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Increase of available soil silicon by Si-rich manure for sustainable rice production

Zhaoliang Song · Hailong Wang · Peter James Strong · Shengdao Shan

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Abstract Depletion of bioavailable silicon, Si, in paddy soils can decrease the yields of rice. A potential solution is to amend soil with Si-rich organic wastes such as manure from animals fed with rice crop residues. Here, we studied Si in soils from 2000 to 2010 field experiments without manure, with 5 and 10 years of manure, in Eastern China. Results showed that available Si in soils increased from 130 to 270 mg kg⁻¹ after 10 years of manure amendment. This finding is explained either by direct input of available Si or by Si produced by mineralization of Si minerals. To conclude, our results show that amending soil with Si-rich manure in the long term is a solution for sustainable rice production.

Keywords Silicon bioavailability · Fractionation · Noncrystalline Si · Paddy soil · Pig manure · Sustainable rice production

1 Introduction

Rice is the staple food for more than a half of the world's population and has a global distribution area of 155 million ha. More than 90 % of the distribution area is located in Asia, comprising China, India, and Indonesia (Van Soest 2006; Kögel-Knabner et al. 2010). Silicon can improve the quality and yield of rice and other cereals (Matichenkov and Calvert 2002; Richmond and Sussman 2003) by enhancing plant resistance to pests (Nakata et al. 2008) and pathogens (Rodrigues et al. 2003), improving drought resistance (Gong et al. 2005), salt tolerance (Tuna et al. 2008), and heavy metal tolerance (Liang et al. 2005) as well as improving soil nutrient availability (Ma and Takahashi 1991). Rice takes up more Si than other nutrients such as nitrogen during its growth (Van der Vorm 1980; Prakash 2002). Annual rice removal of Si from soils was estimated to range from 205 to 611 kg ha⁻¹, of which approximately 80 % was in the straw (Prakash 2002; Wickramasinghe and Rowell 2006). Thus, depletion of bioavailable Si in paddy soils would occur if crop residues were not incorporated back and cause the decline or stagnation of crop yields (Savant et al. 1997). Silicon fertilization is becoming an increasingly accepted measure in rice and other cereal production via incorporating crop residues into the soil or applying an external source of Si (Savant et al. 1997; Matichenkov and Calvert 2002).

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Rice production generates the largest amount of crop residues globally, in the order of 330 million tons annually (Van Soest 2006). The bran, straw, and hulls of rice are usually rich in Si (about 5 %) and serve as the main feed for animals such as pigs in China and other rice-producing countries (Van Soest 2006; Wickramasinghe and Rowell 2006). As Si is poorly absorbed or digested by animals, the Si content in animal manure from rice-producing areas is generally higher than that from other areas, 5 to 20 g kg⁻¹ total Si (compared to 5 g kg⁻¹ total Si) (this study; Van Soest 2006). Therefore, rice residues (Wickramasinghe and Rowell 2006) as well as animal manure from rice-producing areas may therefore serve as a soil supplement to improve soil available Si content and aid rice production.

Besides primary and secondary crystalline and short-range ordered silicates, Si is also present as water-soluble Si, adsorbed Si, and amorphous Si (Kurtz et al. 2002). Although various Si pools show contrasting reactivities water as well as soil solutions, they can be transformed under certain conditions (Sommer et al. 2006). For example, acidification may disintegrate clay minerals and release Si into soil solution in very acid soils, while the released Si may also precipitate at mineral surfaces forming amorphous Si under other pH conditions (Sommer et al. 2006). The impact of climatic conditions (White and Blum 1995; Sommer et al. 2006), parent material (Höhn et al. 2008), and plant species (Cornelis et al. 2010) on the transformation and uptake of Si in soils has been demonstrated. However, the transformation and fate of external Si in soils remain unclear. This study investigated the effects of Si-rich pig manure amendment on transformation and bioavailability of noncrystalline Si in a paddy soil. The purposes of the study are to assess the fate of Si derived from pig manure and to provide an example for the efficient use of organic wastes in crop production.

