

Original Research

Supplying Amorphous Silicon Fertilizer Reduced Cd Accumulation in Rice (*Oryza sativa* L.) via Increasing the Available Si/Cd Ratio in Paddy Soil

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Abstract

Food security is threatened by cadmium (Cd) contamination of rice fields. *In-situ* immobilization of Cd by silicon (Si) fertilizers is one of the crucial approaches to solving Cd contamination in rice fields. Various mineral Si fertilizers versus liquid Si fertilizers were compared in this study with *in-situ* field experiments to explore their effects and the regulating mechanisms on reducing Cd bioavailability in paddy fields as well as Cd absorption and transport in rice. The results showed that both the sprinkled mineral Si fertilizer and the foliar spray of liquid Si fertilizer significantly reduced the Cd concentration in brown rice, which was linked to reduced Cd availability in soils. Further analysis of the interaction between Si and Cd indicated that the reduced soil Cd availability and Cd accumulation in brown rice was mainly ascribed to an increase in soil pH and the available Si/Cd ratio. Among these Si fertilizers, LS and GS dominated by amorphous Si were more effective in controlling the accumulation of Cd in brown rice and declining the toxic risk of Cd on human health in rice consumption. In conclusion, Si fertilizer reduced Cd concentration in brown rice via increasing rhizosphere soil pH and available Si/Cd ratio.

Keywords: silicon, cadmium, brown rice, translocation, immobilization

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Introduction

Cadmium (Cd) contamination in paddy fields is a severe problem that threatens the nation's food security and public health [1]. A recent survey of 19 main rice-producing provinces in China found that the average concentration of Cd in paddy soils was 0.45 mg/kg, and around one-third of the samples exceeded the risk screening threshold for agricultural land according to the Chinese Soil Environmental Quality Scheme (GB15618-2018). Rice has a remarkable propensity to absorb Cd from paddy soils and accumulates a large proportion of the absorbed Cd in grain, especially in Cd-contaminated acidic soils [2, 3]. Hence, minimizing Cd transfer from paddy soil to brown rice is of great importance for improving food safety.

Our previous studies demonstrated that silicon (Si)-based amendment has the potential to be used as an alternative method of contaminated soil remediation [4]. The reduction in Cd availability caused by Si-based amendments in contaminated soils could be explained by pH-change-induced immobilization, Fe-induced chemisorption, Si-induced co-precipitation, and Ca-induced ion exchange [5]. Meanwhile, Si is an essential mineral element for plant growth and promotes plant resistance to heavy metal toxicity [6]. The mechanisms of Si inhibiting the absorption of heavy metals by plants mainly includes: (1) Si can combine with heavy metals to form silicic acid compounds [7]; (2) Si can reduce the activity of heavy metals by affecting the redox force of the rhizosphere; (3) Si can inhibit plant absorption of heavy metals by affecting soil pH [8]; (4) Si prevents plant uptake by altering the form of heavy metals in the soil [6]; (5) the accumulation of Si in the root of plant hinders the transport of heavy metals to the above-ground parts [9].

For silica-loving crops like rice (*Oryza sativa* L.), the supply of Si from the soil itself is far from sufficient due to the large amount of Si loss caused by long-term cultivation. Si-rich material not only supplies the Si required for rice growth, but it can also minimize Cd accumulation in grains by restricting Cd transfer from roots to shoots via the endodermis and epidermal cell walls [10, 11]. According to some studies, Si fertilizer (foliar or soil Si fertilizer) enhanced the nutritional value of rice grain by increasing silicate and protein content and drastically lowering Cd levels [12, 13]. Mineral Si fertilizer is a type of citrate-soluble, slightly alkaline fertilizer that mostly contains calcium silicate and is rich in the medium and trace elements needed for a variety of crops, including S, Zn, Fe, Mn, and Cu [14, 15]. Mineral Si fertilizer applied to the soil might promote Cd adsorption, strengthen Cd accumulation in the endodermis of rice roots, and inhibit Cd transfer from roots to shoots [10]. Foliar spraying of liquid Si fertilizer could reduce Cd transport from stem to brown rice by reducing Cd concentration in rice stem and improving leaf photosynthesis [16, 17]. Many of the results are based on culture simulation experiments.

However, there are few studies on *in-situ* inhibition control of Si fertilizer to restore Cd-contaminated paddy fields. Furthermore, compared with mineral Si fertilizer, does liquid Si fertilizer have better effects on Cd immobilization in soils and Cd reduction in rice?

In the present study, *in-situ* field experiments were conducted to evaluate the effects of different mineral Si fertilizers and liquid Si fertilizers on Cd bioavailability, absorption, and transport in rice. Additionally, the relationship between the available Si/available Cd ratio in paddy soil and the absorption, transport, and enrichment of Cd in rice was investigated. The results will provide scientific guidance for the effective use of Si fertilizer to restore Cd-contaminated rice fields.

Materials and Methods

Materials

The Si fertilizers used in this study include three mineral Si fertilizers and one liquid Si fertilizer. The mineral Si fertilizers were obtained from Gansu Province, Inner Mongolia Autonomous Region, and Kenya, respectively. The fertilizer was dried and thoroughly mixed. The liquid Si fertilizer was obtained from Shandong Province, China. The basic physical and chemical characteristics of these fertilizers were listed in Table 1, Fig. 1 and Fig. 2. Procedures adopted for fertilizer characterization are reported below.

Experimental Design and Sampling

The field experiment was carried out from June to October 2021 in rice fields in Huangshan, Anhui Province, China (30°7'N, 117°57'E). The amount of Cd in rice exceeded the National Food Safety Standard (GB2762-2017) due to the high background level of Cd in the soil. The soil was sandy loam (57.6% sand, 32.5% silt, and 9.86% clay) with the following properties: pH (H₂O) 5.10; the organic matter was 33.35 g/kg; total nitrogen was 1.65 g/kg; available phosphorus was 29.22 mg/kg; available potassium was 163.13 mg/kg; citric acid-extractable Si was 34.32 mg/kg; available Cd was 0.11 mg/kg; total Cd was 1.32 mg/kg. The soil Cd exceeded the risk screening value of the Risk Control Standard for Soil Contamination of Agricultural Land in China (GB15618-2018), while other heavy metals (i.e., As, Cr, Pb, Cu, Zn) were far below the limit.

Five treatments were used in the trial: liquid Si fertilizer (LS), mineral Si fertilizer from Kenya (KE), mineral Si fertilizer from Inner Mongolia Autonomous Region (IM), mineral Si fertilizer from Gansu Province (GS), and the control (CK). Five replications of each treatment were performed, and 3.0 t/ha of three different mineral Si fertilizer types (GS, IM, and KE) were artificially applied. Liquid Si fertilizer (LS) of 0.3 t/ha

Table 1. The BET surface area (m²/g), pore volume (cm³/g), pore size (nm), pH, and CEC (cmol/kg) of Si fertilizer.

Treatments	BET surface area	Pore volume	Pore size	pH	CEC
GS	33.7091	0.0139	1.6526	8.35±0.03	32.62±0.61
KE	0.5399	0.0003	2.4928	8.99±0.06	0.52±0.01
IM	0	0	0	8.81±0.11	0.21±0.00
LS	-	-	-	6.00±0.00	-

GS, Si fertilizer from Gansu; KE, Si fertilizer from Kenya; IM, Si fertilizer from Inner Mongolia; LS, liquid Si fertilizer.

