\rho$  is the gas density of  $\text{CH}_4$ ,  $\text{CO}_2$ , or  $\text{N}_2\text{O}$  under a standardized state ( $\text{mg cm}^{-3}$ );  $V$  is the volume of the chamber ( $\text{m}^3$ );  $A$  is the surface area of the chamber ( $\text{m}^2$ );  $\Delta c/\Delta t$  is the rate of increase of each gas concentration in the chamber ( $\text{mg m}^{-3} \text{ h}^{-1}$ ) and  $T$  (absolute temperature) is the 273+ mean temperature ( $^\circ\text{C}$ ) of the chamber.

The total amount of the  $\text{CH}_4$ ,  $\text{CO}_2$ , or  $\text{N}_2\text{O}$  emissions was calculated by linear interpolation between consecutive values using the following equation [35,36]:

$$\text{The cumulative emission of CH}_4, \text{CO}_2, \text{ or N}_2\text{O} = \sum_{i=1}^n (F_i + F_{i+1})/2 \times (t_{i+1} - t_i) \times 24 \quad (3)$$

where  $F$  is the emission flow of  $\text{CH}_4$ ,  $\text{CO}_2$ , or  $\text{N}_2\text{O}$  at the  $i$ th measurement;  $(t_{i+1} - t_i)$  is the time length between the two adjacent measurements; and  $n$  is the total measurement number.

The global warming potential (GWP) of the soil in each treatment was calculated as the sum of the  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  fluxes released through heterotrophic respiration by converting each gas concentration to its  $\text{CO}_2$  equivalent over a 100-y time scale by using a conversion factor of 1 for  $\text{CO}_2$  from heterotrophic respiration, 25 for  $\text{CH}_4$ , and 298 for  $\text{N}_2\text{O}$  [33,37].

#### 2.4. Soil Properties

Before the experiment, the soil was air-dried and ground into the 1 mm mesh and 0.25 mm mesh to measure the physical and chemical properties. The soil pH was measured using a glass electrode (PB-10, Sartorius, Göttingen, Germany). The glass electrode was set in a 1:2.5 soil-water solution at room temperature [38]. The available nitrogen (AN) content was determined by the alkaline hydrolysis diffusion method. The available phosphorus (AP) content was extracted by a  $0.5 \text{ mol L}^{-1}$   $\text{NaHCO}_3$  (pH 8.5) solution. The available potassium (AK) content was extracted by using  $1 \text{ mol L}^{-1}$   $\text{NH}_4\text{Ac}$  (pH 7.0) [39]. The soil organic carbon (SOC) was determined by  $\text{K}_2\text{Cr}_2\text{O}_7$  oxidation and  $\text{FeSO}_4$  titration [40].

The SOC storage was calculated as follows [41]:

$$\text{SOC} = 100 \times h \cdot \rho \cdot C \quad (4)$$

where  $h$  represents the soil depth (cm),  $\rho$  is soil bulk density ( $\text{g}\cdot\text{cm}^{-3}$ ), and  $C$  is the content of SOC ( $\text{g}\cdot\text{kg}^{-1}$ ). The soil was collected at 0–20 cm before the rice transplanting and after its harvest, respectively. After being air-dried, the soil sample was brought back into the laboratory and impurities such as the residual roots of plants and gravel were removed. Then, the soil was ground into a 0.25 mm

mesh to measure the SOC. The soil bulk density was determined with the cutting ring before the rice planting and after its harvest.

### 2.5. Rice Organic Carbon Storage

After harvesting, one whole plant was collected. Then we washed the soil attached to the root and the plant was dried so as to be a constant weight. The organic carbon of the rice was measured by  $K_2Cr_2O_7$  oxidation and  $FeSO_4$  titration [42] and was calculated as follows [43]:

$$C_{\text{plant}} = B_1 \times C_1 + B_2 \times C_2 + B_3 \times C_3 + B_4 \times C_4 \quad (5)$$

where  $C_{\text{plant}}$  represents a plant's organic carbon [ $g \cdot (\text{one plant})^{-1}$ ],  $B_1$  is the biomass of the rice foliage [ $g \cdot (\text{one plant})^{-1}$ ],  $B_2$  is the biomass of the rice root,  $B_3$  is the biomass of the rice panicle, and  $B_4$  is the biomass of the rice grain. Similarly,  $C_1$  is the organic carbon of the rice foliage ( $g \cdot kg^{-1}$ ),  $C_2$  is the organic carbon of the rice root,  $C_3$  is the organic carbon of the rice panicle, and  $C_4$  is the organic carbon of the rice grain.

### 2.6. Net Greenhouse Gas Balance

The NGHGB (net greenhouse gas balance) can be converted to its  $CO_2$  equivalent ( $CO_2$ -eq) using the global warming potential [44]. It can be calculated as follows:

$$NGHGB = GWP_{\text{soil}} + GWP_{\text{indirect}} - GWP_{\text{SOC}} - GWP_{\text{plant}} \quad (6)$$

where NGHGB indicates the sink or source of GHG.  $GWP_{\text{SOC}}$  represents the GWP caused by the SOC change in the soil. It can be calculated as follows:

$$GWP_{\text{SOC}} = SOC_A - SOC_B \quad (7)$$

$SOC_A$  ( $kg \cdot hm^{-2}$ ) and  $SOC_B$  represent the carbon storage after rice harvesting and before rice planting, respectively.

