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A potential of iron slag-based soil amendment as a suppressor of greenhouse gas (CH_4 and N_2O) emissions in rice paddy

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Iron slag-based silicate fertilizer (SF) has been utilized as a soil amendment in rice paddy fields for over 50 years. SF, which contains electron acceptors such as oxidized iron (Fe^{3+}) compounds, is known to reduce methane (CH_4) emissions, which have a global warming potential (GWP) of 23, higher than that of carbon dioxide (CO_2). However, the dynamics of nitrous oxide (N_2O), which has a GWP of 265, were questionable. Since the reduced Fe (Fe^{2+}) can react as an electron donor, SF application might suppress N_2O emissions by progressing N_2O into nitrogen gas (N_2) during the denitrification process. To verify the influence of SF application on two major greenhouse gas (GHG) dynamics during rice cultivation, three different kinds of SF were prepared by mixing iron rust (>99%, Fe_2O_3) as an electron acceptor with different ratios (0, 2.5, and 5%) and applied at the recommended level (1.5 Mg ha^{-1}) for rice cultivation. SF application was effective in decreasing CH_4 emissions in the earlier rice cropping season, and seasonal CH_4 flux was more highly decreased with increasing the mixing ratio of iron rust from an average of 19% to 38%. Different from CH_4 emissions, approximately 70% of seasonal N_2O flux was released after drainage for rice harvesting. However, SF incorporation was very effective in decreasing N_2O emissions by approximately 40% over the control. Reduced Fe^{2+} can be simultaneously oxidized into Fe^{3+} by releasing free electrons. The increased electron availability might develop more denitrification processes into N_2 gas rather than NO and N_2O and then decrease N_2O emissions in the late rice cultivation season. We could find evidence of a more suppressed N_2O flux by applying the electron acceptor-added SFs ($SF_{2.5}$ and $SF_{5.0}$) to a 49%–56% decrease over the control. The SF application was effective in increasing rice productivity, which showed a negative-quadratic response to the available silicate (SiO_2) concentration in the soil at the harvesting stage. Grain yield was maximized at approximately 183 mg kg^{-1} of the available SiO_2 concentration in the Korean rice paddy, with a 16% increase over no-SF application. Consequently, SF has an attractive potential as a soil amendment in rice paddy to decrease GHG emission impacts and increase rice productivity.

KEYWORDS

silicate fertilizer, methane, nitrous oxide, electron transfer, iron

1 Introduction

Iron slag-based silicate fertilizer (SF) has been utilized as a soil amendment for >50 years to improve soil productivity in East Asian rice paddies (Ohta et al., 1953; Park, 2001; Makabe-Sasaki et al., 2014). SF, which is made from blast furnace slag (BFS), a byproduct from iron-making factories, primarily consists of silicate (SiO_2) and calcium oxide (CaO) derived from iron ore and added lime, respectively (Horii et al., 2015; Piatak et al., 2015). In Korea and Japan, SF has been subsidized by the government to improve soil quality and rice productivity (Park, 2001; Makabe-Sasaki et al., 2014).

SF application can improve plant resistance against climatic vulnerabilities and abiotic–biotic stresses (Bokor et al., 2021). In particular, rice uptakes SiO_2 by approximately 10% of its own biomass (Luyckx et al., 2017). Since SiO_2 accumulates in the epidermal cell, it is known to protect itself against pathogens and lodging damage (Ma et al., 2006; Meharg and Meharg, 2015). On the other hand, the accumulated SiO_2 can improve rice plant erectness and then enhance photosynthetic activity (Cooke and Leishman, 2011; Dorairaj et al., 2017). In a 28-year field experiment in Korea, 1.5 Mg ha^{-1} of periodic SF application enhanced rice grain productivity by an average of 14% over no amendment (Lim et al., 2022).

SF also contains high contents of oxidized iron (Fe^{3+}) and was known to decrease methane (CH_4) emissions during the rice cropping period (Ali et al., 2008; Wang et al., 2019; Galgo et al., 2022). CH_4 is biologically formed via the decomposition of organic matter and the reaction of carbon dioxide (CO_2) and hydrogen (H_2) by methanogens under strongly anaerobic conditions (less than minus 200 mV of soil Eh value) (Christy et al., 2014). The activities of electron acceptors and donors can play a dynamic role in regulating CH_4 production and consumption (Madsen, 2011). The oxidized ion can accept free electrons under extremely reduced soil conditions and suppress methanogenesis. However, its acceptability has higher power in the order of O_2, NO_3, Mn^{4+}, Fe^{3+}, SO_4^{2+}, and CO_2 (Keller et al., 2009; Gao et al., 2019). Overall, the electron acceptors, which have higher acceptability than CO_2,

