

## Article

# Manganese Slag Amendment Reduces Greenhouse Gas Emissions from Paddy Soil

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**Abstract:** Increasing crop productivity and minimizing greenhouse gas emissions from paddy fields are increasingly receiving attention. Slag application not only can maximize the use of solid wastes as beneficial resources for agricultural production, but it also reduces greenhouse gas emissions. In order to determine the most effective slags as soil amendments for greenhouse gas emission reduction, three major slags, i.e., steel, titanium and manganese slags, were applied as soil amendments to paddy soils; correspondingly, the greenhouse gas emissions, cumulative emissions and global warming potential of the soils during one growing season were measured. It was found that applying all these three slags could reduce the methane emission rates and the cumulative methane emissions. Manganese slag significantly decreased methane emissions by 55% compared with the control. Carbon dioxide caused no significant changes among different slag treatments; however, the cumulative carbon dioxide emissions from fields treated with steel and manganese slags were lower than those from control fields. The global warming potential of paddy soil with manganese application was 63% lower than that of the control. Finally, manganese oxide was found to have a negative relation with greenhouse gas emissions. It was inferred that the electron acceptors and the photocatalysis of manganese oxide minerals might have been the main reasons for greenhouse gas reduction. This preliminary result could be further applied to utilizing solid wastes as beneficial resources and to developing carbon fixation and greenhouse gas reduction fertilizers.

**Keywords:** slag application; greenhouse gases; manganese slag



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## 1. Introduction

Carbon dioxide, methane and nitrous oxide are three major greenhouse gases (GHGs), and according to the data from the World Meteorological Organization, their concentrations have been found to reach 416 ppm, 1908 ppb and 335 ppb, respectively [1]. Increased greenhouse gases can induce global warming (an increase of 1.5 °C in 2021–2040), cause unavoidable increases in multiple climate hazards and present multiple risks to ecosystems and human beings [2]. Natural processes and anthropogenic activities are two main emission sources of greenhouse gases. For instance, food systems contribute 19–29% of the global anthropogenic GHG emissions, and about 80–86% of the total food system emissions are attributed to agricultural production [3]. Paddy fields are an important emission source of greenhouse gases, and their methane emissions are as high as 48% of those of farmland ecosystems [4]. Rice production in China accounts for 27.7% of the world's rice production and has annual methane emissions of up to 8.11 Tg CH<sub>4</sub> yr<sup>-1</sup> [5,6]. It is of great significance to determine the dynamics of GHG emissions from Chinese paddy

soil and to develop effective GHG mitigating measures for their implications in regional and global climate change.

In light of global climate changes and their impacts on global food production, future agricultural production is expected to encounter multifaceted challenges derived from global climate changes [7]. The biggest challenge that agriculture faces is to produce more grain at lower environmental costs and with lower GHG emissions [8,9]. Natural Climate Solutions (NCS) are strategies and innovative interventions for climate mitigation in the land use sector that either increase carbon storage or avoid GHG emissions [10]. In recent years, a large number of agricultural strategies have been adopted to reduce GHG emissions from rice fields, including water management [8], and film mulching or improved farming measures [11–13]. In addition, substrate additions and fertilizer management are the most common strategies for reducing GHG emissions [14,15]. Therefore, the global trend is to find new substrates with lower greenhouse emissions that are environmentally friendly. Because it has a low price, it is easy to obtain and it contains a lot of elements that benefit plant growth, slag has gradually entered the field of vision. Slag recycling was firstly used in agriculture to help in the remediation of soil acidity, the reduction in industrial waste water organic load or the releasing of potassium and silicate fertilizers [16,17]. In recent years, more and more researchers have realized the value of slags in greenhouse gas reduction and soil carbon fixation [18,19]. It is reported that steel slag, a typical material containing high concentrations of electron acceptors, has decreased methane and nitrous oxide emissions from paddy fields in China [20]. However, the effectiveness of steel slags in mitigating CO<sub>2</sub> emissions is not clearly understood. Unlike methane, CO<sub>2</sub> production requires different environments. Therefore, more attention needs to be paid to the cumulative emissions and overall warming potential of rice cultivation during the whole growing season after slag application. Furthermore, slag is rich in various mineral elements, especially semiconductor minerals with photoelectric response, which can directly affect carbon emissions from paddy soil [21]. Despite this broader knowledge, the detailed understanding of whether these mineral additions can have the effect of reducing GHG emissions from rice fields and of their specific mechanism of emission reduction is lacking, as these topics have not been studied in depth, and currently, these are considered as research gaps.