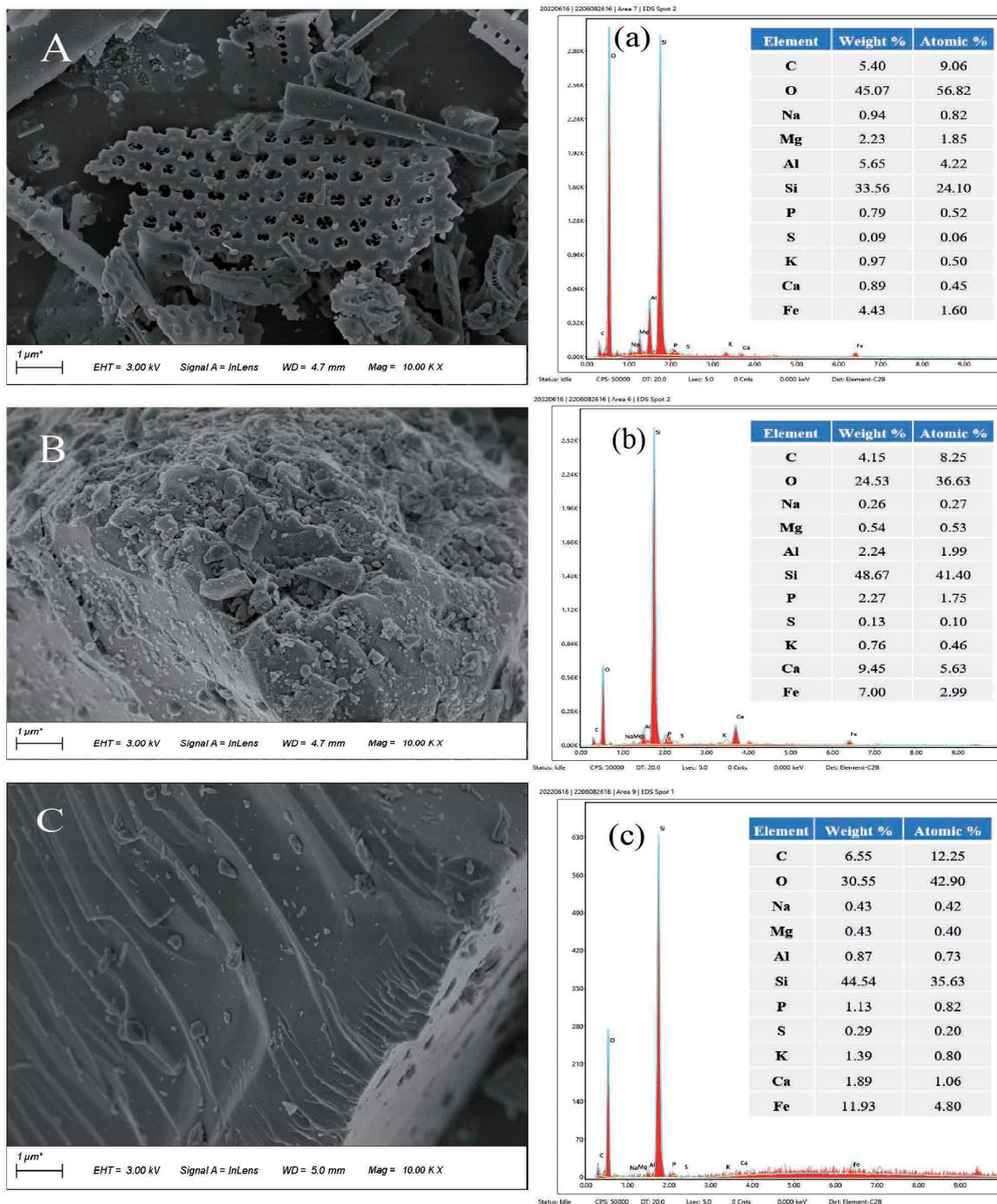


Fig. 1. SEM images of (A) GS, (B) KE, and (C) IM, EDS spectra are shown in a), b), and c), respectively. GS, Si fertilizer from Gansu; KE, Si fertilizer from Kenya; IM, Si fertilizer from Inner Mongolia.

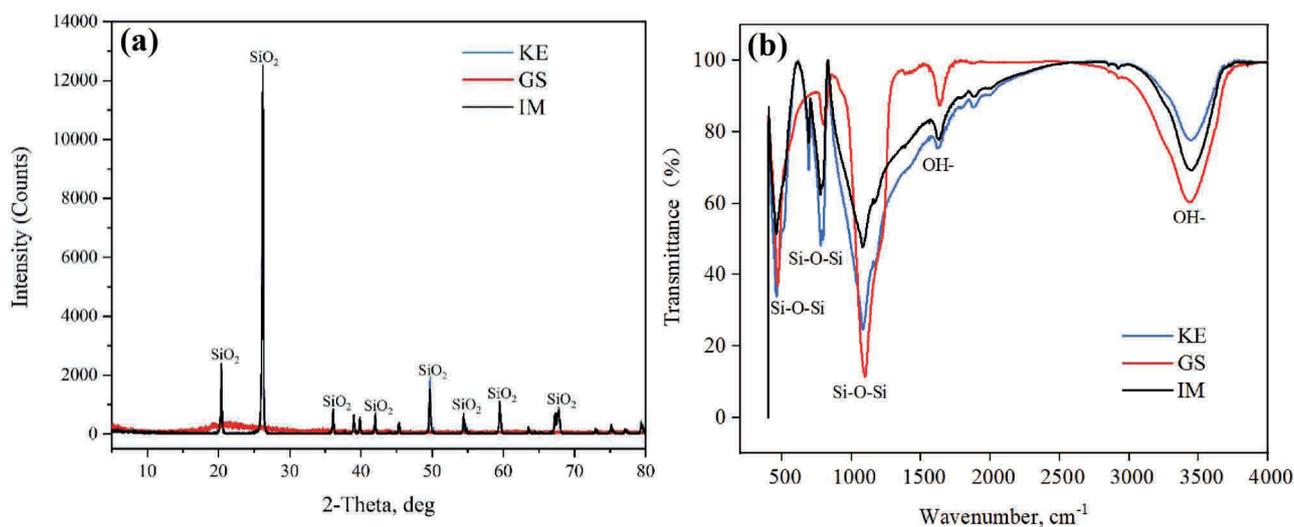


Fig. 2. a) XRD pattern and b) FTIR spectra of mineral Si fertilizers. GS, Si fertilizer from Gansu; KE, Si fertilizer from Kenya; IM, Si fertilizer from Inner Mongolia.

was applied by an unmanned aerial vehicle, and 200 times the diluent was sprayed on the leaf surface four times, at the jointing stage, booting stage, heading stage, and grouting stages of rice, respectively. N, P, and K fertilizers were applied using normal fertilizer dosage, water and fertilizer management should adhere to regional norms. The hybrid rice-Indica 21 (late rice variety) varieties were examined.