2 Materials and methods

In order to test the fractionation and bioavailability of noncrystalline Si in a paddy soil amended with Si-rich pig manure, a 10-year field experiment with two rice cropping systems per year from 2000 to 2010 was conducted at the Mabaoliang farm, Pinghu City, Zhejiang Province, Eastern China (30°39'43" N, 121°00'59" E). The site has an altitude of about 6 m and a subtropical climate controlled by the East Asian monsoon. The average annual temperature is 16 °C, and the annual rainfall is approximately 1,170 mm. The soil is composed of 25 % sand, 63 % silt, and 12 % clay and classified as Gleyed paddy soil according to the Chinese soil

classification system and Gleysols according to the Food and Agriculture Organization soil classification system. The experimental trial site was reclaimed and planted with rape, alfalfa, and rice for more than 20 years prior to the experiment. The initial properties of the surface soil (0–20 cm depth) were as follows: pH 6.12±0.13, soil organic matter content of 55.16±3.27 g kg⁻¹, P content of 1.64±0.17 g kg⁻¹, total SiO₂ of 603.8 g kg⁻¹, and available Si of 142.7 mg kg⁻¹.

The area of each plot is approximately 66.7 m², with a length of 10 m and a width of 6.67 m. The experiment was conducted with three replications. The long-term Si-rich pig manure fertilization experiment was based on normal chemical fertilization with full recommended N, P, and K fertilizer doses of 120–24–36 and 90–18–27 kg ha⁻¹ in early and late season rice, respectively. The Si-rich pig manure fertilization experiment was conducted with the following three treatments: control (without manure), 5-year manure, and 10-year manure. The rate of manure application was 35 Mg ha⁻¹ year⁻¹. The pig manure had a pH value of 7.50±0.40, total organic matter content of 480±12 g kg⁻¹, total P content of 7.3±2.3 g kg⁻¹, and total Si content of 8.5±1.5 g kg⁻¹.

The mature crop was harvested manually at 5 cm above the ground level. The annual yields of rice grain ranged from 10 to 12 Mg ha⁻¹. The ratio of straw to grain of rice was approximately 1.1. The Si content of rice was 23.1±3.2 g kg⁻¹. Annual rice removal of Si from soils was estimated to range from 200 to 370 kg ha⁻¹.

2.1 Soil sampling and treatment

Soil samples from were hand collected horizontally from five depths: 0 to 10, 10 to 20, 20 to 30, 30 to 40, and 40 to 70 cm. For soil pH analyses, samples were air-dried, crushed, and passed through a 2-mm sieve (after removing visible stones, roots, and crop residues). Subsamples were ground to a size that would pass a 100-mesh sieve and then used for chemical analyses to determine contents of other parameters such as organic matter and different fractions of noncrystalline Si.

2.2 Physical and chemical analysis

Soil pH was determined in a ratio of 1:2.5 soil/water suspension with a PHS-3C precision pH meter. Organic carbon was analyzed using a wet oxidation method with dipotassium chromate and concentrated sulfuric acid to determine the chemical oxygen demand, from which the soil organic matter content was calculated (Nelson and Sommers 1982). Soil samples were fused in nickel crucible with sodium hydroxide at 650 °C and neutralized with dilute hydrochloric acid. The concentrations of Si and P in the prepared sample solution

were determined colorimetrically by the molybdate–ascorbic acid method (Mortlock and Froelich 1989; Murphy and Riley 1962). Available Si in soil was extracted with acid sodium acetate (Lu 2000).

2.3 Fractionation of noncrystalline Si

Four “operationally defined” soil noncrystalline Si fractions including acid Na acetate–Si, H_2O_2 –Si, $NH_2OH\cdot HCl$ –Si, or $NaOH$ –Si were isolated in sequence (Table 1) to represent available Si, organic Si, Fe–Mn oxide Si, and amorphous Si, respectively. A portion of each extract was pipetted into a 50-mL centrifuge tube and centrifuged (Sorvall, Model RC2-B) at 16,300g at 0 °C for 10 min; Si was then determined colorimetrically using the molybdate–ascorbic acid procedure (Mortlock and Froelich 1989). All Si measurements were done in triplicate. The data were analyzed by ANOVA, and means were compared with Duncan’s test using the SPSS software (SPSS 11.5 for windows).