Previous studies proved that steel slag could reduce methane and nitrous oxide emissions [20]. However, it is not known whether slag application can decrease the cumulative GHG emissions and overall warming potential during the whole growing season of rice or not. Moreover, it is worthwhile to discover other slags capable of increasing rice yield and reducing greenhouse gas emissions. To fill the above-mentioned knowledge gap, the study presented in this paper was aimed at determining (1) GHG emission reduction and cumulative GHG emissions during the whole growing season of rice after the application of three different slags and (2) the role that semiconductor minerals in slags could play in GHG emissions from paddy soil.

## 2. Materials and Methods

### 2.1. Experiment Location and Design

#### 2.1.1. Location

The study was conducted at Experiment Farm, Southwest University of Science and Technology in Mianyang City, Sichuan (104.7° E, 31.5° N; 582 m above sea level). The farm is in an area with subtropical monsoon humid climate with an annual average temperature of 18 °C, annual precipitation of more than 800 mm, and a frost-free period of about 280 days. In this climate, rice and rapeseed are rotated, and double cropping is practiced (with rice being planted from May to September and rapeseed from October to May). In this study, Yixiangyou 2115 was chosen as the experimental material. It was sowed in a dry rice nursery bed on April 17, and uniformly growing seedlings were chosen and transplanted leaving alternated wide and narrow row spaces on May 21. The wide and narrow row spaces were 45 cm and 25 cm, with plant space of 17 cm, respectively. The plots had an area of 48 m<sup>2</sup>. In each of the plots, 1.8 kg of compound fertilizer (equivalent

to 1200 kg / hm<sup>2</sup>, N: P<sub>2</sub>O<sub>5</sub>: K<sub>2</sub>O = 19:10:6) was applied, 50% as the base fertilizer and the remaining 50% as the tillering-promoting fertilizer. From seedling transplanting to June 25, the plots were kept with 3–5 cm deep standing water; then, on June 26 they were drained of their standing water and dried. The other field management procedures were carried out as commonly practiced.

### 2.1.2. Experiment Design

A design of four treatments (steel, titanium and manganese slags, and the other was control) was adopted, and each treatment was repeated three times. The three repetition plots of each treatment were adjacent to each other. These treatment plots were 16 × 3 = 48 m<sup>2</sup>, and neighboring plots were separated with ridges to prevent them from affecting each other in terms of water and fertilization. The main operation to prevent water flowing from one plot to its neighboring ones was to manually form ridges between neighboring plots, and that repaired them when they became dry and hardened. The ridges were 20 cm higher than the standing water surface and were covered with two sheets of black plastic film to protect them. Steel slag was obtained from Anyang iron & steel group Co., Ltd. (Anyang, China) and titanium slag was obtained from Baotai Huashen titanium industry Co., Ltd. (Jinzhou, China), Manganese slag was sampled from a manganese tailing dam, Tongren, Guizhou province, China. The slags were ground with a ball mill for 2 h. Then, one day before transplanting, these slags were applied in a proportion of Fe<sub>2</sub>O<sub>3</sub>: TiO<sub>2</sub>:MnO = 25:5:1. The slag amendment ratio was determined based on the oxide content in paddy soils. Steel, titanium and manganese slags were applied at 4.0 M/ha, 0.8 M/ha and 0.16 M/ha, respectively.

### 2.1.3. Sampling and Measurement

#### Soil Sampling and Soil Physicochemical Parameter Measurement

At the end of the growing season, three soil samples (0–20 cm of soil) were taken for each slag treatment using a soil auger with a diameter of 8 cm. Then, all the samples were placed into self-sealing bags and timely sent to the laboratory. The samples were dried and sieved with 100-mesh sieves for the determination of their organic matter, total nitrogen and phosphorus, pH, XRD (X-ray diffraction) and XRF (X-ray fluorescence).