After harvesting, the complete rice was rinsed with deionized water and separated into five tissue components: roots, stems, leaves, husks, and brown rice. The plant samples were heated for 30 min at 85°C, then oven-dried at 60°C to constant weight. The dried plant samples were ground and sieved (0.15 mm) for analysis. Soil near 2 cm of rice roots was collected. The soils from the rhizosphere were carefully removed from the roots, and the soils from the non-rhizosphere were gathered by shaking the roots. The surface layer (0-20 cm) was sampled using the “S” type multi-point sampling method, and the resulting uniformly mixed soil samples were used as bulk soil. After air drying, the soil was ground and screened with 2 mm, 0.25 mm, and 0.15 mm screens for chemical characteristics.

Chemical Analysis

Fertilizer Characterization

The pH (1:5 H₂O) of fertilizers was measured using a pH meter (PHS-3C, Leici, China). The morphologies of the mineral fertilizers were measured by a scanning electron microscope coupled with an energy-dispersive spectrometer (SEM-EDS, S-4300, Hitachi, Japan). The mineralogical composition of the mineral fertilizers was determined by X-ray diffraction (XRD, XD-6, Beijing general analytical instrument, China) with Cu-K α radiation and scanned from 5° to 80° (2 θ) with

a continuous scan rate of 4°/min. The functional groups in the mineral fertilizers were obtained using Fourier transform infrared (FTIR, Nicolette is 50, Thermo Fisher, USA) spectroscopy. FTIR spectra were recorded between 4000 and 400 cm⁻¹. Discs were prepared by first mixing 1 mg of the dried sample with 500 mg of KBr in an agate mortar and then pressing the mixture at 10 tons cm⁻² for 15 min under a vacuum. The cation exchange capacity of the mineral fertilizers was determined by sodium acetate flame spectrophotometry. The surface area and average pore size of the mineral fertilizers were measured using a Quadrasorb SI-MP surface area analyzer (Quantachrome, USA).

Digestion and Analysis of Plant

The contents of Cd in rice tissues (root, stem, leaf, husk, and brown rice) were digested by HNO₃-H₂O₂ in a microwave digester (MD8H, APL Corporation, China). The concentration of Cd in the digestion was determined by atomic absorption spectrophotometry (AAS, PinAAcle 900T, PerkinElmer, USA). The concentration of Si was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Perkin Elmer, Optima 5300DV, USA) after microwave digestion with a mixture of HNO₃, HCl, and HF [18]. Blank and standard reference materials of plants (GBW-10045, rice, China National Centre for Standard Materials) were used for quality control of analytical procedures. The recovery rates for Si and Cd were within 90±10%.

Soil Properties

The soil available Cd content was determined by DTPA extract and determined by ICP-OES. Soil total Cd was digested by HF-HNO₃-H₂O₂ in a microwave digestion system and determined by ICP-OES. Blanks

and certified references of soil samples (GBW07980, National Center for Standard Materials) were included to ensure the reproducibility and accuracy of the measurements. The available Si in soil was determined by citric acid extraction and silicon molybdenum blue colorimetric method. Soil pH was measured by a glass electrode pH meter (PHS-3C, Leici, China) at a soil-water ratio of 1: 2.5. Soil sand, silt, and clay were analyzed using the hydrometer method. The total nitrogen content of the soil was determined by the Kjeldahl nitrogen method, and the soil's available potassium was determined by neutral NH_4OAc leaching-flame photometry. Soil-available phosphorus was determined by the molybdenum-antimony resistance colorimetric method. Soil organic matter was determined using the $\text{H}_2\text{SO}_4\text{-K}_2\text{CrO}_4$ wet combustion method.

Statistical Analysis

The translocation factor (TF) is the ratio of heavy metal content in the aboveground part of plants to the corresponding heavy metal content in the roots, reflecting the ability of plants to transfer heavy metals from the root to the aboveground part [19].

The values of DIM (mg/person/day) for Cd were calculated using the following relation. These values were derived from Rizwan et al. (2017) [20] with minor modifications.

$$\text{DIM} = \frac{C(\text{metal}) \times C(\text{factor}) \times D}{\text{BW}} \quad (1)$$

Where: C (metal) - Cd accumulated in brown rice (mg/kg); C (factor) - 0.085 which is the correction factor; D - taken as 0.4kg/person/day; BW - applied as 70 kg considering it as an average human adult body weight.

The health risk index (HRI) for Cd was calculated using the following equation reported by Rizwan et al. (2017) [20].

$$\text{HRI} = \frac{\text{DIM}}{\text{RF}} \quad (2)$$

Where: DIM - daily metal intake (mg/person/day); RF - oral reference dose of Cd was 0.001. When $\text{HRI} < 1$, it indicated that Cd in rice would not cause harm to human health. When $\text{HRI} \geq 1$, it indicated that Cd in rice had harmful effects on human health.

The average daily intake (ADD, mg/kg/day) was used to calculate the oral exposure dose for deleterious substances and was determined using the following equation reported by Fan et al. (2017) [21].

$$\text{ADD} = \frac{C \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (3)$$

Where: C - Cd accumulated in brown rice (mg/kg); IR - ingestion rate, the average daily rice intake of adults was estimated to be 0.425 kg; EF - exposure frequency, EF was 74 years (based on age); ED - the exposure

duration was 365 days; BW - the mean body weight was 58.1 kg for adults; AT - average contact time, $27010\text{d} = 365\text{d} \times 74\text{a}$.

The hazard quotient (HQ), defined as a ratio of average daily intake (ADD) to reference dose (RfD) [22], describes the health risk of non-carcinogenic adverse effects caused by toxicant exposure:

$$\text{HQ} = \text{ADD}/\text{RfD} \quad (4)$$

Where: ADD - average daily intake (mg/kg/day); RfD - the estimated maximum permissible dose for humans through daily exposure and is 1.00×10^{-3} (mg/kg/d).

If $\text{HQ} < 1$, adverse health effects would be unlikely experienced, while potential non-carcinogenic effects would occur when $\text{HQ} \geq 1$.

The cancer risk (CR) was determined by multiplying the average daily intake with a cancer slope factor (SF) according to Equation (4). CR was calculated as the incremental probability of an individual developing cancer over a lifetime. The CR of residents induced by potential carcinogen exposure throughout a lifetime was determined using the equation below [22]:

$$\text{CR} = \text{ADD} \times \text{SF} \quad (5)$$

Where: ADD - average daily intake (mg/kg/day); SF - a cancer slope factor and is 6.1 (mg/kg/d).

All data were expressed as the mean of five replications. Statistical analyses (one-way ANOVA) were performed using IBM SPSS Statistics 22 (SPSS Inc., Chicago, USA). The least significant difference (LSD) was used to test for significance at $p < 0.05$ between the means. Pearson correlations were also performed using SPSS, and values were considered significant at $p < 0.05$ and $p < 0.01$. Redundancy analysis (RDA) was conducted to investigate the relationship between Cd uptake in rice and environmental variables using CANOCO 5 software (Microcomputer Power, Inc., Ithaca, NY). Grey correlation analysis was performed to evaluate the correlation between different treatments and various indicators, and then the effects of Si fertilizer on reducing Cd toxicity in rice were compared. The calculation is based on the method of Huang et al. (2019) [23]. Graphical analysis was carried out using Origin 2018 (OriginLab Corporation, Northampton, MA, USA).

