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*Original Research*

# Effects of Reduced Fertilization Combined with Titanium Gypsum on Soil Arsenic and Cadmium and Water Spinach (*Ipomoea aquatica* Forsk) Growth

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## Abstract

Many industrial by-products have been used to fix heavy metals in contaminated soil. In this study, three amendments (titanium gypsum (TG) and two simulated titanium gypsum (STG1; STG2) were used to immobilize arsenic (As) and cadmium (Cd) in soil and reduce their concentration in water spinach. Three fertilization regimes (local conventional fertilization (CK), 30% reduced fertilization (CJ) and 30% nitrogen reduction slow-release fertilizer (WH)) were employed to verify the feasibility of reduced fertilization. The results showed that both TG and STG reduced As and Cd concentrations in soil and water spinach. In this study, TG, STG1 and STG2 reduced soil available As concentration by 3.8%, 4.1% and 6.2%, and soil available Cd concentration by 12.6%, 20.2% and 29.0%, respectively. These amendments increased soil pH without affecting alkali-hydrolyzed nitrogen, available phosphorus, available potassium, and organic matter. Moreover, reduced fertilization was feasible, in this experiment, CJ had no significant effect on soil nutrients and plant growth, and WH increased soil organic matter concentration and spinach biomass. Therefore, TG and STG have excellent soil heavy metal fixation potential, and combined with reducing fertilization, they can not only alleviate the pollution of soil As and Cd, but also improve the efficiency of fertilizer utilization.

**Keywords**: Titanium gypsum, slow-release fertilizer, Arsenic, Cadmium, amendments

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## Introduction

Soil heavy metal pollution is a non-ignorable issue in the agricultural field, and the consequent food safety problem has attracted a large amount of attention [1-4]. There are various sources of heavy metal(loid)s in soil, including discharge of industrial waste [5, 6], mining and smelting of mines [7], application of chemical fertilizers and pesticides [8], irrigation of sewage, discharge of municipal solid waste [9, 10], and volcanic eruption [11]. Heavy metal(loid)s cannot be degraded biologically or chemically. The accumulation of heavy metal(loid)s can lead to soil degradation and ecosystem destruction. Moreover, they can enter the human body through the food chain, thereby endangering human health [12].

The treatment dealing with soil heavy metal(loid)s pollution is mainly carried out from two aspects: removing heavy metal(loid)s from the soil to reduce the degree of pollution; immobilizing heavy metal(loid)s in the soil to alleviate its toxicity [13]. For soils polluted by heavy metal(loid)s, common remediation techniques include physical, chemical and bioremediation techniques. Among them, *in-situ* passivation remediation technology has become a promising solution due to its low cost, wide suitability for different soils, and low impact on soil biomes. Various chemical amendments were applied to fix heavy metal(loid)s in soil, reducing their mobility and bioavailability [14]. For example, lime increases the negative charge of soil by reducing soil $H^+$ and adsorbs more heavy metal cations [15]. Metal oxides passivate soil heavy metals mainly through chemical reactions, charge adsorption and formation of complexes. Hartley et al. [16] pointed out that iron oxides have a lasting fixation effect on soil As, and the adsorption capacity of different iron oxides to As is as follows: iron (III) >iron (II)>iron grit>goethite, of which iron (II) may cause soil acidification.

Arsenic and cadmium are trace toxic metal(loid)s commonly found in dryland soils. They both have serious effects on human body, such as lung cancer, skin cancer, neurological disease and bone damage [17-19]. Studies have shown that the application of Titanium gypsum (TG) could significantly reduce the bioavailability of As, Cu, and Cd in the soil, and increase the number of heavy metal-resistant bacteria in the soil [20]. TG is an industrial by-product in the production of titanium dioxide by the sulfuric acid method. Its main components are dihydrate gypsum ($CaSO_4·2H_2O$) and iron oxide ($Fe_2O_3$) [21]. At present, TG is mainly used in industrial fields, rather than in soil. The abundant calcium and sulfur in TG can provide nutrients to the soil, and iron oxide is also a good soil amendment. As an industrial by-product, TG contains zinc, arsenic, lead and other elements [22], which may have an adverse effect on its passivation capability. Therefore, simulated titanium gypsum (STG) becomes a new option. STG is a mixture of dihydrate gypsum and iron oxide, and different ratios can be adjusted to pursue better fixing effect on As and Cd.

Excessive use of mineral fertilizers is another problem in agricultural production. In China, nitrogen fertilizer is excessively applied for high crop yields. the average nitrogen fertilizer application in China (before 2018) was 305 kg N $ha^{-1}$ $yr^1$, while the world average was 75 kg N $ha^{-1}$ $yr^1$ [23]. Referring to a long-term study [24], soil pH decreased by an average of 0.07 per year under the application of mineral fertilizers. In addition, heavy use of chemical fertilizers can also lead to soil quality degradation, biodiversity reduction, and even environmental pollution [25-27]. In response to these situations, many fertilization measures have been applied, such as reduction fertilization, biochar substitution, and combination application of organic and inorganic fertilizers [28, 29]. Reduced fertilization is a direct solution to excessive fertilization. Study [23] showed that proper management increased yields of maize, rice, and wheat by an average of 10% and reduced nitrogen application by 14%. Compared with single application of chemical fertilizers, organic-inorganic compound fertilizers can provide more organic matter and improve soil physicochemical properties and microbial activity [30, 31]. At the same time, organic fertilizer can also supplement slow-acting nutrients, improve crop growth and increase yield [32].

