

Phosphogypsum and cadmium remediation agents: A synergy for mitigating Cd contamination and CH₄ emissions in rice paddies

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Abstract Rice paddies, a major anthropogenic source of atmospheric methane (CH₄), currently face significant cadmium (Cd) pollution. China has a substantial storage of phosphogypsum intended to enhance arable soil fertility. However, little is known about the impact of phosphogypsum on synergic Cd pollution and CH₄ emission in rice paddies. In this study, we conducted a pot experiment to assess the effects of phosphogypsum, combined with Cd remediation agents such as sulfhydryl-modified palygorskite (SMP), bacillus subtilis (BS), and selenium foliar fertilizer (SFF), on soil and rice Cd contents and CH₄ emissions. We found that a large amount of phosphogypsum (2250 kg ha⁻¹) can significantly reduce the bioavailable Cd content in soils. Combining remediation agents with phosphogypsum effectively reduced Cd levels in brown rice. Phosphogypsum can significantly reduce CH₄ emissions from rice paddies, resulting in cumulative evasion rates of 255.54–633.63 kg hm⁻². Our results demonstrate that phosphogypsum paired with

Cd remediation agents effectively reduces Cd contamination in brown rice and CH₄ emissions from rice paddies, providing insights into the synergistic management of heavy metal pollution and greenhouse gas emissions in agricultural environments.

Keywords Cd · CH₄ flux · Phosphogypsum · Remediation agents · Synergistic effect · Rice paddy

1 Introduction

Global warming, primarily driven by greenhouse gas emissions, is expected to increase the average temperature by 1.5 °C in the next 20 years (IPCC 2013, 2021). Worldwide, rice paddies represent one of the most important anthropogenic methane (CH₄) sources (Carlson et al. 2017). This is especially the case for China, which accounts for 20% of the world's rice cultivation areas (IPCC 2014). The 2014 National Soil Pollution Survey showed serious cadmium (Cd) pollution with a site-exceeding-standard rate of 7.0%. Guizhou, known for karst areas, has carbonate rock accounting for 73% of the entire land areas (Luo et al. 2022). Carbonate rock can lead to the enrichment of heavy metals during weathering and soil formation. Guizhou therefore has a higher geological background value for soil Cd (0.659 mg kg⁻¹) (Luo et al. 2022; Zhang and Song 2018). In addition, anthropogenic activities such as mining, smelting, sewage irrigation, and waste treatment increase the content of soil Cd through surface water and atmosphere (Ke et al. 2015; Tu et al. 2013). This elevated soil Cd content poses an environmental risk to crops (Song et al. 2022) and thus human health (Gu et al. 2019; Li et al. 2014). To address this issue, remediation and safety utilization techniques were proposed. For instance, previous studies have shown that

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spraying selenium foliar fertilizer (SFF) can promote rice growth and significantly reduce Cd content in brown rice (Lin et al. 2012). The application of sulfhydryl-modified palygorskite (SMP) can significantly reduce the available Cd content in rhizosphere soil and thus the Cd content of brown rice (Liang et al. 2017). Li et al. (2022) found that inoculation with *Bacillus subtilis* (BS) significantly reduced the bioavailability of Cd in soil. These measures have been proved effective in the remediation of Cd-polluted soil, but whether they can simultaneously affect CH₄ flux from rice paddy requires further research.

Phosphogypsum, a byproduct of phosphoric acid production, is generated at a ratio of 4.5 tons per ton of acid produced in China (Yang et al. 2016). China produces 76 million tons of phosphogypsum annually, with a storage capacity > 500 million tons (Wang et al. 2022), making its recycling urgent. However, the utilization rate of phosphogypsum is generally < 40% because of high costs and energy consumption (Wang et al. 2022). Phosphogypsum contains the nutrients phosphorus and sulfate, which can improve the fertility of agricultural soils. However, there are concerns regarding the safety of heavy metals present in it (Caires et al. 2022; Shivay et al. 2016; Vaishnav et al. 2022). Gauci et al. (2004) revealed an emergent pattern of decreasing CH₄ emissions from peatlands with increasing sulfate (SO₄²⁻) deposition. Schimel (2000) discovered that sulfate-reducing bacteria can effectively outcompete with methanogens for substrates, primarily because of the energetically favorable nature of SO₄²⁻ reduction compared to methanogenesis. This

competition results in the inhibition of methanogenesis, suggesting that phosphogypsum has potential in CH₄ reduction in rice paddies.

In this context, we conducted pot experiments in 2022 by adding phosphogypsum alone or mixed with SMP, BS, or SFF synergistically. The objectives of this study were to (1) explore the Cd contents in soil and rice and (2) examine CH₄ fluxes and cumulative CH₄ emissions. This study hopes to supplement the knowledge on synergistic control effects of phosphogypsum mixed with remediation agents on Cd remediation and CH₄ emission reduction in rice paddies.

2 Materials and methods

2.1 Pot experiment

The pot experiment was conducted at Guizhou Minzu University in 2022. The average temperature was 15.3 °C, and the relative air humidity was 89.96% within the experimental period (Fig. 1). The experiment was divided into four groups with three parallel samples: (1) CK (no agent was added), (2) MG: SMP + phosphogypsum, (3) SG: BS + phosphogypsum, and (4) FG: SFF + phosphogypsum.

The plastic pots were 50 × 50 × 30 cm (length × width × height) and filled with 36 kg air-dried and uniformly mixed soils, which were collected at a depth of 0–20 cm from karst rice paddies in Guizhou. Chemical properties of soils are shown in Table 1. During the whole

Fig. 1 Changes in temperature and relative humidity during the observation period