Results

Rice Cd and Si Contents

The application of Si fertilizer reduced Cd uptake and accumulation in rice (Fig. 3), particularly the concentration of Cd in roots, which decreased by 64.94%, 60.82%, 54.34%, and 69.9% when compared to CK (Fig. 3a). Liquid Si fertilizer (LS) significantly reduced the Cd content in rice. Among the three

mineral Si fertilizers, only KE significantly reduced Cd accumulation in stems (Fig. 3b), GS significantly reduced Cd accumulation in leaves (Fig. 3c), and GS and IM significantly reduced Cd accumulation in husks and brown rice (Fig. 3d, e). However, the concentration of Cd in each treatment of brown rice still exceeded the limit set by the National Food Safety Standard (GB 2762-2017) (0.2 mg/kg). Except for KE, the application of Si fertilizer effectively reduced the DIM, HRI, HQ, and CR values (Table 2). Nonetheless, the HQ of Cd exceeded 1, indicating that Cd might pose non-carcinogenic dangers to residents. The CR values exceeded 0.0001, suggesting that brown rice consumption poses a significant potential carcinogenic risk. Furthermore, the concentration of Cd in brown rice was positively correlated with Cd in roots, leaves, and husks (Fig. 3f). In conclusion, LS and GS had the best effects on Cd reduction. Additionally, the Cd concentration in rice tissues treated by LS and GS did not vary significantly.

Si content in brown rice and husks were dramatically raised by the use of both liquid and mineral Si fertilizers. Furthermore, the brown rice treated with IM and the husks treated with KE had the highest Si contents (Fig. S1). The concentration of Si in brown rice was positively correlated with Si in husks. Si content in husks had a significant negative relationship with Cd in roots and stems (Fig. 3f).

Cd Transport Factor from Roots to Aboveground Parts

The application of Si fertilizer promoted the transfer of Cd from roots to stems, leaves, husks, and brown rice (Fig. 4). The application of Si fertilizer, in which the $TF_{\text{roots-stems}}$ value of GS was the highest (Fig. 4a) and the $TF_{\text{roots-leaves}}$ value of KE was the highest (Fig. 4b), considerably increased the transfer of Cd from roots to stems and leaves. Si fertilizers had dramatically

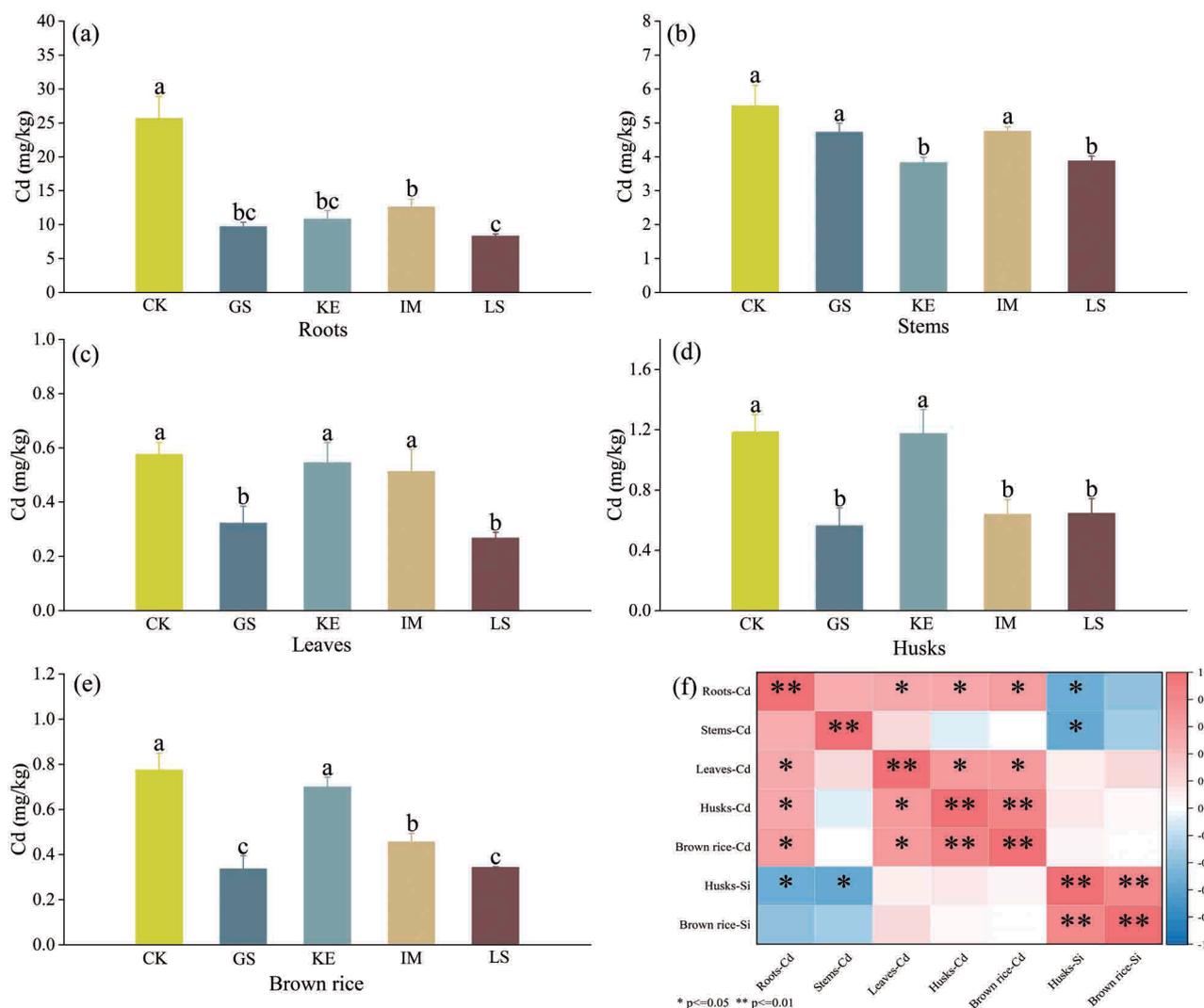


Fig. 3. Effect of Si fertilizer on Cd concentration in a) roots, b) stems, c) leaves, d) husks, e) brown rice, and f) matrix of correlations between Cd content and Si content in different tissues. GS, Si fertilizer from Gansu; KE, Si fertilizer from Kenya; IM, Si fertilizer from Inner Mongolia; LS, liquid Si fertilizer. Error bars represent \pm sd (n = 5). Different letter in the same group indicates a significant difference at 5% level according to the LSD test.

Table 2. Effect of Si fertilizer on daily metal intake of Cd (DIM)(mg/person/day), Cd health risk index (HRI), the average daily intake (ADD, mg/(kg·day)), the hazard quotient (HQ), the cancer risk (CR).

Treatments	DIM	HRI	ADD	HQ	CR
CK	0.00037±0.00a	0.37±0.04a	0.0063±0.00a	6.32±1.51a	0.039±0.02a
GS	0.00016±0.00b	0.16±0.03b	0.0025±0.00b	2.47±0.43c	0.015±0.01c
KE	0.00034±0.00a	0.34±0.02a	0.0051±0.00a	5.12±0.32ab	0.031±0.01ab
IM	0.00022±0.00b	0.22±0.02b	0.0033±0.00b	3.34±0.27bc	0.020±0.00bc
LS	0.00022±0.00b	0.22±0.04b	0.0033±0.00b	3.25±1.28bc	0.020±0.02bc

GS, Si fertilizer from Gansu; KE, Si fertilizer from Kenya; IM, Si fertilizer from Inner Mongolia; LS, liquid Si fertilizer. The data represent the mean±standard deviation (n = 5). Different letters mean significant differences among treatments at $P < 0.05$ level.

different impacts on the transport of Cd from roots to husks and brown rice. LS and KE dramatically boosted the transfer of Cd from roots to husks (Fig. 4c). Only KE's impact on the value of $TF_{\text{roots-brown rice}}$ was significant (Fig. 4d). Therefore, the transfer of Cd from roots to aboveground tissues was significantly enhanced by KE.

