



Effect of Monosilicic and Polysilicic Acids on Cd Transport in Rice, a Laboratory Test

Wei Wei¹ · Xionghui Ji^{2,3} · Liu Saihua^{2,3} · Elena Bocharnikova⁴ · Vladimir Matichenkov⁴

Received: 23 June 2020 / Accepted: 10 February 2021 / Published online: 6 March 2021
© The Author(s), under exclusive licence to Springer Science+Business Media, LLC part of Springer Nature 2021

Abstract

Silicon (Si) has been reported to enhance the plant tolerance to cadmium (Cd) toxicity, while the Si–Cd interactions remain poorly investigated. In a laboratory study, the transport of monosilicic and polysilicic acids in the apoplast and symplast of roots, stems and leaves of rice as well as the effect of Si supplementation on the external solution-to-root-to-stem-to-leaf time-dependent Cd transport through apoplastic and symplastic pathways were investigated. The Cd translocation was very fast and mainly through apoplastic pathway. For 24 h the Cd concentration increased 38–50 times in apoplast and 6–8 times in symplast. In Cd-exposed plants, Cd entry into apoplast was inhibited during the first 2 days, but its massive flow was observed on the 4th day. In Si-supplied plants, the ability of apoplastic barriers to impede Cd root-to-leaf transport was higher during all time of examination. Silicon reduced the Cd transport through the apoplast of roots, stems, and leaves by 50–90%, while the symplast transport of Cd was influenced by Si only in stems. In the apoplast and symplast, soluble Si was presented in the form of both monomers and polymers of silicic acid. Exposure to Cd initiated the uptake by roots and fast redistribution of Si from leaves to roots via mono- and polysilicic acids movement in apoplast and symplast.

Keywords Cadmium · Soluble Si · Rice · Apoplast · Symplast

Introduction

Pollution of the environment with cadmium (Cd) results from industrial wastes, the incineration of garbage, watering fields with wastewater and application of agrochemicals (He et al. 2013; Zaid et al. 2019). Cadmium accumulates in harvested yield in the contaminated area and poses a health risk (Zhao et al. 2014). The mechanisms of Cd uptake by plants have been widely studied, but the regulation of Cd translocation to aboveground tissues remains elusive (Song

et al. 2017; Wu et al. 2019). The absorption of Cd by plant depends on soil properties (pH, chemical and physical properties), a level of pollution, macro- and micronutrients uptake, temperature, and others (Ge et al. 2016; Song et al. 2017). Usually, the absorbed Cd primarily accumulates in the roots (the root apoplast) (Ouariti et al. 1997; Ji et al. 2017). However, in regard to posing a risk to human health, the Cd accumulated in the aboveground organs of plants, except root crops, is crucial.

Cadmium enters the plant from soil mainly via root uptake in the form of accidental transport by specific and non-specific transporters of essential elements such as Fe^{2+} , Ca^{2+} , Zn^{2+} , Cu^{2+} and Mg^{2+} (Roth et al. 2006; Llugany et al. 2012). The root-to-leaf Cd transport occurs through apoplastic and symplastic pathways (Song et al. 2017; Wu et al. 2019). During transportation, Cd is partly precipitated, trapped into cell wall or capsulated by organic or inorganic substances (Rodda et al. 2011). The formation of Cd complexes with organic ligands is recognized as the mechanism of increasing plant tolerance to this toxic metal (Song et al. 2017). However, many heavy metal-transport proteins have not been identified at the molecular level, and the transport function, specificity,

Handling Editor: Rhonda Peavy.

✉ Vladimir Matichenkov
vvmatichenkov@yandex.ru

- ¹ Long Ping Branch, Graduate School of Hunan University, Changsha, China
- ² Institute of Agro-Environment and Ecology, Hunan Academy of Agricultural Science (HAAS), Changsha 410125, China
- ³ Key Laboratory of Agro-Environment in Midstream of Yangtze Plain, Ministry of Agriculture, Changsha, China
- ⁴ Institute Basic Biological Problems, Pushchino, Russia 142290

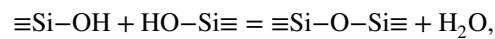
and location of most of them in plants remain unknown. Knowledge of the dynamics of mobile and immobile forms of Cd in different plant organs and tissues is essential in regard to understanding of the process and finding the most effective way to minimize the Cd accumulation in the harvested crop.

Recently many authors reported that Si-rich substances mitigate the Cd-induced negative impact on growth of various plants (Dresler et al. 2015; Vaculík et al. 2015). Indirect effect of Si on Cd-stressed plants is mainly attributed to adsorption of mobile forms of Cd on the surface of soil-applied Si materials (Keller et al. 2005). Silicon applied as soil amendment was efficient in reducing Cd mobility (Treder and Cieslinski 2005).

Additional Si was shown to reduce the Cd toxicity symptoms in cultivated plants via modulating metabolic activities, including photosynthesis process (Zhang et al. 2014; Yu et al. 2016). Silicon-treated plants demonstrated enhanced antioxidant enzyme activities and diminished the lipid peroxidation, resulting in alleviating Cd-induced oxidative damages (Song et al. 2009; Farooq et al. 2016; Kabir et al. 2016). Improved plant Si nutrition was reported to increase the Cd accumulation in the endodermis of rice seedling roots, restricted the Cd transport to shoots, and deposited mainly into the cell walls of endodermis, thus blocking the apoplastic transport of Cd (Shi et al. 2005; Wu et al. 2019). Application of Si substances decreased the Cd uptake by and the root-to-shoot transport inside plants (Ji et al. 2017; Shao et al. 2017; Greger and Landberg 2019). However, the Cd transport in detail as well as the role of apoplastic and symplastic pathways as affected by additional Si remain poorly investigated.

Among soluble forms of Si, monosilicic acid is recognized the most significant for plants (Li et al. 2012; Tubaña and Heckman 2015). Two forms of monosilicic acid are distinguished: orthosilicic acid (H_4SiO_4) and metasilicic acid (H_2SiO_3). Orthosilicic acid is the predominant form of monosilicic acid in aqueous systems and in soil solution (Iler 1979; Dietzel 2002). Metasilicic acid is reported to be hypothetical or unstable form of silicic acid at very low pH (< 3) (Jurkić et al. 2013; Mondal et al. 2009). However, this term is used in many studies conducted with sodium silicate because it contains anion of methasilicic acid (Wu et al. 2013). Determination of monosilicic acid is based on the reaction with ammonium molybdate with the formation of yellow complex (Mullin and Riley 1955). Both forms of monosilicic acid react with ammonium molybdate, so many authors suggest to use the single term “monosilicic acid” (Mullin and Riley 1955; Iler 1979; Dietzel 2002; Jurkić et al. 2013).

Monosilicic acid can polymerize according to the equation:



resulting in the formation of polysilicic acid ($[\text{SiO}_x(\text{OH})_{4-2x}]$) (Dietzel 2002; Jurkić et al. 2013). According to Iler (1979), polysilicic acid is silicic acid containing more than 2 atoms of Si. The mechanism of the polysilicic acid formation is not fully understood to date (Kley et al. 2017). Polymers consist of silica tetrahedrons that are linked via silicon–oxygen–silicon bonds. The formation of polysilicic acid may be described according to the equation: $\equiv\text{Si}-\text{OH} + \text{HO}-\text{Si}\equiv = \equiv\text{Si}-\text{O}-\text{Si}\equiv + \text{H}_2\text{O}$ (Iler 1979). Among polysilicic acids, molecules with up to ten atoms of Si are called oligomers (Igarashi et al. 2017).

Both monomers and polymers of silicic acid are water-soluble, while their chemical and biochemical properties highly vary.

Plants absorb Si from soil solution in the form of monosilicic acid (Ma and Takahashi 2002). Negative charge resulting from dehydration contributes to the chemical and biochemical activity of monosilicic acid (Iler 1979). The significant role of monosilicic acid in plant, soil, and water is well documented (Ji et al. 2016; Bosnic et al. 2019).

Unlike monosilicic acid, polysilicic acid is less chemically active because the surface charge, arising from dissociation, is neutralized by the molecule itself due to its flexible structure (Iler 1979). Polysilicic acid does not react with ammonium molybdate and cannot be determined by the classical molybdenum blue colorimetric method. It is interesting that polysilicic acid or Si gel is exploited in low temperature synthesis of many organic molecules as catalyst (Banerjee et al. 2001). There is the hypothesis that polysilicic acid can adsorb and capsulate organic and inorganic molecules (Nguyen et al. 2017). Polysilicic acid may participate in the transport and translocation of Si in plant organs (Matichenkov et al. 2018). Unfortunately, information about the role and functions of polysilicic acid in plant is extremely limited.