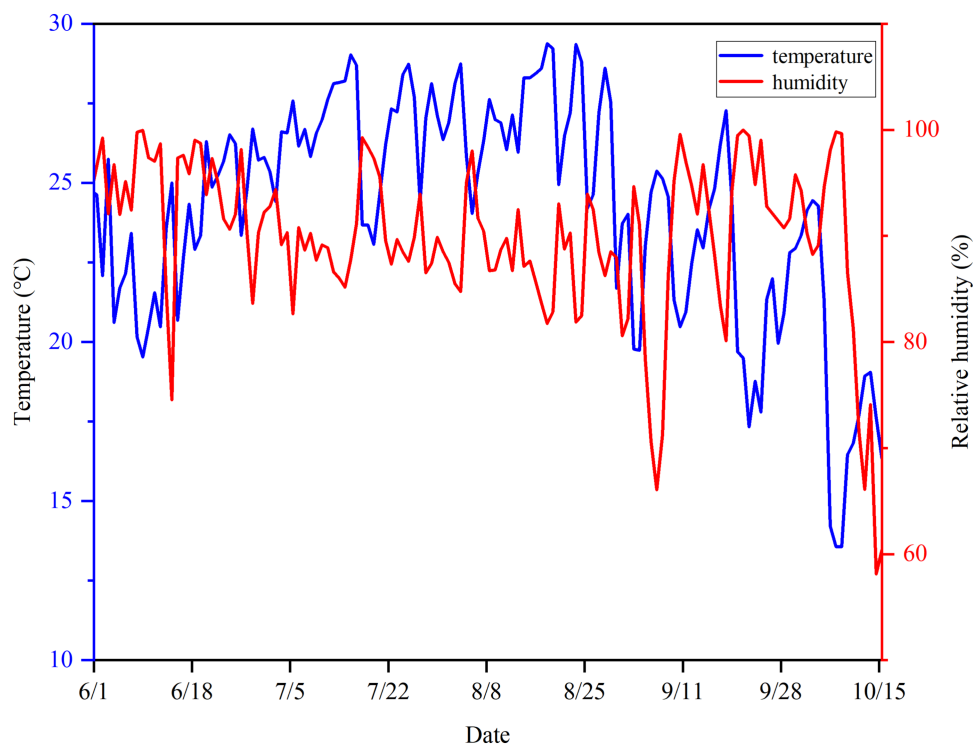


Table 1 Chemical properties of soils

pH	OM (g kg ⁻¹)	NO ₃ ⁻ N (mg kg ⁻¹)	NH ₄ ⁺ N (mg kg ⁻¹)	TP (mg kg ⁻¹)	Available P (mg kg ⁻¹)	Available K (mg kg ⁻¹)	Cd Content (mg kg ⁻¹)	Available Cd (mg kg ⁻¹)
6.98	95.86	96.07	40.89	109.74	12.57	198.38	1.44	0.69

growing season, water management was intermittent irrigation (naturally falling dry to a moist state after 5-cm depth water irrigation), and the water was cut off 1 week before harvest. Detailed information about experiments is shown in Table 2.

The washed phosphogypsum was provided by Guizhou Phosphating Co., Ltd., and the content of water-extractable sulfate in the phosphogypsum was 30.95 mg g⁻¹. SMP was developed and produced by the Chinese Academy of Agricultural Sciences. It also passed through a 100-mesh sieve and contained 1.21% CaO, 10.43% Al₂O₃, 1.54% Na₂O, 20.48% MgO, 64.42% SiO₂, 0.11% K₂O, and 0.89% Fe₂O₃ (Liang et al. 2017, 2013). BS (150 kg ha⁻¹) was provided by Shandong Lihaoyuan Biotechnology Co., Ltd. SFF was provided by Nanjing Ainuo Biotechnology Co., Ltd.

2.2 CH₄ flux measuring

Gas samples were collected using a static chamber at 3–22 day intervals after transplantation. The transparent chambers were 50×50×100 cm (length×width×height). Two electric fans were installed at the top of the chamber to mix the air. Two holes for gas collection and pressure balancing were drilled at the top with a 9.5 mm diameter. Given CH₄ fluxes were influenced by diurnal temperature, those were specifically measured near the daily average temperatures (Dai et al. 2019; Parkin and Venterea 2010). Five samples were collected using 30-mL plastic syringes at

6-min intervals. Soil pH and temperature were measured at 5 cm depth. Gas samples were analyzed immediately using a modified gas chromatography system (GC9790 plus, Fuli Instrument Co., Ltd., China) equipped with a flame ionization detector (FID). CH₄ fluxes and cumulative CH₄ emissions were calculated according to the following equations.

$$F = \rho \cdot \frac{\Delta C}{\Delta t} \cdot H \cdot \frac{273.15}{273.15 + T} \quad (1)$$

F is the CH₄ flux (mg m⁻² h⁻¹). ρ is the density of CH₄ in standard state (0.714 kg m⁻³). $\Delta C/\Delta t$ is the change rate of gas concentration (μl l⁻¹ h⁻¹). T is air temperature in the chamber in Celsius (°C). H is the distance from the top of the chamber to the water surface (m).

$$CE = \sum \left[\left(\frac{F_i + F_{i+1}}{2} \right) \times 10^{-2} \times d \times 24 \right] \quad (2)$$

CE is the cumulative CH₄ emission (kg hm⁻²). i is the number of each sampling. d is the number of days between two consecutive samplings.

2.3 Cd analysis

Rhizosphere soil was collected after the rice harvest, and the soil samples were air-dried and then sifted through a 10-mesh sieve to eliminate debris and pebbles. Subsequently, the samples were ground using an agate mortar and

Table 2 Treatment of pot experiments

Treatment	Date	Specific measures
Seeding	April 10	Sowed rice seeds uniformly in the rice paddy field
Base fertilizer application	June 16	Applied compound fertilizer (N:P:K = 15:15:15, 750 kg ha ⁻¹)
Phosphogypsum, SMP, and BS application	June 16	MG group: Added 0.05% SMP and 0 kg ha ⁻¹ phosphogypsum (MG0), 0.05% SMP and 750 kg ha ⁻¹ phosphogypsum (MG1), 0.05% SMP and 2250 kg ha ⁻¹ phosphogypsum (MG2). Refer to Liang et al. (2017) and He et al. (2018) SG group: Added BS (150 kg ha ⁻¹) and 0 kg ha ⁻¹ phosphogypsum (SG0), BS and 750 kg ha ⁻¹ phosphogypsum (SG1), BS and 2250 kg ha ⁻¹ phosphogypsum (SG2)
Transplanting	June 17 (Day 1)	Selected 4 seedlings with similar growth condition and planted in each pot (distance between each seedling was ~25 cm)
Earing fertilizer application	July 17 (Day 33)	Applied urea and potassium fertilizer (total N ≥ 46.2%, 164 kg ha ⁻¹) (total K ₂ O ≥ 60%, 224 kg ha ⁻¹)
SFF spraying	August 12 (Day 35) and September 4 (Day 83)	FG group: Added SFF and 0 kg/ha phosphogypsum (FG0), SFF and 750 kg ha ⁻¹ phosphogypsum (FG1), SFF and 2250 kg ha ⁻¹ phosphogypsum (FG2). Sprayed SFF until the leaf surface was totally wet. Refer to Liu (2019)
Harvesting	October 9 (Day 123)	Collected rhizosphere soil, root, stem, leaf, and rice