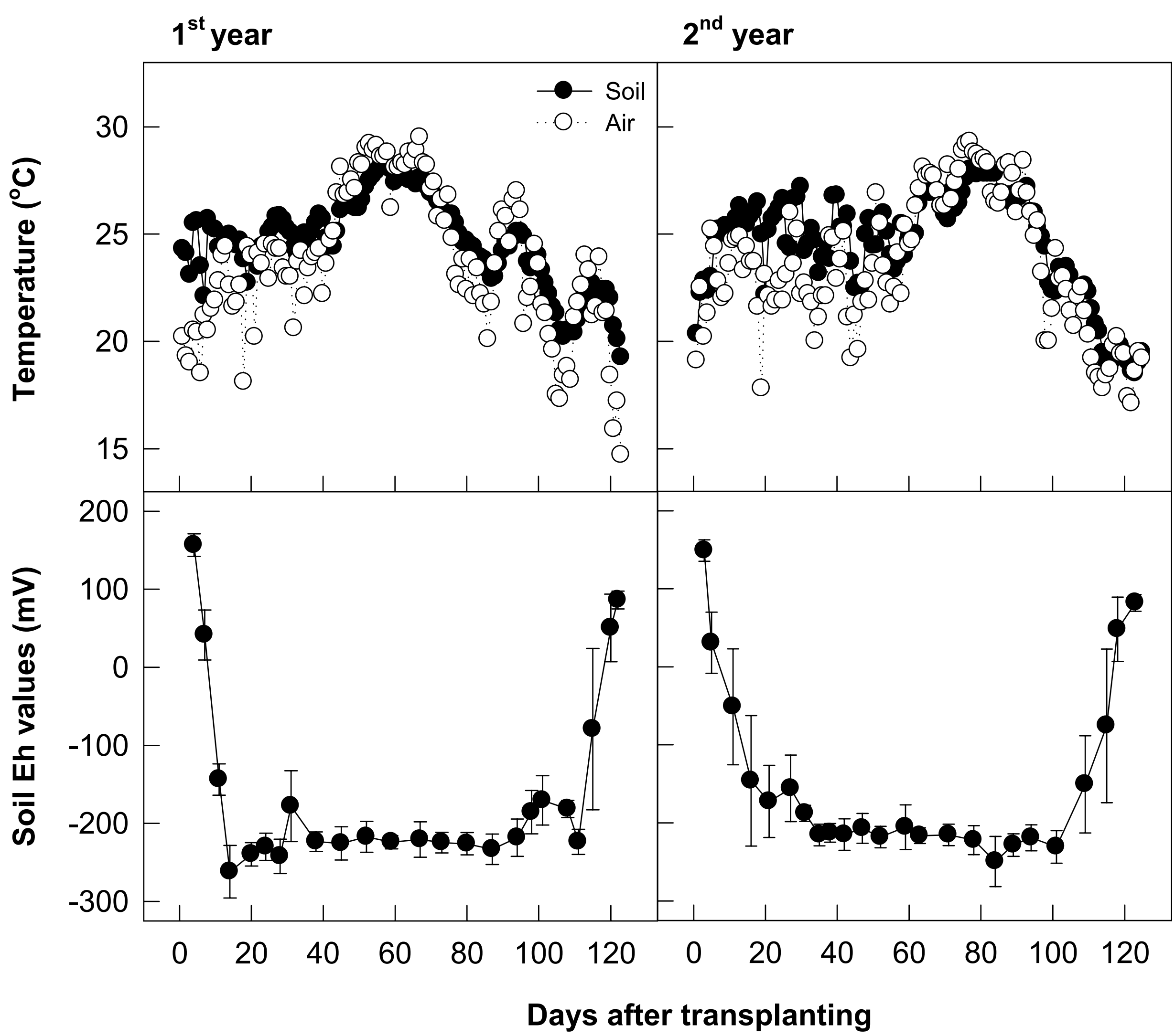

FIGURE 1
Changes in soil and air temperatures and soil Eh values during rice cultivation.

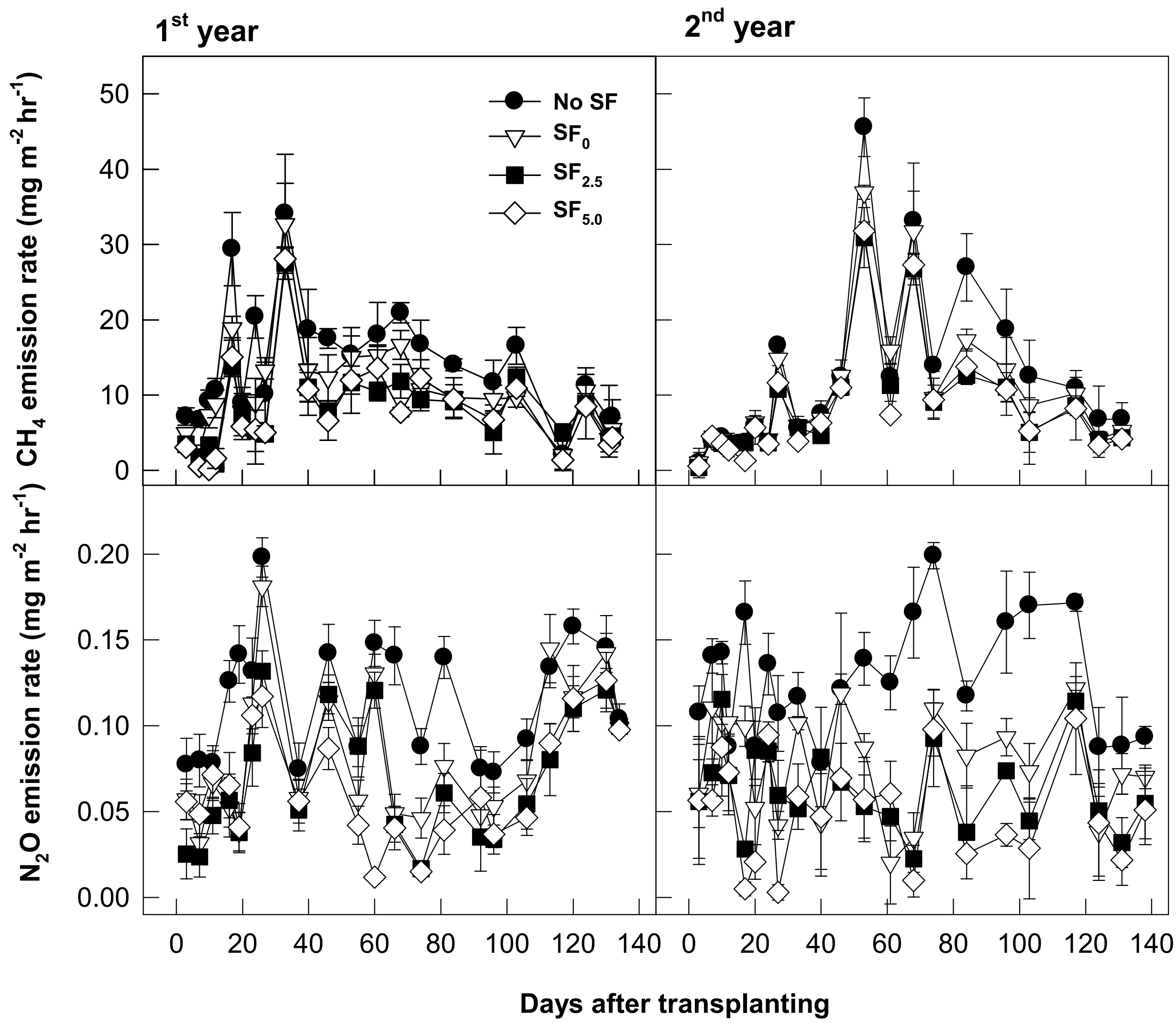

FIGURE 2
Changes in greenhouse gas (CH_4 and N_2O) emission rates in rice paddy soils amended with silicate fertilizer.

can compete with methanogens and then suppress methanogenesis (Frenzel et al., 1999; Kumaraswamy et al., 2001).

Nitrous oxide (N_2O) is biologically formed by denitrification from nitrite (NO_2^-), which is an electron-donating process (Schreiber et al., 2012; Heil et al., 2016). NO_2^- can be denitrified into nitrogen oxide (NO), N_2O, and nitrogen gas (N_2); however, with higher amounts of free electrons, NO_2^- might be converted into N_2 gas rather than NO and N_2O (Chandran et al., 2011). This implies that N_2O flux can theoretically be determined by electron availability (Kool et al., 2011). Fe^{3+}, which was added by SF, might react as an electron acceptor and then suppress methanogenesis by consuming free electrons, especially during the earlier rice cropping season. However, floodwater is generally drained 1 month before harvesting in rice paddy, and subsequently, the reduced soil is oxidized at the later cropping season. We hypothesized that reduced Fe (Fe^{2+}) can be simultaneously oxidized, which can donate more free electrons to the denitrification process. This process can develop a stronger denitrification process into N_2 gas rather than NO and N_2O (Wang et al., 2016; Wang et al., 2020). Therefore, SF addition might decrease N_2O flux in rice paddy, especially during the later rice cropping season. Since N_2O has 265 times higher GWP than CO_2, a small reduction in N_2O flux can strongly influence mitigating global warming. However, the effect of SF on N_2O flux was not properly verified during rice cropping season.