The main aim of this study was to investigate the impact of mono- and polysilicic acids on the external solution-to-root-to-stem-to-shoot transport of Cd through the apoplastic and symplastic pathways in rice plants.

Materials and Methods

In a pot experiment, seedlings of rice (*Oryza sativa* L. cv. Lu Liang You 996) were cultivated in paddy soil (moist, poorly drained, silt loam, formed on Ultisol), which had the following characteristics: pH 6.5 ± 0.1 ; C_{org} $44.2 \pm 0.4 \text{ g kg}^{-1}$; CEC $9.4 \pm 0.2 \text{ cmol kg}^{-1}$; total Cd $0.05 \pm 0.01 \text{ mg kg}^{-1}$; total nitrogen (N) $3.08 \pm 0.04 \text{ g kg}^{-1}$; total phosphorus (P) $1.11 \pm 0.04 \text{ g kg}^{-1}$; total potassium (K) $25.3 \pm 0.5 \text{ g kg}^{-1}$; sand content $29.3 \pm 1.5\%$; clay content $30.2 \pm 3.5\%$;

water-extractable Si $3.5 \pm 0.2 \text{ mg kg}^{-1}$ and acid-extractable Si $125 \pm 15 \text{ mg kg}^{-1}$. The total soil content of Cd, P and K was analyzed after a $\text{HNO}_3\text{-H}_2\text{O}_2$ microwave digestion and then solutions were analyzed by ICP-MS I Cap-Q (USA) (Aldabe et al. 2013).

To analyze water-soluble Si in soil: (1) $6.0 \pm 0.1 \text{ g}$ of fresh sample was placed into a 100-mL plastic vessel; (2) 30-mL of water was added to each vessel; (3) after 1 h shaking, a sample was filtered and a clean extract was analyzed for monosilicic acid using the Mullin and Riley method (1955). The acid extraction procedure was as follows: (1) $2 (2.0 \pm 0.1) \text{ g}$ of an air-dried soil sample was placed in a 100 mL polyethylene cup; (2) 20 mL of 0.1 M HCl was added and the mixture was agitated at 200 rpm for 30 min; (3) After standing overnight, the mixture was agitated again for 30 min, then the supernatant was centrifuged at 7000 rpm for 15 min. Si was analyzed in cleaned extract by the method mentioned above.

As evident from the water-extractable and acid-extractable Si values, the experimental soil was critically deficient in plant-available and potentially plant-available Si (Matichenkov et al. 2018). The rice was grown in a climatic chamber for 30 days at the following conditions: air temperature $26 \pm 4 \text{ }^\circ\text{C}$ during the day and $22 \pm 2 \text{ }^\circ\text{C}$ during the night; the light period was 12 h at intensity of $200 \text{ } \mu\text{mol photons m}^{-2} \text{ s}^{-1}$ by UV/Vis lighting, and the relative air humidity was $85 \pm 5\%$ during the day and $78 \pm 5\%$ during the night. Plants were irrigated with distilled water (DW) for keeping soil moisture between 20 and 40%.

One-month-old plants were removed carefully from soil, then roots were washed with DW and 5 plants were put into each 250-mL glass flask containing 200 mL of a solution.

The following solutions were used:

- (1) Control (DW);
- (2) Cd, $50 \text{ } \mu\text{M}$;
- (3) Si, 1 mM ;
- (4) Cd, $50 \text{ } \mu\text{M}$ + Si, 1 mM .

Each treatment was conducted in ten replications with five plants in each flask to have enough material for plant analyses. The Cd solution was prepared from $\text{Cd}(\text{NO}_3)_2$, the Si solution was prepared from concentrated monosilicic acid (Fisher Scientific, CAS-No 7699-41-4). Only low concentrations of Cd and monosilicic acid were used to prevent the Cd precipitation. Before experiment, to verify the absence of precipitation, the solution #4 was kept for a week and then analyzed for Cd and monosilicic acid. The results showed that the concentrations of Cd and monosilicic acid did not change. In Cd-free solutions, nitrate introduced by $\text{Cd}(\text{NO}_3)_2$ was supplemented with $\text{Ca}(\text{NO}_3)_2$.

Each flask was covered with aluminum foil to keep dark and minimize water evaporation. To compensate the water losses by leaf transpiration, DW was added to flask daily to maintain a volume of 200 mL. Every day the aeration

of the water was conducted using EcoPlus 126 GPH (480 LPH, 3 W) Air Pump during 10 min. All flasks were satay in climatic chamber with same condition as were used for rice growing.

Daily for a week, five plants from each treatment were pulled out of the flasks and roots were washed with DW. Then roots, stems and leaves were separated. The soluble forms of Cd and monosilicic acid in the apoplast and symplast of roots, stems, and leaves were analyzed using the following technique. A fresh plant sample of $0.20 \pm 0.01 \text{ g}$ was cut into 1–2 cm pieces and put into a plastic bottle. Then, 50 mL of DW was added and the mixture was agitated for 24 h to provide diffusion of apoplast solution into external solution (Kursanov 1968, 1976; Matichenkov et al. 2008). The mixture was filtrated and a cleaned solution was analyzed for monosilicic acid, polysilicic acid and Cd. The plant tissues after filtering were homogenized to crush all cell walls. Homogenized slurry was mixed with 50 mL of DW and agitated for 1 h. As a result, the diluted symplast solution was obtained and analyzed after centrifugation for monosilicic acid, polysilicic acid and Cd. Based on the data on plant tissue moisture, the concentrations of monosilicic acid, polysilicic acid and Cd were calculated on a dry weight.

The concentration of monosilicic acid in a solution was tested by the molybdate method (Mullin and Riley 1955). To measure polysilicic acid, $0.10 \pm 0.01 \text{ g}$ of NaOH was added to an aliquot (20–25 mL) of tested solution, then the solutions stayed for 2 weeks at $+4 \text{ }^\circ\text{C}$ in refrigerator to achieve complete depolymerization (Matychenkov and Snyder 1996). After that, the concentration of monosilicic acid was measured and the concentration of polysilicic acid was estimated on a difference between Si values after and before depolymerization.

On the first and the last days of the experiment, plant samples were analyzed for total Si and Cd. To analyze Si, a plant sample of $0.20 \pm 0.01 \text{ g}$ was placed into a Teflon tube and 4 mL of 50% NaOH was added. After standing for 12 h, 2 mL of 30% H_2O_2 was added; the tubes were kept for 30 min, capped, and placed into the microwave (CEM MARS 6 MS5181) for 30 min. To analyze total Cd, a plant sample of $0.20 \pm 0.01 \text{ g}$ was predigested in a mixture of 4 mL of concentrated HNO_3 and 2 mL of 30% H_2O_2 overnight followed by microwave digestion for 30 min. Silicon was analyzed by the molybdate method (Mullin and Riley 1955). Cadmium, P and K in solutions were analyzed by ICP-MS I Cap-Q (USA).

Statistical Analysis

Plants were sampled in five replications. All data obtained were subjected to a statistical analysis based on comparative

methods using Duncan's multiple range tests for mean separation at the 5% level of significance (Duncan 1957).

Results

Biomass of roots, stems and leaves is presented in Table 1. On the 7th day, fresh weights of the roots, stems and leaves in Cd solution were significantly lower than those in DW, Si treatment, or Si + Cd treatment, whereas the corresponding dry weights stayed equal in all solutions.

On the 7th day, the total plant Si was significantly increased in Si treatment and especially in Cd + Si treatment. In Cd + Si treatment, the root, stem and leaf Si increased from 2.18, 1.79, and 1.23 to 2.28, 1.85, and 1.34%, respectively, as compared to the Si-exposed plants (Table 2).

On the 7th day of the experiment, an increase in the total Cd was determined in Cd-exposed plants. Among different plant organs, a higher increase was observed in roots, up to 1.25 mg kg⁻¹ of Cd in Cd + Si treatment in comparison with 0.42 mg kg⁻¹ in control. The maximum values of the stem and leaf Cd were detected in alone Cd treatment. The presence of monosilicic acid in Cd solution resulted in a reduction from 0.28 to 0.21 and from 0.25 to 0.15 mg kg⁻¹ of Cd in the stems and leaves, respectively.

