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RESEARCH ARTICLE

Mitigation of cadmium and arsenic in rice grain by applying different silicon fertilizers in contaminated fields

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Abstract A field experiment was established to support the hypothesis that application of different silicon (Si) fertilizers can simultaneously reduce cadmium (Cd) and arsenic (As) concentration in rice grain. The "semi-finished product of Si-potash fertilizer" treatment at the high application of 9000 kg/ha (NP+S-KSi9000) significantly reduced the As concentration in rice grain by up to 20.1 %, compared with the control. Si fertilization reduces the Cd concentration in rice considerably more than the As concentration. All Si fertilizers apart from sodium metasilicate (Na_2SiO_3) exhibited a high ability to reduce Cd concentration in rice grain. The Si-calcium (CaSi) fertilizer is the most effective in the mitigation of Cd concentration in rice grain. The CaSi fertilizer applied at 9000 kg/ha (NPK+CaSi9000) and 900 kg/ha (NPK+CaSi900) reduced the Cd concentration in rice grain about 71.5 and 48.0 %, respectively, while the Si-potash fertilizer at 900 kg/ha (NP+KSi900), the semi-finished product of Si-potash fertilizer at both 900 kg/ha (NP+S-KSi900) and 9000 kg/ha (NP+S-KSi9000), and the rice straw (NPK+RS) treatments reduced the Cd concentration in rice grain about 42, 26.5, 40.7, and 23.1 %, respectively. The results of this investigation demonstrated the potential effects of Si fertilizers in reducing Cd and As concentrations in rice grain.

Keywords Field experiment · Arsenic · Cadmium · Mitigation · Silicon fertilizer · Rice grain

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Introduction

Rice (*Oryza sativa* L.) is a staple food that supports almost half of the world's population (Sun et al. 2012). Unfortunately, rice is also the major contributor to the human intake of the toxic trace elements such as cadmium (Cd) and arsenic (As) worldwide, especially in Asia (Meharg et al. 2009; Williams et al. 2009). Human exposure to As and Cd by means of daily consumption in food is a concern in many areas of China, where farming and mining coexist (Williams et al. 2009; Sun et al. 2012). Arsenic, especially inorganic form, is classified as a non-threshold class 1 human carcinogen and can cause serious health problems such as skin cancer and lung, bladder, kidney, and other diseases (Bernard and Lauwerys 1986; Ng et al. 2003; Halim et al. 2009). Cd has been linked to diseases including lung cancer, pulmonary adenocarcinomas, prostatic proliferative lesions, bone fractures, kidney dysfunction, and hypertension (Bernard and Lauwerys 1986).

Rice consumption is a major source of Cd and As for the global human population (Sun et al. 2008; Williams et al. 2009). Cd has relatively high mobility in paddy soil and can be easily absorbed into rice root using the same transport pathways as micronutrients such as Fe^{2+}, Zn^{2+}, and Ca^{2+} (Clemens 2006; Verbruggen et al. 2009; Clemens et al. 2013). Arsenic is particularly easily accumulated in rice grain compared with other cereals, because the bioavailability of As is markedly enhanced in flooded environments and the

released As is absorbed into the rice root through silicic acid transporters, which are widely distributed in rice plants (Zhao et al. 2009). Contamination of As and Cd in rice grain may pose a risk to human health through the food chain. Thus, practical solutions are urgently needed to mitigate the accumulation of Cd and As in rice grain.

Various actions have been undertaken to reduce the uptake of Cd and As by rice. Evidence has suggested that silicon (Si) fertilizers are effective in reducing the concentration of Cd (Shi et al. 2005; Kim et al. 2014) or As in rice grain (Guo et al. 2007; Seyfferth and Fendorf 2012). Various Si compounds, such as K_2SiO_3 and silica gel, were chosen as Si fertilizers for hydroponic culture or pot experiments to mitigate Cd or As individually in rice shoots (Zhang et al. 2008; Putwattana et al. 2010; Marmiroli et al. 2014). It can be difficult to compare the effects of various Si fertilizers on reducing Cd or As in rice because of the differences in fertilizer types, dosage, rice cultivation methods, and other confounding factors. In addition, most of the experiments in the previous studies were designed to investigate the reduction effect of single toxic metals such as As or Cd rather than both of them together. These toxic metals commonly coexist in the contaminated fields, especially in the paddy fields of Southern China, which are in the vicinity of large-scale mining or ore-processing facilities and are subject to irrigation water contaminated with multiple elements. About 65 and 50 % of rice from fields that are impacted by the proximity of mines fail Chinese national food standards of As and Cd respectively, and most rice is co-contaminated (Williams et al. 2009). However, the effects of Si fertilizers on simultaneous mitigation of Cd and As in rice are as yet unclear.