In these 2-year field studies, to investigate the influence of Fe^{3+} as an electron acceptor on two major GHG (CH_4 and N_2O) dynamics, three different kinds (SF_0, $SF_{2.5}$, and $SF_{5.0}$) of SF were prepared by mixing the different rates (0, 2.5, and 5%, respectively) of iron rust (>99% Fe_2O_3) as an electron acceptor, and two GHG fluxes were characterized under the recommended level (1.5 Mg ha^{-1}) of SF application.

2 Materials and methods

2.1 Experimental plot installation and rice cultivation

In the agricultural experimental station (35.15° N, 128.10° E) at Gyeongsang National University, Jinju, South Korea, the

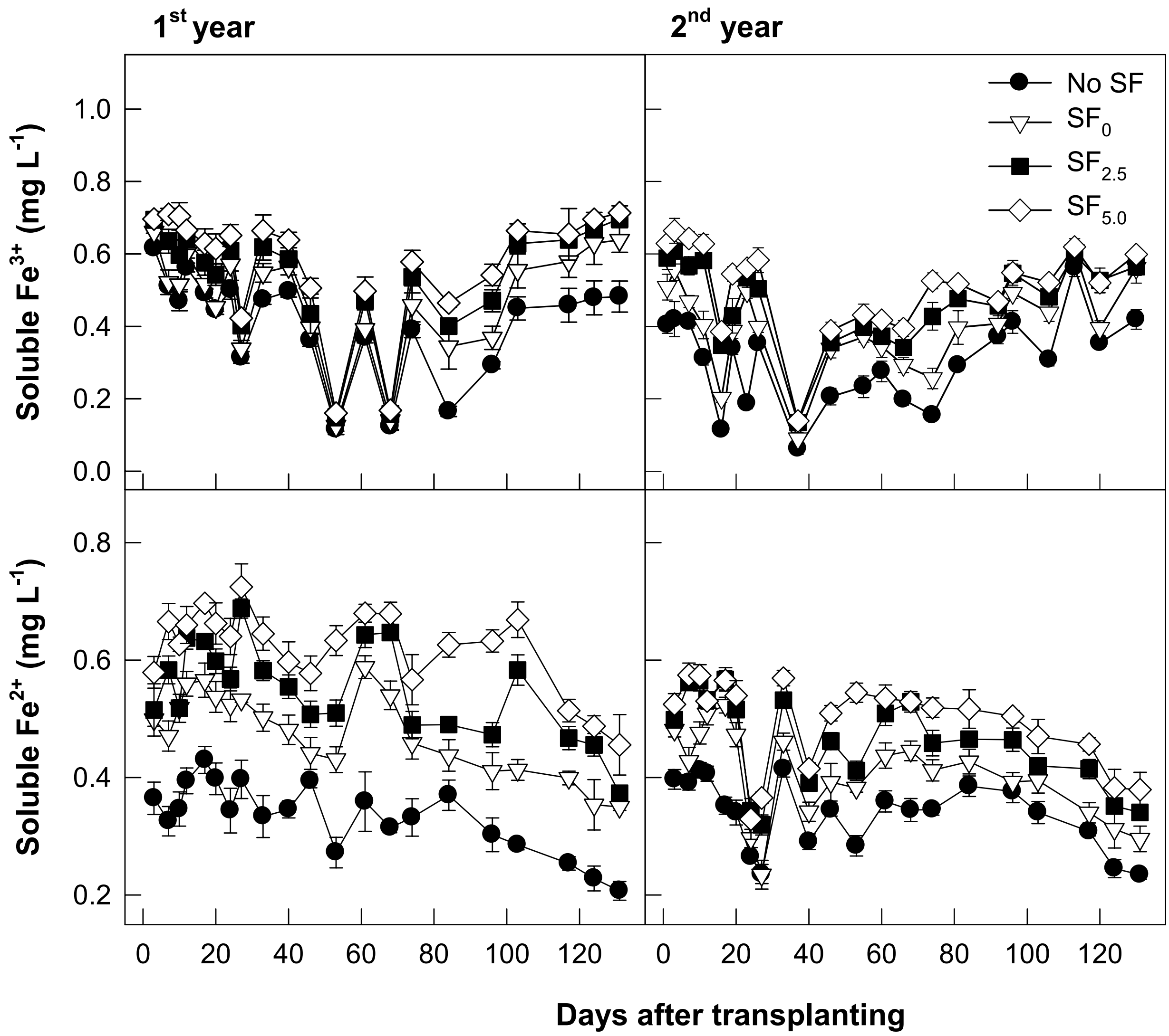

FIGURE 3
Changes in soluble Fe^{3+} and Fe^{2+} concentrations in the floodwater during the rice cropping season.

experimental field was prepared in a typical mono-rice paddy. In the selected rice paddy, only rice was cultivated for over 5 decades during the warm season, but the soil was not managed during the cold fallow season. The field was poorly drained with a silty clay loam (SiCL) texture under the USDA taxonomy classification. Before the experiment, the surface soil (0–15 cm) had a neutral pH (6.1) but low fertility with 16.7 g kg^{-1} of organic matter, 0.88 g kg^{-1} of total nitrogen (N), and 154 mg kg^{-1} of available SiO_2.

SF and no-SF applications were prepared as the main treatment. SF was made from BFS, which primarily consisted of CaO (44%), SiO_2 (35%), and Al_2O_3 (14%), with a high material pH (12.8). In the SF treatment, three different kinds of SFs (SF_0, $SF_{2.5}$, and SF_5) were added as sub-treatments. These SFs were prepared by adding iron rust as an electron acceptor with rates of 0, 2.5, and 5.0% (wt wt^{-1}), respectively. Iron rust had a neutral pH (6.7) and was mainly composed of Fe_2O_3 (>99%) (Galgo et al., 2022). A total of twelve plots (four treatments × three replications) were randomly placed in the selected field. Each plot had a size of 100 m^2 (10 m × 10 m). In the SF treatments, the recommended level (1.5 Mg ha^{-1}) of SF was applied 1 week before rice transplanting and then mechanically plowed within the surface soil (RDA, 2019).

In early June 2020 and 2021, 21 -day-old rice seedlings (Japonica type, Ilmi cultivar) were manually transplanted with a 30 cm × 15 cm planting distance. Except for the SF application, all plots were controlled under the same practices. The recommended levels of chemical fertilizers for rice cultivation were applied with the levels of N–P_2O_5–K_2O = 90–45–57 kg ha^{-1}, respectively. Throughout the rice cropping season, the soil was steadily flooded using groundwater to a depth of 5–10 cm and drained 1 month before rice harvesting. In mid-October of the same years, the aboveground biomass of rice plants was harvested to investigate yield properties.