The concentrations of monosilicic acid in the apoplast of roots, stems, and leaves are presented in Fig. 1. In the root apoplast, the monosilicic acid increased from 114 to 212 ppm of Si in Cd treatment, to 365 ppm of Si in Si treatment, and to 232 ppm of Si in Cd + Si treatment for the first 3 days. After that, the concentration of monosilicic acid remained around 70–120 ppm of Si. The dynamics of monosilicic acid in the stem and leaf apoplast in control and

Table 1 Fresh and dry weights of roots, stems and leaves of rice on the 1st and the 7th days of experiment ($n=5$)

Treatment	Fresh weight			Dry weight		
	Roots	Stems	Leaves	Roots	Stems	Leaves
	g plant ⁻¹					
1st day						
Control	0.352c	0.435c	0.453c	0.054a	0.056a	0.042a
Cd	0.343bc	0.424c	0.445c	0.053a	0.057a	0.043a
Si	0.353c	0.433c	0.441c	0.054a	0.057a	0.043a
Cd + Si	0.355c	0.432c	0.452c	0.053a	0.056a	0.043a
7th day						
Control	0.323b	0.325b	0.334b	0.053a	0.056a	0.044a
Cd	0.122a	0.124a	0.125a	0.053a	0.057a	0.043a
Si	0.344bc	0.353b	0.364b	0.054a	0.058a	0.044a
Cd + Si	0.345bc	0.373b	0.365b	0.055a	0.058a	0.045a

Different letters mean significant differences between the treatments at 0.05% level

Table 2 Total Si and Cd in roots, stems and leaves of rice on the 1st and the 7th days of experiment ($n=5$)

Treatment	Si			Cd		
	Roots	Stems	Leaves	Roots	Stems	Leaves
	%			mg kg ⁻¹		
1st day						
Control	1.94a	1.58a	1.02b	0.45a	0.15a	0.11a
Cd	1.95a	1.57a	1.03b	0.48a	0.15a	0.12a
Si	1.95a	1.58a	1.03b	0.46a	0.13a	0.11a
Cd + Si	1.95a	1.59a	1.02b	0.46a	0.13a	0.11a
7th day						
Control	1.94a	1.59a	1.03b	0.42a	0.14a	0.12a
Cd	1.99b	1.57a	0.94a	1.05b	0.28c	0.25c
Si	2.18c	1.79b	1.23c	0.45a	0.13a	0.11a
Cd + Si	2.28d	1.85c	1.34d	1.25c	0.21b	0.15b

Different letters mean significant differences between the treatments at 0.05% level

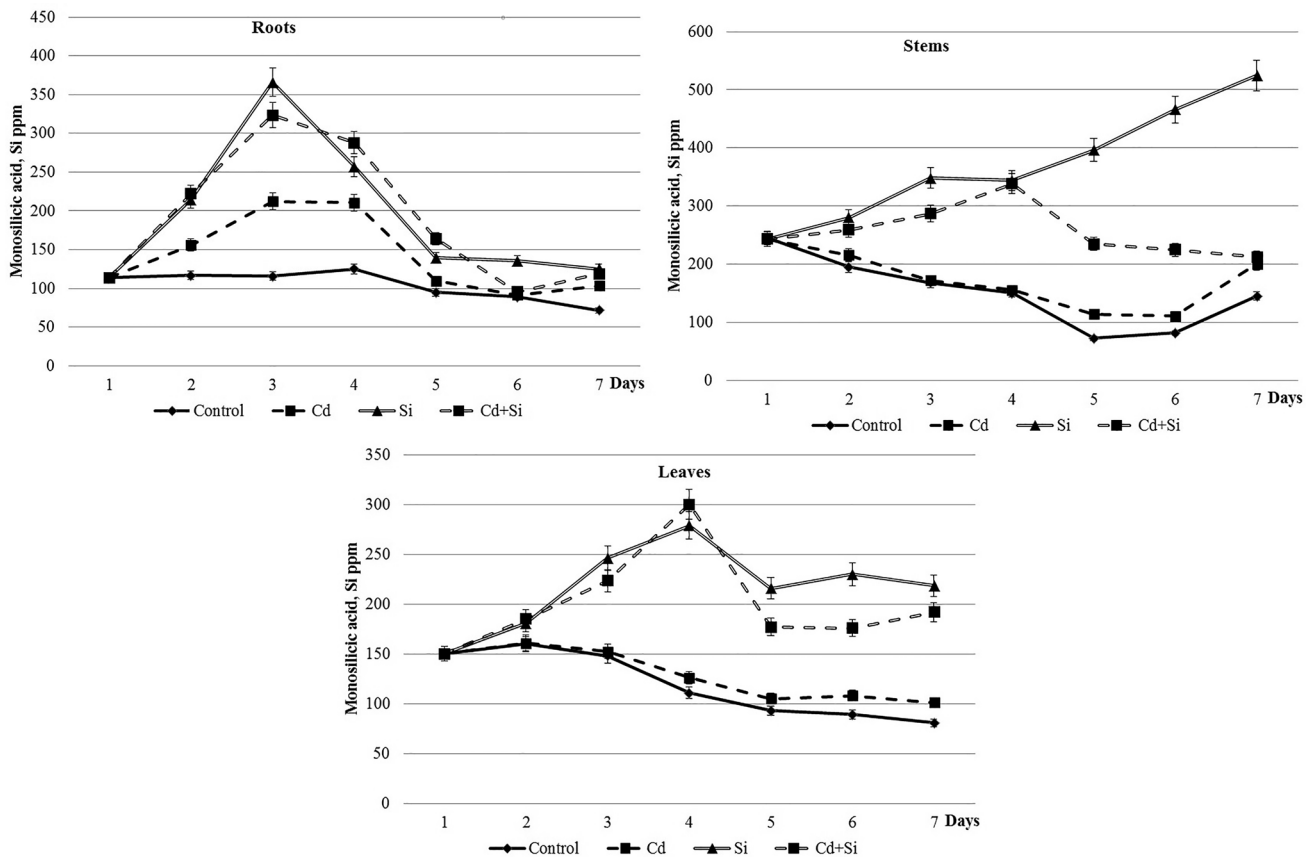


Fig. 1 Concentration of monosilicic acid in the apoplast of roots, stems, and leaves of rice

Cd solution was similar. While in Cd + Si and Si treatment, a gradual increase in soluble Si was observed in the stem apoplast during 4 and 7 days, respectively.

Generally, the concentrations of monosilicic acid in the symplast of roots, stems and leaves were higher than those in the corresponding apoplast (Fig. 2). Initial concentrations of monosilicic acid amounted to 114 and 250; 245 and 300; and 150 and 447 ppm of Si, respectively in the apoplast and symplast of roots, stems, and leaves. The monosilicic acid in the root and leaf symplast gradually decreased in control and Cd treatment within 7 days. In Si or Cd + Si treatment, the monosilicic acid in the root, stem and leaf symplast increased during the first 3–4 days and then decreased.

The dynamics of polysilicic acid in the apoplast and symplast of rice is presented in Figs. 3 and 4. Polysilicic acid in the root apoplast gradually reduced from 228 to 91 ppm of Si in control. In Cd solution, the root apoplast polysilicic acid significantly increased on the 2nd day of the experiment, but then gradually decreased up to 97 ppm of Si. In Si or Cd + Si treatment, the polysilicic acid in the stem apoplast increased for the first 4 days and then decreased. In the stem apoplast, the dynamics of polysilicic acid was the same in control and Cd treatment, demonstrating a gradual reduction, whereas in

Si and Cd + Si treatment a maximum increase in polysilicic acid was observed on the 2nd day, having reached up to 810 and 568 ppm of Si, respectively. The dynamics of polysilicic acid in the leaf apoplast was different. In control and Cd solution, the polysilicic acid concentration was markedly reduced on the 2nd day, but then gradually increased up to 249 and 263 ppm of Si, respectively. In Si or Cd + Si solution, the leaf apoplast polysilicic acid continually increased up to 417 and 360 ppm of Si, correspondingly.

In control, the root symplast polysilicic acid gradually declined within 3 days and then stabilized at the level of 127 ppm of Si. In Cd-exposed plants, this parameter increased from 204 to 236 ppm of Si on the 1st day and then gradually decreased to 172 ppm of Si. In Si or Cd + Si solution, the root symplast polysilicic acid sharply increased on the 2nd day, which demonstrate higher values in the presence of Cd.