#### Greenhouse Gas Sampling and Measurements

Three static chambers were prepared for each treatment. These static chambers were divided into two parts, bottom and top boxes, whose dimensions were 50 cm high × 50 cm wide × 20 cm high and 50 cm high × 50 cm wide × 100 cm high, respectively, and a 12 V exhaust fan was installed in one of the top corners of the chambers for air blending. A sensor was placed in the chambers to measure the air temperature. Before each measurement, the static chambers were placed in the field for 15 min; then, the fans were turned on for air blending. Sampling was conducted at 9:00 a.m. Samples were taken every 10 min. In each box, sampling was carried out four times (0, 10, 20 and 30 min). Samples thus obtained were kept in vacuum tubes. The temperature in the static chambers and the water table of paddy soil were recorded when the air samples were taken. After sampling, the top boxes were taken away, and the bottom ones were kept in place, so that rice growth was not negatively affected. The samples were sent to Northwest A & F University to determine the concentrations of carbon dioxide, methane and nitrous oxide using gas chromatography. Gas collection was carried out 1, 7, 49, 81, 103 and 125 days after seedling transplanting.

The greenhouse gas emission flux was calculated using the following formula:

$$J = \frac{dc}{dt} \times \frac{M}{V_0} \times \frac{P}{P_0} \times \frac{T_0}{T} \times H \quad (1)$$

where  $dc/dt$  is the rate of concentration change over time;  $M$  is the molar mass of CH<sub>4</sub>;  $P$  is the atmosphere pressure in the sampling site;  $T$  is the absolute temperature at sampling;  $V_0$ ,  $P_0$  and  $T_0$  are the molar volume, the atmosphere pressure and the absolute temperature

under the standard conditions, respectively; and  $H$  is the chamber height above the water surface defining the actual gas volume in the column.

The cumulative greenhouse gas emissions during the whole growing season of rice were calculated using the following formula:

$$E_c = 24 \times 0.01 \left[ \sum_{i=1}^n \left[ \frac{F_i + F_{i+1}}{2} (t_{i+1} - t_i) \right] + \frac{F_1 + F_n}{2} \right] \quad (2)$$

where  $E_c$  is the cumulative greenhouse gas emission during the whole growing season of rice in  $\text{mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ;  $n$  is the number of samples taken;  $F_i$  and  $F_{i+1}$  are greenhouse gas emission fluxes at the sampling times of  $i$  and  $i + 1$ ; and  $t_i$  and  $t_{i+1}$  are the intervals of time between the sampling times of  $i$  and  $i + 1$ .

The global warming potential of greenhouse gases with different treatments was calculated using the warming potential coefficient of greenhouse gases over 100 years in IPCC 2013 (GWP) ( $\text{kg}\cdot\text{hm}^{-2}$ ), and one research paper [8] shows  $\text{GWPC}_{\text{CH}_4} = 28 \text{ N}$  and  $\text{GWPN}_{\text{N}_2\text{O}} = 265 \text{ N}$ .

**Agronomic and yield characteristics:**

**Plant height:** In each plot, ten plants were tagged, and their tillers were tallied every 10 days until their numbers were stable.

**1000-grain weight and yield:** In each plot, 5 plants with typical fruiting panicles were tagged, harvested and put into seed bags. After they were dried, they were threshed, and their 1000-grain weights were measured. **Yield and yield characteristics:** In each plot, 20 rice panicles were randomly taken, placed into nylon net bags, air-dried and threshed. Once the rice grains thus obtained were dried to have a water content of less than 13.5%, they were weighed after their blighted grains were removed; their weights were used to calculate the rice yield of the plot in question. Each treatment was repeated three times.

## 2.2. Data Analysis

The mean greenhouse gas emissions following each treatment were calculated by averaging the emissions of its replicates at each sampling point. Analysis of variance was employed to test if the mean greenhouse emissions among the different treatments differed significantly. The mean soil organic matter and the nitrogen and phosphorus total contents following each treatment were also calculated by averaging those of its three replicates. The significances of the differences among the different treatments were statistically tested at  $p < 0.05$ . SPSS 20.0 for Windows was employed to conduct data processing, and sigmaplot 12.0 was employed to draw all the relevant graphs.