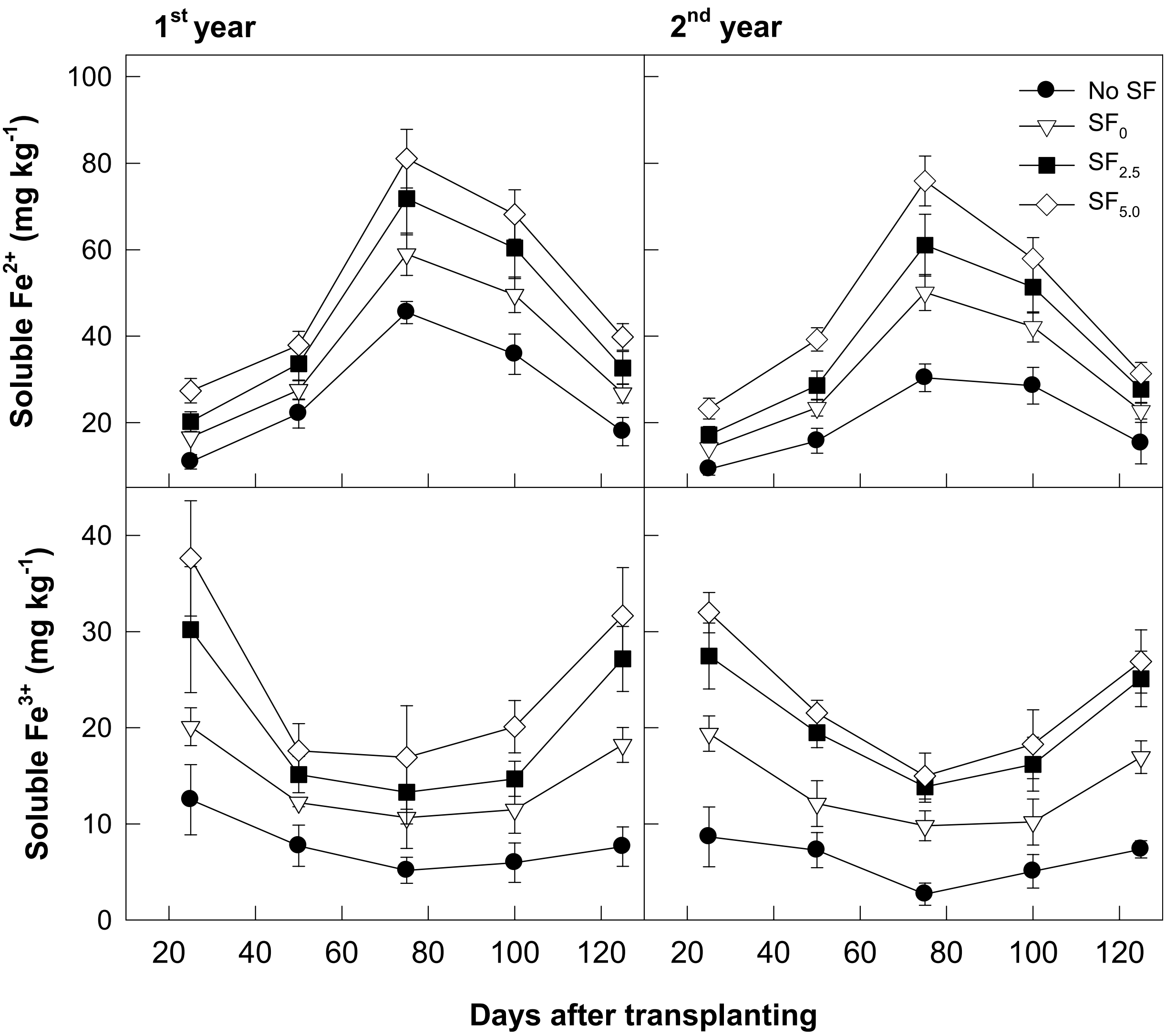

FIGURE 4
Changes in soluble Fe^{3+} and Fe^{2+} concentrations in the soil during the rice cropping season.

2.2 Greenhouse gas flux measurement

To evaluate GHG (CH_4 and N_2O) fluxes, the static chamber method was used (Rolston, 1986). During rice cultivation, three sets of rectangular parallelepiped acrylic chambers (H. 120 cm x W. 60 cm x L. 60 cm) were installed in each plot. A thermometer and two electrical fans were equipped to record the temperature and homogenize the gas inside the chamber, respectively. A total of eight rice plants were transplanted into the chamber with the same planting distance on the outside. The chambers were kept open during the entire investigation period, except for gas sampling.

Before the start of regular gas samplings, the research protocol was established to set sampling conditions such as sampling hours, intervals, and times. In the preliminary measurement, 30 min was selected as the chamber lid closing hour to collect gas samples since the positive linear relationships between gas concentration and chamber closing hour (0, 10-, 20-, 30-, and 60-min chamber closing) were found.

Gas samples were collected weekly between 10:00 and 11:00 a.m., at 0 and 30 min after the chamber closing. Gases were sampled using an air-tight plastic syringe (30 mL) and then directly transferred into 20-mL vacuumed glass vials for analysis. Gas chromatography (GC) was used to quantify CH_4 and N_2O concentrations. A ShinCarbon ST micropacked column and a flame ionization detector (FID) with a methanizer were used to analyze CH_4 concentration. A ^{63}Ni electron capture detector (ECD) and capillary column (HP-PLOT/A capillary column) were selected to evaluate the N_2O concentration. The column, injector, and detector were programmed with a constant temperature of 35, 200, and 200 C, respectively.

The increased concentration was used to calculate gas emission rates (Rolston, 1986).

$$\text{Emission rate } (\text{mg m}^{-2}\,\text{h}^{-1}) = \Delta C/\Delta T \times (V/A) \times \rho \times (273/T),$$