3 Results and discussion

3.1 Manure impact on soil parameters

The pH value in surface soil of 0 to 10 cm depth increased from 5.92 to 7.18 with the cumulative additions of pig manure (Table 2). As a major component of soil, SiO_2 content did not show an increasing trend with manure amendment in most depths of soil profiles. Soil organic matter and total P content in upper soil profiles such as 0 to 30 cm depth increased with the cumulative additions of pig manure from lower than 52 to 63 g kg^{-1} and from lower than 1.6 g kg^{-1} to higher than 4.6 g kg^{-1} , respectively. Available Si throughout soil profiles increased from

133 mg kg^{-1} to higher than 267 mg kg^{-1} with manure amendment. Generally, the impact of manure amendment on soil parameters in upper soils such as surface soil was more significant than that in bottom soils, as soil organic matter may degrade, and mineral elements may deposit or be adsorbed by secondary minerals during their vertical transport with irrigation water. However, the fluctuation of pH and SiO_2 in bottom soils may be affected by other factors such as groundwater level fluctuation and soil heterogeneity.

3.2 Manure impact on soil noncrystalline Si distribution

Generally, major noncrystalline Si fractions in soils were $NaOH$ –Si and $NH_2OH\cdot HCl$ –Si, while minor amounts of acid Na acetate–Si and H_2O_2 –Si were also present (Figs. 1, 2, 3, and 4).

Acid Na acetate–Si in soil profiles increased from 130 mg kg^{-1} to higher than 270 mg kg^{-1} with the cumulative additions of pig manure (Fig. 2). The percentage of acid Na acetate–Si in the four noncrystalline Si forms throughout soil profiles showed a similar increasing trend. The percentage of acid Na acetate–Si increased from 3.4 % to higher than 6 %. The increasing trend is more obvious in the upper part of soil profiles such as 0 to 20 cm than that in the bottom soil. The increase soil of acid Na acetate–Si content and percentage is due to the high efficiency of available Si release from manure degradation.

H_2O_2 –Si content in soils of 0–40 cm increased from lower than 215 to 245 mg kg^{-1} with the cumulative additions of pig manure due to organic Si input from manure (Fig. 3). However, the mass ratio of acid Na acetate–Si/ H_2O_2 –Si increased from 0.62 to 1.09 with the cumulative additions of pig manure in the upper parts (0 to 20 cm) of soil profiles as the organic Si

Table 1 Soil noncrystalline Si fractionation procedure modified after Tessier et al. (1979), Lu (2000), and Kurtz et al. (2002)

Step	Si fraction	Conditions	Characteristics
1	Acid Na acetate–Si	Add 30 mL 1 mol L^{-1} acid Na acetate buffer solution at pH 4.0 to 0.75 g soil in a 50-mL centrifuge tube, shake for 16 h, centrifuge	Bioavailable and mobile Si directly exchangeable with soil solution
2	H_2O_2 –Si	Add 5 mL 30 % H_2O_2 to the residue from step 1, heat to 85 ± 2 °C for 1 h twice, add 30 mL 1 mol L^{-1} acid Na acetate buffer solution at pH 4.0, shake for 16 h, centrifuge	Labile Si associated with humic compounds
3	$NH_2OH\cdot HCl$ –Si	Add 30 mL 0.5 mol L^{-1} $NH_2OH\cdot HCl$ to the residue from step 2, wrap the tubes with foil, shake for 16 h, centrifuge	Labile Si chemisorbed to Fe and Mn compounds
4	$NaOH$ –Si	Add 30 mL 0.5 mol L^{-1} $NaOH$ to the residue from step 3, treat with ultrasonic bath for 1 h, shake for 16 h, centrifuge	Weakly labile Si fixed in noncrystalline or short-range crystal-order silicates

Table 2 Selected physical and chemical properties of the soils used in this study