Water spinach is a leafy vegetable widely grown in Guangdong Province, China, which is susceptible to As, Cd contamination [33]. But at present, there are few studies on the effects of TG and STG on heavy metals in soil and water spinach. Therefore, this study aimed to compare the remediation effects of TG and STG on As and Cd in soil and water spinach by a pot trial, to study the effect of reduced fertilization and organic-inorganic slow-release fertilizer on soil fertility and growth of water spinach, and to explore locally appropriate fertilization and passivation methods.

## Materials and Methods

### Experiment Material

#### *Gypsum Passivation Materials*

Three materials were used in this experiment, namely titanium gypsum, dihydrate gypsum ($CaSO_4·2H_2O$) and ferric oxide ($Fe_2O_3$). Titanium gypsum was taken from a company in Zhenjiang, Jiangsu Province, which produced titanium dioxide by the sulfuric acid method. Titanium gypsum was passed through 20-mesh sieves and 100-mesh sieves for use. The main components of titanium gypsum are calcium sulfate ($CaSO_4$), iron oxide ($Fe_2O_3$) and crystal water. And the ratio of $CaSO_4·2H_2O/Fe_2O_3$ in titanium gypsum ranges from 7.36 to 10.88. The pH value of the titanium gypsum used in this experiment was 8.55, the Cd concentration was 0.41 mg/kg, and the As concentration was 159.25 mg/kg. The dihydrate gypsum and iron trioxide were provided by Sinopharm Chemical Reagent Company.

### Test Fertilizer

Norway (N-$P_2O_5$-$K_2O$: 15-15-15) compound fertilizer (conventional fertilizer widely used in the vegetable fields of the Pearl River Delta, purchased from Yaran Trading Shanghai Co., Ltd.)

Wanli Shennong (N-$P_2O_5$-$K_2O$: 8-4-8) organic-inorganic slow-release fertilizer (organic matter content >25%, including modified lignin, ultra-fine pulverized cellulose and humic acid, etc. purchased from Wanli Shennong Co., Ltd.)

### Test Plant

The test plant was water spinach (*Ipomoea aquatica* Forsk) widely grown in the Pearl River Delta region, purchased from Guangzhou Hualu Seed Co., Ltd. After the seeds were propagated and cultivated in a temperature-controlled growth room, healthy seedlings with a length of about 3 cm were selected as the test plants.

### Test Soil

The test soil used in this experiment was vegetable soil contaminated by heavy metals in Foshan City, Guangdong Province (22°59′3″N, 112°53′6″E). Topsoil samples (0-20 cm) were collected by S-type sampling method at 5 sub-points, and passed through 10-mesh and 100-mesh sieves after air-drying. Physico-chemical characteristics of the tested soils are shown in Table 1.

## Experiment Method

The experiment was performed with a completely randomized experiment including two factors (three fertilization methods and four passivation materials), which gave a total of 12 treatments, and each treatment was set with three repetitions. Three fertilizer treatments were as follows: (1) CK, conventional fertilization (Norwegian compound fertilizer N-$P_2O_5$-$K_2O$: 15-15-15, 750 kg/ha); (2) CJ, 30% reduction in conventional fertilization; (3) WH, nitrogen reduction 30% slow-release fertilizer (slow-release fertilizer N-$P_2O_5$-$K_2O$: 8-4-8, 975 kg/ha). All fertilizers are applied in the form of basal fertilizer. Four passivation materials were as follows: (1) CT, no addition; (2) TG, Titanium gypsum; (3) STG1, 90% Dihydrate gypsum + 10% Ferric oxide; (4) STG2, 70% Dihydrate gypsum + 30% Ferric oxide. Considering the toxic effect of high concentrations of sulfur or iron on crops, the ratio of the added passivation materials was 0.3% [34, 35] (Table 2).

The experiment was carried out in the smart greenhouse of Zhejiang A&F University in March 2018 (30°19’N, 119°35’E). Referring to Fan et al. [36], 1.5 kg of test soil and amendment were mixed according to different treatments and placed in ceramic pots (diameter: 20 cm, high: 19 cm). Each treatment was replicated three times. The pots were set in natural light and at a temperature of 25-33ºC. The soil moisture was adjusted to 80% degree of water holding capacity. After 15 days of stable cultivation, each pot was planted with three water spinach seedlings, watered once a week, and kept loosening the soil and preventing pests. Finally, plant and soil samples were collected after 40 days of water spinach growth.

