TECHNICAL ARTICLE

Effect of Si on As Speciation and Distribution in Rice near the Shimen Realgar Mine

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Abstract

Protection of natural water and cultivated crops from contamination in mining-affected areas is a problem in many regions. Wastewater and waste residuals from the Shimen realgar mine in Hunan Province, China, pose a high risk of arsenic (As) poisoning. The potassium silicate (PS)-assisted mechanisms of As mobility and accumulation reduction in a paddy soil–plant system were investigated. In a vegetation experiment, rice was grown in moderately and highly As-polluted soil (30.6 and 66.9 mg kg^{-1} of As, correspondingly) with and without PS. Total As and silicon (Si) in roots, shoots, and grains and the forms of As in the grains were analyzed. Sequential extraction of the As in the soil showed that the PS significantly reduced the mobility of As in the soil and its accumulation by rice. Several PS-mediated mechanisms were discussed: (1) dissolution of PS monosilicic acid enhances the sorption capacity of Si-based minerals for As; (2) increased pH in the soil solution provides higher As sorption by soil; (3) Si-induced competitive inhibition of As(III) transport initiated by *Lsi1* and *Lsi2*. The results indicate the potential of using soluble Si to reduce As mobility and biotoxicity at sites with high levels of As in wastewater, tailings, and waste residuals.

Keywords As(V) · As(III) · Dimethylarsinic acid · Potassium silicate · Sequential soil extraction

Introduction

Arsenic (As) is a widespread environmental pollutant and a Group I human carcinogen (Bradham et al. 2018; Martinez et al. 2011). The main sources of As in the soil are weathering of As-containing rocks, coal combustion, As-based pesticides and herbicides, chromated copper arsenate for wood preservation, and mining (Kumar et al. 2016). Arsenate (As(V)) and arsenite (As(III)) are the dominant inorganic forms of As in the environment. Arsenate is mostly present in aerated soils and arsenite is prevalent in paddy soils (Takahashi et al. 2004). The transformation of As(V) to As(III) can result in retention of the element in plants, mostly in the roots, and its subsequent compartmentalization in the root vacuoles as arsenite-phytochelatins (Li et al. 2016). Silicon (Si) transporters are able to load As(III) into the xylem or exude As(III) outside of the roots (Zhao et al. 2010). The competition between As(III) and silicic acid inhibits As(III) uptake (Fleck et al. 2013).

The Shimen realgar mine (29°38′11″–29°38′42″N, 111°2′06″–111°2′22″E) is located in Shimen County, Hunan Province. This mine is the largest deposit of realgar in Asia, with a mining history of more than 1500 years, until it closed in 2011 (Yang et al. 2018). The mining there has resulted in As pollution of a large area including agricultural land e, with soils containing up to 5240 mg kg^{-1} of As (Tang et al. 2016). The former mining and transport of As and disposal of mine tailings, wastewater, and waste residuals caused severe As pollution in both the nearby Huangshui River and the Xieshui River, which is only a few kilometers further away from the mine (Chi et al. 2017; Zheng et al. 2012). Water from these rivers is used to irrigation the rice paddies.

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Rice (*Oryza sativa* L.) is a staple crop in a large part of the world, especially in East Asia. Rice accumulates high quantities of As in grains, compared to other cereals such as wheat and barley (Su et al. 2010). In rice paddy soils, total As content typically ranges between 4 and 8 mg kg^{-1}, but it can reach up to 83 mg kg^{-1} in areas where the land has been irrigated with As-contaminated water (Williams et al. 2007). Arsenic(III) is a dominant form of As under paddy conditions, but monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), and arsenate are also present in flooded soils (Abedin et al. 2002). Arsenic toxicity causes inhibition of adenosine triphosphate (ATP) formation, which adversely impacts yield (Panaullah et al. 2009). Toxicity symptoms such as retarded development, brown spots, and scorched spots were observed on plants in soils containing > 60 mg kg^{-1} of As (Choudhury et al. 2011; Khan et al. 2010). Arsenic(III) reacts with sulphydryl groups of enzymes and proteins and disturbs cellular functions. At the metabolic level, As triggers the generation of reactive oxygen species (ROS), thus leading to oxidative stress (Shrivastava et al. 2015).

Silicon is considered to be a quasi-essential element for plants (Luyckx et al. 2017), which absorb Si as monosilicic acid [Si(OH)$_4$]. Rice is recognized as a Si accumulator and plant tissue can contain more than 10% Si (dry weight; Yamamoto et al. 2012). Silicon protects plants against numerous biotic and abiotic stresses through: (1) a physical or mechanical protection; (2) physiological reinforcement of the cell and inter-cell organelles and membranes, including chlorophylls and mitochondria; (3) chemical precipitation of inorganic pollutants, and (4) a biochemical response triggering metabolic changes (Meharg and Meharg 2015; Vaculik et al. 2015). Over the last 5–10 years, many authors have reported that Si-rich substances alleviate the negative influence of As on various plants (Fleck et al. 2013; Gupta and Khan 2015; Sanglard et al. 2016; Seyfferth et al. 2018; Silva et al. 2015). For example, it has been shown that Si reduces plant uptake and translocation of As by competition for transport (Fleck et al. 2013; Gupta and Khan 2015; Sanglard et al. 2016; Seyfferth et al. 2018; Tripathi et al. 2013). Improved Si nutrition was also reported to mediate photosynthetic performance and enhance antioxidant enzyme activity in As-exposed plants (Gupta and Khan 2015; Sanglard et al. 2016; Silva et al. 2015; Tripathi et al. 2013). While most studies focus on the plant mechanisms responsible for the Si-induced alleviation of As stress, it is also important to consider the soil–plant system. The effect of Si-rich materials applied to soil on As adsorption, precipitation, and complexation is poorly studied. Some authors observed an increase in As mobility through replacement of As anion by silicic acid (Seyfferth et al. 2018). Our previous study evidenced higher As adsorption by sand and different Si minerals with increasing amounts of monosilicic acid (Ji et al. 2017). The main aim of this investigation was to determine the effect of applying potassium silicate (K$_2$SiO$_3$) to soil on As mobility in soil and its translocation to rice.