Depth (cm)	Treatment	pH	SiO ₂ (g kg ⁻¹)	Soil organic matter (g kg ⁻¹)	P (g kg ⁻¹)	Available Si (mg kg ⁻¹)
0–10	No manure	5.92±0.08c	601±2a	52.0±4.0b	1.59±0.06c	133±10c
	5-year manure	6.67±0.14b	605±14a	60.0±5.3ab	2.56±0.27b	162±10b
	10-year manure	7.18±0.14a	606±18a	63.2±3.6a	4.65±0.66a	267±24a
10–20	No manure	6.40±1.03a	620±36a	47.3±5.6b	1.58±0.04b	149±16c
	5-year manure	7.16±0.84a	620±15a	59.5±6.4a	2.03±0.78b	188±8b
	10-year manure	7.29±0.08a	618±6a	62.1±5.8a	4.96±0.05a	247±17a
20–30	No manure	7.23±0.64a	624±29a	31.1±6.9b	1.28±0.64b	195±19c
	5-year manure	7.82±0.48a	642±29a	42.0±8.6ab	1.51±0.25b	236±12b
	10-year manure	7.73±0.79a	624±6a	47.3±7.0a	3.97±1.93a	279±14a
30–40	No manure	7.59±0.07b	615±12a	13.4±8.4a	0.84±0.24a	239±6b
	5-year manure	8.07±0.01a	646±22a	17.4±4.5a	1.06±0.65a	262±16a
	10-year manure	8.08±0.08a	639±24a	23.2±4.2a	2.04±1.93a	263±15a
40–70	No manure	7.68±0.09b	621±7b	8.6±0.8a	0.63±0.10a	261±7b
	5-year manure	8.01±0.07a	637±3a	6.4±0.5a	0.67±0.04a	274±12b
	10-year manure	7.94±0.09a	642±12a	8.9±2.3a	0.64±0.35a	297±6a

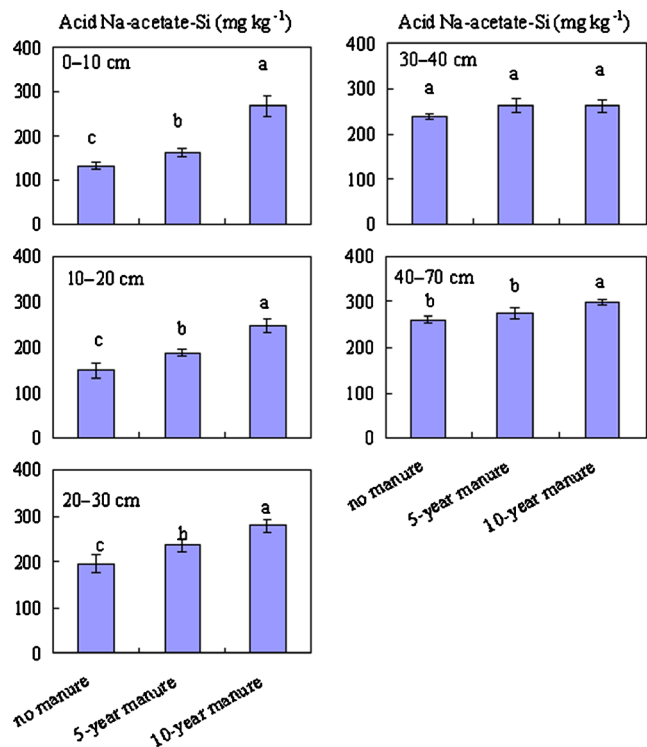
Values followed by the same letter of a soil depth within the same column are not significantly different at $P < 0.05$

released to soil may degrade to form water-soluble or exchangeable inorganic Si.

NH₂OH·HCl–Si content in soils of most depths except 30–40 cm increased slightly from lower than 620 to 650 mg kg⁻¹ during the first 5 years of manure amendment and declined to lower than 570 mg kg⁻¹ during the next 5 years of manure amendment (Fig. 4). The first increase of NH₂OH·HCl–Si content in soils is probably due to the high efficiency of Fe–Mn oxides in adsorption of bioavailable Si released from manure degradation. However, the late decline of NH₂OH·HCl–Si content in soils is probably the result of Fe–Mn oxide dissolution under high organic acid conditions (Chen et al. 2003) created with incomplete degradation of pig manure. The mass ratio of acid Na acetate–Si/NH₂OH·HCl–Si increased from 0.21 to 0.46 with the cumulative additions of pig manure in the middle to upper parts (0 to 40 cm) of soil profiles

**Fig. 1** Extensive and intensive production of rice in China

due to Fe–Mn oxide dissolution under high organic acid conditions (Chen et al. 2003).