## 3. Results

### 3.1. Physicochemical Parameters of Different Slags and Slag-Treated Paddy Soils

Slag application to paddy fields clearly affected their soil chemical properties. The TN, TP and soil organic matter (SOM) contents were significantly different among slag treatments. The TN and TP contents with steel slag treatment were higher than those of the control and of fields that received the other treatments (Table 1). The SOM contents with steel slag application were the highest and significantly higher than those with manganese slag treatment. It was shown in the XRD analysis that  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{MgO}$  were the most abundant oxides in steel slag. In manganese slag, the main oxides were  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SO}_3$ ,  $\text{CaO}$  and  $\text{MnO}$ , with  $\text{SO}_3$  reaching 32%. In titanium slag,  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were the most abundant oxides, with  $\text{TiO}_2$  reaching 88% (Table 2).

**Table 1.** Soil physicochemical characteristics following different treatments. Different letters indicate significant difference ( $p < 0.05$ ).

Slag Type	pH	TN %	TP %	SOM mg/kg
Steel slag	7.61 ± 0.04	0.153 a ± 0.0009	0.068 a ± 0.0011	2.369 a ± 0.050
Manganese slag	7.69 ± 0.02	0.135 c ± 0.0006	0.066 ab ± 0.0004	2.015 c ± 0.083
Titanium slag	7.83 ± 0.02	0.141 b ± 0.0008	0.064 bc ± 0.0005	2.261 ab ± 0.097
CK	7.58 ± 0.01	0.137 c ± 0.0007	0.062 c ± 0.0004	2.178 ab ± 0.065

**Table 2.** Oxide compositions of the different slags. Oxide levels were measured using XRF.

Slag Type	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	TiO <sub>2</sub>	CaO	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	MgO	BaO	MnO	Rb <sub>2</sub> O	ZrO <sub>2</sub>	Na <sub>2</sub> O	Nb <sub>2</sub> O <sub>5</sub>	F	V <sub>2</sub> O <sub>5</sub>	NiO
Steel slag	19.60	4.88	17.22	0.10	1.89	38.96	1.72	1.21	10.37	0.06	2.71	/	0.03	0.11	0.09	0.30	0.29	0.20
Manganese slag	28.17	7.85	4.89	1.61	0.39	17.83	0.50	32.21	2.06	0.09	3.68	0.01	/	0.51	/	/	/	/
Titanium slag	1.69	1.36	4.00	0.03	87.92	0.25	/	1.64	0.56	/	1.93	/	0.32	0.14	0.11	0.03	0.02	0.01

### 3.2. Grain Yield and Yield Components

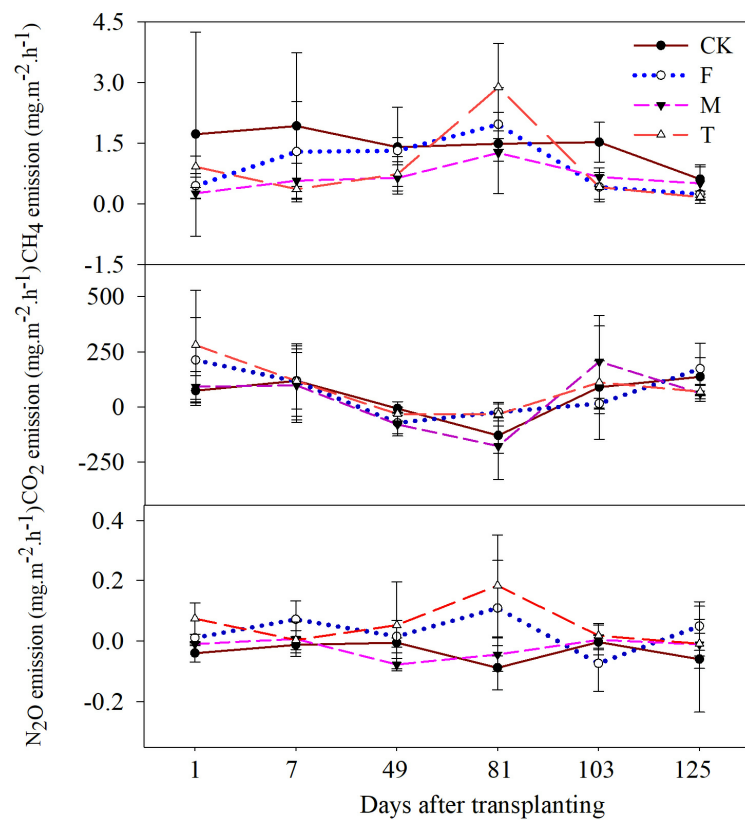
The yield of rice did not significantly differ among treatments, but all the yields following the application of the different amendment slags were higher than those of the control (Table 3). The yield increased by 1% with steel slag application compared with that of the control. Slag application had no significant effects on the tiller numbers and 1000-grain weights. The plant height of rice was significantly higher when steel slag ( $136 \pm 1.4$  cm) and titanium slag ( $130 \pm 1.4$  cm) were applied. The plant height of rice was significantly lower with manganese slag application ( $123 \pm 0.5$  cm) than that of the control ( $125 \pm 0.5$  cm) (Table 3).