The concentration of polysilicic acid in the stem symplast in Si-free solutions was slightly decreasing, then stabilized within the first 4 days, and then reduced to 188 and 120 ppm of Si in control and Cd treatment, respectively. In the presence of monosilicic acid, the dynamics in the stem symplast polysilicic acid has changed considerably. For the first

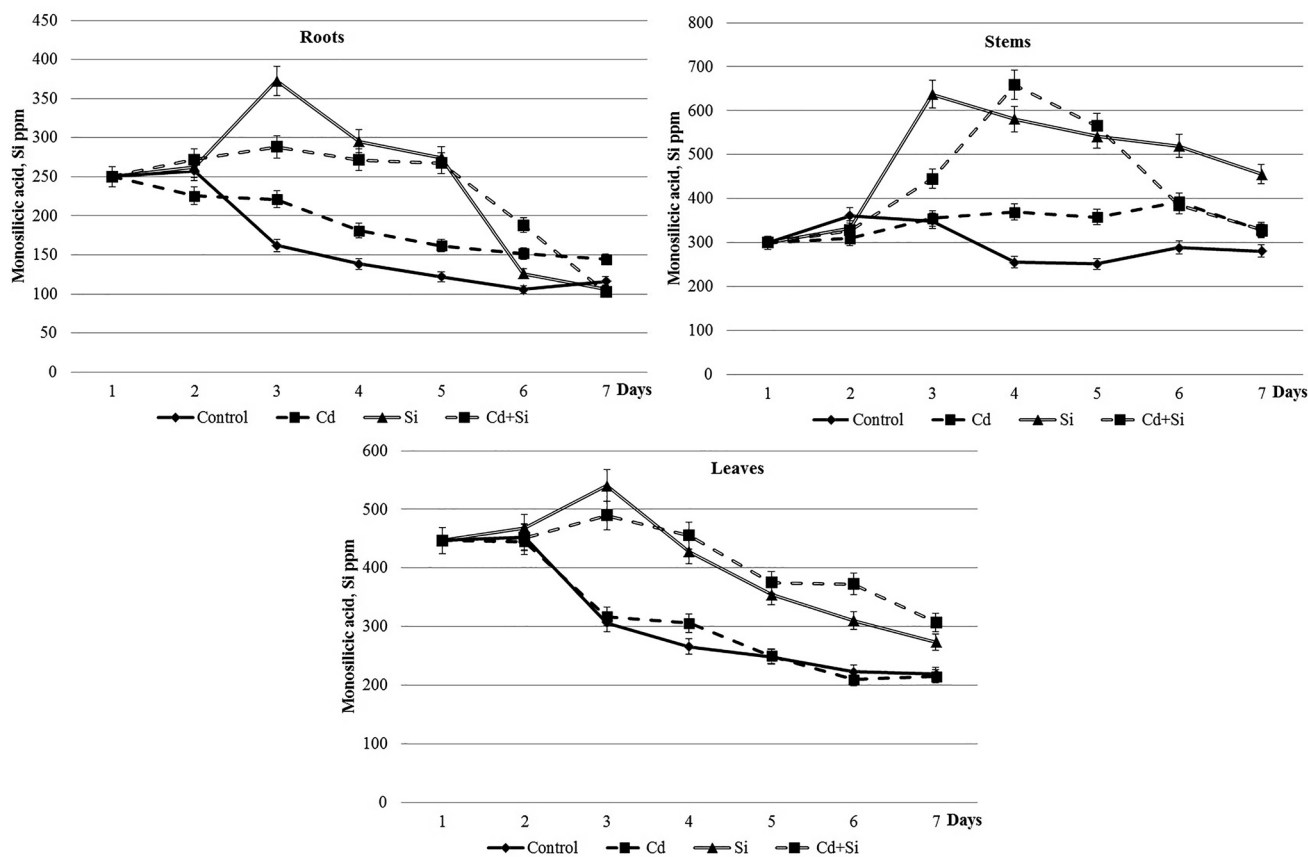


Fig. 2 Concentration of monosilicic acid in the symplast of roots, stems, and leaves of rice

4 days, polysilicic acid reached up to 666 and 703 ppm of Si in Si and Cd + Si treatment, correspondingly. After that, it began to decline.

The leaf symplast polysilicic acid in Si-free solution first gradually decreased and then stabilized. In Si or Cd + Si treatment, the leaf symplast polysilicic acid was increasing from the 2nd day to the 5th day and reached 500 and 594 ppm of Si, respectively.

The dynamics of soluble Cd in plant tissues are presented in Figs. 5 and 6. In control and Si solution, soluble Cd in the apoplast and symplast of roots, stems and leaves was very low, in range of 8–9 to 125–128 ppm of Si, and did not alter in the course of experiment. Lesser concentrations of Cd were detected in the leaf apoplast and higher ones—in the root symplast.

In Cd-exposed plants, the dynamics of soluble Cd was more complicated. The maximum values of Cd were observed in the root apoplast on the 4th day of the experiment and reached up 32,838 ppm of Cd in Cd treatment. In Cd + Si treatment, the root apoplast Cd did not exceed 3807 ppm, being maximum on the 5th day of experiment. Similar dynamics was observed in the stem and leaf apoplast, although the Cd values were significantly lower in

comparison with the roots. The maximum stem apoplast Cd amounted to 24,432 and 5390 ppm in Cd and Cd + Si treatment, respectively. The corresponding values in the leaf apoplast did not exceed 12,958 and 2662 ppm.

The Cd content in the root symplast of Cd-free plants was almost fivefold higher than that in the root apoplast—123 vs 25 ppm of Cd. On the contrary, Cd in the root symplast of Cd-exposed plants was much lower than that in the apoplast. Besides, the dynamics in the root symplast Cd was different. For the first 2 days, the Cd sharply increased and then altered slightly. It is important that some increase in the root apoplast Cd, from 3265 to 3798 ppm, was detected in Cd + Si treatment as compared to that in Cd treatment.

The dynamics of Cd in the symplast and apoplast of stems was very similar—maximum on the 4th day, followed by a sharp decrease. In Cd + Si treatment, both the symplast and apoplast Cd were much lower in comparison with those in Cd treatment. The dynamics of Cd in the leaf apoplast was identical to that in the stems. But the dynamics of the leaf symplast Cd was different compared to the root or stem symplast. There was a gradual increase for the first 4 days and some reduction after that. The addition of Si in Cd treatment markedly reduced the leaf symplast Cd.