passed through a 100-mesh nylon sieve. The outer husks of the rice grains were removed. The plant samples (brown rice, root, stem, and leaf) were oven-dried at 50 °C for 3 days and then finely powdered using an agate mortar. The soil-available Cd (Cd-DTPA) was determined using DTPA [$c(\text{DTPA}) = 0.005 \text{ mol/L}$, solid-to-solution ratio 1:2, extraction time 2 h] solution extraction and flame atomic absorption spectrophotometer. Soil samples were digested with a mixture of high-purity HNO_3 , HF, and HCl, while plant samples were digested with concentrated HNO_3 . Cd concentrations of all samples were measured using ICP-MS (Thermo Fisher Scientific, USA) in State Key Laboratory of Environmental Geochemistry. More details refer to the procedures proposed by Li et al. (2017).

2.4 Soil chemical property measurement

Soil pH was measured using the water extraction method. Soil organic matter (SOM) was measured using the element analyzer (vario MACRO cube, Germany). Soil NO_3^- -N and NH_4^+ -N were extracted using potassium chloride solution and determined by spectrophotometry. TP was determined using hydrochloric acid extraction and molybdenum antimony resistance colorimetric method. SO_4^{2-} was determined by ion chromatography.

2.5 Statistical analysis

The statistical relationships among all data were analyzed using one-way analysis of variance (ANOVA). All

the figures were drawn by Origin 2021 (OriginLab Corp., Northampton, MA, USA) and CorelDRAW X8 (Corel Corp., Ottawa, Canada).

3 Results

3.1 Physical and chemical properties of soil

Chemical properties of the sampled soil are shown in Fig. 2. Soil pH ranged from 7.38 to 7.64, and the average pH values of CK, MG, SG, and FG groups were 7.44, 7.52, 7.51, and 7.39, respectively. The FG group had lower soil pH compared to other groups. There was no significant difference in SOM contents among groups, ranging from 108.01 to 121.75 g kg^{-1} . MG group showed an increasing trend with the increase of phosphogypsum content.

The average NH_4^+ -N content of CK, MG, SG, and FG groups were 19.09, 21.33, 21.34, and 21.19 mg kg^{-1} , respectively. The average NO_3^- -N contents were respectively 14.44, 11.86, and 19.98 mg kg^{-1} in the MG, SG, and FG groups. The NH_4^+ -N content in each treatment group increased generally relative to the CK, and the SG2 group stood out with the highest NH_4^+ -N content, which was significantly reduced by 52.33% compared to the CK group.

The TP content varied within a range of 93.34 to 151.62 mg kg^{-1} . The average TP levels in the MG, SG, and FG groups were 117.05, 116.92, and 124.92 mg kg^{-1} , respectively, demonstrating an increase of 2.35%, 2.23%, and 9.23% over the CK group. Notably, the TP content in the

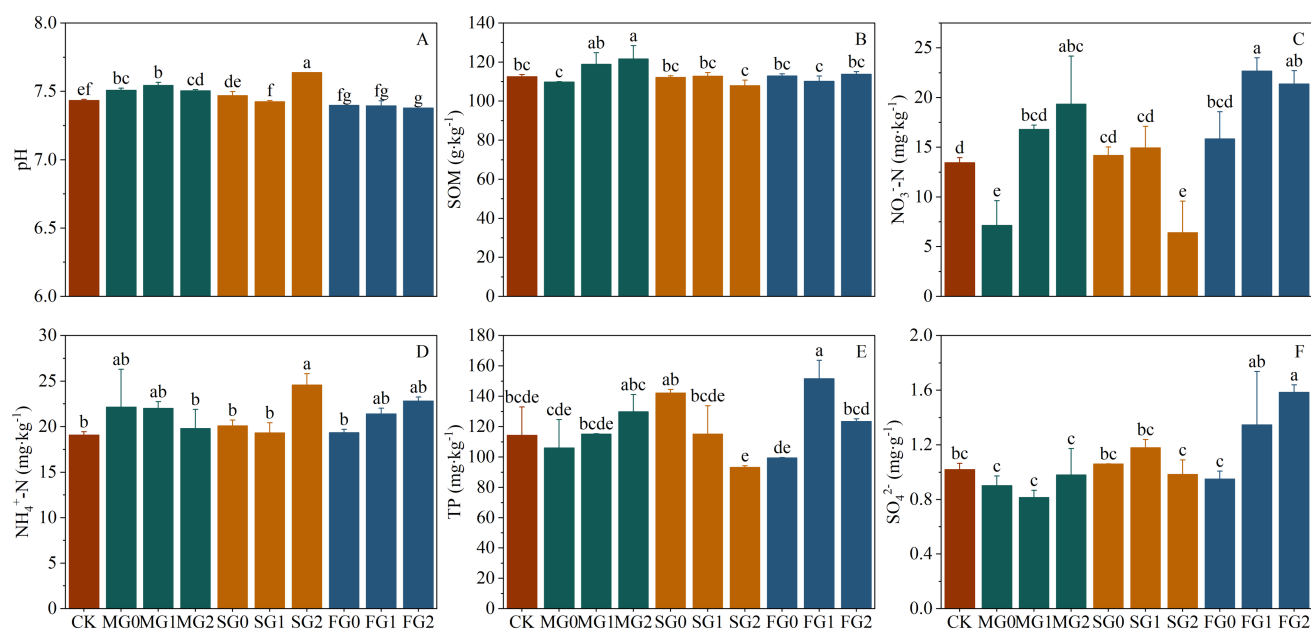


Fig. 2 Chemical properties of the soils. The bars with whiskers show mean $\pm$ standard deviation. Different letters represent significant statistical differences between the treatments

SG group exhibited a decline as the phosphogypsum content increased, contrasting with the MG and FG groups, where the addition of phosphogypsum led to a rise in TP content.

The SO_4^{2-} content, as depicted in Fig. 2F, ranged from 0.82 to 1.59 mg g^{-1} . The average SO_4^{2-} content for the MG, SG, and FG groups was 0.90, 1.01, and 1.30 mg g^{-1} , respectively. The incorporation of phosphogypsum significantly elevated the SO_4^{2-} content, with the MG and FG groups showing the highest levels at high phosphogypsum concentrations, whereas the SG group displayed the opposite trend.