## Measurement Items and Methods

### Soil Analyses

Soil pH was determined by potentiometric method after ultrapure water extraction (soil: water ratio 1:2.5), soil organic matter by potassium dichromate oxidation-heating method, and then titrated with 0.2 mol/L $FeSO_4$ solution. Alkali-hydrolyzed nitrogen by alkaline-hydrolysis diffusion method. Soil available phosphorus was extracted with $NaHCO_3$ and measured by molybdenum antimony colorimetric method. Soil available potassium was measured by atomic adsorption spectrophotometer [24]. The available heavy metals in soil were extracted by 0.1 mol/L HCl, and then determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 2000, PerkinElmer Co., USA).

### Plant Samples Determination

Height of water spinach was measured by a tape before harvesting. The plant samples were rinsed with tap water, then soaked with 10 mmol/L $Na_2$-EDTA, and finally washed with deionized water, then oven dried at 105ºC for 15 minutes, then at 80ºC to constant weight. After oven drying, the dry weight was measured as the biomass of water spinach [37].

Plant samples were digested with $H_2SO_4$-$H_2O_2$, then the total nitrogen concentration was measured by distillation nitrogen determination method, total phosphorus concentration by the vanadium molybdenum

Table 1. Basic nutrients, and Available As and Cd concentrations on the collected soils.

| pH | Organic matter (g/kg) | Alkaline N (mg/kg) | Available P (mg/kg) | Available K (mg/kg) | Available As (mg/kg) | Available Cd (mg/kg) |
|---|---|---|---|---|---|---|
| 7.69 | 16.21 | 87.56 | 80.75 | 240.67 | 1.78 | 0.225 |

Table 2. Fertilizer and amendment additions in pot experiment.

| Treatment | Fertilizer | Amendment |
|---|---|---|
| CK1 | 10 g Norwegian compound fertilizer | CT |
| CK2 | | 4.5g TG |
| CK3 | | 4.5g STG1 |
| CK4 | | 4.5g STG2 |
| CJ1 | 7 g Norwegian compound fertilizer | CT |
| CJ2 | | 4.5g TG |
| CJ3 | | 4.5g STG1 |
| CJ4 | | 4.5g STG2 |
| WH1 | 13 g slow-release fertilizer | CT |
| WH2 | | 4.5g TG |
| WH3 | | 4.5g STG1 |
| WH4 | | 4.5g STG2 |

CT means no addition, TG: titanium gypsum, STG1: 90% dihydrate gypsum + 10% ferric oxide, STG2: 70% dihydrate gypsum + 30% ferric oxide.

yellow colorimetric method, total potassium concentration by atomic adsorption spectrophotometer. Arsenic and cadmium in water spinach were extracted by $HNO_3$/$H_2O_2$ digestion (EPA Method 3050B), and then determined by inductively coupled plasma emission spectroscopy (ICP-OES, Optima 2000, PerkinElmer Co., USA) [38].

### Statistical Analysis

SPSS 22.0 was used for experimental data processing and statistical analysis, and Origin 2018 was applied for graph drawing. All data were presented in forms of mean±standard deviation. Two-way analysis of variance (ANOVA) was used to determine significant differences among treatments at the 0.05 level, and comparisons of means were carried out by Duncan's multiple range test.

## Results and Analysis

### Two-way ANOVA for Fertilizer and Amendment

The two-way ANOVA results are shown in Table 3. The interaction of fertilizers and amendments was not statistically significant for the studied variables of soil and water spinach. Therefore, the differences of soil and water spinach in treatments related to fertilization and amendment were further analyzed. Fertilization significantly affected soil available nutrients, soil available As, plant height, dry weight and total potassium ($p<0.05$). Amendment had significant effect on available As, Cd of the soil and water spinach.

### Physico-Chemical Properties of Soil in Different Treatments

#### *pH*

Compared with the original soil pH 7.69 (Table 1), both fertilization and amendment treatments decreased soil pH, the range was 7.33-7.43, 7.32-7.42, respectively (Fig. 1). Compared with conventional fertilization treatments (CK) and reduced fertilization 30% treatments (CJ) (Fig. 1a), slow-release fertilizer (WH) significantly increased soil pH by 1.36% and 1.22%, respectively ($p<0.05$). Compared with control treatments (CT) (Fig. 1b), the addition of amendments increased soil pH, and the pH order of the treatments was TG>STG2>STG1>CT.