**Table 3.** Agronomic traits of rice plants following different slag treatments. Different letters indicate significant difference ( $p < 0.05$ ).

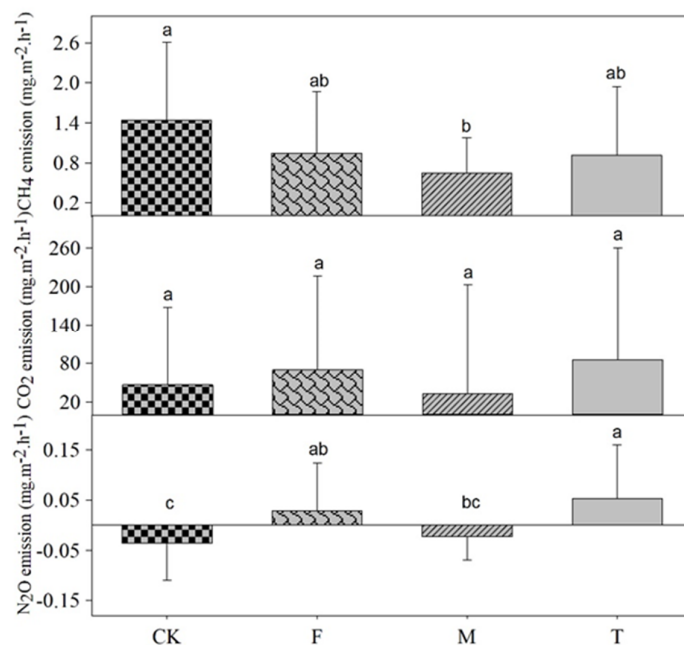
Slag Type	Height (cm)	Tillers (No.)	1000-Grain Weight (g)	Yield (kg/ha)
Steel slag	136 a ± 2.7	12 a ± 3.0	29.8 a ± 0.5	7948 a ± 287
Manganese slag	123 c ± 1.3	8.7 a ± 0.6	29.1 a ± 0.7	7897 a ± 222
Titanium slag	130 b ± 2.4	9 a ± 1.0	29.5 a ± 0.9	7900 a ± 222
CK	125 c ± 3.6	10.3 a ± 1.0	29.4 a ± 0.8	7872 a ± 287

### 3.3. Greenhouse Gas Emissions of Paddy Soil with Different Slag Treatments

The seasonal variations in GHG emissions with the application of the three slags to paddy soil are shown in Figure 1. After seedling transplanting, the methane emissions gradually increased, peaked in 81 days and then declined drastically with all slag treatments (Figure 1). After seedling transplanting, carbon dioxide decreased and reached its lowest value on the 81st day; then, it increased with all slag treatments. The nitrous oxide emissions with steel and manganese slag application showed a trend similar to that of methane emissions. Following the different treatments, methane and nitrous oxide were shown to differ significantly among slag treatments ( $p < 0.05$ ). With manganese slag application, methane emissions significantly decreased, by 55%, compared with the control (Figure 2). Carbon dioxide emissions were shown not to significantly differ among slag treatments (Figure 2). Nitrous oxide emissions were shown to be significantly different among slag treatments. The application of steel and titanium slags significantly increased nitrous oxide emissions.



**Figure 1.** Greenhouse gas emission rates with time versus the different slag treatments. CK—control; F—steel slag application; M—manganese slag application; T—titanium slag application.