Soil Available Cd, Available Si, and pH Values

The application of Si fertilizer decreased the available Cd in the rhizosphere, non-rhizosphere, and bulk soil (Fig. 5a), while the effect on the available Si was less obvious (Fig. 5b). LS significantly reduced the available Cd in the rhizosphere, non-rhizosphere, and bulk soil. GS had a greater impact on Cd reduction than

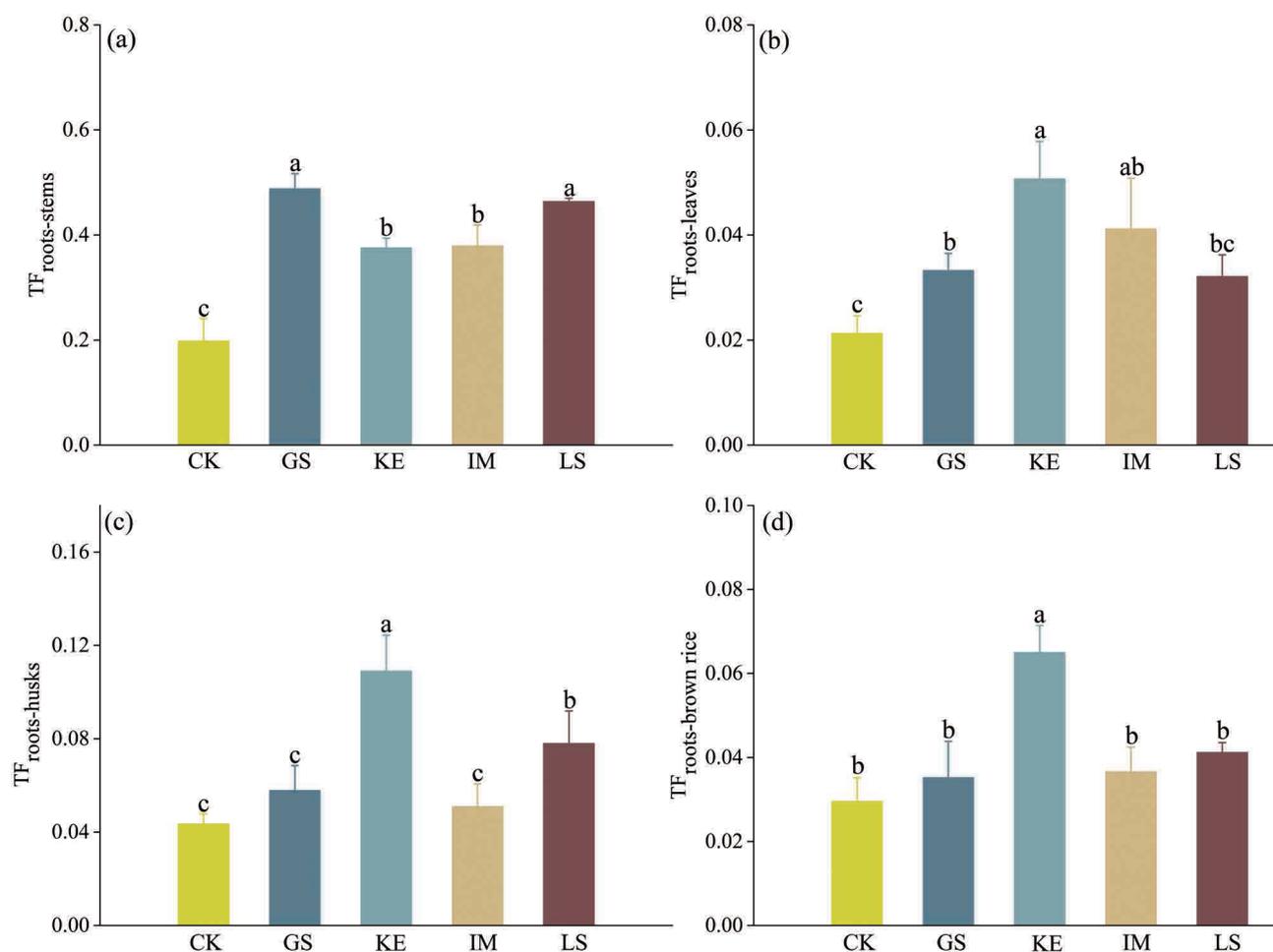


Fig. 4. Effect of Si fertilizer on Cd-TFs in a) stems, b) leaves, c) husks, and d) brown rice. GS, Si fertilizer from Gansu; KE, Si fertilizer from Kenya; IM, Si fertilizer from Inner Mongolia; LS, liquid Si fertilizer. Error bars represent ±sd (n = 5). Different letter in the same group indicates a significant difference at 5% level according to the LSD test.