Materials and Methods

Two paddy soils differing in total As (30.6 and 66.9 mg kg^{-1} in moderately and highly polluted soil) were selected. Soil samples were collected near the realgar (arsenic sulfide mineral) mining area. The coordinates of the first site were E111°3′30.2″, N29°39′46.3″ and of the second site—E111°2′51.1″, N29°39′44.3″. Rice has been grown in both fields for more than 50 years. Soils were sampled from a 0–10 cm depth, air-dried at room temperature (25–28 °C), ground, and passed through a 2-mm sieve. The basic soil properties were analyzed using standard procedures (Sparks et al. 1996). The data obtained is presented in Table 1.

Rice (*O. sativa* L. cv. Yuzhenxiang) seeds were obtained from the Institute of Rice (Hunan Province). Seeds were soaked in 10% H$_2$O$_2$ for 10 min, rinsed in double-distilled water, and germinated in autoclave-sterilized water. After 6 days of germination, plants were transferred to aerated nutrient solution. The solution was prepared according to Kukier and Chaney (2002) using deionized water, as follows: 126 mg L^{-1} KNO$_3$, 33 mg L^{-1} CaCl$_2$, 60 mg L^{-1} MgSO$_4$, 68 mg L^{-1} KH$_2$PO$_4$, 66 mg L^{-1} (NH$_4$)$_2$SO$_4$, 7.6 mg L^{-1} Fe–EDTA, 0.002 mg L^{-1} Na$_2$MoO$_4$, 0.12 mg L^{-1} H$_3$BO$_3$, 0.12 mg L^{-1} MnCl$_2$, 0.32 mg L^{-1} CuSO$_4$, 0.32 mg L^{-1} ZnSO$_4$. The final pH was adjusted to 5.5 with 1 N NaOH or 1 N HNO$_3$ and monitored throughout the experimental period. Growth solution was changed every 5 days for 30 days. Six seedlings were put into a pot at the 3-leaf stage

Table 1 Selected chemical properties of the paddy soils

Soil	pH	Organic matter (g kg^{-1})	Alkali-hydrolyzed N (mg kg^{-1})	Na$_2$HCO$_3$ extracted P (mg kg^{-1})	Water-soluble K (mg kg^{-1})	Total Fe (mg kg^{-1})	Total As (mg kg^{-1})	Total Ca (%)
Medium contaminated soil (Soil 1)								
I	5.43	30.4	206.6	3.44	96.8	23.1	30.6	0.106
Highly contaminated soil (Soil 2)								
II	5.46	29.4	152.5	0.41	106.3	23.3	66.9	0.121

(5 kg of soil, 25 cm diameter, and 20 cm height). Nitrogen as urea at 200 mg kg^{-1}, P as CaH_2PO_4 at 150 mg kg^{-1}, and K as KCl at 200 mg kg^{-1}, were applied to the soil before planting the rice. Silicon was then added as K_2SiO_3 (PS) as follows: soil 1, no Si (T1SiCK); soil 1, 150 mg kg^{-1} Si (T1Si1); soil 1, 300 mg kg^{-1} Si (T1Si2); soil 2, no Si (T2SiCK); soil 2, 150 mg kg^{-1} Si (T2Si1); soil 2, 300 mg kg^{-1} Si (T2Si2). The rice was grown under waterlogged conditions with 2–3 cm of water above the soil surface. Deionized water was added every 2 days to maintain the same approximate level of flooding. The temperature regime was 26 ± 2 °C during the day and 24 ± 2 °C at night. The light and night periods were each 12 h, with a light intensity of 950 mmol photons m^{-2} s^{-1}. The air humidity was $75 \pm 5\%$ during the day and $70 \pm 5\%$ at night.

Plants were harvested after maturity (105 days after transplanting) and the biomass of the roots, shoots, and grains were measured. The collected plant tissues were dried at + 65 °C for 24 h and weighed. Soils were sampled with harvesting, air-dried at room temperature, ground, and passed through a 1 mm sieve.

Plant Analysis

The total As in the roots, shoots and grain was analyzed by the following method. Dried, milled and passed through a 0.2-mm sieve plant sample (0.5 g) was put into a conical flask with 5 mL of concentrated nitric acid (HNO_3) The prepared solution was kept overnight at room temperature and then heated using a hot block at 12 °C until the extracts became clear. The digested solution was made up to a volume of 20 mL using deionized water and analyzed for As by atomic fluorescence spectrometry (AFS-7300).

The method of evaluating As speciation [As(V), As(III), and DMA] has been described by Shi et al. (2013). A milled sample of grain (1.0 ± 0.01 g) was put into a 50 mL centrifuge tube and extracted with 20 mL of 1% HNO_3 at 95 °C for 1.5 h. Then samples were cooled to room temperature and centrifuged at 5000 rpm for 10 min. The supernatant solution was filtered through a 0.22 μm filter. Arsenic was analyzed by HPLC-HG-AFS (Shimadzu LC-15C Suzhou Instruments Co., China; HG-AFS, AFS8230, Beijing Jitian Instruments Co., China).

To analyze total Si in plant tissue, a dried and ground plant sample of 0.20 ± 0.01 g was placed into a Teflon tube, then 4 mL of 50% NaOH was added. After standing overnight, 2 mL of 30% H_2O_2 was added, then the tubes were kept for 30 min, capped and placed into the microwave (CEM MARS 6 MS5181) for 30 min. Silicon in the obtained solution was analyzed by the Mullin and Riley method (1955).