**Fig. 2** Distribution of acid Na acetate–Si in soils of different depths after 0 to 10 years of manure amendment. Values followed by the same letter of a soil depth within a figure are not significantly different at $P < 0.05$. Acid Na acetate–Si in soil profiles increased from 130 mg kg⁻¹ to higher than 270 mg kg⁻¹ with the cumulative additions of pig manure due to the high efficiency of available Si release from manure degradation

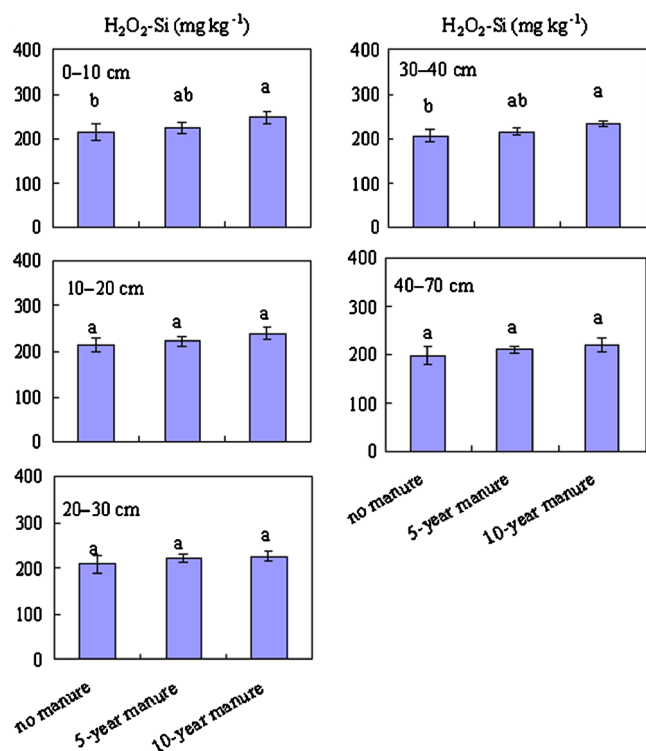


Fig. 3 Distribution of $\text{H}_2\text{O}_2\text{-Si}$ in soils of different depths after 0 to 10 years of manure amendment. Values followed by the same letter of a soil depth within a figure are not significantly different at $P < 0.05$. $\text{H}_2\text{O}_2\text{-Si}$ content in soils of 0–40 cm increased from lower than 215 to 245 mg kg^{-1} with the cumulative additions of pig manure due to organic Si input from manure

NaOH-Si content in soil profiles increased from lower than 2,800 mg kg^{-1} to higher than 3,800 mg kg^{-1} with the cumulative additions of pig manure, as is more obvious in the upper parts of soil profiles (i.e., 0 to 40 cm) due to the release of amorphous Si from manure (Fig. 5). The mass ratio of acid Na acetate-Si/ NaOH-Si increased from 0.046 to 0.070 with the cumulative additions of pig manure in the mid-upper parts (0 to 40 cm) of soil profiles due to a higher dissolution rate of amorphous Si in organic materials than in soils (Frayse et al. 2009).

3.3 Transformation and bioavailability of manure Si in soils

The distribution of noncrystalline Si in soil profiles (Table 2, Figs. 1, 2, 3, and 4) indicates that pig manure amendment controls the distribution, transformation, and bioavailability of manure Si in the upper parts from 0 to 40 cm depth of soil profiles.

The changes of relative bioavailability of soil Si with the cumulative additions of pig manure can be characterized according to the changes of acid Na acetate-Si percentage in noncrystalline Si (Tessier et al. 1979; Lu 2000). The relative increase in acid Na acetate-Si in the noncrystalline Si with

cumulative additions of pig manure (Fig. 2) indicates that the bioavailability of Si increased with cumulative additions of pig manure.