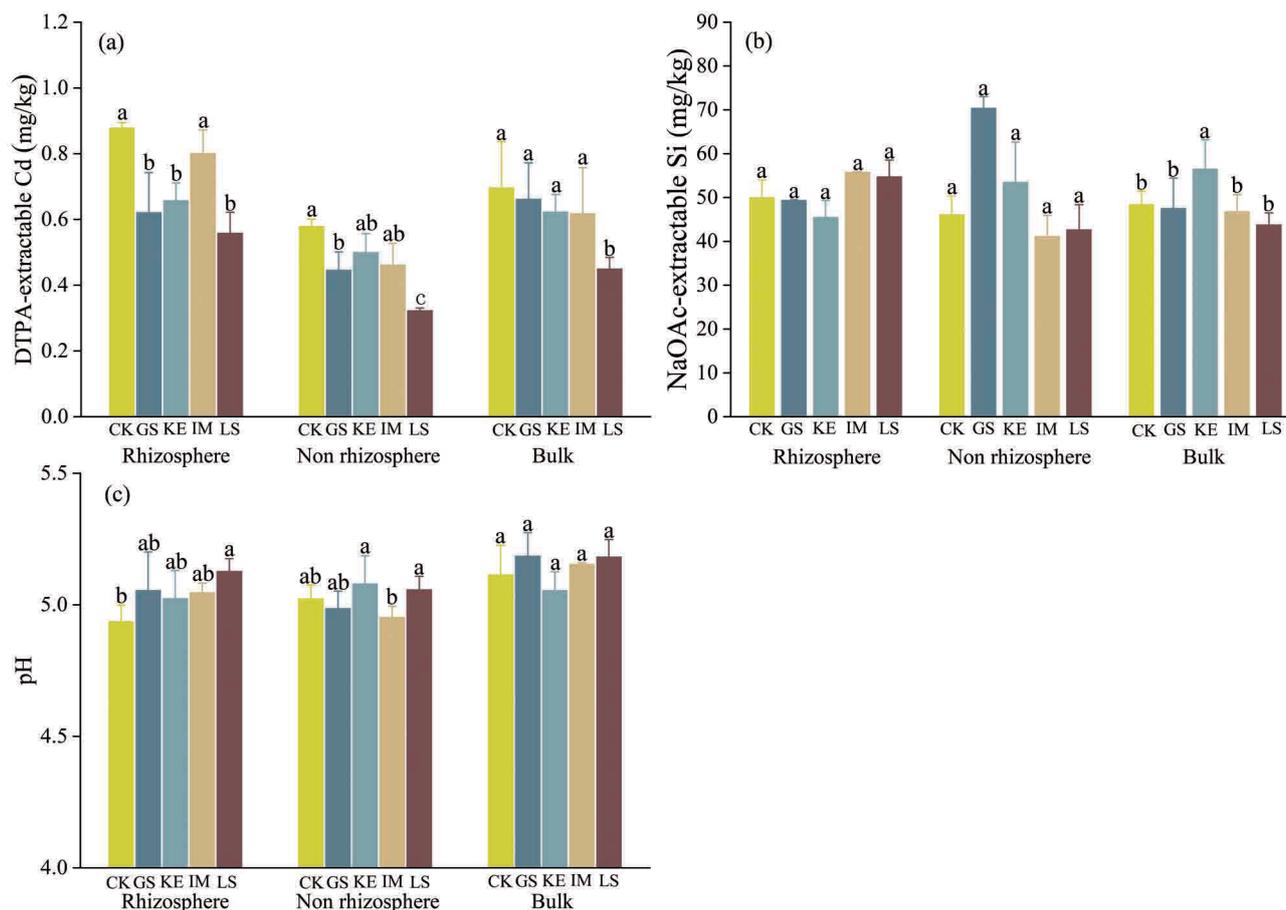


Fig. 5. Effect of Si fertilizer on a) available Cd, b) available Si, and c) pH of soil. GS, Si fertilizer from Gansu; KE, Si fertilizer from Kenya; IM, Si fertilizer from Inner Mongolia; LS, liquid Si fertilizer. Error bars represent \pm sd ($n = 5$). Different letter in the same group indicates a significant difference at 5% level according to the LSD test.

KE and IM (Fig. 5a). The application of Si fertilizer increased the pH value of rhizosphere soil, and LS had the greatest impact. However, there was no distinct difference between the Si fertilizer treatments for bulk soil and non-rhizosphere soil in terms of pH values (Fig. 5c).

Relationship between Cd in Rice and Soil Properties

Brown rice-Cd was significantly negatively correlated with bulk soil pH and soil available Si/available Cd ratio, according to Pearson's correlation matrix analysis. In addition, husks-Cd was negatively correlated with the pH of rhizosphere soil as well as bulk soil, leaves-Cd was negatively correlated with the pH of rhizosphere soil, roots-Cd was negatively correlated with the pH of bulk soil, DTPA-Cd was negatively correlated with the pH of non-rhizosphere soil. Noteworthy, the available Si/available Cd ratio showed a positive correlation with pH (Fig. 6a). The RDA was performed to clarify the relationship between Cd in rice tissues and soil properties. The concentration of Cd in rice tissues was positively correlated with soil-available

Cd, and negatively correlated with soil-available Si and pH (Fig. 6b).

Discussion

The Effect of Si Fertilizer on Soil Cd Immobilization

The bioavailability of Cd in soils was decreased by the application of Si fertilizer (Fig. 5a). It was found that the application of Si fertilizer reduced the concentration of available Cd in rhizosphere soil, non-rhizosphere soil, and bulk soil (Fig. 5a). Three principal mechanisms could explain the results above. Firstly, the addition of Si regulated the bioavailability of Cd by affecting soil pH [24]. Changes in pH are important for Cd stabilization in contaminated soils. It was found that the application of Si fertilizer significantly increased the pH value of rhizosphere soil from 4.94 to 5.13 (Fig. 5c). This is mostly due to the mineral Si fertilizer's high alkalinity (Table 1), which immediately raised soil pH while introducing relevant accompanying ions (e.g., K^+ , Na^+ , Ca^{2+} , Mg^{2+}) into the soil, which is consistent with

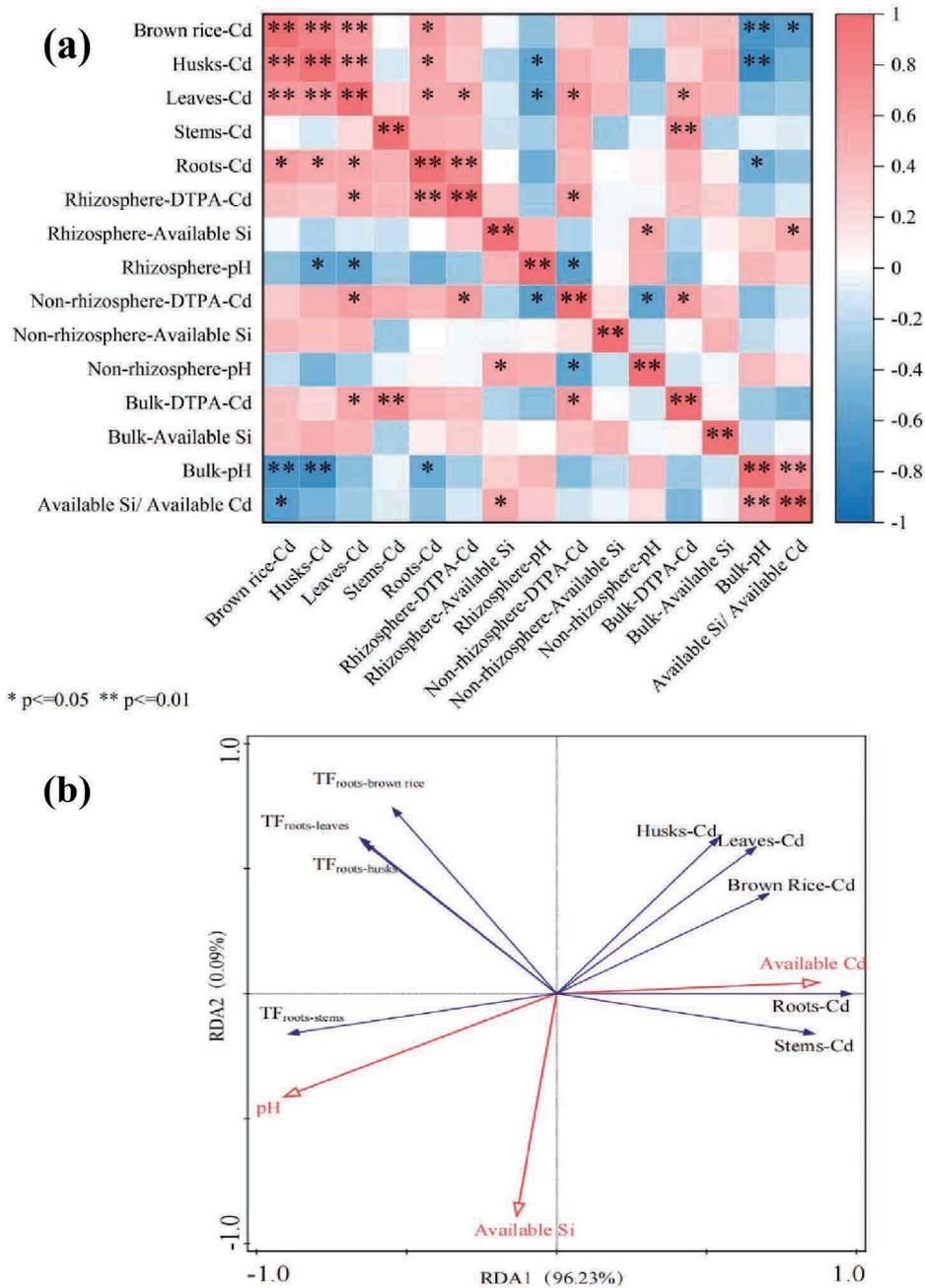


Fig. 6. a) Correlation matrix analysis and b) Redundancy analysis (RDA) of plant and soil properties. Plant variables are indicated by blue arrows. Soil variables are indicated by red arrows.