Table 3. Two-way ANOVA for fertilizer and amendment.

| Source of variation | Soil | | | | | | |
|---|---|---|---|---|---|---|---|
| | pH | OM | AN | AP | AK | As | Cd |
| Fertilizer | 0.048 | 0.360 | 0.012 | <0.001 | 0.038 | 0.048 | 0.168 |
| Amendment | 0.232 | 0.702 | 0.736 | 0.817 | 0.831 | 0.001 | <0.001 |
| F×A | 0.869 | 0.874 | 0.998 | 0.998 | 0.964 | 0.384 | 0.132 |
| Source of variation | Water spinach | | | | | | |
| | Height | D.W. | TN | TP | TK | As | Cd |
| Fertilizer | 0.003 | 0.023 | 0.994 | 0.886 | 0.007 | 0.319 | 0.127 |
| Amendment | 0.590 | 0.978 | 0.143 | 0.699 | 0.463 | 0.034 | <0.001 |
| F×A | 0.884 | 0.998 | 0.743 | 0.619 | 0.143 | 0.744 | 0.596 |

The data in the table are all p-values. F×A means Fertilizer × Amendment, OM: organic matter, AN: Alkali-hydrolyzable nitrogen, AP: available phosphorus, AK: available potassium, D.W. means dry weight, TN: total nitrogen, TP: total phosphorus, TK: total potassium

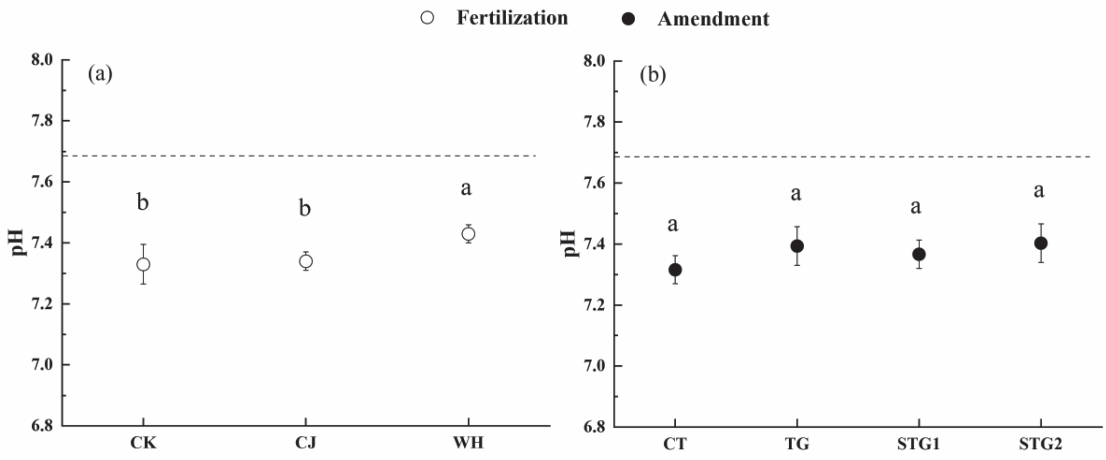

Fig. 1. Soil pH with different fertilization and amendment treatments. The dotted line represents the soil pH background value. Different lowercase letters indicate significant a difference at $P<0.05$ between different treatments.

### *Available Nutrients*

The difference of soil nutrients between treatments was mainly related to different fertilization measures, rather than amendments (Table 4). Compared with the background value of soil alkali-hydrolyzed nitrogen (87.56 mg/kg, Table 1), different fertilization treatments can significantly increase the soil nitrogen concentration in the soil ($p<0.05$). The soil alkali-hydrolyzed nitrogen concentration of CK was the highest, reaching 134.9 mg/kg, which was 54.1% higher than the soil background value. The corresponding nitrogen concentration of CJ was significantly lower than that of CK and WH. The soil available phosphorus concentrations of fertilization treatments were ranked as CK>WH>CJ, and the available phosphorus concentration of CJ was significantly lower than that of CK and WH, which decreased by 17.3% and 16.8%, respectively. Among the fertilization treatments, WH had the highest concentration of soil available potassium. There was no significant difference in soil organic matter concentration among the treatments.

## Concentrations of As and Cd in Soils

Soil available As was significantly affected by fertilization and amendments (Fig. 2). In the fertilization treatments, the soil available As concentration of CJ was the highest, which was 1.51 mg/kg, and the soil available As concentration of CK was the lowest. On the other hand, compared to the treatments without amendments, the addition of amendments significantly reduced the concentration of soil available As ($p<0.05$, Fig. 2a). The concentration of available As in the soil of each treatment was CT>TG>STG1>STG2, and STG2 was 6.2% lower than CT (Fig. 2b).

Soil available Cd was mainly affected by amendments. The available Cd concentration of different amendment treatments ranged from 0.164 to 0.231 mg/kg (Fig. 2d). The addition of amendments significantly reduced the concentration of soil available Cd. Compared with CT, the TG, STG1 and STG2 decreased the available Cd concentration by 12.6%, 20.2% and 28.9%, respectively.