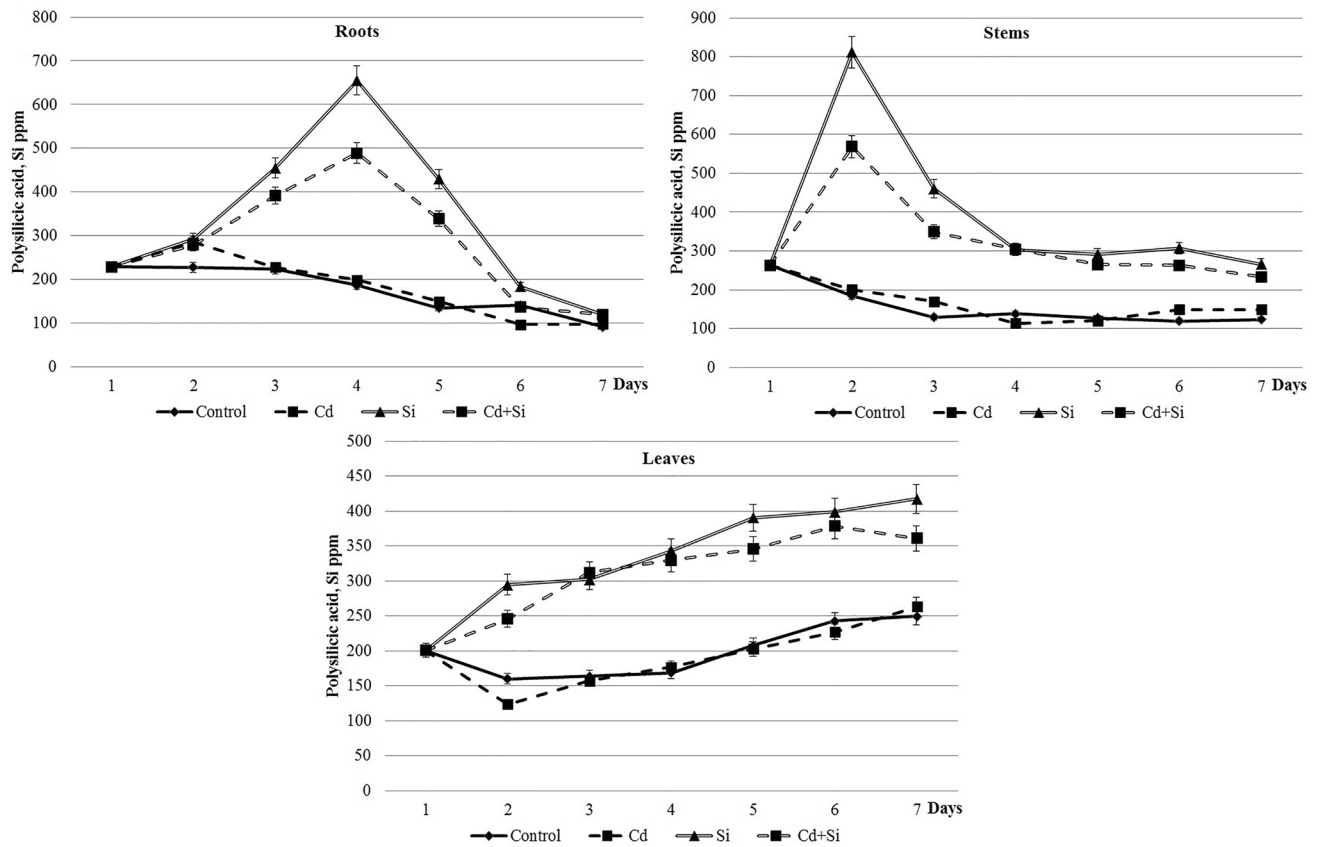


Fig. 3 Concentration of polysilicic acid in the apoplast of roots, stems, and leaves of rice

Discussion

In the current experiment, the concentrations of Cd in the apoplast and symplast ranged between 9 and 126 ppm and between 322 and 12,528 ppm of Cd in the control and Cd-exposed plants, respectively. The monosilicic acid concentrations ranged between 66.4 and 870.6 ppm of Si in the apoplast and from 244.5 to 1036.3 ppm of Si in the symplast. Therefore, intercellular and intracellular solutions in plant can be characterized as saturated or hyper saturated. The direction and rate of chemical and biochemical reactions in hyper saturated solutions are poorly understood and can differ as compared with diluted solutions (Chang and Myerson 1985; Okutsu et al. 2007; Hussner et al. 2016).

Immediately after putting plants into Cd solution, Cd began to move from roots to leaves very fast, predominantly via the apoplastic pathway. The apoplastic pathway includes endodermal barriers, such as Casparian strips and supra-cellular suberin deposition (Barberon et al. 2016). In 3–4 days, the Cd concentrations reached 32.8; 24; and 13 g kg⁻¹, respectively in the apoplast of roots, stems, and leaves. Thus, the reductions in the apoplast Cd concentrations accounted for 26.8% from root to stem and 45.8% from stem to leaf.

Dehydration of plant tissue is well recognized symptom of physiological and biochemical destructive processes in plant cell (Sundari 2014). We hypothesize that critically high values of Cd in the apoplast may damage entire transport system, including the transport of water and nutrients. As a result, there was dehydration of Cd-exposed plants.

The dynamics of the stem symplast Cd was similar to that in the apoplast of root, stem and leaf, but differed from the root and leaf symplast. Perhaps, the Cd concentration in stem symplast is controlled by direct translocation from stem apoplast because the stem symplast is parallel to the apoplast and has much lower volume compared to the root and leaf symplast.

Regarding Si, several transport genes have been identified so far in different plants, for example Lsi1, Lsi2 in rice, HvLsi1 and HvLsi2 in barley, ScLsi1 in cucumber (Hosseini et al. 2017; Sahebi et al. 2017; Sun et al. 2017). Numerous investigations have shown that plant absorbs only monomer of silicic acid or its anion (Ma and Takahashi 2002; Ma and Yamaji 2015). Two types of Si transporters have been reported: channel-type transporter and efflux transporter. The channel-type Si transporter (Lsi1) facilitates the passive transport of Si across the plasma membrane between the external solution (i.e. apoplast) and the plant cell (Ma

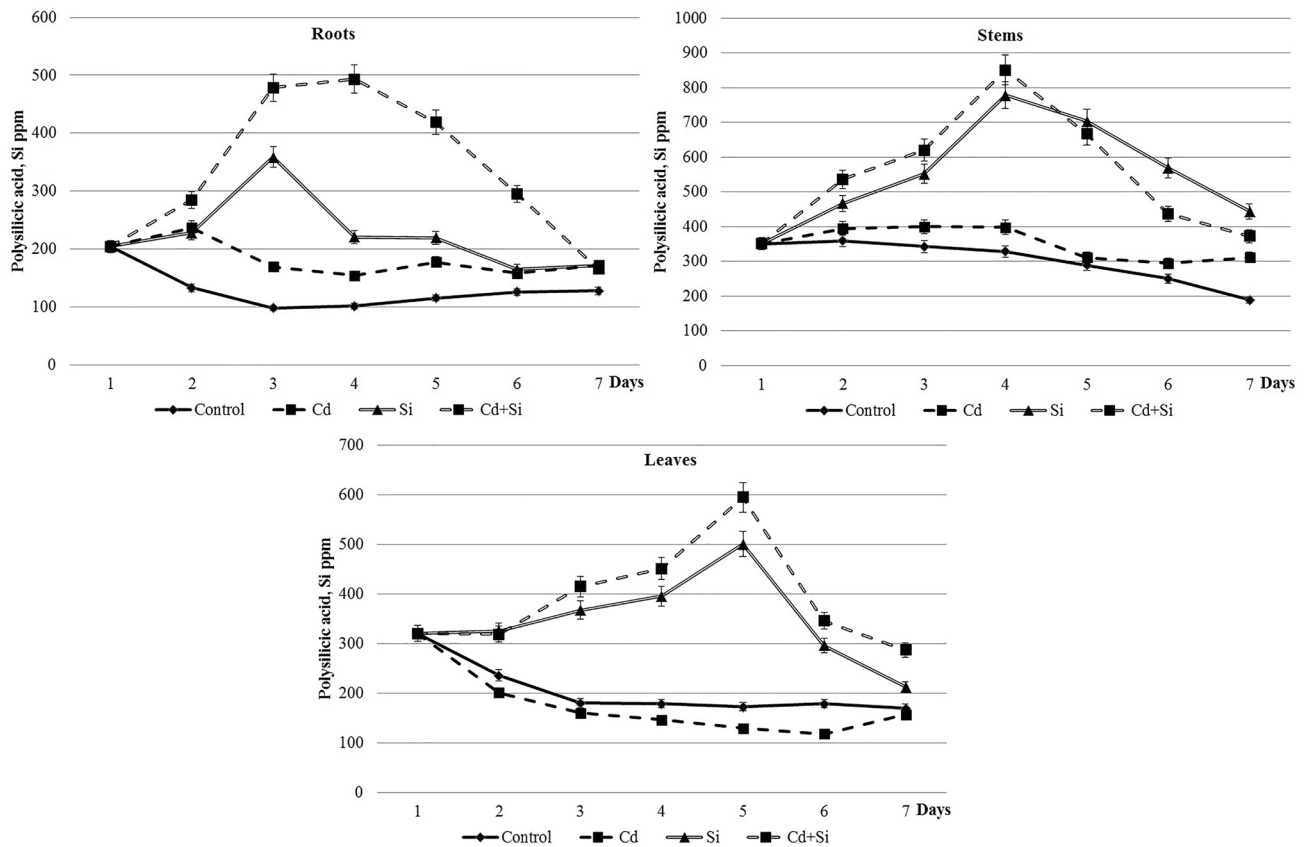


Fig. 4 Concentration of polysilicic acid in the symplast of roots, stems, and leaves of rice

and Yamaji 2015). The efflux transport of Si by Lsi2 is an active process that is driven by the proton gradient across the plasma membrane (Ma et al. 2007).

In the current and previous studies, at least two forms of soluble Si present in the plant apoplast and symplast were detected: monosilicic acid and polysilicic acid (Matichenkov et al. 2008; Ji et al. 2017). Atomic absorption or ICP spectroscopy doesn't analyze these forms of Si separately. However, monomers of silicic acid react with molybdenum ammonia, while polymers don't (Iler 1979). This feature makes possible to distinguish both forms of soluble Si.

Reducing the leaf Si and significantly increasing the root Si evidence the reverse leaf-to-root translocation under Cd exposure. It is possible to assume that Si can move through the apoplast as monomers and polymers of silicic acid. We suppose that in response to Cd exposure, plants induce signaling mechanisms for Si transport to Cd-stressed tissue. The Si redistribution within plant and accumulation in the stressed tissue has been reported in our earlier investigations (Matichenkov et al. 1999, 2000).