previous study findings [25]. The mineral Si fertilizer also contains a lot of calcium hydroxide and basic oxide (Fig. 2a). Accordingly, the results of Pearson’s correlation matrix analysis showed that soil pH was significantly negatively correlated with soil available Cd (Fig. 6a). Secondly, the application of Si fertilizer promoted the adsorption of Cd in acidic soil and inhibited the desorption of Cd. According to Zhao et al. (2020) [24], Si enhanced Cd adsorption and decreased the concentration of Cd in soil solution. However, in this study, the application of Si fertilizer did not increase the soil available Si (Fig. 5b). The possible reason is that the formation of insoluble hydroxy aluminosilicate from

the addition of Si will lower the efficiency of Si when the soil pH is less than 5.5 [26]. Thirdly, the absorption of Si fertilizer on Cd in soil [27]. Functional hydroxyl (-OH) groups in Si fertilizer could be utilized for Cd binding (Fig. 2b). In addition, the abundant Ca, Mg, and Fe oxides in the Si fertilizers served as efficient Cd adsorbents (Fig. 1).

The Cd-fixing effect of GS was better than that of KE and IM in mineral Si fertilizer (Fig. 5a). GS exhibited a large specific surface area and pore volume (Table 1), and its porous structure was visible in the SEM analysis (Fig. 1a). The key physical parameters that determine the metal sorption capacity of Si fertilizer are surface

area and porosity. The incorporation of GS into soil increased soil sorption capacity for Cd while reducing Cd mobility in soil and availability to rice. Thus, in Cd-contaminated soils, the application of Si fertilizer with high adsorption capacity has been recommended as an efficient method of reducing Cd mobility by *in situ* fixing. Furthermore, GS has a greater CEC than KE and IM (Table 1), implying that more metal exchange might occur in the GS structure. According to XRD analysis, SiO₂ was dominant in KE and IM, and both of these Si fertilizers had high crystallinity and very similar mineral composition (Fig. 2a). However, no crystal structure could be detected in GS (Fig. 2a). The XRD and FTIR analysis revealed that the GS has an amorphous structure, and the Si-O in the GS dissolved into the soil, improving Cd adsorption capacity. Amorphous Si is the most common kind of Si that plants could utilize. Plants acquire silicic acid from soil solution, which is mostly deposited in the shoots as particulate amorphous silica [28]. Furthermore, it can be seen from a comparison of the spectral curves of the three types of mineral Si fertilizer that the distinctive peak of GS had a different wave number from that of KE and IM (Fig. 2b). More specifically, FTIR showed that the characteristic peaks at 704 cm⁻¹ and 625 cm⁻¹ belonged to Si-O-Si tensile vibration, that the Si-O-Si tensile vibration was a high-intensity wide-band with 1084 cm⁻¹ as the center, and that the absorption peak at 3500 cm⁻¹ was mainly the intermolecular -OH stretching vibration peak (Fig. 2b).

The liquid Si fertilizer (LS) had a better immobilizing effect on soil Cd than mineral Si fertilizer (Fig. 5a), which might be because it increased the concentration of silicate ions in the soil solution when it was sprayed on the soil surface, leading to the formation of coprecipitates or complexes with Cd in the soil [15, 29]. Plants may take up mono silicic acid from the soil directly, but they can also co-precipitate with HMs to create slightly silicates (Si-HMs complexes) that are stored in soil [30, 31].

The Effect of Si Fertilizer on the Uptake and Translocation of Cd in Rice

Si fertilizer decreased the uptake and accumulation of Cd in rice (Fig. 3), especially brown rice, a dietary product with potential health implications. In the present study, the application of Si fertilizer decreased HRI by 18.85%~60.86% and CR by 20.51%~61.54% (Table 2), reducing the risk of Cd on human health when rice is consumed. However, the CR values exceeded the maximum allowable threshold. This research indicates that the intake of local brown rice may provide a substantial carcinogenic risk to residents. Cd migration and accumulation in soil-rice systems were influenced by soil physical and chemical properties such as Cd bioavailability [32]. Most importantly, the application of Si fertilizer increased the soil available Si/ available Cd ratio and inhibited the accumulation of Cd in brown rice. In the soil, available Cd in rhizosphere soil decreased by

9.09%~36.48% with the application of Si fertilizer while available Si did not change (Fig. 5a, b). According to the results of statistical analysis, rice Cd has negatively correlated with the soil available Si/ available Cd ratio, and soil available Si/ available Cd ratio has positively correlated with the available Si in rhizosphere soil (Fig. 6). Assessing and enhancing the soil available Si/ available Cd ratio is therefore critical to reducing Cd absorption and its transport to the edible section of rice.

As mentioned above, the application of Si fertilizer significantly reduced Cd accumulation in roots (Fig. 3a). Cd was mainly concentrated in the roots and stems of rice, while it was relatively low in the leaves and brown rice (Fig. 3). Previous studies have found that Si could co-precipitate in the root cell wall of rice to limit the absorption of Cd [33]. Rice roots served as the dominant sink for Cd accumulation [34]. A significant portion of the Si absorbed by the roots was found to be deposited in the cell wall as SiO₂ [35], which increased the cell wall's mechanical strength, promoted the synthesis of lignin, hemicellulose, pectin, and polysaccharides, provided more ligand, and formed stable chelates with Cd, inhibiting the transport of Cd [11]. Gu et al. (2011) [36] found that the co-precipitation of heavy metals and Si in stems was the reason for the low Cd level in leaves. Accordingly, the increase of mono-silicic acid in roots may be an important reason for the decrease in Cd inflow, load, and absorption in rice plants [31]. Moreover, during transportation, Si competes with Cd²⁺ absorption in rice to some extent, inhibiting and controlling Cd absorption in rice [37].

According to the findings of our experiment, the application of Si fertilizer enhanced the TF value of Cd from roots to stems, leaves, husks, and brown rice (Fig. 4), while decreasing the concentration of Cd in stems, leaves, and husks and brown rice (Fig. 3). The contradiction between the increase in transfer factor and the decrease in aboveground concentration caused by Si fertilizer treatment might be explained by a decrease in Cd content in the roots. Furthermore, Si fertilizer treatment greatly boosted rice growth (Table S1) and, as a result, diluted the concentration of Cd in the rice, which is consistent with previous studies [38]. Additionally, *OsNramp* overexpression increased Cd transport to the shoot and raised Cd concentration in the roots [35, 39].