3.2 Cd contents of soil

The content of Cd in the soil samples spanned from 1.10 to 2.48 mg kg^{-1} (Fig. 3A). Within the MG group, the soil Cd content was observed to increase by 14.75% to 40.98%, but the Cd content decreased as the phosphogypsum concentration increased. The average Cd contents for the SG and FG groups were 1.69 and 1.45 mg kg^{-1} , respectively, which corresponded to increases of 38.52% and 18.85% over the CK group. Interestingly, the Cd content in SG2 and FG1 were lower than that in the CK group, with reductions of 9.84% and 2.46%, respectively. These observations indicate a synergistic interaction between phosphogypsum and remediation agents, potentially contributing to the modulation of soil Cd content.

In terms of available Cd, the content ranged from 0.294 to 0.402 mg kg^{-1} (Fig. 3B). The averages in the MG, SG, and FG groups were 0.337, 0.363, and 0.380 mg kg^{-1} , respectively. Notably, MG2, SG2, and FG2 exhibited lower values compared to CK, which decreased by 19.67%, 8.20%, and 7.65%, respectively. This suggests that the combination of remediation agents with high concentrations of

phosphogypsum could effectively reduce the available Cd content in the soil.

3.3 Cd content of plants

As shown in Fig. 4A, the Cd content in brown rice remained below the regulatory threshold of 0.2 mg kg^{-1} , as outlined in the National Food Safety Standard for Pollutant Limits in Food (GB 2762-2022). This observation underscores the compliance with food safety regulations. The variation in the Cd content of brown rice also served as an indicator of the differential heavy metal remediation effects among different experimental groups.

Compared to the CK, the Cd content in brown rice showed a significant reduction across all treatment groups. Specifically, the average Cd levels in brown rice were recorded at 0.038 mg kg^{-1} for the MG group, 0.030 mg kg^{-1} for the SG group, and 0.036 mg kg^{-1} for the FG group, representing a decrease of 30.91%, 45.45%, and 34.55%, respectively. Notably, the MG0, SG0, SG2, and SG1 treatment caused a pronounced reduction in Cd content.

Further analysis of Cd distribution within rice tissues is presented in Fig. 4D, C, and B. In the stems, the average Cd contents were reduced to 0.020 mg kg^{-1} in the MG group and 0.038 mg kg^{-1} in the SG group, corresponding to a decrease of 55.56% and 15.56% from the CK group, respectively. Conversely, in the leaves, the average Cd content increased to 0.024 mg kg^{-1} in the MG group, 0.027 mg kg^{-1} in the SG group, and 0.027 mg kg^{-1} in the FG group, an increase of 14.29%, 28.57%, and 28.57%, respectively, over the CK group. The FG0 recorded the highest Cd content in leaves at 0.033 mg kg^{-1} , a significant increase of 57.14% compared to the CK. However, the combined application of low-concentration phosphogypsum and remediation agents

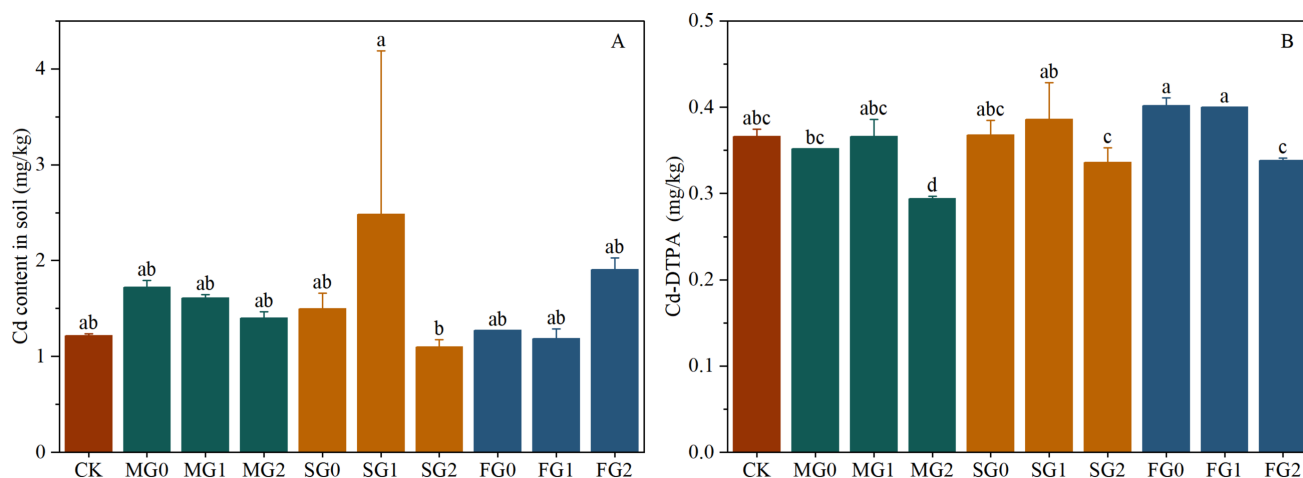


Fig. 3 Soil Cd content across treatments. The bars with whiskers show mean $\pm$ standard deviation. Different letters represent significant statistical differences between the treatments