Soil Analysis

The plant-available Si in the soil was determined by a 3.6 g L^{-1} HCl extract, according to the following procedure: Ten (10.0 ± 0.01) g of an air-dried soil sample was placed in a 100 mL polyethylene cup; 50.0 mL of 3.6 g L^{-1} HCl was added to each cup and the mixture was agitated at 200 rpm for 0.5 h. Then, after standing overnight, the mixture was agitated again for 0.5 h, and then the supernatant was centrifuged at 7000 rpm for 15 min (Matichenkov and Ammosova 1996; NIAES 1987). The Si was analyzed in a centrifuged solution using the Mullin and Riley method (1955). Soil As speciation was evaluated by sequential extraction (Herreweghe et al. 2003), as presented in Table 2.

Statistical Analysis

All data was entered into Microsoft Excel (2007). Analysis of variance was determined using SPSS 17.0. Figures were created by origin 8.0. The absorption factor (AF) was calculated as follows: AF = As concentration in roots/initial As concentration in soil. The arsenic translocation factors (TFs) were calculated as follows (Liu et al. 2014; Ye et al. 2012): TF1 of As from root to shoot = As concentration in roots/As concentration in shoots; TF2 of As from shoot to grain (maturity) = As concentration in grain/As concentration in shoots.

Table 2 Different As fractions of sequential extraction

Stage	Reagents	Procedure	Fraction
1	30 mL 1 mol L^{-1} NH_4Cl	0.5 h shaking	Easily soluble
2	30 mL 0.5 mol L^{-1} NH_4F (pH 8.2)	1 h shaking	NH_4F-extractable
3	30 mL 0.1 mol L^{-1} NaOH	2 h shaking	NaOH-extractable
4	30 mL 0.25 mol L^{-1} H_2SO_4	2 h shaking, 16 h stewing, 2 h shaking	H_2SO_4-extractable
5	4 mL HClconc, 2 mL HNO_3conc and 2 mL HFconc mixture; gently heated until half dry, subsequently reattacked with these three acids, heated until completely dry, redissolved with 20 mL 2.5 N HCl and diluted to 50 mL		Residual

Table 3 Dry weight of roots, shoots and grain (g plant⁻¹)

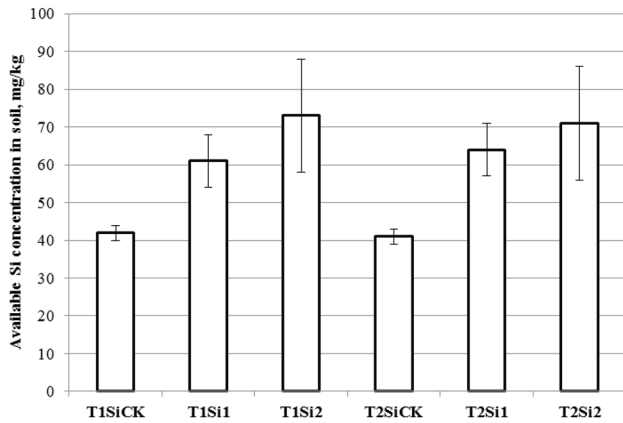| As in soil (mg kg⁻¹)	Si treatment (mg kg⁻¹)	Root (g plant⁻¹)	Shoot (g plant⁻¹)	Grain (g plant⁻¹)
30.6	0	7.76 ± 0.18	33.93 ± 0.99	25.63 ± 0.83
	150	9.18 ± 2.15	38.13 ± 1.05	30.77 ± 1.86
	300	10.00 ± 0.14	46.97 ± 1.12	34.97 ± 0.47
66.9	0	4.85 ± 0.22	30.63 ± 0.76	20.80 ± 1.48
	150	5.67 ± 0.33	34.50 ± 1.15	23.87 ± 0.47
	300	6.38 ± 0.09	38.60 ± 1.08	27.90 ± 1.90

Fig. 1 Soil concentration of acid-extractable Si after experiment, mg kg⁻¹

Results

The biomass of roots, shoots, and grains are shown in Table 3. The weight of roots, shoots, and grains in Soil 2 was 37.5, 9.7, and 18.8% less, respectively, than that in Soil 1. Application of PS significantly increased the biomass of plants. PS at a low rate increased biomass of the roots by 18.3 and 16.9%, biomass of the shoots by 12.3 and 12.6%, and grain yield by 20.1 and 14.8% in Soils 1

and 2, respectively. The higher rate of PS increased the rice biomass by 26.0–38.4% (Fig. 1).

In our study, the 0.1 M HCl extraction method was used to assess soil Si available for plant uptake. Numerous methods have been suggested for determining the plant-available Si in the soil (Bocharnikova and Matichenkov 2012; Miles et al. 2014). The literature indicates that the 0.1 M HCl-extractable Si in the soil correlates better with total plant Si than other Si extraction methods (Bocharnikova and Matichenkov 2012; Matichenkov and Ammosova 1996). The correlation coefficients between 0.1 M HCl-extractable soil Si and plant Si was 0.89–0.95 (Bocharnikova and Matichenkov 2012; Matichenkov 2007), while it did not exceed 0.77 for the $CaCl_2$ extraction method, one of the most commonly used methods of evaluating mobile Si in soil (Georgiadis et al. 2014; Miles et al. 2014). The concentration of plant-available Si in both untreated soils was 43.2 mg kg of Si (Table 4). The K_2SiO_3 addition increased this by 40.6–46.9 and 64.4–67.8%, according to the application rate.

The total content of Si in the roots and shoots differed depending on the level of As soil contamination. Without Si treatment, the root Si was 0.81% of Si in Soil 1 and only 0.56% of Si in Soil 2. The shoot (stem + leaf) Si amounted to 1.68 and 1.16% in Soil 1 and Soil 2, accordingly. Application of PS increased that up to 0.91 and 0.97% of the root Si in Soil 1, but reduced it to 0.52 and 0.50% in Soil 2. The shoot Si was significantly affected by Si added at a low rate (2.24 and 1.49% of Si in Soils 1 and 2), whereas a higher Si rate had little effect (Fig. 2).