$GWP_{\text{plant}}$  ( $kg \cdot hm^{-2}$ ) represents the GWP caused by the carbon storage of plants. It can be calculated as follows:

$$GWP_{\text{plant}} = C_{\text{plant}} \times \text{the quantities of crops per hectare}/1000 \quad (8)$$

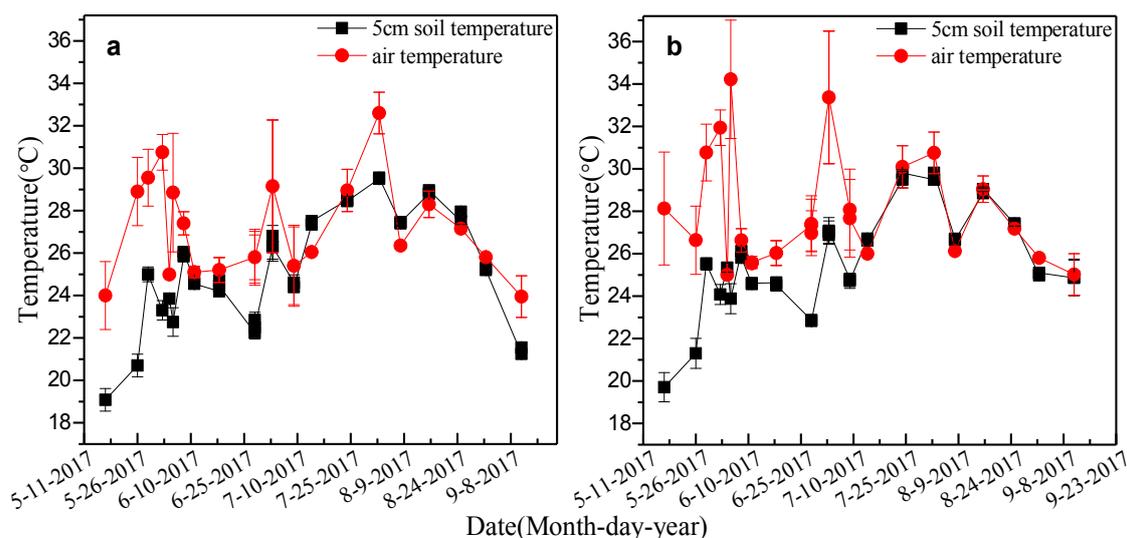
### 2.7. Data and Statistical Analyses

The data were analyzed using Microsoft Excel 2013, SPSS 22.0, and the origin 8.5 software. The differences among the treatments were carried out by one-way analysis of variance (ANOVA) in combination with an LSD test ( $p < 0.05$ ,  $p < 0.01$ ).

## 3. Results

### 3.1. Temperature

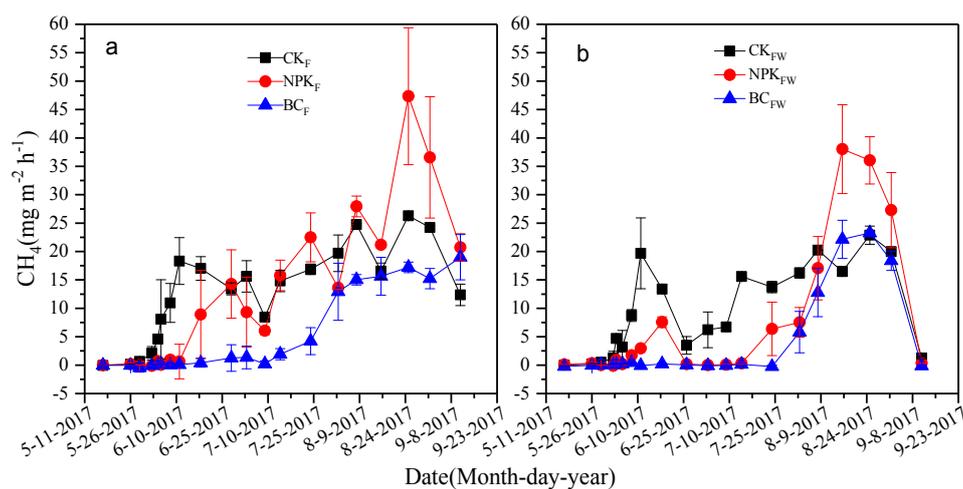
The air temperatures increased from May to August, with a peak at the beginning of August due to the high-temperature weather in Chongqing. The air temperatures, which averaged  $28.2 \pm 3.2$  °C and  $29.1 \pm 3.9$  °C for the F and FW irrigation conditions, respectively, were not significant. The average soil temperatures were  $25.5 \pm 2.5$  °C and  $25.9 \pm 2.2$  °C between May 2017 and September 2017 for the F and FW irrigation conditions, respectively (Figure 3). The soil temperature also changed according to the seasons; it increased from 20.9 °C in May to 28.9 °C in July and August and decreased to 21.9–26.0 °C in September.