Table 4. Soil N, P, K and organic matter concentration of different treatments.

| Treatment | AN (mg/kg) | AP (mg/kg) | AK (mg/kg) | OM (g/kg) |
|---|---|---|---|---|
| CK | 134.90±7.36A | 122.56±9.52A | 284.08±16.38A | 18.16±0.80A |
| CJ | 126.42±5.16B | 101.40±10.41B | 271.23±10.01B | 17.81±0.96A |
| WH | 133.02±4.86A | 121.90±5.30A | 285.78±10.62A | 18.41±0.99A |
| CT | 132.33±6.93a | 119.35±12.65a | 281.89±12.92a | 18.33±0.92a |
| TG | 129.64±7.12a | 114.58±16.85a | 278.11±13.09a | 18.02±0.88a |
| STG1 | 130.93±7.62a | 116.10±11.77a | 283.17±14.56a | 17.85±1.21a |
| STG2 | 132.88±6.27a | 113.11±11.10a | 278.28±16.70a | 18.31±0.71a |

Values are mean±standard deviation. AN means alkaline hydrolyzed nitrogen, AP: available phosphorus, AK: available potassium, OM: organic matter. The different capital letters indicate a significant difference between CK, CJ and WH treatments at $P<0.05$ (Duncan's test). Different lowercase letters indicate significant a difference at $P<0.05$ between CT, TG, STG1 and STG2.

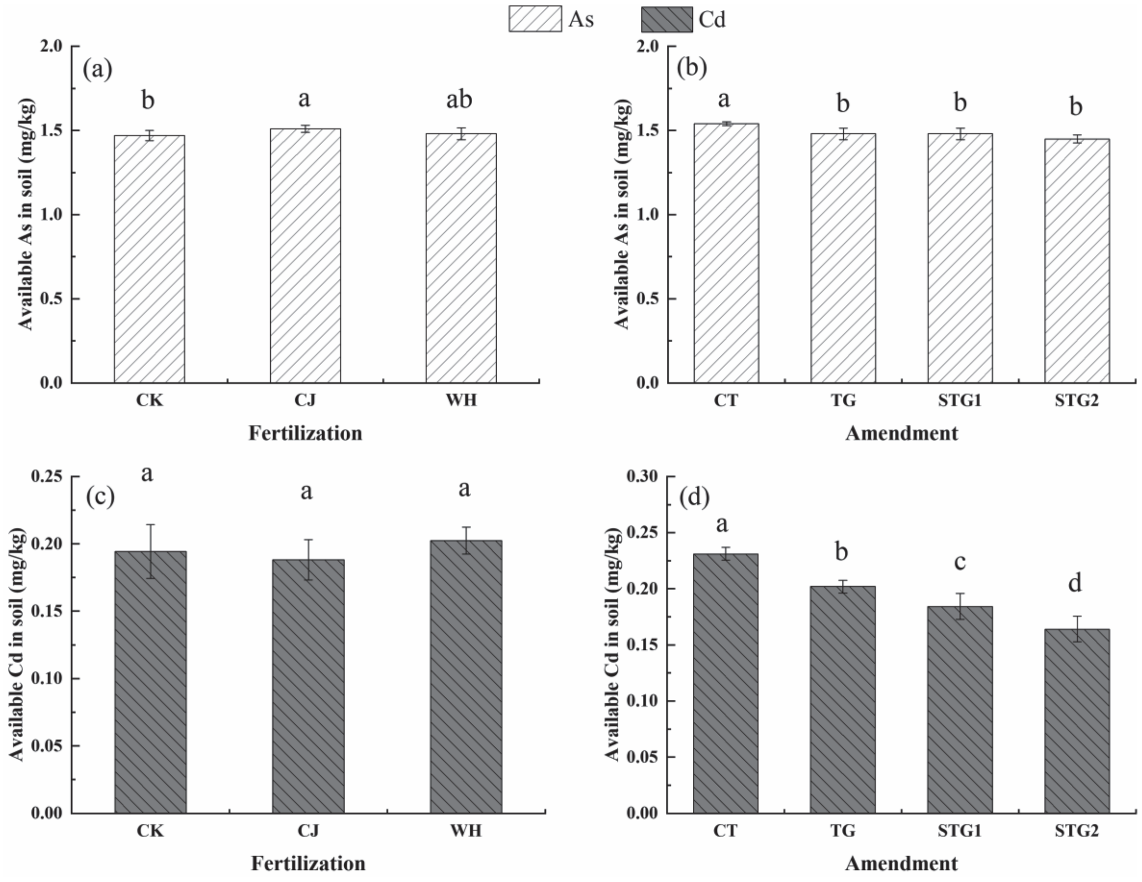

Fig. 2. The available concentration of As and Cd in soil. Different lowercase letters indicate significant differences between treatments ($P<0.05$).

## Growth and Nutrient Concentration of Water Spinach

Fertilization significantly affected water spinach height, dry weight and TK concentration, but had no significant effect on TN and TP (Table 5). The plant height of CJ and WH treatments was significantly higher than that of CK treatments, with an increase of 11.5% and 19.8%, respectively. Compared with conventional fertilization (CK), the addition of slow-release fertilizer (WH) significantly ($p<0.05$) increased the dry weight of water spinach by 29.7%. However, the total potassium concentration of water spinach in CK was the highest at 5.95 g/kg, which was significantly increased by 6.1% compared with CJ, while there was no significant difference between CJ and WH.