The original soils were slightly acid with a pH of 5.43 (Soil 1) and 5.46 (Soil 2). Application of PS increased the pH to 6.06 and 6.17, and to 6.59 and 6.58, in Soils 1 and 2, respectively.

The total As concentrations in the rice plants are presented in Table 5. The most As (90.37 mg kg⁻¹) was observed in the roots of the rice in Soil 2. The shoot As was 89.5% less than in the roots in Soil 1 and 84.3% less in Soil 2. The minimum As was detected in the rice grains (0.46 and 0.81 mg kg⁻¹ of As, accordingly in Soils 1 and 2).

Table 4 Plant-available Si in soil, pH of soil and total Si in the roots and shoots of rice

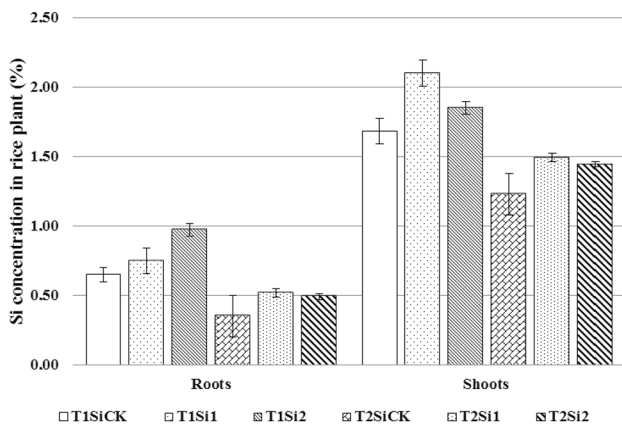| As in soil (mg kg⁻¹)	Si treatment (mg kg⁻¹)	Plant-available Si (mg kg⁻¹)	Total Si in plants		Soil pH
			Roots (%)	Shoots (%)	
30.6	0	42.3 ± 2.0	0.81 ± 0.14	1.68 ± 0.21	5.51 ± 0.10
	150	61.2 ± 7.2	0.91 ± 0.09	2.24 ± 0.19	6.06 ± 0.12
	300	73.4 ± 15.2	0.97 ± 0.05	1.78 ± 0.08	6.59 ± 0.11
66.9	0	41.0 ± 2.3	0.56 ± 0.36	1.16 ± 0.43	5.69 ± 0.14
	150	64.2 ± 7.3	0.52 ± 0.06	1.49 ± 0.10	6.17 ± 0.12
	300	71.2 ± 15.1	0.50 ± 0.05	1.24 ± 0.07	6.58 ± 0.12

Fig. 2 Concentration of total Si in shoots and roots, %

Table 5 Arsenic concentration in shoots, roots and grain of rice under different treatments, mg kg^{-1} As

As in soil (mg kg^{-1})	Si treatment (mg kg^{-1})	Root (mg kg^{-1})	Shoot (mg kg^{-1})	Grain (mg kg^{-1})
30.6	0	81.19 ± 0.29	8.51 ± 0.48	0.46 ± 0.05
	150	75.98 ± 3.05	6.66 ± 0.03	0.34 ± 0.04
	300	46.00 ± 2.85	6.28 ± 2.26	0.31 ± 0.02
66.9	0	90.37 ± 0.40	16.02 ± 0.19	0.81 ± 0.02
	150	66.84 ± 1.37	14.99 ± 0.83	0.70 ± 0.03
	300	61.30 ± 3.10	9.54 ± 2.33	0.69 ± 0.05

The PS significantly decreased the total As in all of the plant parts. The As reductions were greater in the roots and grains (by 43.3 and 32.0%, respectively) in Soil 1 at the higher PS application rate. The shoot As decreased more (by 40.4%) in Soil 2 at the higher PS application rate.

In the rice grains, As was mostly present as As(III) (Table 6). As As increased in the soil, all of the tested forms of As in the grain increased: As(III)—by 79.2%, As(V)—by 7,6%, and DMA—by 187.8%. While the Si application did not significantly affect the As(V) content, it significantly reduced As(III) content in the rice grains by 41.2 and 30.6%,

Fig. 3 Effect of applied PS on the soil pH

when applied at a low rate, and by 51.0 and 42.0% at a high rate, in Soils 1 and 2.

The As content in the different soil fractions is presented in Table 7. In the original Soil 1, the maximum As was observed in fraction 3 (3.68 ± 0.07 mg kg^{-1} As), while the maximum As content in the original Soil 2 was detected in fraction 5 (9.89 ± 0.71 mg kg^{-1} As). Five fractions in total comprised about 33% of the soil As. Application of PS reduced As mobility in the soil. The amount of As in the first two fractions was decreased in both soils and at both Si rates. The NaOH-extractable As was increased in Soil 1 at a higher Si rate and in Soil 2 at both Si rates. The H$_2$SO$_4$-extractable As was insignificantly reduced by Si in Soil 1 and significantly increased in Soil 2. Silicon added at both rates increased the residual As in both soils (Fig. 3).

Discussion

The test soil was collected near Asia's biggest realgar mine. The As concentrations in the Xianyang River range from 0.01 to 28 mg L^{-1} (Chi et al. 2017). Periodic aeration of the soil during rice harvesting initiates As oxidation and transformation into less mobile forms (Geng et al. 2017). Then additional As enters the soil with irrigation.