**Figure 3.** Changes of 0–5 cm in the soil and air temperature during the rice cultivation season for (a) the rice cultivation season in the continuous flooding (F) irrigation condition and (b) the rice cultivation season in the water-saving (FW) irrigation condition.

### 3.2. The CH<sub>4</sub> Emissions of the Soil

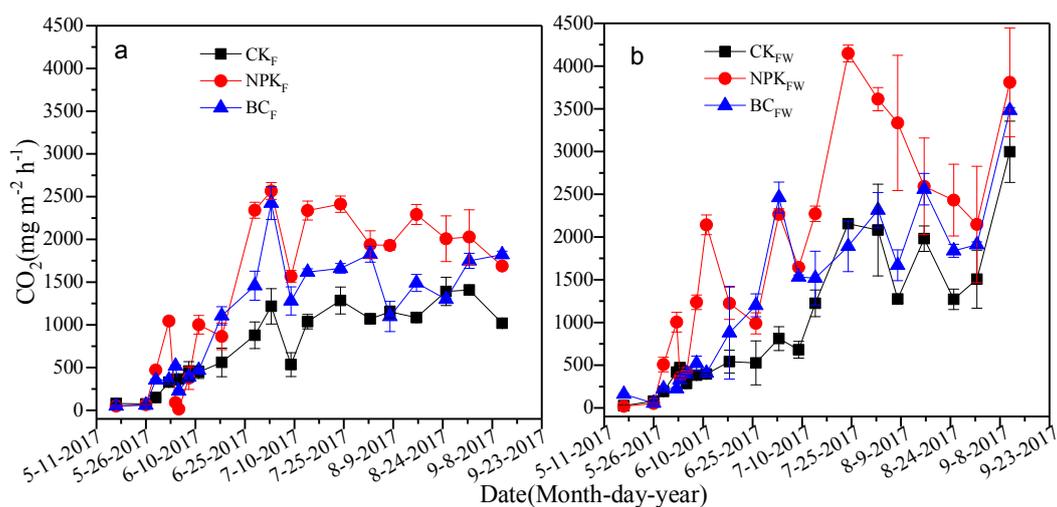
The water-saving irrigation condition reduced the average CH<sub>4</sub> fluxes (Figure 4). The maximum values of the two irrigation treatments were both NPK treatments in the heading stages with CH<sub>4</sub> emission rates of 47.34 mg m<sup>-2</sup> h<sup>-1</sup> in the continuous flooding soil and it decreased by 19.6% in the water-saving irrigation soil. The average CK<sub>FW</sub> treatment's CH<sub>4</sub> emission flux was 9.72 mg m<sup>-2</sup> h<sup>-1</sup>, which decreased by 23.7% more than the CK<sub>F</sub> treatment. The average CH<sub>4</sub> emission flux was 12.34 mg m<sup>-2</sup> h<sup>-1</sup> in the NPK<sub>F</sub> treatment and it was reduced by 40.38% to 7.36 mg m<sup>-2</sup> h<sup>-1</sup> in the NPK<sub>FW</sub> treatment. The least mean CH<sub>4</sub> emission value was 4.15 mg m<sup>-2</sup> h<sup>-1</sup> in the BC<sub>FW</sub> treatment and it was reduced by 20.38% more than BC<sub>F</sub> treatment.



**Figure 4.** The CH<sub>4</sub> flux emission during the rice growth period for (a) the rice cultivation season in the continuous flooding (F) irrigation condition and (b) the rice cultivation season in the FW irrigation condition.

### 3.3. The CO<sub>2</sub> Emissions of the Soil

The mean CO<sub>2</sub> flux emission rate of the soil increased significantly and fluctuated dramatically in the FW irrigation condition (Figure 5b), more so than the flooded one (Figure 5a). The peak value on the CO<sub>2</sub> emission flux of CK<sub>F</sub> was 1407.4 mg m<sup>-2</sup> h<sup>-1</sup> in the milk stage with peak values of 2424.2–2566.4 mg m<sup>-2</sup> h<sup>-1</sup> in the tillering stage in the NPK<sub>F</sub> and BC<sub>F</sub> treatments. The highest CO<sub>2</sub> emission was 4347.7 mg m<sup>-2</sup> h<sup>-1</sup> in the jointing stage of the NPK<sub>FW</sub> treatment and was 2997.0 and 3481.8 mg m<sup>-2</sup> h<sup>-1</sup>, respectively, in the milk stage of the CK<sub>FW</sub> and BC<sub>FW</sub> treatments.