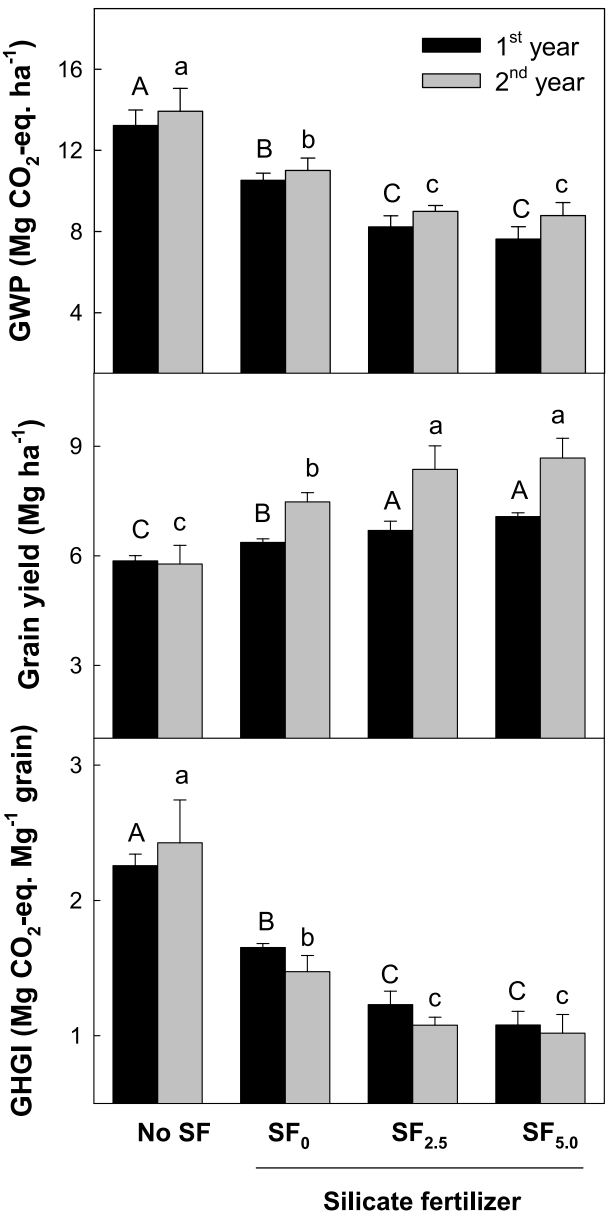

FIGURE 5
Global warming potential, grain yield, and greenhouse gas intensity in rice paddy soils applied with silicate fertilizer. The different letters above the bar indicate a significant difference between treatments (p < 0.05, Tukey test).

where ΔC (mL m^{-3}) and Δt denote the increased gas concentration in the chamber headspace and the chamber closing hour (0.5), respectively. V (m^3) and A (m^2) indicate the volume and surface area of the chamber, respectively. ρ (kg m^{-3}) and T (°K) indicate the gas density (standard condition) and absolute temperature inside the chamber during gas sampling, respectively.

Daily emission rates were integrated to calculate seasonal gas fluxes (Singh et al., 1999).

$$\text{Seasonal gas flux} = \sum_{i}^{n} (F_i \times D_i),$$

where F_i is the daily gas emission rate (g m^{-2} day^{-1}) at the ith sampling; D_i is the interval days between the ith and (i–1)th samplings; and n means the total number of gas samplings.

2.3 Net global warming potential and greenhouse gas intensity

Two GHG (CH_4 and N_2O) fluxes were integrated to calculate the net GWP with the CO_2 equivalent (Mosier et al., 2006).

$$\text{Net GWP}\left(\text{Mg}\,CO_2-\text{eq.}\,\text{ha}^{-1}\right) = CH_4\ \text{flux x}\ 28 + N_2O\ \text{flux x}\ 265.$$

GHG intensity (GHGI) was calculated using the net GWP per grain productivity to compare the yield scale GHG emission impact among the treatments (Shang et al., 2011).

$$\text{GHGI}\left(\text{Mg}\,CO_2-\text{eq.}\,\text{Mg}^{-1}\,\text{grain}\right) = \text{Net GWP}\left(\text{Mg}\,CO_2-\text{eq.}\,\text{ha}^{-1}\right) \div \text{Grain yield}\left(\text{Mg}\,\text{ha}^{-1}\right).$$

2.4 Investigation of soil and water properties and rice yield components

Soil temperature and redox potential were continuously monitored using electric sensors and electrodes in the field during rice cultivation. The sensors and electrodes were installed at a 5–10 cm soil depth and connected to a battery-powered data logger and Eh meter, respectively.

Soil samples (0–15 cm) were collected before rice transplanting and after harvesting, air-dried, and meshed (<2 mm) to analyze chemical properties. Soil pH was measured using a water suspension (1:5 with H_2O). Organic C and total N contents were quantified using the Walkley–Black and Kjeldahl digestion method, respectively. The available P_2O_5 concentration was measured using the Lancaster method (RDA, 2019). Exchangeable Ca^{2+}, Mg^{2+}, and K^+ concentrations were analyzed using an ICP spectrometer (PerkinElmer) after 1 M NH_4-acetate (pH 7) extraction. The available SiO_2 content was analyzed using the molybdenum blue method after 1 N Na-acetate extraction (pH 4) (Yoshida et al., 1959).

Soil and floodwaters were periodically sampled during rice cultivation to monitor the changes in soluble Fe^{3+} and Fe^{2+} concentrations. Floodwater samples were simultaneously collected with gas sampling, but the soil was sampled at monthly intervals. To assay soluble Fe^{3+} and Fe^{2+} concentrations in the soil, fresh soil was extracted using distilled water. The extracted water and collected floodwater were filtered. The Fe^{2+} concentration was analyzed using a 1,10 phenanthroline reagent in dark conditions to prevent photoreduction of Fe^{3+} at 510 nm (UV spectrophotometer) (Loeppert and Inskeep, 1996). The total Fe concentration was measured through the reduction of Fe^{3+} to Fe^{2+} by adding 10% hydroxylamine hydrochloride as a reducing agent. The Fe^{3+} concentrations were estimated using the difference between the total Fe and Fe^{2+} concentrations (Olson and Ellis, 1982).

Rice plants were harvested at the maturity stage. Ten representative rice plants were collected manually from each plot. The harvested rice was air-dried, and the grain and straw were

TABLE 1 Rice yield components.

Year (A)	Treatment (B)	Tiller number	Grain number per panicle	Ripened grains (%)	1,000 grain weight	Grain yield (Mg ha^{-1})
1st	No SF	15	91	89	22	5.9
	SF_0	15	92	92	23	6.4
	$SF_{2.5}$	16	92	92	22	6.7
	$SF_{5.0}$	16	92	90	24	7.1
2nd	No SF	16	88	88	21	5.8
	SF_0	17	93	90	23	7.5
	$SF_{2.5}$	18	98	92	24	8.4
	$SF_{5.0}$	18	99	92	24	8.7
Statistical analysis						
A		ns	*	ns	ns	*
B		***	***	***	***	***
A*B		ns	***	***	*	**

separated. Rice yield components such as tiller number, panicles per hill, 1,000 grain weight, and ripened ratio were measured according to the Korean standard for investigating rice yield properties (RDA, 2019).

2.5 Statistical analysis

IBM SPSS version 20 (SPSS Inc., Chicago, IL, United States) was selected for analyzing statistical characteristics. Variance (ANOVA) analysis was applied to all datasets, and the differences among treatments were compared using the honestly significant difference (HSD) test at a $p < 0.05$ probability level. Regression analyses between GHG fluxes and soluble Fe^{3+} and Fe^{2+} concentrations were conducted using SigmaPlot10.

3 Results

3.1 Changes in temperatures and soil Eh values

Soil temperature similarly fluctuated with air temperature changes (Figure 1). However, soil temperatures were not different among treatments. It gradually increased after rice transplanting, peaked at the reproductive stage between 56 and 77 days after transplanting, and thereafter gradually decreased. However, air and soil temperatures were slightly higher in the second year than in the first year. The cumulative air temperature was 2,913°C and 2,942 C in the first and second years of rice cultivation, respectively. The higher temperature in the second year might influence better rice development and higher productivity.

Soil Eh values changed with a typical pattern in the rice cropping environment. These values sharply decreased to minus 150–260 mV within 2 weeks after flooding (Figure 1). The extremely reduced soil condition, having less than minus 200 mV of soil Eh value, was maintained until water drainage for rice harvesting practices. However, soil Eh values were not different among the treatments.