Table 6 Content of As(III), As(V) and DMA in rice grain

Treatment	As(III) (mg kg^{-1})	As(V) (mg kg^{-1})	DMA (mg kg^{-1})	Inorganic As (%)
T1SiCK	0.284 ± 0.023 d	0.104 ± 0.016 a	0.066 ± 0.001 a	85.4
T1Si1	0.167 ± 0.003 b	0.109 ± 0.041 a	0.066 ± 0.005 a	80.7
T1Si2	0.139 ± 0.013 a	0.095 ± 0.060 a	0.080 ± 0.010 b	74.6
T2SiCK	0.509 ± 0.007 e	0.112 ± 0.012 a	0.190 ± 0.017 c	76.6
T2Si1	0.353 ± 0.007 c	0.113 ± 0.017 a	0.238 ± 0.010 d	66.2
T2Si2	0.295 ± 0.023 d	0.117 ± 0.022 a	0.276 ± 0.011 e	59.9

Inorganic arsenic (%) = [(inorganic As)/(species sum)] × 100

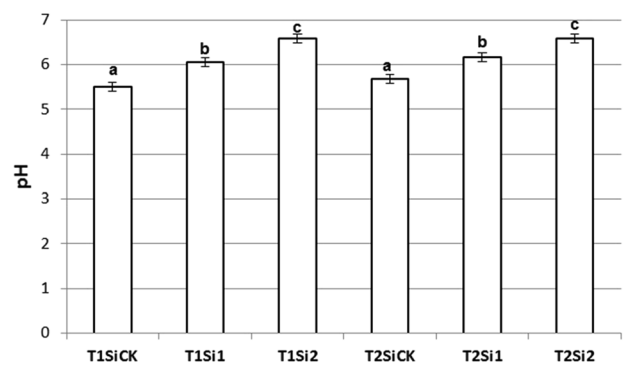Value within a column followed by the same letter are not different using Duncan's Multiple Range test (P < 0.05)

Table 7 Content of As in sequential extraction fractions in the soil

As in soil (mg kg^{-1})	Si treatment (mg kg^{-1})	Fractions of As				
		1 (mg kg^{-1})	2 (mg kg^{-1})	3 (mg kg^{-1})	4 (mg kg^{-1})	5 (mg kg^{-1})
30.6	0	0.31 ± 0.04	2.03 ± 0.39	3.68 ± 0.07	1.31 ± 0.07	2.72 ± 0.85
	150	0.28 ± 0.01	1.72 ± 0.23	3.58 ± 0.07	1.19 ± 0.09	3.46 ± 0.48
	300	0.23 ± 0.03	1.91 ± 0.26	3.94 ± 0.06	1.22 ± 0.18	6.03 ± 0.76
66.9	0	0.38 ± 0.02	2.40 ± 0.36	6.95 ± 0.19	2.84 ± 0.34	9.89 ± 0.71
	150	0.33 ± 0.06	2.19 ± 0.43	7.62 ± 0.37	3.21 ± 0.44	10.64 ± 0.84
	300	0.29 ± 0.03	2.05 ± 0.45	7.66 ± 0.18	3.17 ± 0.16	12.52 ± 2.03

Table 8 Adsorption and translocation factors of As

Treatment	AF	TF1	TF2
T1SiCK	2.65 ± 0.01 a	0.10 ± 0.01 a	0.04 ± 0.01 a
T1Si1	2.48 ± 0.10 b	0.09 ± 0.02 a	0.05 ± 0.01 a
T1Si2	1.50 ± 0.09 c	0.14 ± 0.04 a	0.06 ± 0.02 a
T2SiCK	1.35 ± 0.01 a	0.18 ± 0.01 b	0.04 ± 0.01 a
T2Si1	1.00 ± 0.02 b	0.23 ± 0.02 a	0.03 ± 0.01 a
T2Si2	0.92 ± 0.05 b	0.16 ± 0.01 b	0.05 ± 0.04 a

Value within a column followed by the same letter are not different using Duncan's Multiple Range test ($P < 0.05$)

As(V) is the dominant form of the element in aerobic soils. Because of adsorption to iron (Fe), aluminum (Al), and manganese (Mn) oxides and hydroxides, soluble forms of As are low (Inskeep et al. 2002). In flooded fields, Fe^{3+} is reduced to Fe^{2+} and As is released into the soil solution. In addition, As(V) is reduced to As(III), which is more mobile than arsenate (Takahashi et al. 2004). However, continuous changes in the redox state for many years have led to strong As fixation in Soil 2. As a result, the more soluble forms of As (fraction 1) were similar in Soils 1 and 2. But the more contaminated Soil 2 had a greater content of the less soluble forms of As (fractions 3–5) than Soil 1. This can be attributed to the process of As chemical fixation, which proceeds more actively in the more contaminated Soil 2.

Although the soluble forms of As were similar in the two soils, there was significantly more biomass in Soil 1 (by 16.4% for whole plants and 37.5% for roots) than in Soil 2. This suggests that even soil-bound As might have a deleterious effect on plant growth and that it could be partially transformed into plant-available As during the growing season. The AF for the control plants in Soil 1 was twice as high as that in Soil 2 (Table 8). In our study, a large difference in the AF values between two soils is attributed mostly to the difference in the total soil As, whereas plant-available forms in both soils as well as the root content of As did not differ much.

It is important that the control plants in Soil 1 had a much lower TF1 than Soil 2. Therefore, natural plant mechanisms responsible for restricting root to shoot As translocation were more efficient in the less contaminated soil. The TF2 was the same for the control plants in both soils. According to Gupta et al. (2011), retention can be mediated through As compartmentation in vacuoles, complexation by glutathione and peptides, transformation into non-toxic organic forms, and volatilization into the atmosphere.

Soil-applied PS significantly reduced AF values in both soils, and the effect was increased at a greater PS rate. As in the control plants, TF1 was less in the less contaminated Soil 1 than in Soil 2, but a direct correlation between PS application and TF1 was not observed. The TF2 values differed insignificantly in both PS-treated soils. Apparently, the PS mostly impacted the transfer of As from soil to root.