The information from field experiments about Si for Cd and As reduction in rice grain is limited, even though many laboratory experiments have shown the efficacy of As and Cd reduction in rice grain by Si application (Wang et al. 2000; Zhang et al 2008; Guo et al. 2009). The field experiment is necessary to confirm the effects of Si fertilizers on heavy metal mitigation, especially in the paddy fields contaminated with multiple elements. Silicon fertilizers such as Si-calcium fertilizer and Si-potash fertilizer have been extensively applied in rice fields for increasing productivity (Ma et al. 2001; Meharg and Meharg 2015).

In this study, several Si fertilizers (Si-calcium fertilizer, Si-potash fertilizer, sodium metasilicate, semi-finished product of Si-potash fertilizer) were chosen as Si sources to investigate their capacities of reducing Cd and As concentrations in rice grain. About 5–10 % of Si exists in rice straw as phytolith which is a kind of amorphous Si (Marschner and Rimmington 1988). As a Si hyper-accumulator, rice straw can also be regarded as a type of Si fertilizer (Epstein 1994; Liang 1999; Ma et al. 2001) because of the higher solubility of amorphous Si (1.8–2.0 mM Si) in rice straw than crystalline counterpart quartz (0.1–0.25 mM Si) (Drees et al. 1989; Fraysse et al. 2006). Considering the ubiquity of rice straw being returned to paddy fields, rice straw was also selected as a potential Si fertilizer to study its effect on reducing Cd and As concentrations in rice grain.

The aims of the present study were to investigate (1) the effect of Si fertilizers on reducing Cd and As concentration in rice grain in paddy field and (2) the relative efficacy of various Si fertilizers in reducing Cd and As concentrations at the same time.

Materials and methods

Materials

The field experiment was conducted in city of Qiyang (Hunan Province, China). The concentrations of some toxic elements in the study soil are listed in Table 1. As and Cd concentrations slightly exceed the Chinese standard for agricultural land (30 mg/kg for As and 0.4 mg/kg for Cd) (GB15618-1995). The rice cultivar utilized in this study is *Xiangfengyou 186*.

Methods

The experiment was established using a completely randomized design with three replicates per treatment (27 plots in total). The area of each plot was 30 m^2. The Si fertilizers used in the experiment were Si-potash fertilizer (KSi, 50 % water soluble and 50 % citrate soluble potassium), Si-calcium fertilizer (CaSi), a semi-finished product of Si-potash fertilizer (S-KSi, citrate soluble potassium), and sodium metasilicate (Na_2SiO_3). Rice straw (RS) was also applied as a type of Si fertilizer in this study. Basal fertilizers supplied were nitrogen (N) 230 kg/ha as urea, phosphorus (P) 625 kg/ha as calcium superphosphate, and potassium (K) 150 kg/ha as potassium chloride. All Si fertilizers were applied together with basal fertilizers onto the field before transplantation, and in the plots with KSi and S-KSi fertilizers, no extra potassium chloride was applied as K fertilizer. Si fertilizers were applied at 900 kg/ha. Tillering fertilizers supplied before the tillering stage were N 100 kg/ha as urea and K 50 kg/ha as potassium

Table 1 The concentrations of toxic elements in soil (mg/kg)

Toxic elements	mg/kg
As	37.5±3.7
Cu	26.6±5.7
Mn	136.0±17.7
Pb	36.8±1.2
Cd	0.4±0.04
Zn	117.7±17.6
Cr	71.8±7.2

chloride. Six plots with tenfold additional CaSi and S-KSi fertilizers (9000 kg/ha) were used to investigate the dose response of As and Cd accumulations in rice grain to Si fertilizer application. Control plots were established without fertilization. Rice was transplanted by hand and grown in flooded fields until maturity.