3.2 Changes in methane and nitrous oxide fluxes

Regardless of soil amendment management, CH_4 emission rates sharply increased after flooding for rice transplanting, peaked at the panicle initiation stage, and thereafter slowly decreased to the background level at the maturity stage (Figure 2). In the control treatment, an average of 12.53 Mg CO_2-eq. ha^{-1} of seasonal CH_4 fluxes was observed. This flux was mostly released in the early stage of rice cultivation, with approximately 80% coverage of the total flux. The conventional SF (SF_0) application significantly reduced the seasonal CH_4 flux by an average of 19% over the control, but CH_4 emission was mostly suppressed at the early rice growing season. The electron acceptor-added SFs ($SF_{2.5}$ and $SF_{5.0}$), which incorporated 2.5% and 5% of iron rust into BFS, were more effective in suppressing CH_4 fluxes. These two SFs increased the suppression effect of seasonal CH_4 flux by approximately 36%–38% over the control, but there was no big difference between $SF_{2.5}$ and $SF_{5.0}$.

Different from CH_4 emission changes, N_2O was emitted without any specific patterns (Figure 2). In comparison, more N_2O was emitted after drainage for rice harvesting. In all treatments, approximately 30% of seasonal N_2O flux was observed in the early rice cropping season, but 70% of total N_2O flux appeared after drainage for rice harvesting. In the control, approximately 1.0 Mg CO_2-eq. ha^{-1} of N_2O was emitted during the rice cultivation period, but the conventional SF (SF_0) application significantly decreased this flux by approximately 40%. The electron acceptor-added SFs ($SF_{2.5}$ and $SF_{5.0}$) were more effective in decreasing seasonal N_2O flux by 48%–56% over the control.

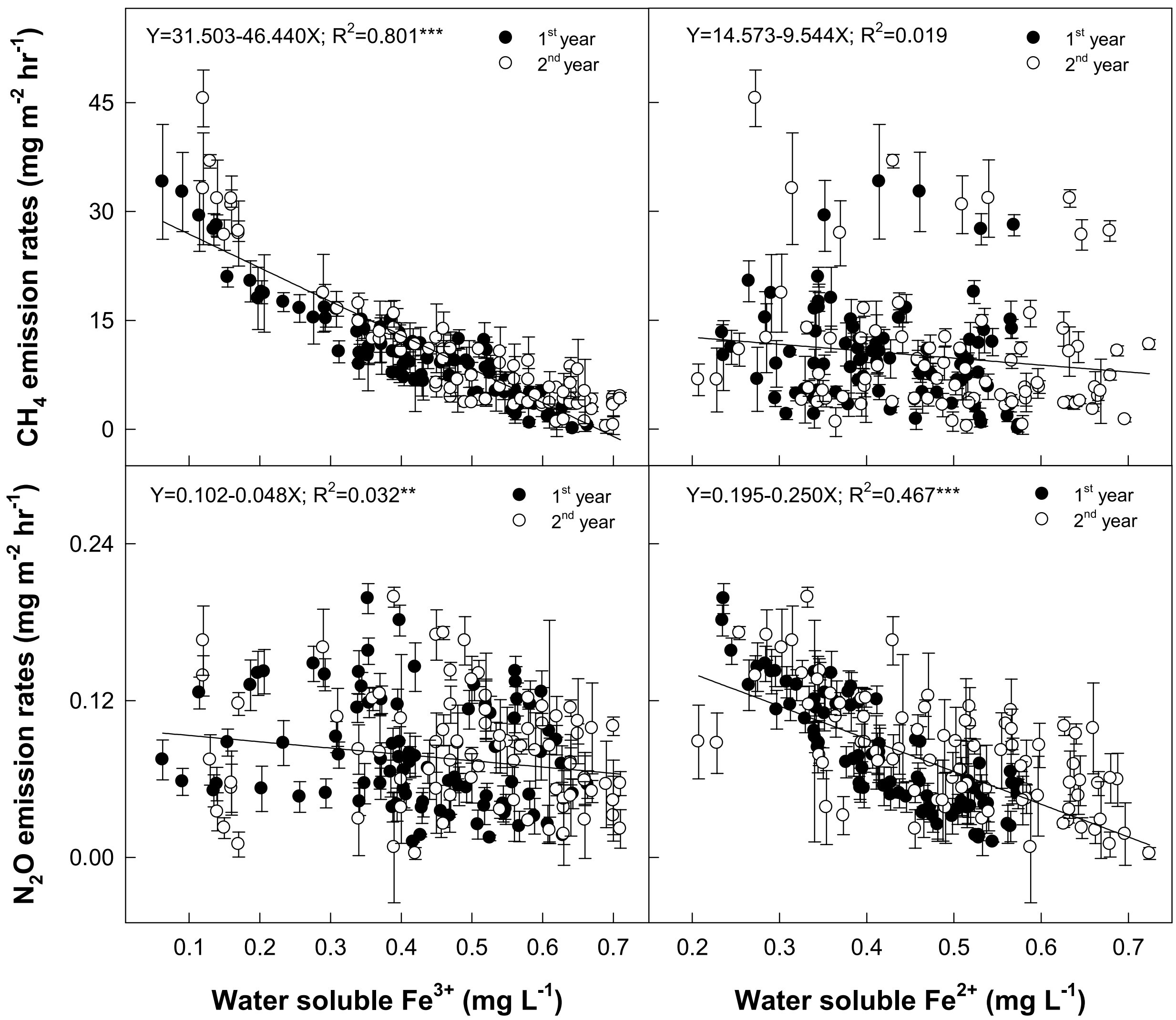

FIGURE 6
Relationship between CH_4 and N_2O emissions rates and soluble Fe^{3+} and Fe^{2+} in the floodwater.

3.3 Changes in iron concentration in floodwater and soil

The changes in soluble Fe^{3+} and Fe^{2+} concentrations were monitored in the floodwater during rice cultivation (Figure 3). The soluble Fe^{3+} and Fe^{2+} concentrations fluctuated in a different pattern throughout the investigation period. Irrespective of the SF application background, the soluble Fe^{2+} concentration rapidly increased after irrigation, peaked at the tillering stage on 27–30 days after transplanting, and then slowly decreased to background levels after drainage for rice harvesting. In comparison, the soluble Fe^{3+} concentration rapidly decreased at the early stage of the rice growing season but increased again in the later stage. The conventional SF (SF_0) application clearly increased Fe^{2+} and Fe^{3+} concentrations in the floodwater. However, the electron acceptor-added SFs ($SF_{2.5}$ and $SF_{5.0}$) more highly increased these two different forms of Fe concentrations in floodwater.