The PS application significantly decreased the mobility of As in the soil and its accumulation by the rice. At the same time, the amount of strongly adsorbed As are increased. Therefore PS application stabilized the As in the soil–plant system. Several mechanisms could be suggested to explain the PS effect on As behavior.

The first mechanism is based on a PS-mediated increase in soil sorption capacity. Our previous experiments on As sorption showed that the sorption capacity of Si-rich minerals rises with increasing monosilicic acid concentration (Ji et al. 2017; Peng et al. 2017). The dissolution of PS and the formation of monosilicic acid could be responsible for enhanced As sorption to the soil. In the scientific literature on As adsorption, many studies focus on the role of Fe-based minerals in As immobilization. Monosilicic acid was reported to compete with As for adsorption on different Fe minerals, thus decreasing the metalloid retention (Möller and Sylvester 2008). However, this data was not obtained for soil, but for chemically pure Fe-based minerals and at high pH levels. In our work, the soils were characterized by pH of about 5.6 and a predominance of silicates in mineral composition. There was only 23.1–23.3 mg kg^{-1} of total Fe in the soil, so the role of Fe minerals in As fixation was low. We suspect that monosilicic acid, a product of PS dissolution, is initially adsorbed on Si-based minerals due to their

chemical affinity, thus forming additional As-adsorbing sites (Ji et al. 2017; Peng et al. 2017).

Another possible PS-mediated mechanism is related to the observed increased pH in the tested soil, which would slightly decrease the sorption of As(V) and DMA, but increase sorption of As(III) (Smith et al. 1998). Considering that As(V) is reduced to As(III) under flooded conditions, total As adsorption could be enhanced.

During the first 30 days of the current study, all rice plants were grown at a low level of Si, mostly the Si available in grain husks (about 1 mg of Si grain^{-1}). However, this period is characterized by enhanced vegetative growth and consequent high Si uptake (Ma and Takahashi 2002). After this period, the biomass production rate decreases and the demand for Si diminishes as well. After replanting, the plant's Si absorption was not intensive and as a result, the total Si in the control and Si-treated mature plants differed insignificantly.

The application of PS significantly reduced the total As in all of the analyzed parts of the rice plant. This data is consistent with other studies (Fleck et al. 2013; Gupta and Khan 2015; Sanglard et al. 2016; Seyfferth et al. 2018; Silva et al. 2015). PS was selected as a common source of monosilicic acid in soil-rice system research (Buck et al. 2008; Raj and Pannu 2017). This substance totally dissolves, forming monosilicic acid, the only Si form that is taken up by plants (Ma and Takahashi 2002). Therefore, it is possible to state that there was a monosilicic acid-induced effect on As transport in rice plants. There are a lot of Si-rich materials that can serve as a source of monosilicic acid: diatomites, zeolites, amorphous silica, some Si-based industrial by-products (Bakhat et al. 2018; Ji et al. 2017; Wei et al. 2018). In this study, we used chemically pure PS to eliminate the influence of solid particles on the As behavior in soil. Our previous investigations and other reports, conducted with diatomite, calcium silicate slag, and amorphous silica have shown that improved plant Si nutrition reduced the root to leaf transport of inorganic pollutants via apoplast and symplast in rice plants (Ji et al. 2017; Wei et al. 2018). We have also shown that added Si reduced the stem to leaf As transport in rice more intensively than the root to stem transport (Wei et al. 2018).

In the grain, the PS application reduced the concentration of As(III), while its influence on As(V) was insignificant. According to Ma et al. (2007, 2008), arsenite is taken up by the rice roots via *Lsi1* and/or *Lsi2*. The same transporters facilitate Si accumulation by rice. The competition between Si and As(III) transport could be responsible for: less Si accumulation in rice in the more contaminated Soil 2, and less As accumulation in both soils with the PS application.

Conclusion

The current study demonstrates that PS applied to As-contaminated paddy soil had a combined impact on the As behavior via soil and plant mechanisms. It contributed to: (a) reduced As bioavailability by altering As speciation in the soil, with increasing fixation in the residual fraction; (b) decreased As uptake by and translocation within rice plants; and (c) mitigation of biotoxicity through transformation of the highly toxic As(III) into the less toxic organic As. The PS application resulted in an increase in the root, leaf, and grain biomass of the rice plants by 12–36%, while the As content in the rice grains decreased by 14–32%, due to less As(III); the As(V) content did not change and the organic As increased.

References

Abedin MJ, Feldmann J, Meharg AA (2002) Uptake kinetics of arsenic species in rice plants. Plant Physiol 128:1120–1128. https://doi.org/10.1104/pp.010733Abedin

Bakhat HF, Bibi N, Zia Z, Abbas S, Hammad HM, Fahad S, Ashraf MR, Shah GM, Rabbani F, Saeed S (2018) Silicon mitigates biotic stresses in crop plants: a review. Crop Prot 104(1):21–34. https://doi.org/10.1016/j.cropro.2017.10.008

Bocharnikova EA, Matichenkov VV (2012) Influence of plant associations on the silicon cycle in the soil–plant system. Appl Ecol Environ Res 10(4):547–560. https://doi.org/10.15666/aeer/1004_547560

Bradham KD, Diamond GL, Burgess M, Juhasz A, Klotzbach JM, Maddaloni M et al (2018) In vivo and in vitro methods for evaluating soil arsenic bioavailability: relevant to human health risk assessment. J Toxicol Environ Health Part B 21(2):83–114. https://doi.org/10.1080/10937404.2018.1440902

Buck GB, Korndörfer GH, Antonio Nolla A, Coelho L (2008) Potassium silicate as foliar spray and rice blast control. J Plant Nutr 31(2):231–237. https://doi.org/10.1080/01904160701853704

Chi S, Hu J, Zheng J, Dong F (2017) Study on the effects of arsenic pollution on the communities of macro-invertebrate in Xieshui River. Acta Ecol Sin 37(1):1–9. https://doi.org/10.1016/j.chnaes.2016.09.003