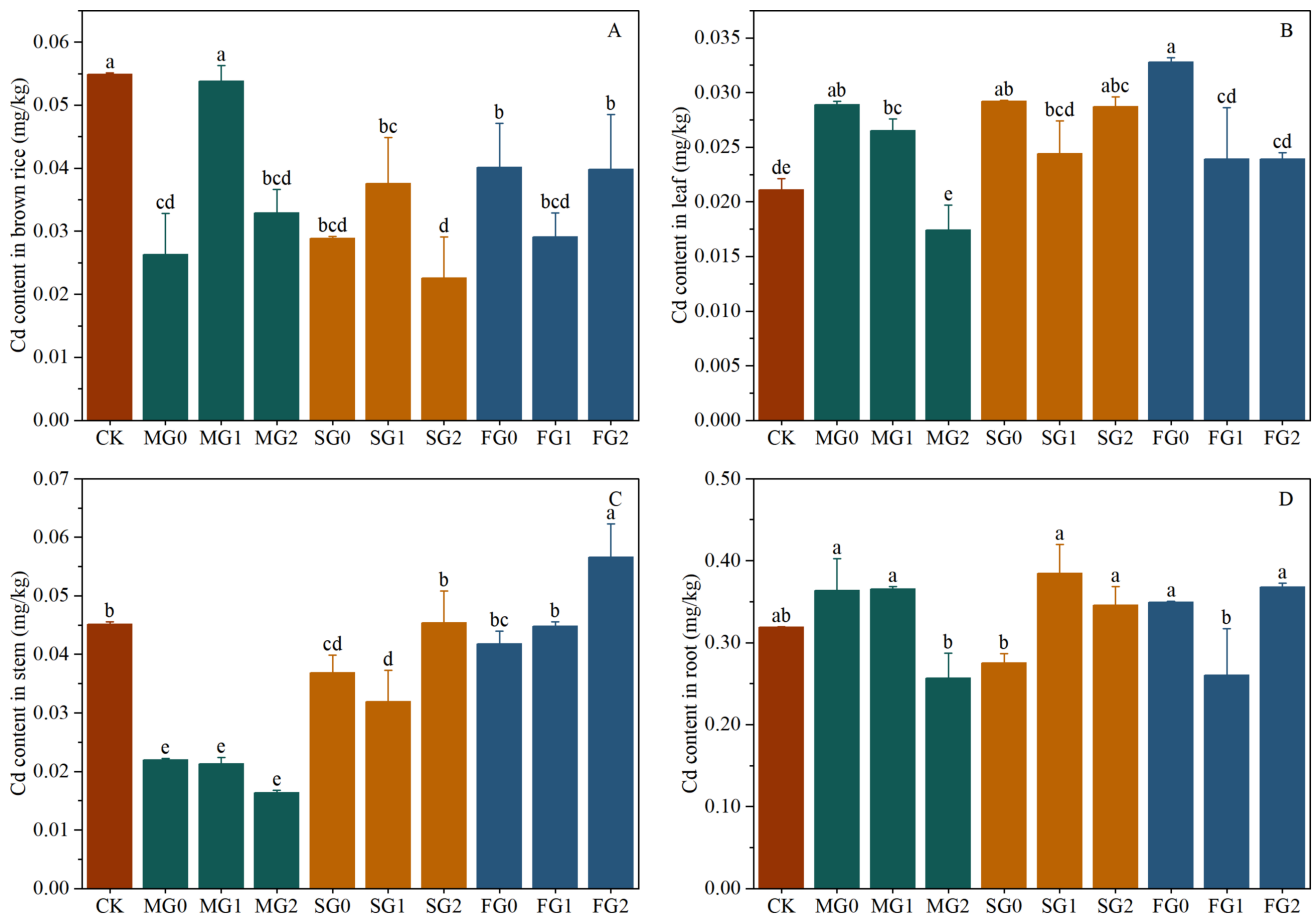


Fig. 4 Cd content in different parts of rice. The bars with whiskers show mean $\pm$ standard deviation. Different letters represent significant statistical differences between the treatments

was observed to effectively lower the Cd content in leaves. In the roots, the average Cd content was 0.329 mg kg^{-1} for the MG group, 0.335 mg kg^{-1} for the SG group, and 0.326 mg kg^{-1} for the FG group.

3.4 CH₄ fluxes and cumulative CH₄ emissions

The temporal dynamics of CH₄ flux and cumulative emission are illustrated in Figs. 5 and 6; they initially rose and then declined during the growing season. The CH₄ flux varied widely, from 0.15 to $21.76 \text{ mg m}^{-2} \text{ h}^{-1}$, with a notable surge observed across nearly all experimental groups on the 72nd day after transplanting.

Cumulative CH₄ emissions ranged from 255.54 to $633.63 \text{ kg hm}^{-2}$, with the CK group showing the highest and the BS2 group the lowest emissions. The average cumulative CH₄ emissions for the MG, SG, and FG groups were calculated at 406.87 , 437.35 , and $406.60 \text{ kg hm}^{-2}$, respectively. Compared to the CK group, these values show substantial reductions of 28.42% , 35.79% , 30.98% , and 35.83% , respectively. Furthermore, the emissions from MG2, SG2, and FG2

were markedly reduced, with decreases of 56.04% , 59.67% , and 53.73% relative to the CK group, respectively.

4 Discussion

4.1 Cd remediation agents

Previous studies have shown that hydroxyl and thiol groups on the SMP surface can form chelates with Cd^{2+} , thereby diminishing the bioavailability of Cd^{2+} (Liang et al. 2014, 2017). The outer surface of BS contained rich functional groups that can adsorb Cd^{2+} , and under Cd stress, BS can produce low-molecular-weight organic acids that can chelate Cd into Cd-organic acid complexes, facilitating the binding of Cd to the cell wall and inhibiting its subsequent translocation into cellular compartments (Xie et al. 2021). However, our results show that there was no significant change in soil-available Cd and root Cd in the SG0. Cd content decreased significantly in the stem yet increased markedly in the leaves. We suggest that low-level BS may lead to insufficient