Sampling and sample preparation

The rice was planted in July 2014 and harvested in October 2014. After maturation, four intact rice plants were randomly collected from every plot. The straw and grain were separated and washed with deionized water to remove soil and dust particles. After washing, they were air dried at room temperature (25 °C) until they reached a constant weight. The complete root systems, together with adhering soil, of the four rice plants were carefully removed from the soil. The soil was obtained through vigorously shaking the root by hand for 5 min. The rhizosphere soil was collected after removing loosely adhering soil by vigorous shaking. The soil samples were also air dried.

Grain was dehulled in a motorized dehusker (JLGJ4.5, TZYQ, Zhejiang, China) to obtain brown rice. All of the plant samples were milled to fine powder using a blender (Langjia, China). Air-dried soil samples were ground into powder with a mortar and pestle, passed through a 0.15-mm sieve, and then further dried in the oven at 70 °C until they reached a constant weight. GBW 07602 (GSV-1) rice flour was used as the standard reference material (SRM) for rice grain; GBW07603 (GSV-2) bush twigs and leaves were used as the SRM for rice straw, and GBW 07405 (GSS-4) soil was used as the SRM for soil samples.

Digestion and analysis

The digestion procedure for all plant material samples followed the protocol of Sun et al. (2010). Briefly, 0.2 g of rice grain or straw powder was transferred into 50-mL polyethylene centrifuge tubes with HNO_3 (2 mL) added and then incubated overnight at room temperature (~25 °C). Three samples of each SRM (GSV-2) for straw, three SRM of rice flour (GSV-1), and three blanks were prepared at the same time for quality control. All samples were microwave digested (MARS, Matthew Inc., USA) using the reported temperature program (Sun et al. 2010). Briefly, the temperature was increased to 55 °C within 5 min and maintained for 10 min, increased to 75 °C within 5 min and maintained for 10 min, and finally increased to 95 °C within 5 min and maintained for 30 min. After digestion, the samples were cooled and then diluted to 50 mL with Millipore ultrapure water (Millipore Milli-Q).

Soil samples (0.25 g) were weighed into block digestion tubes (100 mL). In each tube, 5 mL of aqua regia was added and incubated overnight and then heated at 120 °C for 12 h. Next, 4 mL of perchloric acid ($HClO_4$) was added to each tube and heated at 140 °C for 24 h. The cooled digests were filtered and diluted to 50 mL with Millipore ultrapure water. Two blanks and two samples of SRM for soil (GBW07405) were prepared and digested at the same time for quality control.

Inductively coupled plasma mass spectrometry (ICP-MS, 7500, Agilent Technologies) was used to analyze total As and Cd. Indium (In) was measured as an internal standard and all samples were randomized prior to analysis.

Soil pH was measured (soil/water ratio of 1/2.5) using a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd. Shanghai, China) with pH electrode (Inlab HA405-DPA, Mettler Toledo Instruments Co. Ltd. Shanghai, China). Soil samples (2 g) and Millipore ultrapure water (5 mL) were mixed in a 10-mL centrifuge tube, then agitated (150 rpm) at 25 °C for 20 min, then left to stand for 30 min. Finally, the electrode of the pH meter was inserted into the soil and water interface until a constant reading was attained. Fertilizers were milled and sieved through a 0.3-mm sieve, and the pH values were also measured at a fertilizer/water ratio of 1/2.5. The concentrations of available Si in fertilizers were measured using the molybdate blue colorimetric method (King et al. 1955). Fertilizer samples (0.2 g) were weighed into volumetric flasks (500 mL). In each flask, 10 mL of HCl (5 mol/L) was added and diluted to 500 mL with Millipore ultrapure water and then shaken (150 rpm) for 30 min at 25 °C. The flasks were left to stand for 30 min after shaking, then the supernatants (2.5 mL) were taken to 50-mL centrifuge tubes and 5 mL of H_2SO_4 (0.3 mol/L), 5 mL of $N_2H_8MO_2O_7$ (50 g/L), 5 mL of $C_2H_2O_4$ (50 g/L), and 5 mL of $FeSO_4$ (50 g/L) were sequentially added. The mixture was then diluted to 50 mL with Millipore ultrapure water. The absorbance at 690 nm was measured using a spectrophotometer (Beijing Purkinje General Instrument Co, Ltd, China).