Choudhury B, Chowdhury S, Biswas AK (2011) Regulation of growth and metabolism in rice (*Oryza sativa* L.) by arsenic and its possible reversal by phosphate. J Plant Interact 1:15–24. https://doi.org/10.1080/17429140903487552

Fleck AT, Mattusch J, Schenk MK (2013) Silicon decreases the arsenic level in rice grain by limiting arsenite transport. J Plant Nutr Soil Sci 176:785–794. https://doi.org/10.1002/jpln.201200440

Geng A, Wang X, Wu L, Wang F, Chen Y, Yang H, Zhang Z, Zhao X (2017) Arsenic accumulation and speciation in rice grown

in arsanilic acid-elevated paddy soil. Ecotoxicol Environ Saf 137(1):172–178. https://doi.org/10.1080/00380768.2011.565479

Georgiadis A, Sauer D, Herrmann L, Breuer J, Zarei M, Stahr K (2014) Testing a new method for sequential silicon extraction on soils of a temperate–humid climate. Soil Res 52(7):645–657. https://doi.org/10.1071/SR14016

Gupta M, Khan E (2015) Mechanism of arsenic toxicity and tolerance in plants: role of silicon and signalling molecules. In: Tripathi BN, Muller M (eds) Stress responses in plants. Springer, Cham, pp 143–157

Gupta M, Srivastava S, Huang HG, Romero-Puertas MC, Sandalio LM (2011) Arsenic tolerance and detoxification mechanisms in plants. In: Sherameti I, Varma A (eds) Detoxification of heavy metals. Springer, Berlin, pp 169–179

Herreweghe SV, Swennen R, Vandecasteele C, Cappuyns V (2003) Solid phase speciation of arsenic by sequential extraction in standard reference materials and industrially contaminated soil samples. Environ Pollut 122:323–342. https://doi.org/10.1016/S0269-7491(02)00332-9

Inskeep WP, McDermott TR, Fendorf S (2002) Arsenic (V)/(III) cycling in soils and natural waters: chemical and microbiological processes. In: Frankenberger JWT (ed) Environmental chemistry of arsenic. Marcel Dekker, New York, pp 183–215

Ji X, Liu S, Hua P, Bocharnikova EA, Matychenov VV, Khomyakov DM (2017) Cadmium and arsenic adsorption in aqueous systems in the presence of monosilicic acid. Mosc Univ Soil Sci Bull 72(5):199–206. https://doi.org/10.3103/s0147687417050040

Khan MA, Stroud JL, Zhu YG, McGrath SP, Zhao FJ (2010) Arsenic bioavailability to rice is elevated in Bangladeshi paddy soils. Environ Sci Technol 44:8515–8521. https://doi.org/10.1021/es101952f

Kukier U, Chaney RL (2002) Growing rice grain with controlled cadmium concentrations. J Plant Nutr 25(9):1793–1820

Kumar M, Ramanathan AL, Rahman MM, Naidu R (2016) Concentrations of inorganic arsenic in groundwater, agricultural soils and subsurface sediments from the middle Gangetic plain of Bihar, India. Sci Total Environ 573:1103–1114. https://doi.org/10.1016/j.scitotenv.2016.08.109

Li N, Wang J, Song WY (2016) Arsenic uptake and translocation in plants. Plant Cell Physiol 57(1):4–13. https://doi.org/10.1093/pcp/pcv143

Liu J, Qu P, Zhang W, Dong Y, Wang M (2014) Variations among rice cultivars in subcellular distribution of Cd: the relationship between translocation and grain accumulation. Environ Exp Bot 107:25–31. https://doi.org/10.1016/j.envexpbot.2014.05.004

Luyckx M, Hausman JF, Lutts S, Guerriero G (2017) Silicon and plants: current knowledge and technological perspectives. Front Plant Sci 8:411. https://doi.org/10.3389/fpls.2017.00411

Ma JF, Takahashi E (2002) Soil, fertilizer, and plant silicon research in Japan. Elsevier, Amsterdam

Ma JF, Yamaji N, Mitani N, Tamai K, Konishi S, Fujiwara T, Katsuhara M, Yano M (2007) An efflux transporter of silicon in rice. Nature 448:209–212. https://doi.org/10.1038/nature05964

Ma JF, Yamaji N, Mitani N, Xu XY, Su YH, McGrath SP, Zhao FJ (2008) Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. PNAS 105:9931–9935. https://doi.org/10.1073/pnas.0802361105

Martinez VD, Vucic EA, Becker-Santos DD, Gil L, Lam WL (2011) Arsenic exposure and the induction of human cancers. J Toxicol. https://doi.org/10.1155/2011/431287

Matichenkov VV (2007) Soil gradation on deficiency of plant-available Si. Agrochemistry 7:22–31

Matichenkov VV, Ammosova YM (1996) Effect of amorphous silica on soil properties of a sod-podzolic soil. Eurasian Soil Sci 28:87–99

Meharg C, Meharg AA (2015) Silicon, the silver bullet for mitigating biotic and abiotic stress, and improving grain quality, in

rice? Environ Exp Bot 120:8–17. https://doi.org/10.1016/j.envexpbot.2015.07.001

Miles N, Manson AD, Rhodes R, van Antwerpen R, Weigel A (2014) Extractable silicon in soils of the South African sugar industry and relationships with crop uptake. Commun Soil Sci Plant 45(22):2949–2958. https://doi.org/10.1080/00103624.2014.956881

Möller T, Sylvester P (2008) Effect of silica and pH on arsenic uptake by resin/iron oxide hybrid media. Water Res 42(6–7):0–1766

Mullin JB, Riley JP (1955) The colorimetric determination of silicate with special reference to sea and natural waters. Anal Chim Acta 12:162–176. https://doi.org/10.1016/S0003-2670(00)87825-3