The ratio of acid Na acetate-Si to other noncrystalline Si in soils reflects the relative bioavailability of other noncrystalline Si (Tessier et al. 1979; Lu 2000). The relative bioavailability of $\text{H}_2\text{O}_2\text{-Si}$, $\text{NH}_2\text{OH}\cdot\text{HCl-Si}$, and NaOH-Si increased with the cumulative additions of pig manure in the upper parts (0 to 20 cm) of soil profiles from 0.62 to 1.09, 0.21 to 0.46, and 0.046 to 0.070, respectively (Figs. 1, 2, 3, and 4). The higher relative bioavailability of $\text{H}_2\text{O}_2\text{-Si}$ and $\text{NH}_2\text{OH}\cdot\text{HCl-Si}$ than NaOH-Si was also observed in other natural ecosystems such as rainforests (Alexandre et al. 1997; Farmer et al. 2005; Conely et al. 2008). However, the increasing trend of relative bioavailability of $\text{H}_2\text{O}_2\text{-Si}$, $\text{NH}_2\text{OH}\cdot\text{HCl-Si}$, and NaOH-Si with accumulation of organic matter has not been observed. This difference in relative bioavailability of Si between our manure amendment ecosystems with other natural ecosystems may be due to a relatively higher solubility of Si in manure

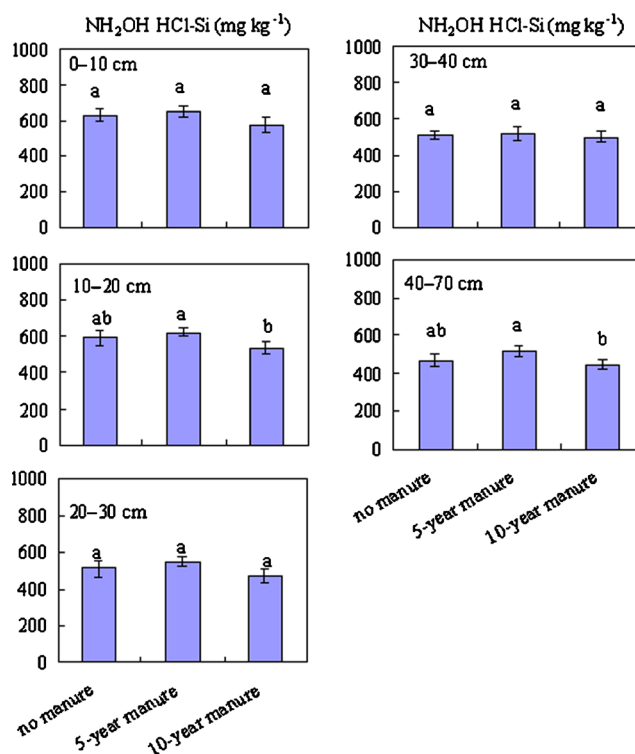


Fig. 4 Distribution of $\text{NH}_2\text{OH}\cdot\text{HCl-Si}$ in soils of different depths after 0 to 10 years of manure amendment. Values followed by the same letter of a soil depth within a figure are not significantly different at $P < 0.05$. $\text{NH}_2\text{OH}\cdot\text{HCl-Si}$ content in soils of most depths except 30–40 cm increased slightly from lower than 620 to 650 mg kg^{-1} during the first 5 years of manure amendment due to the high efficiency of Fe–Mn oxides in adsorption of bioavailable Si released from manure degradation and declined to lower than 570 mg kg^{-1} during the next 5 years of manure amendment due to Fe–Mn oxide dissolution under high organic acid conditions (Chen et al. 2003) created by incomplete degradation of pig manure