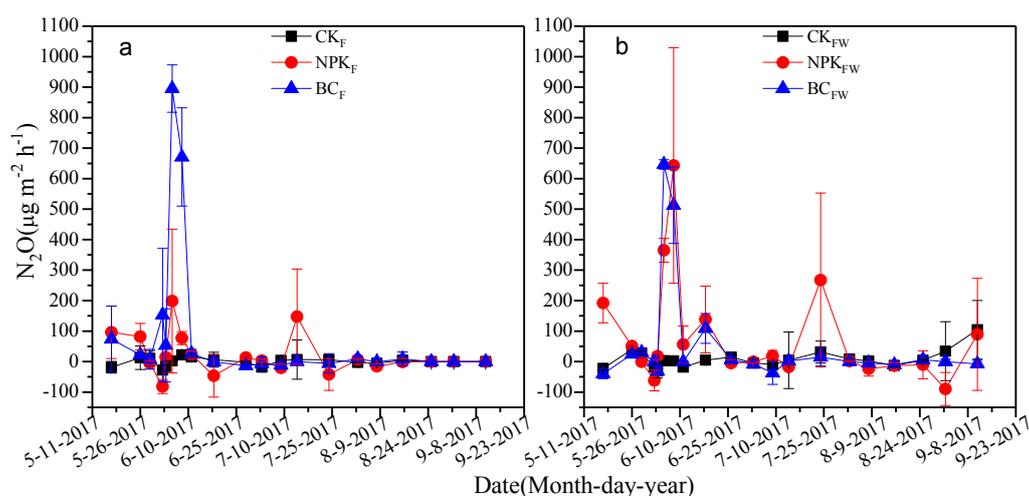


**Figure 5.** The CO<sub>2</sub> flux emission during the rice growth period for (a) the rice cultivation season in the continuous flooding (F) irrigation condition and (b) the rice cultivation season in the FW irrigation condition.

The effect of the fertilizer application on the CO<sub>2</sub> emission was more noticeable than that of the biochar application treatment under the two irrigation conditions. The mean CO<sub>2</sub> emission flux was 1354.09 mg m<sup>-2</sup> h<sup>-1</sup> in the NPK<sub>F</sub> treatment and increased by 81.72% and 27.43%, respectively, more than the CK<sub>F</sub> and BC<sub>F</sub> treatments. The mean CO<sub>2</sub> emission flux was 1854.63 mg m<sup>-2</sup> h<sup>-1</sup> in the NPK<sub>FW</sub> treatment and increased by 92.11% and 43.51%, respectively, more than CK<sub>FW</sub> and BC<sub>FW</sub> treatment.

### 3.4. The N<sub>2</sub>O Emissions of the Soil

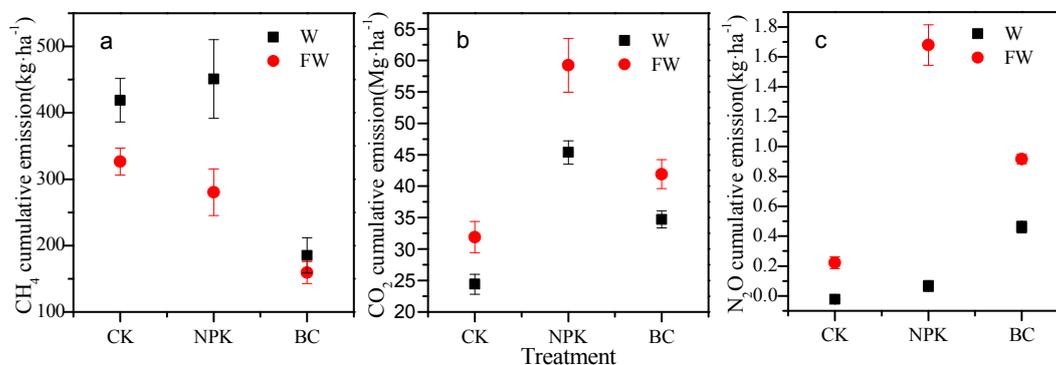
The N<sub>2</sub>O emission increased significantly in the water-saving irrigation treatment, more than in continuous flooding irrigation (Figure 6), especially for the NPK<sub>FW</sub> treatment. The change curves of the N<sub>2</sub>O emission flux in the two irrigation treatments were very affected by the chemical fertilizer. The N<sub>2</sub>O emission flux of the flooded condition was between −309.39 and 895.48 μg m<sup>2</sup> h<sup>-1</sup> and the N<sub>2</sub>O emission fluxes of the water-saving irrigation treatment was from −271.05 to 1029.08 μg m<sup>-2</sup> h<sup>-1</sup>. The peak curves all turned up a week after the chemical fertilizers were added and the highest N<sub>2</sub>O emission fluxes were 22.2, 198.6, and 895.5, respectively, in the CK<sub>F</sub> (No fertilizer), NPK<sub>F</sub>, and BC<sub>F</sub> treatments. Similarly, the peak values were 643.2 and 646.6 a week after the chemical fertilizers application in the NPK<sub>FW</sub> and BC<sub>FW</sub> treatments, respectively, while the peak value of the CK<sub>FW</sub> was 104.4 μg m<sup>2</sup> h<sup>-1</sup> in the milk stage.



**Figure 6.** The  $N_2O$  flux emissions during the rice growth period for (a) the rice cultivation season in the continuous flooding (F) irrigation condition and (b) the rice cultivation season in the FW irrigation condition.