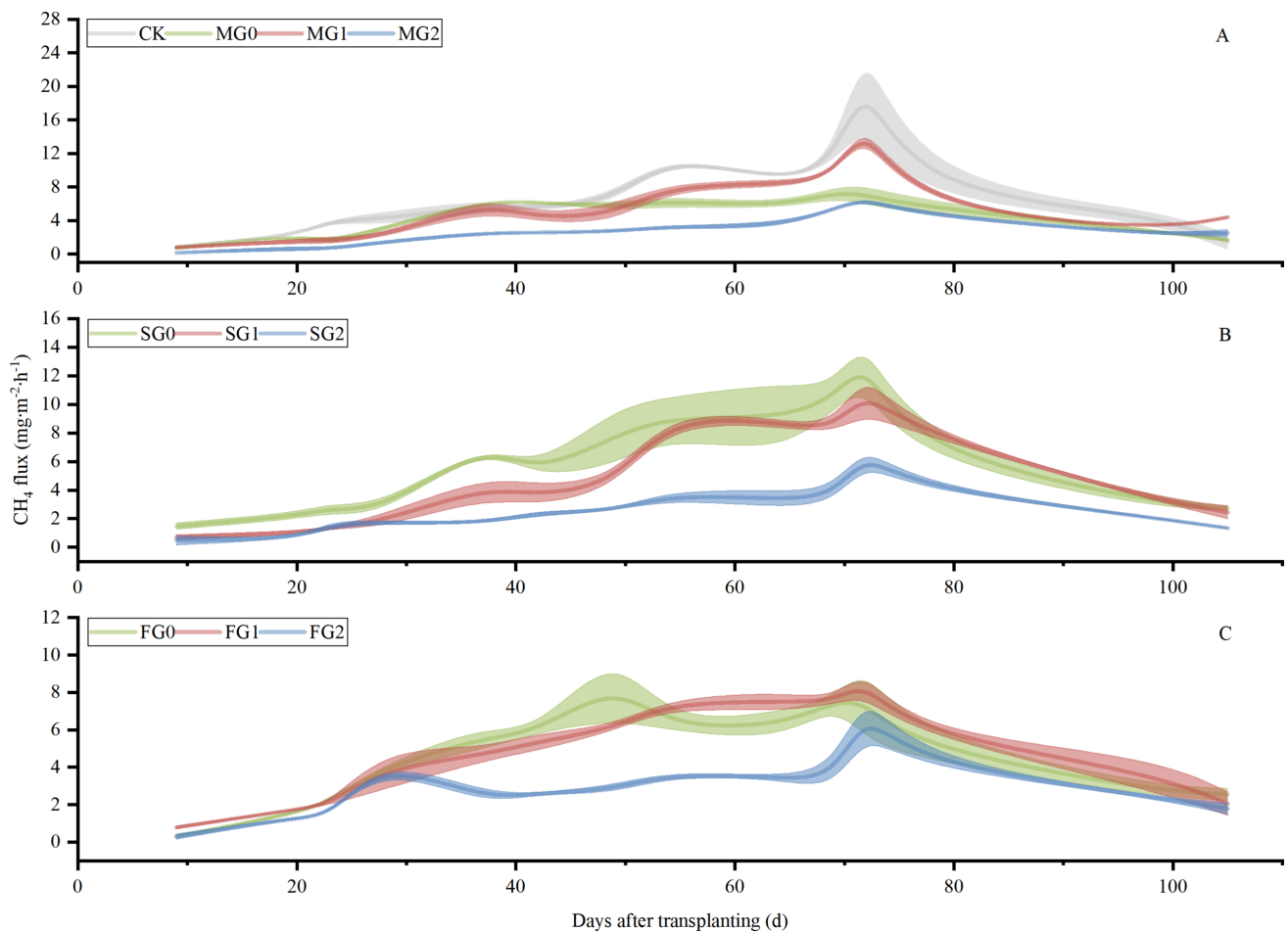


Fig. 5 Soil CH₄ fluxes during the whole growing season. The symbols with whiskers show mean $\pm$ standard deviation

reduction of soil-available Cd. Li et al. (2022) also indicated that large-dosage inoculation significantly reduced soil Cd bioavailability and its mobility into plants. Brown rice Cd is sourced mostly from two pathways: (1) during the vegetative growth period, Cd is transferred from other rice tissues to brown rice via the phloem; (2) during reproductive growth, root Cd enters brown rice directly through the xylem (Rodda et al. 2011). Once BS enters the rice plant through the roots, it can move to the leaves and bind Cd as well as prevent its further transport to brown rice. The Cd content in MG0 stems significantly decreased, reducing its entry into brown rice through pathway.

Our results revealed a significant increase in Cd content in the leaves of the FG0. Selenium fertilizer applied via foliar spray can be absorbed and utilized by plants through the leaf cuticle or stomata, directly inhibiting the transport of Cd from leaves to brown rice (pathway 1) (Lan et al. 2023). Furthermore, selenium enhances the production of plant chelating agents, forming Se–Cd complexes in the roots and limiting Cd transport to aboveground parts (Huang et al. 2018; Rizwan et al. 2020). He et al. (2022) reported that

the application of selenium could reduce the Cd content in brown rice by 36.10% to 48.70%. Sodium selenite reduces Cd accumulation and inhibits its uptake and transport to aboveground parts instead of immobilizing it in the soils. Our results also showed insignificant changes of Cd in FG0 root, stem, and soils. Therefore, SFF mainly reduced the Cd content in brown rice by inhibiting the transport of Cd from leaves to brown rice. Ultimately, MG0 treatment, when used alone, was the most effective for Cd remediation.

Furthermore, our results showed that SG0 and FG0 significantly reduced CH₄ emissions. The incorporation of microbial fertilizers into the soil ecosystem can significantly influence the soil microbial community. Upon application, microbial fertilizers may engage in competition with indigenous root-associated microorganisms for nutrients and ecological niches, potentially altering the composition of these microbial communities (Trabelsi and Mhamdi 2013). The alterations can affect methanogenic archaea and methanotrophic bacteria activity, in turn mediating CH₄ emissions. Additionally, selenium stimulates plant growth and bolsters plant resilience to a variety of stressors (Chu et al. 2010; Yao