Statistical analysis and quality control

The least square difference (LSD) test was used to compare the means between the different treatments. All statistical analyses were conducted using SPSS 17.0. The As recoveries for rice flour, straw, and soil were 127, 110, and 104 %, respectively, while the Cd recoveries for rice flour, straw, and soil were 106, 114, and 118 %, respectively.

Results

Plant growth and biomass

In general, fertilizer application significantly improved grain yields and straw biomass relative to the control (Table 2), but no significant differences were observed between the different fertilizer types (including NPK treatments) or their different dosages. Neither grain yield nor straw biomass were

Table 2 The weight of rice grain and straw biomass under different fertilization regimes (kg/ha)

Treatment	Rice grain	Relative yield	Straw biomass	Relative yield
Control	3633±255a	1.00	2150±272a	1.00
NPK	6734±368b	1.83	4136±701b	1.92
NP+KSi900	6738±298b	1.85	3462±1114b	1.61
NP+SKSi900	6744±270b	1.86	4144±919b	1.93
NP+SKSi9000	6492±424b	1.79	4333±364b	2.02
NPK+$Na_2SiO_3$900	7077±465b	1.95	3441±1030b	1.60
NPK+SiCa900	7262±496b	2.00	4646±962b	2.16
NPK+SiCa9000	6924±464b	1.91	3922±481b	1.82
NPK+RS	6944±177b	1.91	4300±544b	2.00

RS, CaSi, KSi, S-KSi, and Na_2SiO_3 represent rice straw, Si-calcium fertilizer, Si-potash fertilizer, semi-finished product of Si-potash fertilizer, and sodium metasilicate fertilizer, respectively. Different letters indicate significant differences at $p<0.05$

significantly increased following treatments with Si fertilizers in our experiment when compared with the NPK treatment, although it is well known that Si fertilizers can promote plant growth which has been observed in many plants, including peanut, maize, and cucumber (Zhu et al. 2004; Da Cunha and Do Nascimento 2009; Shi et al. 2010). This may be because not enough available Si was added to the soil to significantly influence grain yield and straw biomass or the amount of available Si in the soil is already high enough for rice growth.

Arsenic concentration in grain and straw

The average As contents of the rice samples from the control and NPK treatment were 0.45±0.13 and 0.41±0.08 mg/kg, respectively, higher than the food standard As limit (0.2 mg/kg) for rice in China (GB2762-2012). NPK and NPK+RS treatments significantly increased As concentration in grain by 12.6 and 26.4 %, respectively, with a corresponding As concentration increase in rice straw of 15.9 and 20.5 %, respectively (Fig. 1a). Total As concentration was significantly decreased in the NP+S-KSi9000 treatment by as much as 29.1 and 32.4 % relative to the NPK treatment and by 20.1 and 21.6 % relative to the control for rice grain and straw, respectively. The NPK+CaSi9000 and NP+S-KSi900 treatments also substantially reduced total As in rice grain by 22.4 and 20.1 % relative to the NPK treatment and by 12.6 and 10.1 % relative to control for rice grain and straw, respectively. The high Si amendments (9000 kg/ha) substantially decreased the rice As concentration relative to the low Si amendments (900 kg/ha). Of all the Si fertilizers utilized, the semi-finished product of Si-potash fertilizer achieved the best As reduction in rice. While the other Si amendments (900 kg/ha) did not significantly decrease As concentration in rice grain, the treatment of NP+S-KSi reduced As by 20.1 % relative to NPK. The As concentration in rice grain is closely related to that in straw (R^2=0.82) (Fig. 1b), indicating that Si fertilizers significantly reduce the As concentration in straw.

Cadmium concentration in rice grain and straw

The Cd contents in rice samples from the control and NPK treatments were 0.70±0. 11 and 0.69±0.08 mg/kg, respectively, and exceeded the national food standard limit of 0.2 mg/kg