Water-soluble Fe^{3+} and Fe^{2+} concentrations in the soil were analyzed at a 1-month interval (Figure 4). Two different forms of Fe concentration were reversely changed during rice cultivation. Water-soluble Fe^{3+} concentration in soils decreased with decreasing soil Eh value at the early rice growing season but increased after water drainage at the late rice cultivation season. In contrast, the soluble Fe^{2+} concentration was highly increased with developing anoxic soil conditions, peaked at approximately 70–80 days after transplanting, but thereafter, rapidly decreased to the background level. However, soluble Fe^{3+} and Fe^{2+} concentrations entirely increased with SF application and correspondingly responded to iron rust addition.

3.4 Global warming potential

SF application was effective in suppressing two major GHG (CH_4 and N_2O) fluxes during rice cultivation. Since CH_4 and N_2O

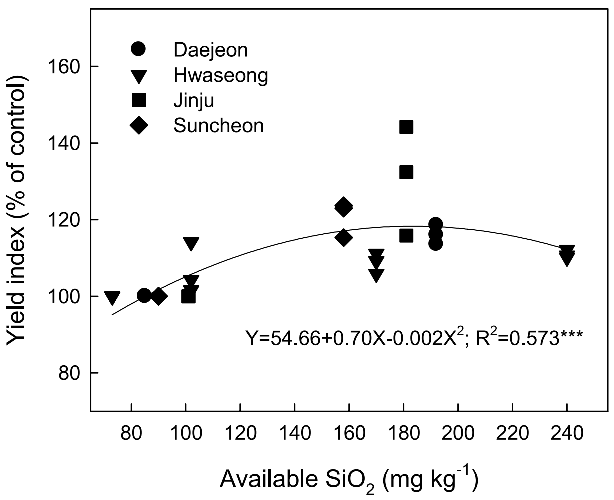

FIGURE 7
Relationship between the grain yield index and available SiO_2 concentration in the soil at the harvesting stage.

have very big GWP values (23 and 265) over a 100-year time horizon, respectively, the net effect of SFs on mitigating global warming was compared using the net GWP, which was integrated by two GHG fluxes with CO_2 equivalent. In the control treatment, total GWP was approximately 13.6 Mg CO_2-eq ha^{-1}, which was weighed by 92% and 8% of CH_4 and N_2O fluxes, respectively (Figure 5). However, the net GWP was slightly higher in the second year than the first year, mainly due to a higher CH_4 flux.

The conventional SF (SF_0) application significantly decreased the net GWP by 21% over the control. SF_0 decreased 19% and 38% of seasonal CH_4 and N_2O fluxes, respectively, but the reduction in net GWP was mainly affected by decreasing CH_4 flux with 94% coverage. In comparison, the electron acceptor-added SFs ($SF_{2.5}$ and SF_5) were more effective in decreasing the net GWP by 37%–40% over the control. These SFs reduced the seasonal CH_4 and N_2O fluxes by 36%–38% and 49%–56% over the control, respectively. However, the decreased CH_4 flux mainly influenced the significant decrease in net GWP with 94% coverage.

3.5 Rice productivity and greenhouse gas intensity

The conventional SF (SF_0) application significantly increased grain yield by 16% over the control due to the increased grains per panicle and the improved 1,000 grain weight (Table 1). SF application increased grains per panicle and 1,000 grain weight by an average of 3% and 4%, respectively, but there was no change in other yield properties. The electron acceptor-added SFs ($SF_{2.5}$ and $SF_{5.0}$) were more effective in increasing grain productivity by 22%–25% over the control, but there was no big difference between $SF_{2.5}$ and $SF_{5.0}$. This yield increase was also influenced by improving grains per panicle, ripened ratio, and 1,000 grain weight. Iron rust-added $SF_{2.5}$ and $SF_{5.0}$ enhanced grains per panicle, ripened ratio, and 1,000 grain weight by an average of 4, 8, and 11% over the control, respectively.

GHGI, which indicates the net GWP per grain productivity, was 2.3 Mg CO_2-eq Mg^{-1} grain in the control treatment (Figure 5). Conventional SF (SF_0) significantly decreased GHGI by approximately 33% over the control due to a 16% increase in grain yield but a 21% decrease in the net GWP. In comparison, the iron rust-added $SF_{2.5}$ and $SF_{5.0}$ were more effective in decreasing GHGI by approximately 51%–55%. This reduction was affected by a highly reduced net GWP rather than a small yield increase.

4 Discussion

Iron slag-based SF, which contains electron acceptors such as oxidized Fe and Mn compounds, was known to decrease CH_4 emissions during flooded rice cultivation (Ali et al., 2008, Huang et al., 2009; Yang and Lu, 2022). Electron acceptors play an important role in regulating CH_4 production and consumption (Watanabe and Kimura, 1999; Sahrawat, 2004; Karri et al., 2005). CO_2 can accept a free electron under an extremely reduced condition (less than minus 200 mV of the soil Eh value) and then produce CH_4 by methanogens (Chapman et al., 1996). The oxidized ions can react as electron acceptors in anaerobic soils (Keller et al., 2009; Gao et al., 2019). The reduction of electron acceptors follows a sequence in the order of O_2 > NO_3^- > Mn^{4+} > Fe^{3+} > SO_4^{2+} > CO_2 (Keller et al., 2009; Gao et al., 2019). Generally, the electron acceptors, which have higher acceptability than CO_2, can compete with methanogens and then suppress CH_4 production (Frenzel et al., 1999; Kumaraswamy et al., 2001).

In this field study, conventional SF (SF_0), which contains 5.4% and 0.4% of Fe and Mn oxides (Galgo et al., 2022), decreased seasonal CH_4 flux by an average of 19% over the control (Figure 2). Since most of CH_4 is emitted during the rice vegetative growth stage, SF mostly suppressed CH_4 emissions at this early rice growing season. As an electron acceptor, a small addition (2.5%–5.0%, wt wt^{-1}) of iron rust, which is a byproduct of the steel processing industry and contains over 99% of Fe_2O_3 on the iron slag-based SF, highly enhanced the suppression of CH_4 emissions by 36%–38%. We also found a highly negative correlation between CH_4 emission rates and soluble Fe^{3+} concentrations in the floodwater (Figure 6). This implies that a small addition of electron acceptors, which have higher electron acceptability than CO_2, can be a soil management strategy to suppress CH_4 production in rice paddy.

Different from the general CH_4 emission pattern, in which most of CH_4 is emitted during the vegetative growth stage (Canatoy et al., 2023; Song and Kim, 2023), over 70% of seasonal N_2O flux was emitted during the rice maturity stage (Figure 2). During the denitrification process, NO_2^- can progress from NO to N_2O and more to N_2 gas with less O_2 supply (Khalil et al., 2004). Under the extremely reduced soil condition, which has less than minus 200 mV of soil Eh value and can activate methanogenesis, like during the early rice growing season, NO_2^- can be converted into N_2 gas rather than NO and N_2O. Therefore, rice paddy might have a very low N_2O emission factor, which is not comparable with upland soils. The Intergovernmental Panel on Climate Change (IPCC) suggested only 0.3% of the added N source as the default value of N_2O flux in the irrigated rice paddy, while 1% of the added N was emitted into N_2O in the upland soils (IPCC, 2023).