### 3.5. GHG Total Flux

The total  $CH_4$  emissions of CK and NPK during the whole rice growth period significantly decreased by 22.1% and 37.8% in the water-saving irrigation treatments and the continuous flooding irrigation treatment, respectively (Figure 7a). This indicates that the water-saving irrigation condition slowed down the total  $CH_4$  emission more than the flooded one.



**Figure 7.** The effects of the two irrigation conditions and biochar on the greenhouse gas total flux during the rice growth period for (a) the total  $CH_4$  emission; (b) the total  $CO_2$  emission; and (c) the total  $N_2O$  emission.

Although there was no significant trend in the  $BC_F$  and  $BC_{FW}$  treatments, the total amount of  $CH_4$  emissions in the BC treatment was significantly less than that of the CK and NPK treatments in the two irrigation conditions. The total amount of  $CH_4$  emission in the BCF treatment declined by 55.7% and 58.8% more than that of the  $CK_F$  and  $NPK_F$  treatments. The total amount of  $CH_4$  emission in the  $BC_{FW}$  treatment declined by 51.2% and 43.2% more than that of the  $CK_{FW}$  and  $NPK_{FW}$  treatments.

Compared with the continuous flooding irrigation treatment, the water-saving treatment increased the  $CO_2$  emissions (Figure 7b). The total amount of  $CO_2$  emissions ranged between  $24.4 \pm 1.6$  and  $45.4 \pm 1.9$   $Mg\ ha^{-1}$  in the continuous flooding irrigation conditions. The total amount of  $CO_2$  emissions ranged from  $31.9 \pm 2.4$  to  $59.2 \pm 4.3$   $Mg\ ha^{-1}$  in the water-saving conditions. The  $CO_2$  emissions were cut down by 23.5%, 23.4%, and 17.1%, respectively, in the  $CK_F$ ,  $NPK_F$ , and  $BC_F$  treatments compared with those of the water-saving treatments.

The total CO<sub>2</sub> emissions during the whole rice growth period in the NPK and biochar application treatments were significantly higher than that of the CK treatment (Figure 7b). The total CO<sub>2</sub> emissions of the NPK<sub>FW</sub> treatment increased by 85.6% more than that of the CK<sub>FW</sub> treatment.

The N<sub>2</sub>O fluxes increased significantly in the water-saving irrigation condition than in the continuous irrigation condition. The total N<sub>2</sub>O emission in the NPK<sub>FW</sub> treatment was 1.68 kg ha<sup>-1</sup>, that is, 25.3 times that in the NPK<sub>F</sub> treatment. The total amount of N<sub>2</sub>O emissions ranged from -0.02 to 0.46 kg ha<sup>-1</sup> in the continuous flooding irrigation condition and ranged from 0.22 to 1.68 kg ha<sup>-1</sup> in the water-saving irrigation treatment. In the whole period of observation, the N<sub>2</sub>O uptake happened in the soil of the CK<sub>F</sub> treatment while the other treatments were dominated by N<sub>2</sub>O flux. The total N<sub>2</sub>O emissions in the BC<sub>F</sub> treatment were significantly higher than that of the other treatments in the continuous flooding irrigation condition ( $p < 0.01$ ). The total N<sub>2</sub>O emissions in the NPK<sub>FW</sub> treatment were 6 times higher than that of the CK<sub>FW</sub> and increased by 83.2% more than that of the BC<sub>FW</sub> treatment.

### 3.6. Net Greenhouse Gas Balance of the GHG Emissions of the Soil

The GWP of CH<sub>4</sub> and CO<sub>2</sub> occupied 99.6–99.9% of the total global warming potential in the continuous flooding irrigation condition (GWP<sub>F</sub>) and 99.3–99.8% of the total GWP<sub>FW</sub> (global warming potential in the water-saving irrigation level). The total GWP of CK<sub>FW</sub>, NPK<sub>FW</sub>, and BC<sub>FW</sub> grew by 13.3%, 14.9%, and 13.8%, respectively, more than that of the CK<sub>F</sub>, NPK<sub>F</sub>, and BC<sub>F</sub> treatments. The total GWP<sub>F</sub> decreased by 30.2% with the biochar amount of 40 Mg ha<sup>-1</sup> in combination with chemical fertilizers compared to the no biochar amendment (NPK) treatment. Compared with the CK treatment, the effects of the chemical fertilizer application on the GWP under the two irrigation conditions were obvious. The GWP of NPK<sub>F</sub> and NPK<sub>FW</sub> significantly increased by 63.1% and 66.3%, respectively, more than that of the CK<sub>F</sub> and CK<sub>FW</sub> conditions. The application of the 40 Mg ha<sup>-1</sup> biological carbon with the decrease in the chemical fertilizer cut down the most GHG emissions compared to the application of pure fertilizer.