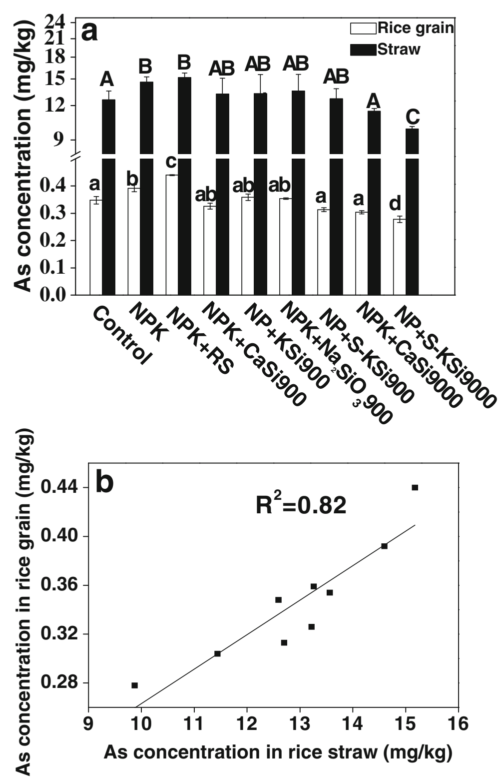

Fig. 1 Arsenic concentrations in rice grain and straw (dry weight) (**a**), and the correlation coefficient (R^2) between them under different Si fertilizers and dosages (**b**). RS, CaSi, KSi, S-KSi, and Na_2SiO_3 represent rice straw, Si-calcium fertilizer, Si-potash fertilizer, semi-finished product of Si-potash fertilizer, and sodium metasilicate fertilizer, respectively. *Different letters above bars* indicate difference at $p<0.05$ (*A–C* represent significant differences between different treatments for rice straw, and *a–d* represent significant differences between different treatments for rice grain)

Cd for rice in China (GB2762-2012). All Si fertilizers significantly reduced Cd concentration in rice grain and straw, except for Na_2SiO_3 (Fig. 2a). The capacity of different Si fertilizers to reduce Cd concentration in rice grain decreased in the following order: NPK+CaSi9000 (71.5 %)>NPK+CaSi900 (48.0 %)>NP+S-KSi9000 (42.0 %)>NP+KSi900 (40.0 %)>NP+S-KSi900 (26.5 %)>NPK+RS (23.1 %). High Si (9000 kg/ha) application decreased the grain Cd more than the corresponding low Si amendments (900 kg/ha). The most effective treatment was NPK+CaSi9000 treatment, which reduced the total Cd in rice grain and straw by 71.5 and 76.7 %, respectively (Fig. 2a). At the normal level of Si application (900 kg/ha), CaSi fertilizer exhibited a higher ability to reduce grain Cd than other Si fertilizers, even though the available Si in the CaSi fertilizer is less than that in KSi fertilizer. Similarly to As, a close linear relationship was observed between the Cd concentration in rice grain and straw (R^2=0.85) (Fig. 2b). This suggests that transfer coefficients from straw to grain are similar, and absorption of Cd from roots may be important for reducing rice Cd.

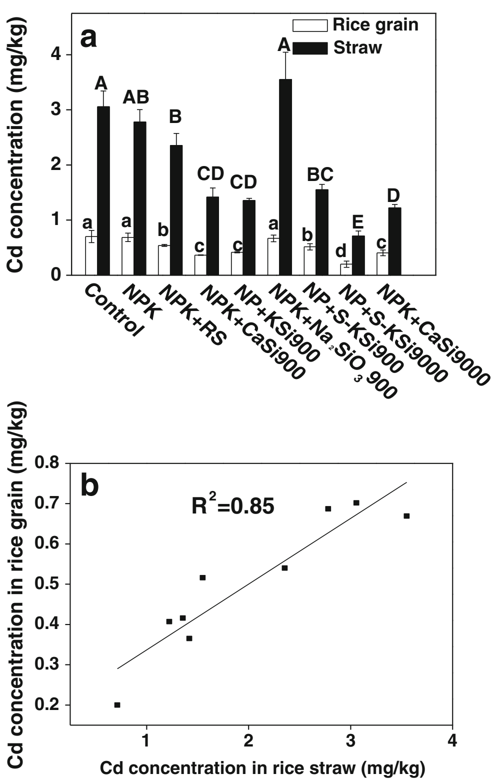

Fig. 2 Cd concentration in the rice grain and straw (dry weight) (**a**), and the correlation coefficient (R^2) between them under different Si fertilizers and dosages (**b**). RS, CaSi, KSi, S-KSi, and Na_2SiO_3 represent rice straw, Si-calcium fertilizer, Si-potash fertilizer, semi-finished product of Si-potash fertilizer, and sodium metasilicate fertilizer, respectively. *Different letters above bars* indicate difference at $p<0.05$ (*A–E* represent significant differences between different treatments for rice straw, and *a–d* represent significant differences between different treatments for rice grain)