Amendments only significantly affected the total nitrogen of water spinach. The total nitrogen

Table 5. Growth and nutrient concentration of water spinach in different treatments.

| Treatment | Height (cm) | D.W. (g/pot) | TN (g/kg) | TP (g/kg) | TK (g/kg) |
|---|---|---|---|---|---|
| CK | 39.98±1.57B | 2.12±0.28B | 31.44±3.23A | 1.31±0.11A | 5.95±0.30A |
| CJ | 44.56±6.87A | 2.33±0.27AB | 31.53±2.72A | 1.34±0.19A | 5.61±0.35B |
| WH | 47.89±3.95A | 2.75±0.69A | 31.41±2.37A | 1.35±0.23A | 5.60±0.22B |
| CT | 45.41±4.87a | 2.44±0.51a | 29.61±3.10b | 1.31±0.17a | 5.76±0.35a |
| TG | 42.91±4.25a | 2.34±0.59a | 31.79±2.32ab | 1.28±0.16a | 5.82±0.26a |
| STG1 | 43.04±3.17a | 2.40±0.62a | 32.67±1.97a | 1.40±0.20a | 5.67±0.32a |
| STG2 | 45.22±8.88a | 2.42±0.43a | 31.78±2.75ab | 1.34±0.19a | 5.63±0.40a |

D.W. means dry weight, TN: Total Nitrogen, TP: Total Phosphorus, TK: Total Potassium. Values are mean±standard deviation. The different capital letters indicate a significant difference between CK, CJ and WH treatments at $P<0.05$. Different lowercase letters indicate significant a difference at $P<0.05$ between CT, TG, STG1 and STG2.

concentration of water spinach under the amendments treatments was 29.61-32.67 g/kg, and the order of total nitrogen concentration in each treatment was STG1> TG>STG2>CT, and STG1 increased by 10.3% compared with TG.

### Concentrations of As and Cd in Water Spinach

The As and Cd concentrations of water spinach with different amendments are shown in Fig. 3. The As concentration in the water spinach in different treatments was 3.40-3.65 mg/kg, and the Cd concentration was 1.68-1.85 mg/kg. Compared to CT treatment, the addition of amendments reduced the concentration of As in water spinach, TG and STG2 significantly ($p<0.05$) reduced plant As concentrations by 6.1% and 6.8%, respectively, while STG1 had no significant effect on plant As concentrations. At the same time, amendments significantly reduced the concentration of Cd in water spinach. TG, STG1, STG2 decreased plant Cd concentrations by 7.6%, 8.9% and 9.3%, respectively, compared with CT. The available As and Cd of the water spinach were 3.44-3.56 mg/kg and 1.71-1.74 mg/kg in the fertilization treatment, and fertilization had no significant effect on As and Cd concentrations in water spinach (Fig. 3).

### Pearson Correlation Analysis of Soil and Water Spinach Related Indicators

The correlation analysis between the indicators was shown in Fig. 4. Soil alkaline-hydrolyzed nitrogen, soil available phosphorus and soil available potassium were extremely significantly positively correlated with each other. In addition, soil As was extremely significantly positively correlated with As and Cd in water spinach, and water spinach Cd was extremely significantly positively correlated with soil Cd and water spinach As.

## Discussion

### Effects of Fertilization and Amendments on Soil Physicochemical Properties

Excessive use of chemical fertilizers would lead to soil acidification [25], and soil pH in all treatments was lower than the background value. Compared with the control, the addition of amendments increased soil pH to varying degrees and slowed soil acidification caused by fertilization. This is mainly due to the large amount of alkaline oxide such as $Fe_2O_3$ contained in TG and STG. Studies have shown that titanium gypsum has high acid neutralization capability and good