In the presence of Cd, Si supplementation enhanced the Si uptake and accumulation by all organs of rice. We assume that Cd stress activates both the Si absorption and redistribution to reinforce plant tolerance. These data are consistent

with our and literary findings that any abiotic or biotic stress initiates the additional Si absorption by plants (Dresler et al. 2015; Matichenkov et al. 2000, 2018).

Generally, two main Si-mediated impacts on the Cd biotoxicity can be distinguished: through soil and directly through plant (Emamverdian et al. 2018). In soil, Si detoxification mechanisms include change in chemical speciation of Cd via increasing pH, adsorption, complexation and precipitation that lead to the immobilization of toxic ions (Matichenkov and Xiao 2019). In plant, monosilicic acid can also precipitate Cd with the formation of silicates such as CdSiO_3 or Cd_2SiO_4 (Ji et al. 2016). Cadmium precipitation in the roots, trapping by cell walls, capsulation by polymers of silicic acid, and extension of apoplastic barriers are among the major Si-induced mechanisms responsible for decreased the Cd translocation from roots to aerial plant organs (Wu et al. 2019; Ji et al. 2017; Sohail et al. 2020). Our data have revealed that the Cd root-to-leaf transport occurred predominantly in the apoplast. The dynamics of Cd differed between apoplast and symplast. The accumulative curve that described the Cd dynamics in the root and leaf symplasts suggests a passive transport of Cd. A 2 or 3-day delay in entering of Cd into apoplast confirms the availability of specific mechanisms for minimizing Cd transport.

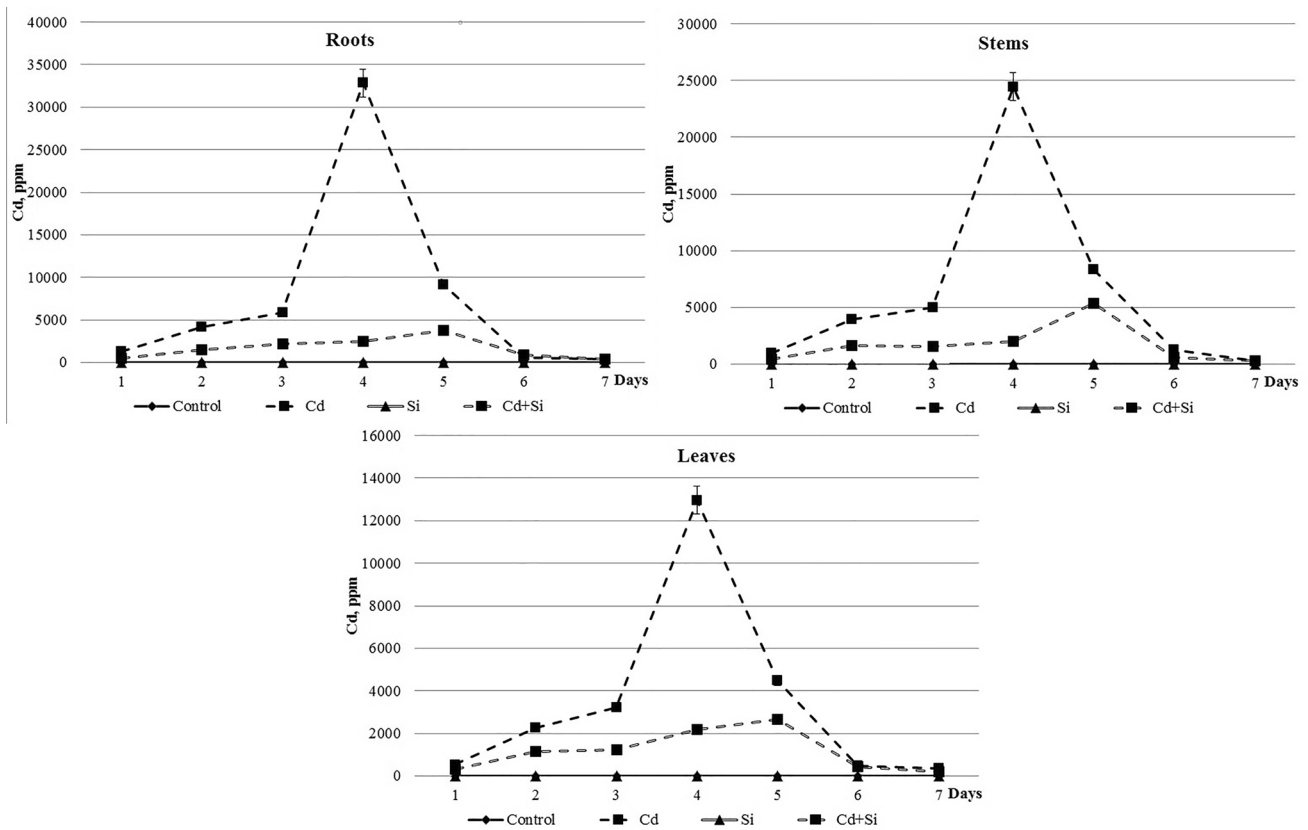


Fig. 5 Cadmium in the apoplast of roots, stems, and leaves of rice

A sharp increase in Cd on the 4th to 5th day indicates the impairment of apoplastic barriers, ultimately resulting in plant death. Supplemental Si reinforced these mechanisms and prevented massive Cd transport. Detailed physiological, biochemical and morphological investigations of Si-assisted mechanisms are required.

Conclusions

The present study evidences that the external solution-to-root-to-stem-to-leaf transport of soluble forms of Cd is very fast, the Cd concentrations increased 38–50 times and 6–8 times, respectively in the apoplastic and symplastic pathways for 24 h.

In Cd-exposed plants, apoplastic barriers inhibited Cd transport during only several days, whereas Si supplementation promoted the efficacy of apoplastic barriers during all time of examination.

The dynamics of Cd transport through the stem symplast and apoplast was the same, but differed from the root and leaf symplast, probably due to direct apoplast-to-symplast Cd translocation in stem.

In the apoplast and symplast, soluble Si was in the form of both monomers and polymers of silicic acid.

Exposure to Cd accelerated Si uptake by roots and redistribution from stem and leaf to root as being Cd-stressed.

Acknowledgements This study was supported by National Science Foundation of China (Project 2013BAD03B02) and Natural Science Foundation of Hunan Province in China (Project 2016JJ6066) and by the Ministry of Science and Higher Education of RF, theme #AAAA-A17-117030110137-5 and #AAAA-A17-117030110139-9.

Author Contributions WW—collection of the samples, conduction of the analysis, work for Introduction. XJ—participation in the experiment design, works for articles; LS—conduction of the analysis and participation in discussion. EB—condition of analysis, works for text of manuscript. VM—conduction of the experiment, analysis and writing of manuscript.