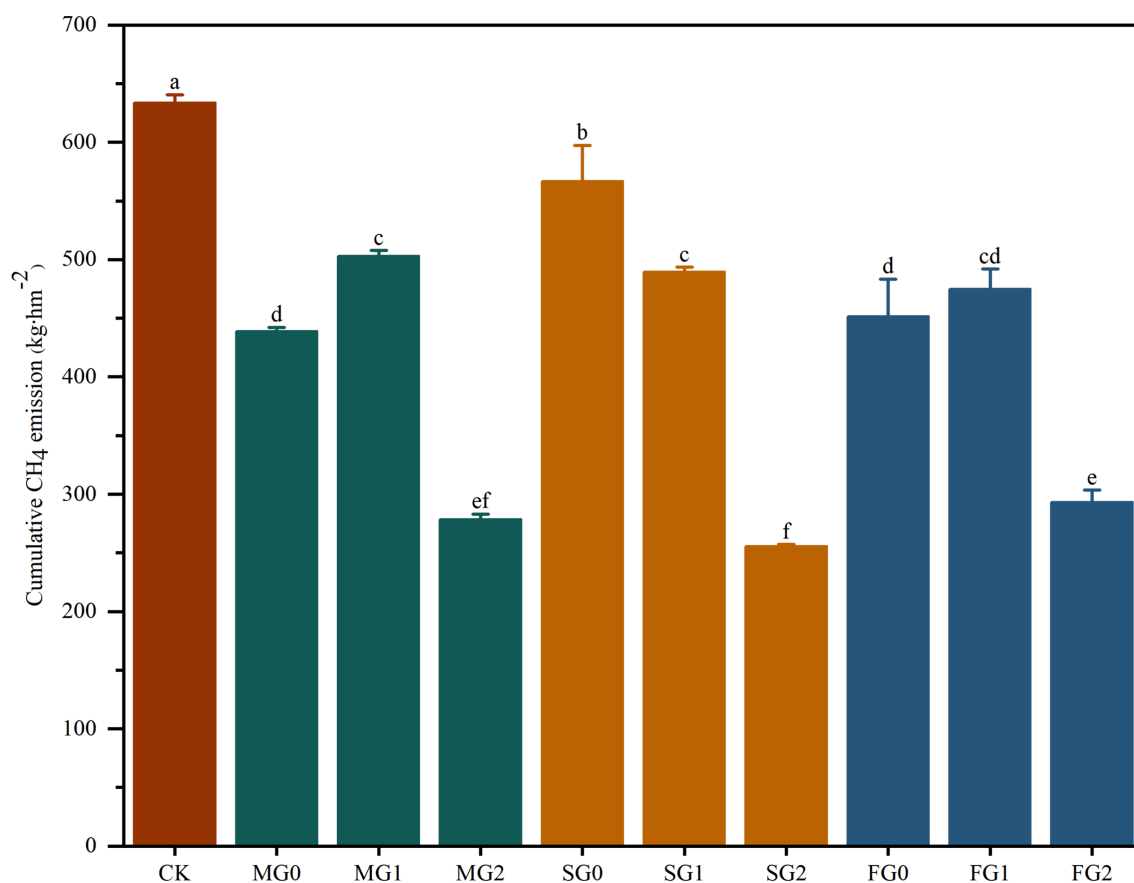


Fig. 6 Cumulative CH₄ emissions from different treatments. The bars with whiskers show mean $\pm$ standard deviation. Different letters represent significant statistical differences between the treatments

et al. 2009). Liu et al. (2024) reported that low-concentration selenium treatment promoted rice seedling growth by enhancing biomass, root length, and antioxidant capacity. An extensive root system can augment the capacity for oxygen secretion by rice roots, which may facilitate the oxidation of CH₄ and consequently contribute to a reduction in CH₄ emissions (Zheng et al. 2018). The addition of SMP also significantly reduced CH₄ emissions from rice paddies. The decreased SOM in the MG0 may constrain CH₄ production (Conrad 2007). In addition, soil pH in MG0 increased significantly, which potentially affects soil microbial activity and leads to a reduction in CH₄ emissions (Wang et al. 1993; Bender and Conrad 1995).

4.2 The role of SO₄²⁻

During the flooding period, the soil conditions diverged significantly from those in the drainage period. In the flooded state, the soil was in an anaerobic environment, leading to a low redox potential. Under these conditions, the SO₄²⁻ in phosphogypsum was reduced to S²⁻. As previously reported by Fulda et al. (2013) and Wu et al. (2019), the S²⁻ could

readily react with Cd²⁺ to form CdS precipitates. This chemical transformation played a crucial role in impeding the translocation of Cd²⁺ into rice plants. The continuous flooding regime further enhanced the rate of sulfate reduction, thereby promoting the precipitation of metal sulfides. Eventually, CdS became the dominant form, and it was non-bioavailable, effectively reducing the environmental risk and bioaccessibility of cadmium (Wu et al. 2019).

Our study corroborates and extends these findings, showing a significant reduction in available Cd in the context of the combined high-concentration phosphogypsum with remediation agents. In the MG and SG groups, Cd concentrations in brown rice initially increased and then decreased, exhibiting a biphasic response to increasing phosphogypsum content. This pattern aligns with the observations reported by Huang et al. (2021), indicating that even low sulfur inputs can enhance Cd transport from stems to leaves, regardless of soil Cd concentrations. Concurrently, sulfur application stimulates the movement of Cd from leaves to rachises through the phloem, directly impacting Cd levels in brown rice. The direct absorption of sulfates from phosphogypsum by plant roots (Hernández

et al. 2015) may lead to an increase in leaf sulfur content, which in turn can elevate the production of cysteine—a key amino acid that may enhance Cd mobility within the plant (Rauser 1999). Our results showed that Cd content in MG1 and SG1 brown rice, respectively, increased by 107.69% and 31.03% compared with MG0 and SG0. However, brown rice Cd decreased when phosphogypsum application increased, suggesting that: (1) a further increase in phosphogypsum did not enhance root or leaf S uptake (Huang et al. 2021); (2) high-concentration phosphogypsum significantly reduced available Cd content in soils. Nevertheless, foliar selenium fertilizer impedes Cd transfer from leaves to brown rice, thereby countering the sulfur-induced increase in Cd mobility. Therefore, the Cd content in FG1 brown rice decreased.

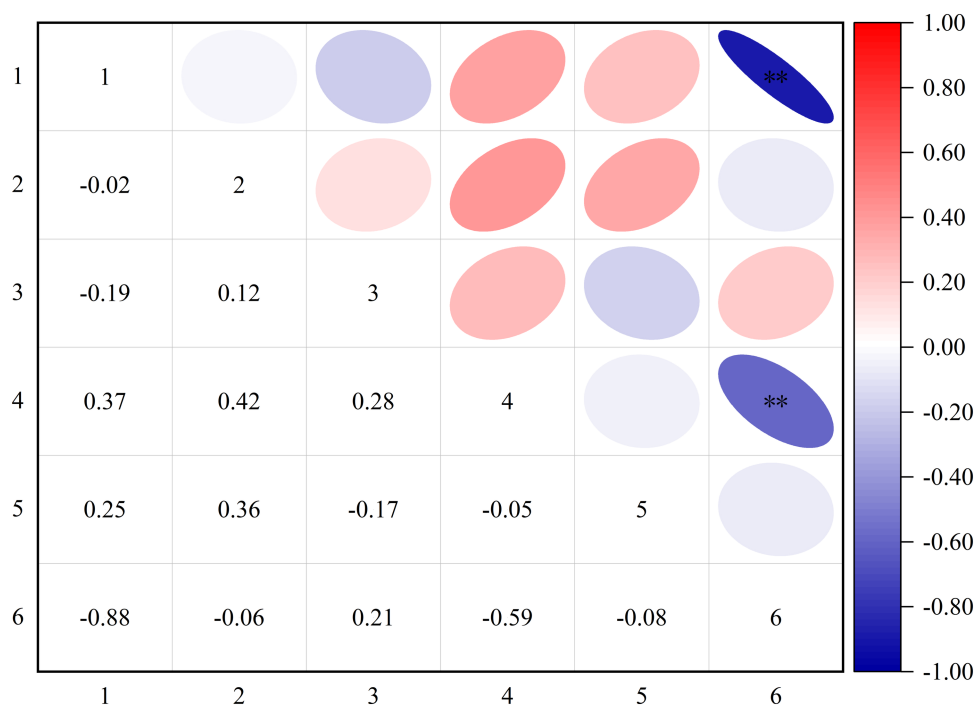
In addition, SO_4^{2-} can enhance the activity of sulfate-reducing bacteria in the soil. Sulfate-reducing bacteria competed with methanogenic archaea for substrates and inhibited the production of CH_4 (Gauci et al. 2004; Gauci and Chapman 2006; Theint et al. 2016). The mixed application of each remediation agent with phosphogypsum reduced CH_4 emission in rice paddies, particularly for high-concentration phosphogypsum. Correlation analysis also showed a significant negative correlation ($p \leq 0.01$) between sulfate content and CH_4 emissions (Fig. 7). Our findings support the view that the competitive sulfate-reducing bacteria with methanogenic archaea reduce substrate availability during methanogenesis processes, restricting CH_4 production in soil environments (Malyan 2017; Sun et al. 2018).