The changes of pH in soil after Si fertilization

The soil pH substantially affects the bioavailability of As and Cd and their absorption by plants (Reddy and Patrick 1977; Masscheleyn et al. 1991; Marin et al. 1993; Naidu et al. 1994; Chan et al. 2008). The soil was slightly acidic with pH 6.0 (Table 3). Application of Si fertilizers increased the pH values of soil except in the case of the RS treatment, and the highest pH was shown in the NPK+CaSi9000 treatment ($p<0.01$) and the NP+S-KSi9000 treatment ($p<0.05$) (Table 3). The pH value increased substantially with increased Si fertilizer application rate, which is reasonable because all applied Si fertilizers have high pH in the range of 9.9–11.9 (Table 4).

Discussion

Effect of Si on As concentration in rice grain

Several Si fertilizers were investigated to reduce As accumulation in rice grain in the field, and differences were observed in these effects between fertilizer types. Compared with the NPK treatment, NP+S-KSi900, NP+S-KSi9000, and NPK+CaSi9000 treatments significantly reduced As concentration in rice grain. This inhibitory effect of Si is supported by many laboratory experiments (Bogdan and Schenk 2008; Li et al. 2009; Fleck et al. 2013; Tripathi et al. 2013). Areao et al. (2009) reported that the soil Eh value decreased rapidly during the flooded period. In this case, arsenite as the predominant form of As species in paddy soils (reducing environments) is actually present in solution predominantly as an undissociated molecule at pH <8. This is because p*K*a of arsenous acid ($As(OH)_3$) is 9.22, which is similar to the value for silicic acid

Table 3 The soil pH under different treatments

Treatment	pH value
Control	6.00±0.23a
NPK	5.99±0.17a
NP+KSi900	6.48±0.23a
NP+SKSi900	6.30±0.11a
NP+SKSi9000	6.59±0.21b
NPK+$Na_2SiO_3$900	6.10±0.14a
NPK+CaSi900	6.11±0.11a
NPK+CaSi9000	6.71±0.08b
NPK+RS	5.78±0.41a

RS, CaSi, KSi, S-KSi, and Na_2SiO_3 represent rice straw, Si-calcium fertilizer, Si-potash fertilizer, semi-finished product of Si-potash fertilizer, and sodium metasilicate fertilizer, respectively. Different letters indicate significant differences at $p<0.05$

Table 4 The pH and available Si in Si fertilizers

Fertilizer type	pH value	SiO_2 (%)
KSi	9.9±0.2	31.0±1.5
SKSi	10.2±0.1	23.3±0.4
Na_2SiO_3	11.9±0.1	13.2±0.9
CaSi	10.1±0.1	24.2±0.6

RS, CaSi, KSi, S-KSi, Na_2SiO_3 represent rice straw, Si-calcium fertilizer, Si-potash fertilizer, semi-finished product of Si-potash fertilizer, sodium metasilicate fertilizer, respectively

(p*K*a of 9.3). Both molecules are tetrahedral with similar sizes (Raven et al. 1998), so arsenite uptake shares the Si pathway of entry to root cells and transfer towards the xylem (Zhao et al. 2009). Additional Si, originated from Si fertilizers, increased the bioavailability of Si. It competed with arsenite, and thus mitigated As absorption in rice and decreased the As contents in rice straw, followed by a decreased As level in rice grain (Fig. 1), especially with large amounts amendments of Si fertilizers (9000 kg/ha) (Fig. 1).