SF application significantly decreased seasonal N_2O flux by 38% over the control (Figure 2). N_2O is biologically formed via electron donation from NO_2^- and NO. NO_2^- might be converted into N_2 gas rather than NO and N_2O with more free electrons (Pan et al., 2013; Young et al., 2022). Fe was known as a key factor in regulating N_2O flux (Carlson et al., 2013; Zhu et al., 2013). Fe^{3+}, which was supplied by SF application, might react as an electron acceptor and then suppress methanogenesis by consuming free electrons, especially in the earlier rice cropping season. However, water is drained 1 month before rice harvesting, and then the reduced soil is oxidized at the later cropping season. Fe^{2+} can be simultaneously oxidized into Fe^{3+} by releasing free electrons. The increased electron availability might develop more denitrification processes into N_2 gas, rather than NO and N_2O, and then decrease N_2O emissions in the late rice cultivation season. We could find a clue from the more suppressed N_2O flux by adding the electron acceptor-added SFs (49%–56% decrease over the control by $SF_{2.5}$ and $SF_{5.0}$, respectively) (Figure 2). The N_2O emission rates were negatively correlated with soluble Fe^{2+} concentrations in the floodwater (Figure 6).

In rice fields, the net GWP, which was integrated by seasonal CH_4 and N_2O fluxes with CO_2 equivalent (IPCC, 2023), was mostly determined by CH_4 flux and not N_2O flux. In the control, the net GWP was 13.58 Mg CO_2-eq. ha^{-1}, which was contributed by 93% and 7% of seasonal CH_4 and N_2O fluxes, respectively (Figure 5). The conventional SF (SF_0) application decreased the net GWP by 20% over the control. This reduction was mainly attributed to a significant reduction in CH_4 flux with 94% coverage of the net GWP. The SF application decreased seasonal N_2O flux by 38%, but this reduction did not significantly change the net GWP. The electron acceptor-added SFs ($SF_{2.5}$ and $SF_{5.0}$) more effectively decreased net GWP by 37%–40% over the control, but this decrease came from the big suppression of CH_4 emissions, with 93%–94% of the contribution to the net GWP. This suggests that in rice paddies, a big reduction in CH_4 emissions might contribute to decreasing the impact of global warming.

SF application was very effective in increasing rice productivity and improving rice quality (Table 1). The conventional SF (SF_0) increased rice grain productivity by approximately 16% over the control. This was mainly caused by the increase in grains per panicle and 1,000 grain weight. Rice accumulated SiO_2 in approximately 10% of its own biomass (Luyckx et al., 2017). This accumulated SiO_2 can enhance photosynthetic activity and then increase rice productivity (Cheng, 1982; Cooke and Leishman, 2011; Dorairaj et al., 2017; Galgo et al., 2022). It was known for SF to improve plant resistance against lodging damage and pathogen attack (Ma and Yamaji, 2006; Meharg and Meharg, 2015). In this study, SF application increased grains per panicle and 1,000 grain weight by an average of 3% and 4%, respectively, but there was no change in other yield properties. In addition, the iron rust-added SFs ($SF_{2.5}$ and $SF_{5.0}$) increased rice productivity by 22%–25% over the control. Iron, as an essential element, can enhance plant photosynthesis capacity and then increase productivity (Yadavalli et al., 2012). A high concentration of soluble Fe may lead to Fe toxicity, while Fe toxic levels range from 10 to 1,000 mg Fe kg^{-1} in soils with poor nutrient conditions (Becker and Asch, 2005; Zahra et al., 2021). However, this toxicity was rarely found in rice fields due to Fe precipitation by O_2 released from rice roots (Atulba et al., 2015). In addition, in our long-term study for 28 years, we found that the long-term SF application improves soil properties and rice productivity and quality without any toxicity (Lim et al., 2022).

In the rice cropping area, iron slag-based SF has been used as a soil amendment only in Korea and Japan. Two countries have subsidized SF, but the management standard is slightly different between nations. In Korean and Japanese rice paddies, the SF application level is basically determined by multiplying the constant and difference between the optimum and present levels of the available SiO_2 concentration in soils (RDA, 2019). The constant was determined using the relationship between rice grain productivity and the available SiO_2 concentration in soils after rice harvesting. However, to maximize rice productivity, Korea and Japan recommended 157 and 150–300 mg kg^{-1} of the available SiO_2 concentration as the optimum levels, respectively (NARO, 2009; RDA, 2019). In this study, we analyzed the responses of grain yield index to the available SiO_2 concentration in soils using RDA (Song et al., 2007) and our investigation data (Supplementary Tables S1, S2). The rice grain yield index was negatively and quadratically changed by the available SiO_2 concentration in soils, with a very high correlation coefficient (R^2 = 0.573***) (Figure 7). Rice grain yield increased with the increasing available SiO_2 concentration in soils and maximized at 183 mg kg^{-1} of the available SiO_2 concentration, with a 16% yield increase over no-SF application. This implies that the optimum level of available SiO_2 should be enhanced from the present level (157 mg SiO_2 kg^{-1}) to approximately 183 mg SiO_2 kg^{-1} for maximizing rice grain productivity in the Korean rice paddy.

GHGI, which indicates net GWP per crop productivity (Mosier et al., 2006), was utilized as a standard to compare the net influence of agricultural practices on GHG emission density under the same crop productivity (IPCC, 2023). The conventional SF (SF_0) application significantly decreased GHGI by 33% over the control, mainly due to a highly decreased net GWP rather than a yield increase. In comparison, the iron rust-added SFs ($SF_{2.5}$ and $SF_{5.0}$) were more effective in decreasing GHGI by 51%–55% over the control. This suggests that GHG emission impacts can be significantly decreased using effective soil amendments like SF while improving soil quality and crop productivity in rice paddies.

5 Conclusion

A prospective soil amendment like SF can significantly decrease GHG emission impacts in rice paddies, while also improving soil quality and rice productivity. SF, which is made from iron slag and contains high amounts of Fe and Mn oxides as electron acceptors, was very effective in suppressing CH_4 emissions during the early rice growing season as well as mitigating N_2O emissions during the late rice developing stage. The functionality of SF in decreasing GHG emissions and increasing rice productivity could be highly improved by adding small amounts of electron acceptors like iron rust, which is a byproduct of the steel-making process and contains over 99% of Fe_2O_3. SF was very effective in increasing rice productivity and quality, but the optimum level of available SiO_2 concentration could be better enhanced from the present level (154 mg SiO_2 kg^{-1}) to approximately 183 mg SiO_2 kg^{-1} in the Korean rice paddy for maximizing rice productivity. In conclusion, the functionalized SF could be a prospective soil amendment to mitigate GHG emission impacts in rice paddy and improve rice productivity.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

Author contributions

SG: data curation, investigation, and writing–original draft. RC: data curation and writing–review and editing. JL: data curation and writing–review and editing. HP: data curation and writing–review and editing. PK: conceptualization, supervision, and writing–review and editing.

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Conflict of interest

Author HP was employed by POSCO Co., Ltd.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvs.2024.1290969/full#supplementary-material

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