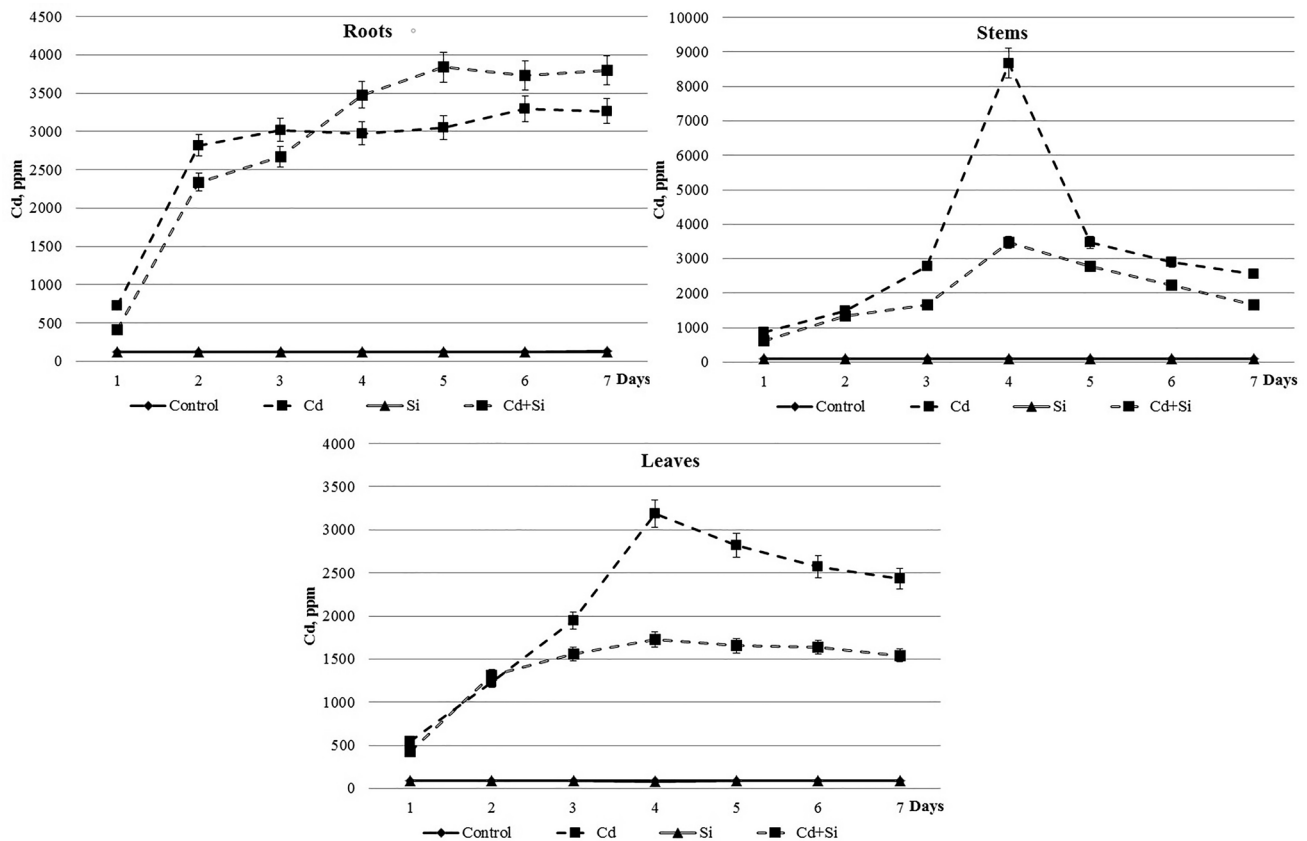


Fig. 6 Cadmium in the symplast of roots, stems, and leaves of rice

Compliance with Ethical Standards

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

References

- Aldabe J, Santamaria C, Elustondo D, Lasheras E, Santamaria JM (2013) Application of microwave digestion and ICP-MS to simultaneous analysis of major and trace elements in aerosol samples collected on quartz filters. *Anal Methods* 5(2):554–559
- Banerjee AK, Mimo ML, Vegas WV (2001) Silica gel in organic synthesis. *Russ Chem Rev* 70(11):971–990
- Barberon JE, Vermeer D, De Bellis P, Wang D, Naseer P, Andersen S, Geldner N (2016) Adaptation of root function by nutrient-induced plasticity of endodermal differentiation. *Cell* 164:447–459. <https://doi.org/10.1016/j.cell.2015.12.021>
- Bosnic P, Pavlicevic M, Nikolic N, Nikolic M (2019) High monosilicic acid supply rapidly increases Na accumulation in maize roots by decreasing external Ca²⁺ activity. *J Plant Nutr Soil Sci* 182(2):210–216
- Chang YC, Myerson AS (1985) The diffusivity of potassium chloride and sodium chloride in concentrated, saturated, and super-saturated aqueous solutions. *AIChE J* 31(6):890–894. <https://doi.org/10.1002/aic.690310603>
- Dietzel M (2002) Interaction of polysilicic and monosilicic acid with mineral surfaces. In: Stober I, Bucher K (eds) *Water-rock interaction*. Water science and technology library, vol 40. Springer, Dordrecht, pp 207–235. https://doi.org/10.1007/978-94-010-0438-1_9
- Dresler S, Wojcik M, Bednarek W et al (2015) The effect of silicon on maize growth under cadmium stress. *Russ J Plant Physiol* 62(1):86–92. <https://doi.org/10.1134/S1021443715010057>
- Duncan DB (1957) Multiple range tests for correlated and heteroscedastic means. *Biometrics* 13(2):164–176. <https://doi.org/10.2307/2527799>
- Emamverdian A, Ding Y, Xie Y, Sangari S (2018) Silicon mechanisms to ameliorate heavy metal stress in plants. *Biomed Res Int* 2018:1–10. <https://doi.org/10.1155/2018/8492898>
- Farooq MA, Detterbeck A, Clemens S et al (2016) Silicon-induced reversibility of cadmium toxicity in rice. *J Exp Bot* 67(11):3573–3585. <https://doi.org/10.1093/jxb/erw175>
- Ge L, Cang L, Yang J, Zhou D (2016) Effects of root morphology and leaf transpiration on Cd uptake and translocation in rice under different growth temperature. *Environ Sci Pollut Res* 23(23):24205–24214. <https://doi.org/10.1007/s11356-016-7696-8>
- Greger M, Landberg T (2019) Silicon reduces cadmium and arsenic levels in field-grown crops. *Silicon* 11:2371–2375
- He B, Yun Z, Shi J, Jiang G (2013) Research progress of heavy metal pollution in China: sources, analytical methods, status, and toxicity. *Chin Sci Bull* 58(2):134–140. <https://doi.org/10.1007/s11434-012-5541-0>