NPK application also clearly increased As level in rice grain (12.6 %). NPK fertilizers are normally applied into the soils to increase crop yield. The As concentration in basal fertilizers (NPK) is low (0.03–5.2 mg/kg), suggesting the increase of As in grain is not due to the application of basal fertilizers. The most plausible explanations are (a) the competition between phosphate (PO_4^{2-}) originating from the NPK fertilizers and arsenate in the soil may release As into pore water (Peryea and Kammereck 1997; Peryea 1998; Wang et al. 2002), leading to increased As bioavailability and higher uptake of As by the plants, or (b) the NPK fertilizers may stimulate microbial activity, which reduces Fe or As in soil, releasing the As adsorbed on the Fe minerals and causing increased availability of As. The addition of rice straw into the soil (NPK+RS) significantly increased the As concentration in rice grain by 12.2 and 26.4 % compared with the NPK and control treatments, respectively. There are two possible explanations for this result. Firstly, the rice straw contained high level of As that can be released into soil through decomposition. The released As is bioavailable and causes higher As accumulation in rice grain. Secondly, the organic matter released from rice straw decomposition facilitated the reduction of Fe/hydroxides in the soil, and As that had been bonded within the Fe/hydroxides was released into the pore water, thus increasing available As in soil and counteracting the Si inhibitory effect (Shuman 1985).

In comparison with the high rate of Si fertilization (9000 kg/ha), the normal level of Si fertilization (900 kg/ha) did not significantly reduce the As concentration in rice grain, except in the case of S-KSi. Interestingly, this occurs despite the fact that the available Si in KSi is about 1.3 times higher than S-KSi, and the reduction effect of S-KSi9000 was greater than CaSi9000, even though the content of available Si in S-KSi is similar to CaSi. Therefore, the S-KSi is most effective for reducing As concentration in rice grain. We will investigate this finding more deeply in future research.

Effect of Si on Cd concentration in rice grain

All Si fertilizers except Na_2SiO_3 significantly reduce Cd concentration in rice grain, and the transfer coefficient from straw to rice grain is similar (R^2=0.85). The NPK+CaSi9000 treatment showed the greatest decrease in the rice Cd concentration (up to ~73 %). These results were partially because of Cd immobilization caused by silicate-induced pH change in the soils, the increase of pH (Table 3), which altered the Cd distribution in soil fractions, reduced the phytoavailable Cd, and increased the allocation of metals into more stable fractions (Naidu et al. 1994; Liang et al. 2005; 2007). This resulted in the observed significant decrease of Cd concentration in straw and grain. This supports other studies that showed that slag alkaline Si-containing materials at high dosages can induce an increase in soil pH which consequently increases the proportion of non-exchangeable heavy metals (Chen et al. 2000; Li et al. 2012). Another possible explanation is that Si restricted the transport of Cd from roots to shoots. In rice plants, Si plays an important role as a structural component of the cell wall; Si-mediated formation of colloidal silica in the cell walls has a strong affinity to heavy metals, and Cd is mainly deposited in cell walls through the co-precipitation of Cd and Si (Epstein 1999; Wang et al. 2000; Shi et al. 2010). The co-precipitation of Cd and Si in cell walls via Si-wall-Cd complexation may be one of the key target mechanisms for the reduction of Cd transportation from roots to shoots and thus the mitigation of Cd accumulation in rice grain. Furthermore, Si deposition in the vicinity of the endodermis can partially block the apoplast bypass-flow across the roots and inactivate Cd apoplastic transport from roots to shoots (Shi et al. 2005).

Clearly, the mitigation of Cd accumulation by Si fertilizers is more effective for rice grain than the mitigation of As accumulation, with the greatest reduction percentage about 20 % for As and 72 % for Cd. As shown in Fig. 2, the CaSi fertilizer is the most effective for Cd reduction in rice grain, while the S-KSi is the most effective for As reduction. Several studies have shown that access via Ca^{2+} transporters is one of the main molecular pathways of Cd^{2+} uptake into plant cells (Clemens 2006; Verbruggen et al. 2009). Therefore, the reduced Cd concentration in rice grain after addition of CaSi fertilizer may indicate that Ca plays a role as antagonist in Cd uptake mechanisms. This may explain why CaSi fertilizer is much more effective than KSi fertilizer for Cd mitigation in rice.

Conclusions

Most Si fertilizers can successfully reduce Cd and As concentration in the rice grain grown on paddy soils polluted with heavy metals. Different Si fertilizers have different effects on the reduction of As and Cd concentrations in rice grain. The S-KSi fertilizer is the most effective for As reduction, while CaSi fertilizer is the optimal choice for Cd mitigation in rice grain. This study shows that application of Si fertilizers can be effective in reducing the As and Cd concentrations in rice grain and thus reducing the health risk for people living in the heavy metal-contaminated area.

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