4.3 Other factors

Under flooded conditions, SOM decomposed into small molecule compounds, which were further decomposed into CH_4 by methanogenic archaea (Conrad 2007). With the increase of phosphogypsum content, increased SOM content in the MG group accelerates the emission of CH_4 . Similar results were found by Huang et al. (2022); phosphogypsum significantly increased crop yield, soil fertility, and SOM in the rice cropping systems. However, our results showed that the addition of phosphogypsum had no significant effect on SOM content in the SG and FG groups. In addition, it was noteworthy that the optimal pH range for the activity of most methanogenic archaea was between 6.9 and 7.2 (Wang et al. 1993), while methanotrophic bacteria showed optimal activity at a pH of 7.0 to 7.5 (Bender and Conrad 1995; Dunfield et al. 1993). Soil pH of the SG group rose significantly with high concentrations of phosphogypsum (reaching 7.64 in SG2), which may have affected methanogenic archaea activity and inhibited CH_4 production.

In general, our treatments resulted in a reduction of Cd content with CH_4 emission. The incorporation of remediation agents, either alone or in combination with phosphogypsum, can synergistically mitigate Cd pollution and CH_4 emissions in rice paddies. Alterations in soil adsorption and other physical and chemical properties are responsible for this reduction. The SO_4^{2-} in phosphogypsum was particularly effective in curtailing the production of CH_4 . Consequently, we propose reducing CH_4 emissions from

Fig. 7 Pearson's correlation between sulfate content and Cd accumulation and CH_4 emission. (1) Cumulative CH_4 emissions, (2) Cd contents in root, (3) Cd contents in stem, (4) Cd contents in leaves, (5) Cd contents in brown rice, (6) SO_4^{2-} contents in soil. * $p \leq 0.05$, ** $p \leq 0.01$. The inclination of the ellipse to the right (red) indicates a positive correlation, while the inclination of the ellipse to the left (blue) indicates a negative correlation. The correlation coefficient was directly proportional to the eccentricity of the ellipse and inversely proportional to the area of the ellipse



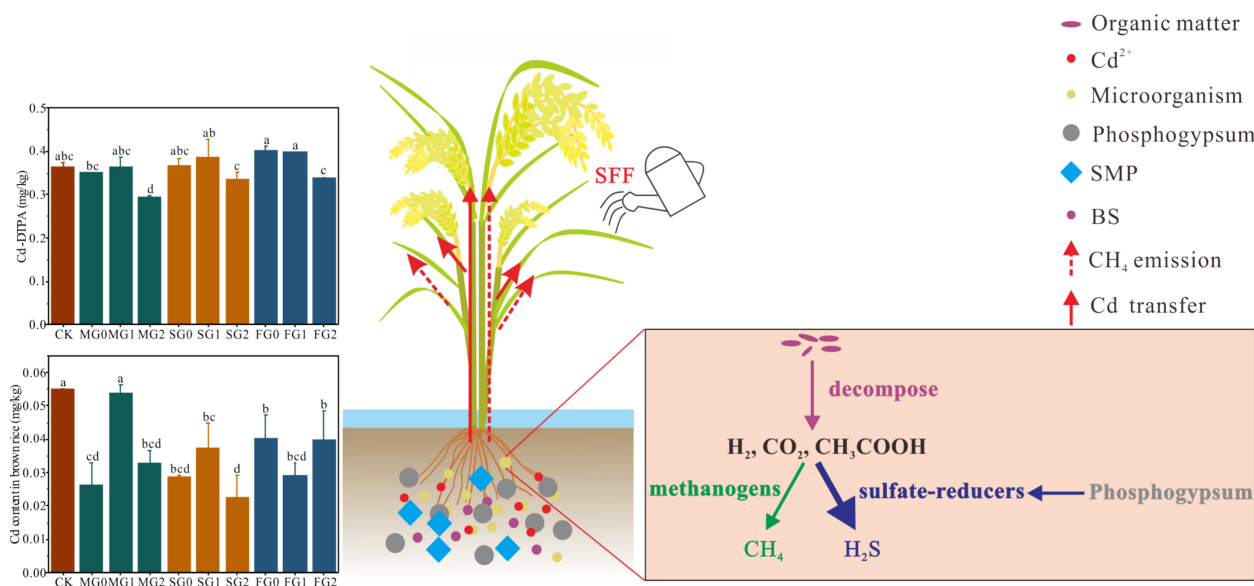


Fig. 8 Effects of different treatments on CH_4 emissions and Cd^{2+} migration. The width of the arrow represents the strength of the reaction

high-concentration phosphogypsum combining with remediation agents (Fig. 8).

5 Conclusions

In this study, we highlight that the combined application of phosphogypsum with Cd remediation agents effectively reduced Cd pollution and CH_4 emissions in rice paddies. Specifically, the integration of phosphogypsum with specific remediation agents such as SMP, BS, and SFF diminished the bioavailability of Cd because of Cd adsorption by remediation agents and CdS formation catalyzed by SO_4^{2-} . Spraying foliar fertilizer can significantly increase the Cd content in the leaves and inhibit Cd transport to brown rice. We found that SO_4^{2-} in phosphogypsum enhanced sulfate-reducing bacterial activity in soils, competitively inhibiting methanogenic archaea and ultimately reducing CH_4 production. This study elucidated the synergistic effects of phosphogypsum in mitigating heavy metal pollution and greenhouse gas emissions in rice paddies, offering valuable insights for sustainable agricultural practices.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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