- Hosseini SA, Maillard A, Hajirezaei MR et al (2017) Induction of barley silicon transporter *hvlsl1* and *hvlsl2*, increased silicon concentration in the shoot and regulated starch and abscisic acid homeostasis under osmotic stress and concomitant potassium deficiency. *Front Plant Sci*. <https://doi.org/10.3389/fpls.2017.01359>
- Hussner A, Mettler-Altmann T, Weber A, Sand-Jensen K (2016) Acclimation of photosynthesis to supersaturated CO₂ in aquatic plant bicarbonate users. *Freshw Biol* 61(10):1720–1732. <https://doi.org/10.1111/fwb.12812>
- Iler RK (1979) The chemistry of silica. Wiley, New York
- Igarashi M, Matsumoto T, Yagihashi F, Yamashita H, Ohhara T, Hanashima T et al (2017) Non-aqueous selective synthesis of orthosilicic acid and its oligomers. *Nat Commun* 8(140):1–8
- Jurkić LM, Cepenec I, Pavelić SK, Pavelić K (2013) Biological and therapeutic effects of ortho-silicic acid and some ortho-silicic acid-releasing compounds: new perspectives for therapy. *Nutr Metab* 10(1):2. <https://doi.org/10.1186/1743-7075-10-2>
- Ji X, Liu S, Huang J et al (2016) Monosilicic acid potential in phytoremediation of the contaminated areas. *Chemosphere* 157:132–136. <https://doi.org/10.1016/j.chemosphere.2016.05.029>
- Ji X, Liu S, Juan H et al (2017) Effect of silicon fertilizers on cadmium in rice (*Oryza Sativa*) tissue at tillering stage. *Environ Sci Pollut Res* 24(2):1–9. <https://doi.org/10.1007/s11356-017-8730-1>
- Kabir AH, Hossain MM, Khatun MA, Mandal A, Haider SA (2016) Role of silicon counteracting cadmium toxicity in alfalfa (*Medicago sativa* L.). *Front Plant Sci* 7:1117. <https://doi.org/10.3389/fpls.2016.01117>
- Keller C, Marchetti M, Rossi L, Lugon-Moulin N (2005) Reduction of cadmium availability to tobacco (*Nicotiana tabacum*) plants using soil amendments in low cadmium-contaminated agricultural soils: a pot experiment. *Plant Soil* 276(1–2):69–84. <https://doi.org/10.1007/s11104-005-3101-y>
- Kley M, Kempter A, Boyko V, Huber K (2017) Silica polymerization from supersaturated dilute aqueous solutions in the presence of alkaline earth salts. *Langmuir* 33(24):6071–6083. <https://doi.org/10.1021/acs.langmuir.7b00887>
- Kursanov AL (1968) Free space and transport of metabolites in parenchymal tissues. *Abhandlungen der deutschen Akademie der Wissenschaften zu Berlin. Aka-demie-Verlag, Berlin*, pp 63–80
- Kursanov AL (1976) Assimilate transport in plants. Nauka, Moscow
- Li ZY, Yangali-Quintanilla V, Valladares-Linares R et al (2012) Flux patterns and membrane fouling propensity during desalination of seawater by forward osmosis. *Water Res* 46(1):195–204. <https://doi.org/10.1016/j.watres.2011.10.051>
- Llugany M, Miralles R, Corrales I et al (2012) *Cynara cardunculus* a potentially useful plant for remediation of soils polluted with cadmium or arsenic. *J Geochem Explor* 123:122–127. <https://doi.org/10.1016/j.gexplo.2012.06.016>
- Ma JF, Takahashi E (2002) Soil, fertilizer, and plant silicon research in Japan. Elsevier, Amsterdam
- Ma JF, Yamaji N (2015) A cooperated system of silicon transport in plants. *Trends Plant Sci* 20(7):435. <https://doi.org/10.1016/j.tplants.2015.04.007>
- Ma JF, Yamaji N, Mitani N et al (2007) An efflux transporter of silicon in rice. *Nature* 448(7150):209–212. <https://doi.org/10.1038/nature05964>
- Matichenkov VV, Snyder GH (1996) The mobile silicon compounds in some South Florida soils. *Eurasian Soil Sci* 12:1165–1180
- Matichenkov V, Xiao W (2019) Reduction Cd in soil-rice by Si: theory and practice. Nova Publisher, New York
- Matichenkov V, Calvert D, Snyder G (1999) Silicon fertilizers for citrus in Florida. *Proc Florida State Hort Soc* 112:5–8
- Matichenkov VV, Calvert DV, Snyder GH (2000) Prospective of silicon fertilization for citrus in Florida. *Ann Proc Soil Crop Sci Soc Florida* 59:137–141
- Matichenkov VV, Bocharnikova EA, Kosobryukhov AA, Biel KY (2008) Mobile forms of silicon in plants. *Dokl Biol Sci* 418(1):39–44. <https://doi.org/10.1007/s10630-008-1013-8>
- Matichenkov VV, Fomina IR, Biel KY (2018) Protective role of silicon in living organisms. In: Fomina I, Biel K, Soukhovolsky V (eds) *Complex biological systems: adaptation and tolerance to extreme environments*. Wiley, Hoboken, pp 175–208
- Mondal B, Ghosh D, Das AK (2009) Thermochemistry for silicic acid formation reaction: prediction of new reaction pathway. *Chem Phys Lett* 478(4–6):115–119. <https://doi.org/10.1016/j.cplett.2009.07.063>
- Mullin JB, Riley JP (1955) The colorimetric determination of silicate with reference to sea and natural waters. *Anal Chem Acta* 12:162–176. [https://doi.org/10.1016/S0003-2670\(00\)87825-3](https://doi.org/10.1016/S0003-2670(00)87825-3)
- Nguyen MN, Picardal F, Dultz S, Nguyen-Thanh L, Dam T, Nguyen KM (2017) Effect of silicic acid on the aggregation properties of goethite. *Eur J Soil Sci* 68(5):650–657. <https://doi.org/10.1111/ejss.12453>
- Okutsu T, Sugiyama K, Furuta K, Watanebe I, Mori H, Obi K (2007) Photochemically induced nucleation in supersaturated and undersaturated thaumatin solutions. *J Photochem Photobiol A* 190(1):88–93. <https://doi.org/10.1016/j.jphotochem.2007.03.016>
- Ouariti O, Boussama N, Zarrouk M, Cherif A, Ghorbal MH (1997) Cadmium- and copper-induced changes in tomato membrane lipids. *Phytochemistry* 45(7):1343–1350. [https://doi.org/10.1016/S0031-9422\(97\)00159-3](https://doi.org/10.1016/S0031-9422(97)00159-3)
- Rodda MS, Li G, Reid RJ (2011) The timing of grain Cd accumulation in rice plants: the relative importance of remobilization within the plant and root Cd uptake post-flowering. *Plant Soil* 347(1–2):105–114. <https://doi.org/10.1007/s11104-011-0829-4>
- Roth U, von Roepenack-Lahaye E, Clemens S (2006) Proteome changes in *Arabidopsis thaliana* roots upon exposure to Cd²⁺. *J Exp Bot* 57:4003–4013. <https://doi.org/10.1093/jxb/erl170>
- Sahebi M, Hanafi MM, Rafii MY, Azizi P, Abiri R, Kalhori N (2017) Screening and expression of a silicon transporter gene (*Isi1*) in wild-type indica rice cultivars. *Biomed Res Int* 2:9064129. <https://doi.org/10.1155/2017/9064129>
- Shao JF, Che J, Yamaji N, Shen RF, Ma JF (2017) Silicon reduces cadmium accumulation by suppressing expression of transporter genes involved in cadmium uptake and translocation in rice. *J Exp Bot* 68:5641–5651. <https://doi.org/10.1093/jxb/erx364>
- Shi X, Zhang C, Wang H, Zhang F (2005) Effect of Si on the distribution of Cd in rice seedlings. *Plant Soil* 272(1–2):53–60. <https://doi.org/10.1007/s11104-004-3920-2>
- Sohail MI, ur Rehman MZ, Rizwan M, Yousaf B, Ali S, ul Haq MA et al (2020) Efficiency of various silicon rich amendments on growth and cadmium accumulation in field grown cereals and health risk assessment. *Chemosphere* 244:125481. <https://doi.org/10.1016/j.chemosphere.2019.125481>
- Song A, Li Z, Zhang J, Xue G, Fan F, Liang Y (2009) Silicon-enhanced resistance to cadmium toxicity in *Brassica chinensis* L. is attributed to Si-suppressed cadmium uptake and transport and Si-enhanced antioxidant defense capacity. *J Hazard Mater* 172(1):74–83. <https://doi.org/10.1016/j.jhazmat.2009.06.143>
- Song Y, Jin L, Wang X (2017) Cadmium absorption and transportation pathways in plants. *Int J Phytoremediat* 19(2):133–141. <https://doi.org/10.1080/15226514.2016.1207598>
- Sun H, Guo J, Duan Y, Zhang T, Huo H, Gong H (2017) Isolation and functional characterization of *clsli1*, a silicon transporter gene in *Cucumis sativus*. *Physiol Plant* 159(2):201–214. <https://doi.org/10.1111/ppl.12515>
- Sundari SK (2014) Impact of biotic, abiotic stressors: biotechnologies for alleviating plant stress. In: Miransari M (ed) *Use of microbes for the alleviation of soil stresses*. Springer, New York, pp 87–120
- Treder W, Cieslinski G (2005) Effect of silicon application on cadmium uptake and distribution in strawberry plants grown

- on contaminated soils. *J Plant Nutr* 28:917–929. <https://doi.org/10.1081/PLN-200058877>
- Tubaña BS, Heckman JR (2015) Silicon in soils and plants. In: Rodrigues F., Datnoff L. (eds) *Silicon and plant diseases*. Springer, Cham, pp 7–51. https://doi.org/10.1007/978-3-319-22930-0_2
- Vaculík M, Pavlovič 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>
- Wu J, Shi Y, Zhu Y, Wang Y, Gong H (2013) Mechanisms of enhanced heavy metal tolerance in plants by silicon: a review. *Pedosphere* 23(6):815–825. [https://doi.org/10.1016/S1002-0160\(13\)60073-9](https://doi.org/10.1016/S1002-0160(13)60073-9)
- Wu J, Mock HP, Giehl RF, Pitann B, Mühling KH (2019) Silicon decreases cadmium concentrations by modulating root endodermal suberin development in wheat plants. *J Hazard Mater* 364:581–590. <https://doi.org/10.1016/j.jhazmat.2018.10.052>
- Yu HY, Ding X, Li F, Wang X, Zhang S, Yi J, Liu C, Xu X, Wang Q (2016) The availabilities of arsenic and cadmium in rice paddy fields from a mining area: the role of soil extractable and plant silicon. *Environ Pollut* 215:258–265. <https://doi.org/10.1016/j.envpol.2016.04.008>
- Zaid A, Bhat JA, Wani SH, Masoodi KZ (2019) Role of nitrogen and sulfur in mitigating cadmium induced metabolism alterations in plants. *J Plant Sci Res* 35(1):121–141. <https://doi.org/10.32381/JPSR.2019.35.01.11>
- Zhang Q, Yan C, Liu J, Lu H, Duan H, Du J, Wang W (2014) Silicon alleviation of cadmium toxicity in mangrove (*Avicennia marina*) in relation to cadmium compartmentation. *J Plant Growth Regul* 33(2):233–242. <https://doi.org/10.1007/s00344-013-9366-0>
- Zhao Q, Wang Y, Cao Y, Chen A et al (2014) Potential health risks of heavy metals in cultivated topsoil and grain, including correlations with human primary liver, lung and gastric cancer, in Anhui province, Eastern China. *Sci Tot Environ* 470–471:340–347. <https://doi.org/10.1016/j.scitotenv.2013.09.086>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.