**Figure 2.** Greenhouse gas emission rates with the different slag treatments. Significant differences are indicated by different letters above the error bars ( $p < 0.05$ ). CK—control; F—steel slag application; M—manganese slag application; T—titanium slag application.

The cumulative GHG emissions over the whole growing season are shown in Table 4. All of the cumulative methane emissions during the three slag treatments were lower than those of the control ( $44.46 \pm 19.18$ ). With steel, manganese and titanium slag application,

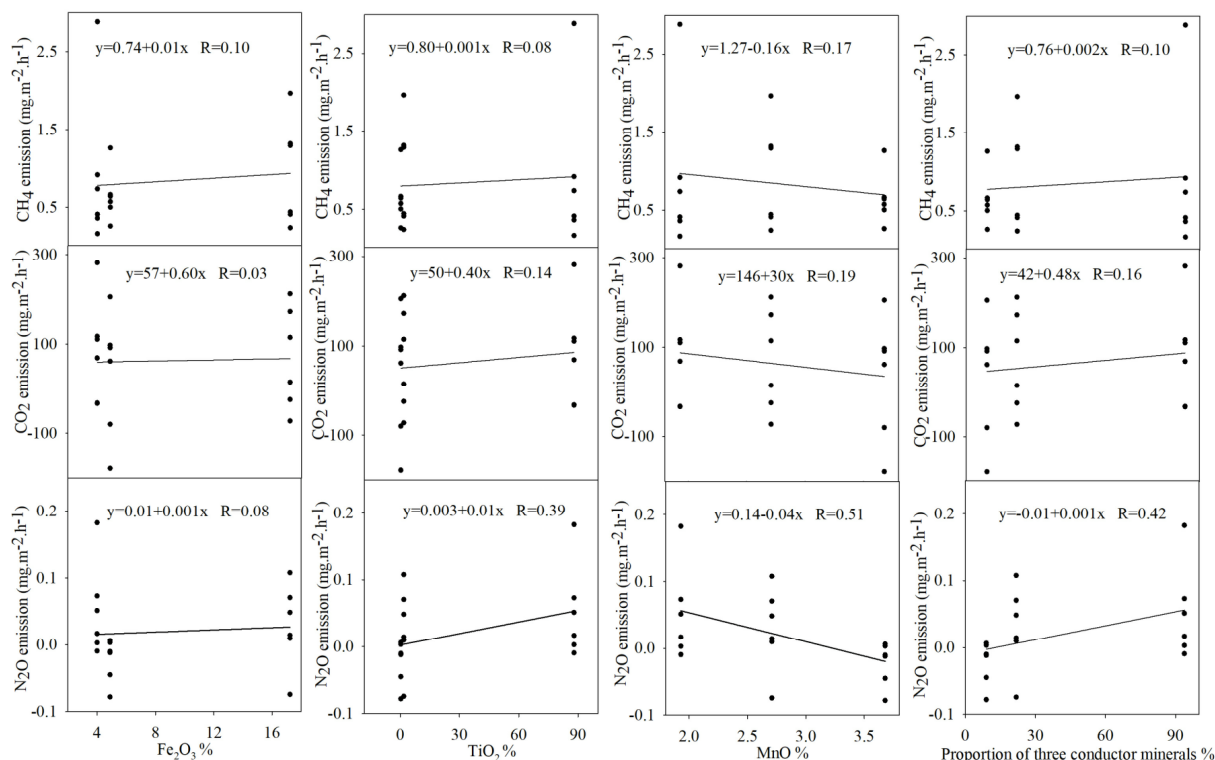
the cumulative methane emissions were decreased by 21%, 50% and 31%, respectively. In addition, with steel and manganese slag application, the cumulative carbon oxide emissions were decreased by 13% and 95%, but with titanium slag application, they were increased by 66%. The cumulative nitrous oxide emissions decreased with manganese slag treatment and increased with the other two treatments. The global warming potential (GWP) for GHG emissions varied among the different gases. The GWP caused by steel and titanium slag amendments increased, and the GWP with manganese slag application decreased by 63%.