## 4. Discussion

### 4.1. Effect of Irrigation Conditions and Biochar Application on the CH<sub>4</sub> Emission of the Soil

The reduction of CH<sub>4</sub> in the control and NPK treatments in the water-saving irrigation was more significant than that of the continuous flooding irrigation and the average CH<sub>4</sub> flux decreased by 23.7% and 40.38%, respectively. In that respect, water management is one of the main agricultural factors that determine the CH<sub>4</sub> emissions in paddy fields [45]. The emissions of methane from the environment were affected by methanogens and methanotrophs [20]. The activities of methanogens promoted methane emissions while that of methanotrophs were inhibited in the paddy soil under the flooding conditions [46]. This eventually caused the methane to be hard to oxidize [47]. The fluctuations of the water table position could kill 50% of the methanogenic bacteria [48]. Therefore, the reduction of the methanogenic bacteria in the soil may also be the reason for the reduction of CH<sub>4</sub> in the water-saving irrigation condition [49]. In addition, the mean CH<sub>4</sub> emissions were the highest in the NPK<sub>F</sub> treatment, followed by the control treatment in the continuous flooding irrigation level condition. In the water-saving irrigation level condition, they were the highest in the CK<sub>FW</sub> treatment, followed by the NPK<sub>FW</sub> treatment.

The effects of the biochar application on the CH<sub>4</sub> emissions were not statistically significant in the two irrigation conditions, probably due to the addition of biochar into soil that could improve the water holding capacity of the soil [19]. The BC<sub>FW</sub> treatment was more tolerant to the drought than the CK<sub>FW</sub> and NPK<sub>FW</sub> treatments. It seemed that the application of biochar allowed the soil to hold water in the water-saving irrigation treatment. Compared with the NPK treatment, the emission of CH<sub>4</sub> was significantly inhibited in the cases of the biochar application treatments in the continuous flooding irrigation conditions. Thereby, the application of the biochar in the flooded paddy field reduces the

CH<sub>4</sub> emissions [19,20]. Although some studies indicate that biochar cannot decrease CH<sub>4</sub> emissions in the water-saving irrigation treatment and in upland soil [45], we found that the BC<sub>FW</sub> treatment reduced more CH<sub>4</sub> emissions (that is, 43.1–51.2%) than that of the CK<sub>FW</sub> and NPK<sub>FW</sub> treatments. This probably happened due to the applications of biochar into soil that promoted the formation of soil structures and increased the soil aeration which oxidized the CH<sub>4</sub> in the soil and plants.

#### 4.2. The CO<sub>2</sub> Emissions of the Soil

The soil ecosystem respiration ( $R_e$ ) (mentioned as the CO<sub>2</sub> flux) can be measured by the opaque static chamber method [50]. Variations of  $R_e$  can be affected by soil environments and agronomic management practices [51]. There was a clear variation of the  $R_e$  between the two irrigation conditions (Figure 5).

The total amount of CO<sub>2</sub> emissions increased by 20.2–33.3% more in the water-saving irrigation condition than in the continuous flooding irrigation condition (Figure 7b). In the suitable soil moisture range, the soil CO<sub>2</sub> emission increased with the increase in the water content [52]. However, in the summer flooded paddy soil, the roots and soil microbial respiration rates slowed down and the CO<sub>2</sub> emissions decreased. This was due to the excessive humidity and insufficient oxygen in the soil. This means that the rate of soil respiration was higher in the dry stage than in the wet stage in the paddy fields [53]. Not only agricultural soil but severely dry and wet alternations also promoted respiration in the forest soils [54].

The application of biochar in the soil did not only improve the soil quality but also influenced the decomposition of the SOC and the carbon circulation in the agricultural ecosystem [17,55]. The effect of the application of the pure chemical fertilizer on the increase of CO<sub>2</sub> emission was more obvious than that of biochar combined with the chemical fertilizer in the water-saving irrigation condition (Figure 7b). This is because, under conditions of sufficient oxygen, the increase of the inorganic nitrogen in the soil promotes the activity of soil microorganisms and the growth of crop roots, as well as the mineralization of SOC [56,57]. The CO<sub>2</sub> emission in the BC treatments cases was cut down by 23.4–29.2% more than in the NPK treatments in the two irrigation conditions. This was probably due to the strong adsorption of the biochar held in the soil nitrogen, phosphorus, and potassium that promoted the formation of the soil aggregates and the physical protection of SOC, thus, slowing down the mineralization of SOC more than in the pure chemical fertilizer treatment condition [58]. Additionally, the interaction of the biochar, soil, and crops may increase the soil carbon utilization efficiency [16,59].

#### 4.3. The N<sub>2</sub>O Emissions of the Soil

The N<sub>2</sub>O emissions of the soil responded sensitively to the two irrigation conditions. The N<sub>2</sub>O emission of the continuous flooding was 49.78–110.73% lower than that of the water-saving irrigation in each treatment (Figure 7c). Haque et al. [5] also found that the seasonal N<sub>2</sub>O fluxes during rice cultivation were approximately three times lower than those during the dried fallow season. Perhaps the main reason for this is that the O<sub>2</sub> content in the long-term flooding condition in the soil was less than that in the water-saving irrigation treatment condition, which inhibited the nitrification of the soil's microorganisms. Meanwhile, the process of soil denitrification was completely carried on and the N<sub>2</sub>O was reverted to N<sub>2</sub>, thereby reducing the N<sub>2</sub>O emissions from the soil [60]. An average decrease of 36% of N<sub>2</sub>O fluxes under high soil moisture conditions, likely induced by the raised abundance of N<sub>2</sub>O-reducing bacteria [61]. Compared with the CK treatment, the cumulative emission of N<sub>2</sub>O significantly increased in both the NPK and biochar treatments under the two irrigation conditions, and this was related to the application of the nitrogen fertilizer [9].