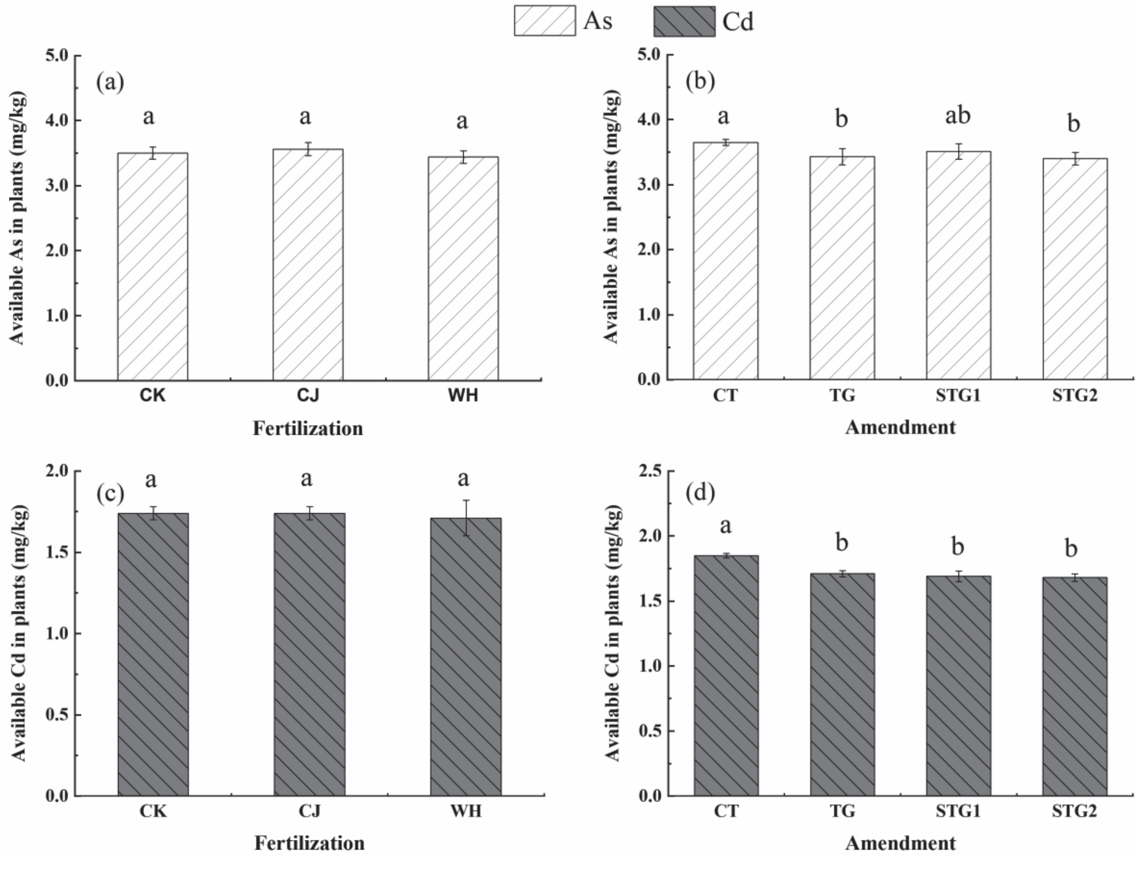

Fig. 3. As and Cd concentration of water spinach. The different lowercase letters indicate significant differences between treatments ($P<0.05$).

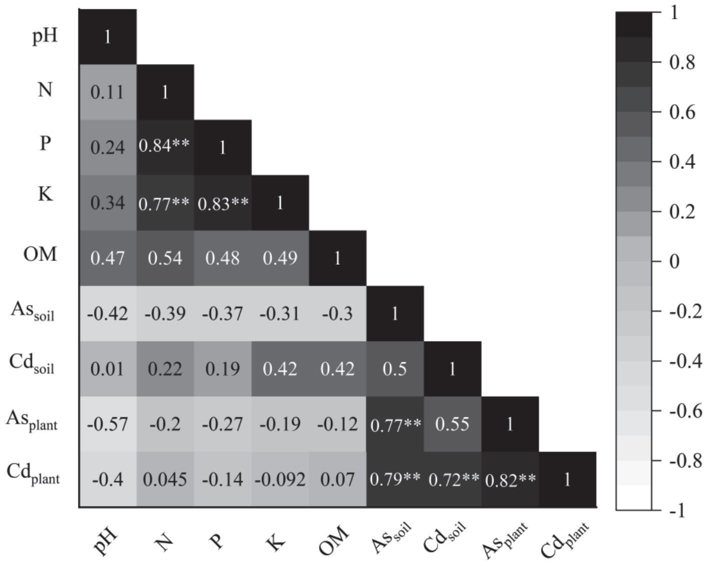

Fig. 4. Pearson correlation analysis of soil and water spinach related indicators. $As_{soil}$: soil As, $Cd_{soil}$: soil Cd, $As_{plant}$: As of water spinach, $Cd_{plant}$: Cd of water spinach. * and ** indicate significant differences between indicators at $P<0.05$ and $P<0.01$, respectively.

resistance to soil acidification [39], and the dihydrate gypsum contained in TG and STG has flocculation effect on heavy metals and can effectively improve soil salinization [40]. In addition, the soil pH in the slow-release fertilizer treatment (WH) was generally higher than that in the other two groups (CK, CJ). It may be attributed to the large amount of active organic matter in the slow-release fertilizer, which enhances the soil's pH buffering capacity [41].

In this study, soil alkali-hydrolyzed nitrogen, available phosphorus, available potassium and organic matter were mainly affected by fertilization, and soil amendments had little effect on them. The concentration of soil nitrogen, phosphorus and organic matter under the slow-release fertilizer treatment was higher than that of the 30% reduction conventional fertilization, which was benefited from the large amount of organic matter contained in the slow-release fertilizer. Studies have shown that organic matter is significantly positively correlated with soil N supply capacity [42], the increase of soil organic matter provides more substrates for microbial activities and accelerates soil N mineralization. And the addition of active organic matter promotes the transformation of microbial phosphorus and improves the bioavailability of phosphorus [43].