**Table 4.** Cumulative greenhouse gas emissions and global warming potential with the different slag treatments.

Treatment	Cumulative Emissions (kg·hm <sup>-2</sup> )			Global Warming Potential (kg·hm <sup>-2</sup> )
	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub> O	
Steel slag	35.14 ± 24.61	624 ± 2322	0.99 ± 2.58	1246 ± 1372
Manganese slag	22.41 ± 14.37	37 ± 3668	−0.98 ± 1.23	368 ± 728
Titanium slag	30.77 ± 12.69	1191 ± 3211	1.77 ± 3.05	1330 ± 1163
CK	44.46 ± 19.18	717 ± 2463	−0.93 ± 1.43	998 ± 915

3.4. Relationships of Greenhouse Gas Emissions and Semiconductor Minerals in Paddy Soil

The major semiconductor minerals identified in the three slags were hematite, rutile and manganosite. A significant correlation was observed between the semiconductor minerals in the applied slags and GHG emissions. Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MnO and their total concentrations significantly affected the GHGs (Figure 3). The GHG emissions increased and were positively correlated with Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and their compositions in the amendment slags. The contents of methane, carbon dioxide and nitrous oxide were negatively correlated with the content of MnO.



**Figure 3.** Scatter plots and fitted regression lines for the greenhouse gas emissions with Fe<sub>2</sub>O<sub>3</sub> (%), TiO<sub>2</sub> (%), MnO (%) and the proportions of the three semiconductor minerals.

## 4. Discussion

### 4.1. Effect of Slag Amendments on GHG Emissions

This study confirmed that steel slag application decreased methane emissions from paddy soil [18,20]. There are two reasons to explain the decrease in methane emissions caused by steel slag application. First, steel slag amendment can increase soil  $\text{Fe}^{3+}$  concentrations, and the increased available  $\text{Fe}^{3+}$  could act as an electron acceptor and thus increase soil reduction capacity [20]. Second, the high silica concentration of steel slag can enlarge the aerenchyma, thereby increasing oxygen transportation from the atmosphere to the rhizosphere, thus enhancing rhizosphere  $\text{CH}_4$  oxidation [22]. With manganese slag treatment in our study, the methane emission rate was also significantly decreased, which was consistent with previous studies that suggested that manganese plays an important role in inhibiting methane emissions and mitigating global warming [23]. Manganese oxides can act as electron acceptors and control the activities of methanogens by limiting their substrate availability [24]. However, titanium slag amendments have no significant effects on methane emissions. This is probably because carbon-cycle-related enzymes show no response to titanium oxide amendment [25]. It was found in this study that slag treatments exerted no significant influences on carbon dioxide emissions, although some studies reported that slag amendment could decrease carbon oxide due to their adsorbent and catalytic abilities [22].  $\text{N}_2\text{O}$  emissions from paddy soil varied considerably among slag treatments. Higher  $\text{N}_2\text{O}$  emissions were observed with steel and titanium slag application, which might have been related to the increased total soil nitrogen content resulted from these amendment slags. In terms of greenhouse gas emission rates, slag application reduced methane emissions and increased nitrous oxide emissions, but it had no obvious impacts on carbon dioxide emissions. The cumulative emissions of methane, carbon oxide and nitrous oxide were significantly lower with manganese slag application than with the other treatments. Thus, paddy fields have the lowest global warming potential if manganese slag is applied to them. It is probably due to the strong oxidant capacity and high redox potential of manganese [26]. Furthermore, in the presence of manganese oxides, organic matter can be oxidized and catalyzed to form relatively stable humus, which can increase the potential of soil carbon fixation [27].