Furthermore, with the GS treatment, we found a remarkable phenomenon: its effect on the yield of rice and Cd reduction was identical to that of liquid Si fertilizer (LS). Even though liquid Si fertilizer has frequently been considered to be superior to mineral Si fertilizer [15, 17]. Si from foliar sprays might be absorbed by rice leaves, forming a double Si cuticle (e.g., a hemicellulose-bound form of Si), which could limit Cd transfer in rice. At the same time, a Si-Cd compound could form in rice stems and leaves, preventing Cd from being transported from the stem to the brown rice. Furthermore, mono silicates present in rice leaves may compete with Cd for the same Si transporter [17].

Table 3. Results of standardization of raw data.

Treatments	Roots-Cd	Stems-Cd	Leaves-Cd	Husks-Cd	Brown rice-Cd
CK	1	0.668	0.651	0.684	0.681
GS	0.621	1	0.659	0.557	0.531
KE	0.599	0.659	1	0.742	0.661
IM	0.648	0.570	0.751	1	0.776
LS	0.681	0.580	0.707	0.801	1

GS, Si fertilizer from Gansu; KE, Si fertilizer from Kenya; IM, Si fertilizer from Inner Mongolia; LS, liquid Si fertilizer.

Table 4. Correlation degree between treatments and indicators.

Treatments	Correlation degree
CK	0.486
GS	0.862
KE	0.482
IM	0.638
LS	0.778

GS, Si fertilizer from Gansu; KE, Si fertilizer from Kenya; IM, Si fertilizer from Inner Mongolia; LS, liquid Si fertilizer.

Further study is needed to elucidate the suppression mechanisms of GS on Cd accumulation in rice. In addition, the combined use of mineral Si fertilizer and liquid Si fertilizer deserves further investigation.

Potential and Prospect of the Si Fertilizers

According to the findings of this study, mineral Si fertilizers and liquid Si fertilizers have the potential to reduce Cd bioavailability and absorption in rice. The soil Cd availability was significantly reduced (Fig. 5a). Meanwhile, Si fertilizer decreased Cd absorption and accumulation in rice (Fig. 3). Si fertilizer also boosted plant-available Si, according to the findings (Fig. S1). An adequate supply of Si is becoming increasingly important for long-term plant productivity. Si is a helpful element that stimulates the growth of plants, strengthens plant defense mechanisms, and reduces heavy metal toxicity. The application of Si fertilizer promoted the growth of rice by increasing the number of effective panicles, grains per ear, and seed setting rate (Table S1). This was attributed to the fact that (1) the application of Si enhanced root activity and decreased cell membrane permeability, hence improving rice resistance to Cd [40]. (2) Si fertilizer had a high concentration of components required for rice growth, such as Si, Ca, Mg, and others (Fig. 1).

The grey correlation analysis approach was utilized to assess the influence of various Si fertilizers on Cd toxicity in rice. Table 3 shows the results of initializing

each parameter index. The grey correlation degrees of several Si fertilizers were determined using grey correlation analysis (Table 4). The findings were $GS > LS > IM > CK > KE$, indicating that GS was more effective in alleviating Cd toxicity in rice.

Although the application of Si fertilizer reduced the Cd accumulation in different tissues of rice, the concentration of Cd in brown rice did not reach the national edible standard (0.2 mg/kg) under the conditions of this study, indicating that under such conditions, the application of Si fertilizer may not be able to solve the problem of Cd in rice, and other measures such as planting low-accumulation rice varieties and flooding irrigation should be combined.

Conclusions

In this study, both the application of mineral Si fertilizer and foliar sprayed liquid Si fertilizer in Cd-contaminated rice fields significantly increased rice yields while reducing the bioavailability of Cd and the risk of Cd migration in the soil-rice-humans circuit. Si application reduced Cd concentration in brown rice by increasing rhizosphere soil pH and available Si/available Cd ratio. In addition, LS and GS fertilizers were more effective in controlling Cd accumulation in brown rice and reducing the risk of Cd toxicity to human health in rice consumption due to their enrichment in amorphous Si. Further research is required to combine mineral Si fertilizer with liquid Si fertilizer, planting low-accumulation rice varieties and flooding irrigation should also be conducted together.

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Conflict of Interest

The authors declare no conflict of interest.

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Supplementary Material

Table S1. Effect of Si fertilizer on rice yield and yield component in Cd-contaminated soils.

Treatments	Effective panicle number (10 ⁴ /ha)	Number of grains per ear	Seed setting rate (%)	1000-grain weight (/g)	Theoretical yield (kg/ha)
CK	228.90	151.40	83.55	22.00	6370.09
GS	293.85	201.80	90.48	21.76	11674.75
KE	404.04	233.80	90.43	22.22	18980.46
IM	339.76	278.00	89.62	20.42	17285.49
LS	303.03	203.20	90.06	22.24	12332.82

GS, Si fertilizer from Gansu; KE, Si fertilizer from Kenya; IM, Si fertilizer from Inner Mongolia; LS, liquid Si fertilizer.

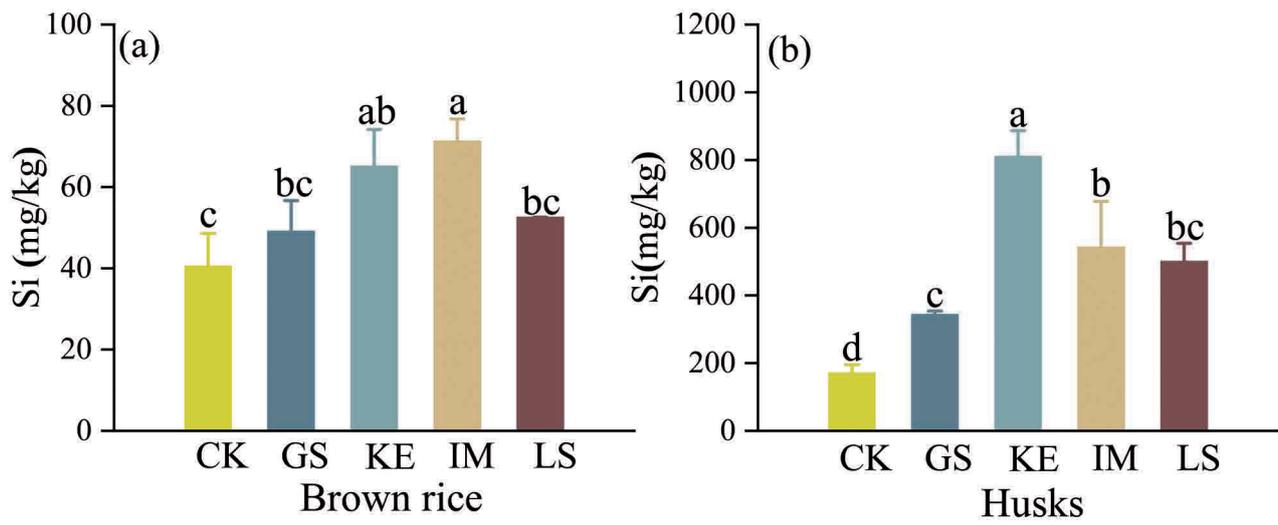


Fig. S1. Effect of Si fertilizer on the concentration of Si in a) brown rice and b) husks. GS, Si fertilizer from Gansu; KE, Si fertilizer from Kenya; IM, Si fertilizer from Inner Mongolia; LS, liquid Si fertilizer. Error bars represent \pm sd (n = 5). Different letter in the same group indicates a significant difference at 5% level according to the LSD test.