The reduction of N<sub>2</sub>O flux in the biochar application under the water-saving irrigation was very significant, however, there was no reduction effect on the N<sub>2</sub>O flux in the continuous flooding irrigation condition (Figure 7c). Zhou et al. [62] also found that the N<sub>2</sub>O flux reduction was only shown in the growing season of wheat (dry land), but there was no significant reduction effect in the growing season

of rice (under flooded conditions). They thought that the effect of biochar on  $N_2O$  differed between different crops, thus, to correct this difference, we planted the same crop. Consequently, the changes of  $N_2O$  flux were not similar in different crops and this was mainly caused by the differential water holding capacity of the soil [23,63]. In the soil with the lower water-filled pore space, the biochar greatly reduces the  $N_2O$  flux, however, there was no significant effect in the soil with the higher water holding capacity [23,63].

The mechanisms of the  $N_2O$  emission reduction in the biochar treatments under the water-saving irrigation condition were mainly included in the following ways: firstly, a large number of active functional groups and porous structures on the surface of the biochar adsorbed  $N_2O$  directly in the soil [18]. In addition, the biochar reduced the content of  $NH_4^+$  and  $NO_3^-$  by physical or chemical adsorption, and by reducing the substrate of nitrification and denitrification, it cut down the  $N_2O$  fluxes [64]. The porous structure of the biochar had been filled with water and could not effectively adsorb  $N_2O$ ,  $NH_4^+$ , and  $NO_3^-$ . Secondly, the application of biological carbon into the soil improved the soil's pH and the activities of  $N_2O$  reductase, which were beneficial to the transformation of  $N_2O$  to  $N_2$  during denitrification [18,65]. The activities of  $N_2O$  reductase were inhibited by the continuous flooding soil condition so that the reduced impact of the biochar on the  $N_2O$  emission in the paddy fields was limited [63]. Thirdly, the application of the biochar into the soil improved the soil structure, increased the soil aeration, and reduced the denitrification intensity [12]. Finally, the increase in  $N_2O$  in the high biochar application treatment under the F irrigation condition may also be related to the different soil types [66]. In our study, the purple paddy soil of high biochar application increased the  $N_2O$  quantity under the continuous flooding irrigation condition. However, the ferric-accumulic Stagnic Anthrosols of the biochar application cut down the  $N_2O$  emissions in the conditions of flooding [67].

#### 4.4. Net Greenhouse Gas Balance of the GHG Emissions of the Soil

The water-saving irrigation reduced the GWP of  $CH_4$  and  $N_2O$  and also saved water. However, under the condition of high temperature in Chongqing, the photosynthesis of paddy fields may not increase while the respiration of plants greatly increase and eventually increased the overall GWP. Compared with the F irrigation condition, the contribution of the  $CH_4$  emissions to GWP decreased from 30.1% to 19.3%; however, the contributions of the  $CO_2$  and  $N_2O$  emissions increased from 70.1% to 79.5% and 0.22% to 1.2%, respectively, in the water-saving irrigation condition in the CK treatment. Additionally, the contribution of the  $CH_4$  emission to the GWP decreased from 19.9% to 10.5%; the contributions of the  $CO_2$  and  $N_2O$  emissions increased from 79.9% to 88.7% and 0.23% to 0.75%, respectively, in the water-saving irrigation condition in the NPK treatment. The changes in  $CH_4$ ,  $CO_2$ , and  $N_2O$  were also applicable to the biochar treatments. With a reduction in the water input, Xu et al. [26] also found that the contribution of  $CH_4$  emissions to the GWP decreased from 71% to 15%; the contributions of the  $CO_2$  and  $N_2O$  emissions increased from 23% to 73% and 6% to 12%, respectively, in a no-till paddy. They found that the GWP of all three GHGs decreased by up to 25% by using water-saving irrigation strategies. In our study, however, the GWP of all three GHGs increased by 13%, 15%, and 15%, respectively, in the CK, NPK, and biochar application treatments using water-saving irrigation strategies. This is perhaps due to the high temperature in Chongqing during summer, especially in the greenhouse, thus, resulting in the severe transpiration of the crop. The transpiration of rice was required for respiration in order to consume organic matter for energy provision. Thus far, the respiration of rice was very high. Consequently, the contribution of  $CO_2$  to GWP was much higher than that reported by Xu et al. [26].