### 4.2. GHG Emission Dynamics and Their Potential Relationship with Soil Minerals

Methane emissions peaked on the 81st day after rice seedling transplanting. This peaking time coincides with the maximum tillering stage of rice [28]. This result is consistent with our previous research results, which indicated that methane emissions were the highest in the tillering stage and had a positive relation with the maximum tiller number [29,30]. Unlike the highest methane emissions on the 81st day after rice seedling transplanting, the results of the study showed a carbon dioxide drop in this stage, because rice paddies always have a  $\text{CO}_2$ -sequestering function and the highest carbon uptake in the tillering stage [31]. The highest carbon dioxide emissions were found 103 days after transplanting, a period of time when there was a lower water table and rice crop was maturing. Thus, higher carbon dioxide emissions contributed to the water management and irrigation of paddy fields. In this study, a traditional irrigation method was adopted for field water management during the whole growing period of rice. In all the growth stages but the late tillering stage, when standing water draining and paddy drying are performed, and the yellow maturity stage, when paddy drying is performed naturally, 3–5 cm deep water was kept. The trend of nitrous oxide emissions was similar to that of methane emissions. In addition to growth stages and water management, more and more attention has been paid to the effects of soil minerals on greenhouse gas emissions. Our previous studies found that respiration in paddy soil was stimulated by semiconductor minerals [21]. In this study, it was also found that there was a positive relation between carbon dioxide emissions and semiconductor minerals, including  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ . It can be seen that the influences of semiconductor minerals on soil carbon cycle are widely present, and their main mechanisms are the photocatalysis of semiconductor minerals under visible light irra-



diation [32]. The photocatalysis of semiconductor minerals on soil surface not only affects soil carbon cycle but also has an important impact on nitrogen oxide conversion [33]. It can be inferred that in the near future, breakthroughs are expected to be made in technology for greenhouse gas emission mitigation using semiconductor minerals, so they are expected to play an important role in reducing greenhouse gas emissions from farmland ecosystems. In particular, it was found in this study that semiconductor mineral manganese oxide had a negative correlation with the emissions of the three greenhouse gases, and its extensive application could have a positive impact on farmland greenhouse gas emission mitigation.

#### 4.3. Effects of Slag Amendments on Rice Productivity

Applying steel slag at  $4 \text{ Mha}^{-1}$ , titanium slag at  $0.8 \text{ Mha}^{-1}$  and manganese slag at  $0.16 \text{ Mha}^{-1}$  increased the grain yield by 76, 28 and 25 kg/ha compared with the control (7872 kg/ha). These increases in rice yield could be attributed to three reasons. First, the most direct reason may be significantly increased soil mass elements after slag application. After slag amendment application, the total N and P contents were significantly increased compared with those in the control field. The soil organic matter contents were increased after steel and titanium slag amendments were applied. Carbon, nitrogen and phosphorus increases provided a good nutritional environment for rice to grow, promoting its yield formation [34]. Second, in this study, there were high contents of CaO (38.96%), SiO<sub>2</sub> (19.60%), Fe<sub>2</sub>O<sub>3</sub> (17.22%) and MgO (10.37%) in steel slag; high contents of SO<sub>3</sub> (32.21%), SiO<sub>2</sub> (28.7%), CaO (17.83%), Al<sub>2</sub>O<sub>3</sub> (7.85%) and Fe<sub>2</sub>O<sub>3</sub> (4.89%) in manganese slag; and high contents of TiO<sub>2</sub> (87.92%), SiO<sub>2</sub> (1.69%), Fe<sub>2</sub>O<sub>3</sub> (4.00%) and MnO (1.93%) in titanium slag. All of these elements are essential nutrients for crop growth. It was reported that Fe<sub>2</sub>O<sub>3</sub> was used to enhance seed germination and increase rich yield [35]. The increased availability of SiO<sub>2</sub> could also greatly boost rice yield and even enhance nitrogen use efficiency [36,37]. TiO<sub>2</sub> could also promote photosynthesis and related metabolic activities in rice [38]. Overall, the increases in soil nutrients were helpful to improve rice yield in the slag-amended plots.

## 5. Conclusions

This study comparatively investigated the effects of the three slag treatments on reducing GHG emissions and enhancing rice production. Its results confirmed that manganese slag, as an effective GHG-reducing material, decreased the methane emission rates by 55% and reduced the global warming potential by 63%. Slag application ( $0.16 \text{ Mg ha}^{-1}$ ) also increased the rice grain yield by 25 kg/ha, compared with the control. The decreases in GHG emissions were attributed to the increased soil active and free iron oxides, which acted as electron acceptors and might have suppressed the activity of methanogens. In addition, the high concentration of silica in slag could increase oxygen transportation and enhance rhizosphere CH<sub>4</sub> oxidation. Furthermore, increases in plant height and biomass after slag application might promote root activity and CH<sub>4</sub> oxidation. Conclusively, manganese slag could be considered as an effective material for reducing GHG emissions, thus mitigating climate change.

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