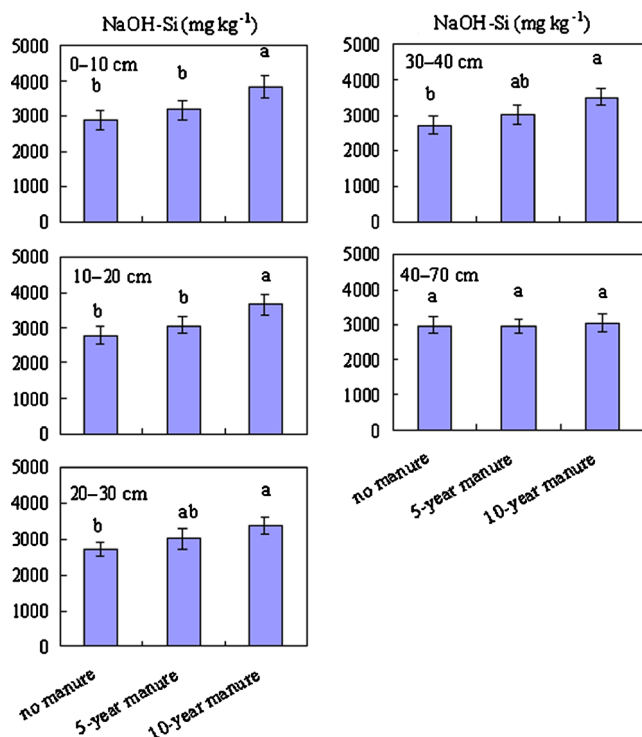


Fig. 5 Distribution of NaOH-Si in soils of different depths after 0 to 10 years of manure amendment. Values followed by the same letter of a soil depth within a figure are not significantly different at $P < 0.05$. NaOH-Si content in soil profiles increased from lower than 2,800 mg kg⁻¹ to higher than 3,800 mg kg⁻¹ with the cumulative additions of pig manure due to the release of amorphous Si from manure

after animal digestion than in natural plant residues. However, this hypothesis requires further examination.

As annual rice removal of Si from soils was estimated to range 205 to 611 kg ha⁻¹ (Prakash 2002; Wickramasinghe and Rowell 2006; this study) during rice production, accumulation of bioavailable Si, and other potential Si forms after manure amendment indicates that long-term pig manure amendment can ameliorate a deficiency of bioavailable Si in soils.

The above observations have broad implications for agricultural production and organic waste treatment. In addition to high rice residue production (about 330 million tons annually), the production of other cereal residues (such as maize residues and wheat residues) is almost equally large and has a similarly high Si content (about 5 %) (Van Soest 2006; Wickramasinghe and Rowell 2006). All these cereal residues are the primary feed for animals in China and other cereal-producing countries (Van Soest 2006). As Si is poorly absorbed or digested by animals, the Si content in animal manure (5 to 20 g kg⁻¹ total Si) is almost equally high (this study; Van Soest 2006). Therefore, the animal manure from all cereal-producing areas of the world may be used to improve soil available Si content to aid cereal production while simultaneously producing an economic value in the form of animal biomass production. A new sustainable

model for agricultural production and organic waste treatment can be illustrated as follows: cereal production, animal raising with cereal residues as the main feed, Si-rich animal manure production, soil incorporation of animal manure after proper treatment, and further cereal production.

4 Conclusions

The results of our investigation show that cumulative manure amendment may increase the content of available Si in soils either directly through manure available Si input or indirectly through mineralization and transformation of other noncrystalline Si forms released from manure degradation. The relative bioavailability of H₂O₂-Si, NH₂OH·HCl-Si, and NaOH-Si increased with the cumulative additions of pig manure in the upper parts (0 to 20 cm) of soil profiles from 0.62 to 1.09, 0.21 to 0.46, and 0.046 to 0.070, respectively. Long-term manure amendment can ameliorate a deficiency of bioavailable Si in soil. We believe that the animal manure from cereal-producing areas of the world may also be used to improve soil available Si content to aid subsequent cereal production while generating an added economic benefit in the form of animal husbandry. Our findings can offer a new sustainable model for agricultural production and organic waste treatment. However, further research is necessary to quantify the amount of animal manure required to fulfill crop Si demand and maintain available Si levels in soils of cereal-producing areas of the world.

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Conflict of interest The authors have declared no conflict of interest.

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