## Effects of Fertilization and Amendments on Soil As and Cd

Arsenic is an element between metals and non-metals, and exists mainly in four oxidation states – arsenate (As (V)), arsenite (As (III)), arsenic (As (0)) and arsine (As (-III)), among them, As (III) is more toxic than As (V), and the bioavailability of arsenic increases with increases of soil pH [44]. Cadmium mainly exists in soil solution as $Cd^{2+}$, and partly as Cd-chelates. $Cd^{2+}$ has high activity under acidic conditions, and forms precipitation with $OH^-$, $CO_3^{2-}$, $PO_4^{3-}$, $AsO_4^{3-}$, $Cr_2O_7^{2-}$ and $S^{2-}$ under alkaline conditions [45]. But in the Pearson correlation analysis, soil pH was negatively correlated with the concentrations of As and Cd, which indicated that the concentrations of As and Cd in soil and spinach decreased with increasing pH under conditions of adding amendments and changing fertilization (Fig. 4).

In vegetable fields, TG and STG reduced soil As concentration to varying degrees, and STG2 with high iron oxide concentration had the best effect. In aerobic soil, As (V) accounts for 73-96% of the total As, and in this case, most As (V) is bound to iron oxides, and the increase of iron oxides favors the fixation of As [46, 47], which is consistent with our results. It was pointed out that gypsum and the low pH environment can promote the absorption of Fe to arsenate, and the co-precipitation of $Ca^{2+}$ and iron (III) enhances the removal of As (Jia and Demopoulos 2005). Fertilizers had little effect on As, and the effective arsenic concentration of WH treatment was higher than that of CK. It may be that the addition of slow-release fertilizers increased soil pH and inhibited the fixation of As.

The soil available cadmium concentration decreased significantly after adding amendments, indicating that both TG and STG can effectively fix cadmium. In soil, decreasing pH increases positive charge on soil particles as well as free $H^+$, leading to increased solubility of heavy metal cations [48]. The addition of amendments increased soil pH and suppressed the release of metal cations. Furthermore, some studies have shown that iron-aluminum oxides such as red mud have strong adsorption effect on Cd, and its internal groups can form stable compounds with Cd and fix exchangeable $Cd^{2+}$ [49]. In this study, soil available Cd concentration in STG2 with high iron oxide was lower than other treatments, which indicated that iron oxide played a major role in Cd fixation in alkaline soil. Amendment is the main factor affecting soil As and Cd, and fertilization had no significant effect on soil Cd (Fig. 3, Table 3).

### Effects of Fertilization and Amendments on Nutrients, As and Cd of Water Spinach

The application of slow-release fertilizer increased dry matter content and height of water spinach, and these phenomena were not found in soil amendments. The reason is that slow-release fertilizers provide more organic matter to the soil, improving soil quality and promoting plant growth. Li et al. [30] pointed out that after adding bio-organic fertilizer, the active organic carbon and available potassium in the soil were effectively improved, and the plant height and biomass of water spinach also increased. On plant nutrients, soil amendments increased water spinach TN concentration, because amendments provided large amounts of sulfur, which is a key substance in many enzymes that synthesize proteins [50]. The TK concentration of water spinach in WH and CJ treatments was lower than that in CK, which may be caused by insufficient potassium fertilizer addition. The combination of slow-release fertilizer with STG2 had the best effect on improving the indicators of water spinach.

Soil amendments led to decreased As and Cd content in water spinach. The decrease of As and Cd bioavailability in soil may be the direct factor leading to the decrease of As and Cd in water spinach, which is also reflected in the As and Cd correlation analysis between soil and water spinach (Fig. 4). Naz et al. [51] showed that the uptake of trace metals by water spinach is largely dependent on the bioavailability of these metals. The uptake of cadmium by plants often occurs in the process of transport proteins absorbing certain essential elements, such as $Fe^{2+}$, $Ca^{2+}$ and $Zn^{2+}$, and the supply of these elements can antagonize cadmium, reduce the concentration of cadmium in plants [52]. Plants take up arsenic in different valences in different ways. As (V) enters plant cells mainly through the Pi transport system, and As (III) is mainly absorbed through aquaporins [53]. A study has shown that the sulfur contained in gypsum can promote the lignification of the water spinach cell wall, further preventing the adsorption and fixation of Cd by plants [52].

## Conclusions

The present study showed that both TG and STG could fix As and Cd in soil, and reduced the concentration of As and Cd in water spinach. In the study, STG2 with high iron content was more effective in reducing soil As and Cd. Compared with the CT, TG and STG increased soil pH, slowed down soil acidification caused by fertilization, and increased the TN concentration of water spinach.

Compared with conventional fertilization (CK), reduced fertilization (CJ, WH) had no significant effect on the concentrations of soil alkali-hydrolyzed nitrogen, available phosphorus and available potassium, and the concentrations of N, P and K in water spinach also did not change significantly. Among them, slow-release fertilizer also increased soil organic matter concentration and water spinach biomass. Soil conditioners (TG and STG) synergized with reduced fertilization not only reduced available As and Cd concentration in soil and water spinach, but also maintained soil fertility and plant growth, among them, the combination of slow-release fertilizer and STG2 has the best effect.

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## Conflict of Interest

The authors declare no conflict of interest.

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