NIAES (1987) Official methods of analysis of fertilizers. Proc Nat Inst Agro Environ Sci 124:36–37

Panaullah GM, Alam T, Hossain MB et al (2009) Arsenic toxicity to rice (Oryza sativa L.) in Bangladesh. Plant Soil 317:31–39. https://doi.org/10.1007/s11104-008-9786-y

Peng H, Ji X, Wei W, Bocharnikova E, Matichenkov V (2017) As and Cd sorption on selected Si-rich substances. Water Air Soil Pollut 228(8):288–298. https://doi.org/10.1007/s11270-017-3473-7

Raj R, Pannu PPS (2017) Management of rice blast with different fungicides and potassium silicate under in vitro and in vivo conditions. Plant Pathol 99(3):707–712. https://doi.org/10.4454/jpp.v99i3.3993

Sanglard LMVP, Detmann KC, Martins SCV et al (2016) The role of silicon in metabolic acclimation of rice plants challenged with arsenic. Environ Exp Bot 123:22–36. https://doi.org/10.1016/j.envexpbot.2015.11.004

Seyfferth AL, Limmer MA, Dykes GE (2018) On the use of silicon as an agronomic mitigation strategy to decrease arsenic uptake by rice. Adv Agron 149:49–91. https://doi.org/10.1016/bs.agron.2018.01.002

Shi GL, Lou LQ, Zhuang S, Cai Q (2013) Arsenic, copper and zinc contamination in soil and wheat during coal mining with assessment of health risks for the inhabitants of Huaibei, China. Environ Sci Pollut Res 20(12):8435–8445. https://doi.org/10.1007/s11356-013-1842-3

Shrivastava A, Ghosh D, Dash A, Bose S (2015) Arsenic contamination in soil and sediment in India: sources, effects, and remediation. Curr Pollut Rep 1:35–46. https://doi.org/10.1007/s40726-015-0004-2

Silva AJD, Nascimento CW, Gouveianeto ADS, Junior EAS (2015) Effects of silicon on alleviating arsenic toxicity in maize plants. Revista Bras De Ciência Do Solo 39(1):289–296. https://doi.org/10.1590/01000683rbcs20150176

Smith E, Naidu R, Altson AM (1998) Arsenic in the soil environment: a review. Adv Agron 64:149–195

Sparks DL, Page AL, Helmke PA et al (1996) Methods of soil analysis: part 3. Chemical methods, vol 5. SSSA Book Ser, Madison

Su YH, McGrath SP, Zhao FJ (2010) Rice is more efficient in arsenite uptake and translocation than wheat and barley. Plant Soil 328(1–2):27–34. https://doi.org/10.1007/s11104-009-0074-2

Takahashi Y, Minamikawa R, Hattori KH, Kurishima K, Kihou N, Yuita K (2004) Arsenic behavior in paddy fields during the cycle of flooded and non-flooded periods. Environ Sci Technol 38:1038–1044. https://doi.org/10.1021/es034383n

Tang JW, Liao YP, Yang ZH, Chai LY, Yang WC (2016) Characterization of arsenic serious-contaminated soils from Shimen realgar mine area, the Asian largest realgar deposit in China. J Soil Sedim 16:1519–1528. https://doi.org/10.1007/s11368-015-1345-6

Tripathi PRD, Tripathi RP, Singh S et al (2013) Silicon mediates arsenic tolerance in rice (Oryza sativa L.) through lowering of arsenic uptake and improved antioxidant defence system. Ecol Eng 52:96–103. https://doi.org/10.1016/j.ecoleng.2012.12.057

Vaculik M, Pavlovic A, Lux A (2015) Silicon alleviates cadmium toxicity by enhanced photosynthetic rate and modified bundle sheath's

cell chloroplasts ultrastructure in maize. Ecotoxicol Environ Saf 120:66–73. https://doi.org/10.1016/j.ecoenv.2015.05.026

Wei X, Liu Y, Zhan Q, Zhang P, Zhao D, Xu B, Bocharnikova E, Matichenkov V (2018) Effect of Si soil amendments on As, Cd, and Pb bioavailability in contaminated paddy soils. Paddy Water Environ 16(1):173–181. https://doi.org/10.1007/s10333-017-0629-4

Williams PN, Villada A, Deacon C, Raab A, Figuerola J, Green AJ, Feldmann J, Meharg AA (2007) Greatly enhanced arsenic shoot assimilation in rice leads to elevated grain levels compared to wheat and barley. Environ Sci Technol 41:6854–6859. https://doi.org/10.1021/es070627i

Yamamoto T, Nakamura A, Iwai H, Ma JF, Yokoyama R, Nishitani K, Satoh S, Furukawa J (2012) Effect of silicon deficiency on secondary cell wall synthesis in rice leaf. J Plant Res 123:771–779. https://doi.org/10.1007/s10265-012-0489-3

Yang F, Xie S, Wei C, Liu J, Zhang H, Chen T, Zang J (2018) Arsenic characteristics in the terrestrial environment in the vicinity of the Shimenrealgar mine, China. Sci Total Environ 626:77–86. https://doi.org/10.1016/j.scitotenv.2018.01.079

Ye X, Ma Y, Sun B (2012) Influence of soil type and genotype on Cd bioavailability and uptake by rice and implications for food safety. J Environ Sci 24(9):1647–1654. https://doi.org/10.1016/S1001-0742(11)60982-0

Zhao FJ, McGrath SP, Meharg AA (2010) Arsenic as a food chain contaminant: mechanisms of plant uptake and metabolism and mitigation strategies. Annu Rev Plant Biol 61:535–559. https://doi.org/10.1146/annurev-arplant-042809-112152

Zheng JX, Zhou LF, Ju-Xiang HU, Wang HJ, Peng Q (2012) Characteristics of zooplankton community in arsenic polluted water of Xieshui River. J Hydrol 33(6):56–61