Compared with the NPK treatment, the application of  $40 \text{ Mg ha}^{-1}$  of biochar in combination with a chemical fertilizer significantly decreased the overall GWP in application two irrigation conditions of paddy fields. The applications of biochar significantly decreased the  $GWP_F$  of paddy soil. The total  $GWP_{FW}$  decreased by 30.8% under application biochar amendment of  $40 \text{ t hm}^{-2}$  compared to application  $NPK_{FW}$  treatment. Zhang et al. [9] also found that the total GWP decreased by 23.8%

and 47.6% with N fertilization, respectively, under application biochar amendment at 20 t·hm<sup>-2</sup> and 40 t·hm<sup>-2</sup> compared to the no biochar amendment of maize yield condition.

The soil carbon sequestration of farmlands was one of the most active and influential carbon pools in the terrestrial ecosystem [68]. The global carbon storage and carbon sequestration capacity of agricultural soils were considered as an important basis for assessing the potential of greenhouse gas emission reduction in the near future [69]. Except for CK<sub>F</sub>, the soil carbon sequestration of other treatments after rice harvest decreased to values lower than that before rice planting (Table 2). The carbon sequestration of BC<sub>F</sub> and BC<sub>FW</sub> was less than that of the other treatments in the rice growth period. This is probably due to the fact that the biochar in the soil played a positive role when it was applied to the soil in the 4 months of rice growth and this was consistent with Singh et al. [70] and Slavich et al. [71]. These scholars also concluded that the effect of biochar in soil disappeared one year after application and that it only affected the stability of soil carbon in the short term [70]. In the three-year field experiment, it was found that the soil SOC reservation increased instead of decreasing [71].

**Table 2.** The net greenhouse gas emissions during the different growth stages in the paddy cropland (CO<sub>2</sub>) kg ha<sup>-1</sup>.

□	GWP <sub>soil</sub>	GWP <sub>soc</sub>	GWP <sub>plant</sub>	Net GHGs
CK <sub>F</sub>	34.87 c	4.22 a	5.54 d	25.11 c
NPK <sub>F</sub>	56.66 a	-1.86 b	10.71 a	47.82 b
BC <sub>F</sub>	39.49 c	-10.47 d	9.88 a	40.08 b
CK <sub>FW</sub>	40.12 b	-2.66 b	4.93 d	37.85 c
NPK <sub>FW</sub>	66.73 a	-2.11 b	10.83 a	58.01 a
BC <sub>FW</sub>	46.16 b	-10.18 d	9.06 b	47.29 b

Note: The same alphabet in the same column indicates that the difference between the two is not significant ( $p > 0.05$ ).

Soil carbon sequestration, plant carbon sequestration, and greenhouse gas emissions in the soil ultimately determine the net greenhouse gas emissions in the farmland ecosystem [72]. In this study, the net greenhouse gas emissions from each treatment were between 25.11 and 59.52 t·hm<sup>-2</sup>, which was the “source” of the greenhouse gases. West and Marland [73] and Baahacheamfour et al. [33] also hold the idea that the net greenhouse gases of the farmland ecosystem were mainly emitted rather than being sequestered. The net GHGS of CK<sub>FW</sub>, NPK<sub>FW</sub>, and BC<sub>FW</sub> increased by 33.6%, 17.6%, and 15.1%, respectively, more than that of the CK<sub>F</sub>, NPK<sub>F</sub>, and BC<sub>F</sub> treatments. The net greenhouse gas emission of BC<sub>F</sub> was 16.1% lower than that of NPK<sub>F</sub>, and that of BC<sub>FW</sub> was 18.5% lower than that of NPK<sub>FW</sub>. This indicated that the effect of 40 t·hm<sup>-2</sup> of biochar application on greenhouse gas emission reduction under the water-saving irrigation condition was better than that under the continuously flooded condition.

## 5. Conclusions

This study provides an insight into greenhouse gas emissions in the sustained flooding paddy field and water-saving irrigation paddy field conditions as impacted by biochar amendments in combination with different proportions of chemical fertilizer in the rice-growing stages in the purple soil in Southwest China. The water-saving irrigation condition reduced the CH<sub>4</sub> emission and promoted the CO<sub>2</sub> and N<sub>2</sub>O emissions compared to that of the sustained flooding condition. The GWP of the water-saving irrigation was also 13–23% higher than that of the flooding one. Proper flooding at the tillering stage contributed to the reduction of the emissions of CO<sub>2</sub> and N<sub>2</sub>O in the soil under the water-saving irrigation condition. Biochar application in the soil reduced the net GHG emissions of CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O in the water-saving irrigation conditions. The net emissions of CH<sub>4</sub> and CO<sub>2</sub> also reduced with the application of biochar, however, the net N<sub>2</sub>O emissions increased in the continuous irrigation condition. The application of 40 t·hm<sup>-2</sup> of biochar in combination with a chemical fertilizer

decreased the GWP of all three GHGs by up to 30.8% in the two irrigation conditions. In conclusion, the application of 40 t·hm<sup>-2</sup> of biochar in combination with an appropriate proportion of chemical fertilizer could offset most of the GHG emissions in the NPK treatment and the effect of the biochar application to the water-saving irrigation on the mitigation of greenhouse gas was better. Thereby, further studies are needed to combine the studied aspects with microorganisms, pH, redox potential, and other factors for more ecological integration.

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