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Key factors influencing arsenic phytotoxicity thresholds in south China acidic soils

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ABSTRACT

Arsenic (As) toxicity threshold values (TTVs) for plants are fundamental to both establishing regional As reference values in soil and performing risk assessment. However, TTVs vary with plant species and soil types. In this study, a hydroponic experiment with 16 plant species was conducted to screen the most As-sensitive plant species. The results showed that the EC_{20} (available As concentration at which shoot biomass or height is inhibited by 20%) values were 1.38–104.4 mg L^{-1} for shoot height and 0.24–42.87 mg L^{-1} for shoot fresh biomass. Rice was more sensitive to As toxicity than the other species. Therefore, it was chosen as the ecological receptor in the pot experiment on As phytotoxicity in nine types of soils collected from Fujian Province in South China. The EC_{10} and EC_{20} with respect to rice shoot height were 3.72–29.11 mg kg^{-1} and 7.12–45.60 mg kg^{-1}, respectively. Stepwise regression analysis indicated that free iron oxide concentration is the major factor that affects As bioavailability in soil, and EC_x ($x = 10$, 20, and 50) of soil available As for shoot height was positively related to free iron oxide concentration in soil. In addition, soil cation exchange capacity, clay (<0.002 mm) content, and exchangeable magnesium content are also important factors influencing As phytotoxicity in acidic soils. The regression models can be used to predict As phytotoxicity in acidic soils.

1. Introduction

Soil contamination by heavy metals has become a worldwide environmental problem. Heavy metal reference values in soil are the basis of risk assessment and soil quality and food safety monitoring. However, there is not a commonly accepted methodology for determination of toxicity threshold value (TTV) for plants [1–3], which often results in controversial conclusions. Besides, many factors affect TTV accuracy, including plant species and soil properties. Plant tolerance to heavy metals is related to the uptake kinetics, complexation, transformation, and phytotoxicity of heavy metals [4]. Heavy metal baseline values in soil as indicated by TTVs for plants vary with different ecological receptors. Therefore, it is critical to select appropriate ecological receptors (plants) for determination of heavy metal TTVs in soils. Some international organizations have developed toxicity test standards or guidelines. For example, the United States Environmental Protection Agency [5–12] established eco-toxicological test methodology for terrestrial

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plants, as well as plant toxicity endpoints; International Standardization Organization (ISO) proposed methods for determination of inhibition of root growth [13] and emergence and growth of higher plants [14].

In addition, soil properties, such as organic matter (OM), pH, cation exchange capacity (CEC), soil texture, mineral composition, and redox potential, tend to affect the sorption-desorption behavior and speciation of heavy metals in soil, which in turn affect the availability and eco-toxicity of heavy metals in soil. It was reported that the availability and eco-toxicity of heavy metals are significantly related to soil properties [15–19]. Thus, to establish the reference values of heavy metals in soil by virtue of TTVs for plants, it is important to determine the most important soil properties and their contributions, which can be used to optimize the reference values. EC_x values have been widely adopted to indicate plant response to heavy metal toxicity [20–22]. For example, EC_{10}, the heavy metal concentration at which crop yield is reduced by 10%, has been used as a threshold to indicate heavy metal phytotoxicity [23]. EC_{50} was used by Rooney [24] as a criterion for nickel contamination in soil.

Posing a great threat to environmental quality and human health, arsenic (As) is one of the most toxic elements in soil [25]. Arsenic contamination is widely reported in Asia [26–28], and determination of As reference values can provide a guideline for establishing regional standards of soil environmental quality. The objectives of this work were to: 1) test the sensitivity of representative crop plant species to As toxicity in order to screen the most sensitive species as ecological receptors, and 2) establish the relationships between As toxicity threshold of plants and soil properties at a regional scale.

2. Materials and methods

2.1. Screening the most as-sensitive crop plant species

In this study, 16 plant species commonly consumed by local people were tested for their sensitivity to As toxicity. These plant species, belonging to nine families, are listed in Table 1. Standard methods or guidelines have been developed for phytotoxicity determination and ecological risk assessment, e.g., generic ecological assessment endpoints (GEAEs) for ecological risk assessment [6], root growth inhibition determination [13], and emergence and growth inhibition determination for higher plants. However, few studies have been conducted to compare As sensitivity and tolerance between plant species. Owing to the complexity of heavy metal uptake and tolerance mechanisms in plants, choosing a proper ecological receptor is very important for phytotoxicity threshold determination.

Sodium arsenate dibasic heptahydrate ($Na_2HAsO_4{\cdot}7H_2O$) (Alfa Aesar, A Jahnson Matthey Company) of analytical grade was used in this study. Soil properties, such as soil OM, pH, CEC, inorganic colloids, and Eh, directly or indirectly influence the availability and phytotoxicity of heavy metal(loid)s by influencing their adsorption-desorption and speciation in soil. Arsenic usually exists in soil as arsenate (As(V)) and arsenite (As(III)), with the former being prevalent. Arsenate dissolves more quickly in water than arsenite and has a higher solubility as well. Similarly, it is more readily adsorbed by soil. In this study, arsenate was mixed thoroughly with soil and let age for 30 d to simulate field conditions, which is a common practice widely adopted by researchers worldwide for phytotoxicity studies [[14,29]].

The hydroponic experiment to monitor shoot and root growth of crop plants was implemented according to the ISO 11269-1 [13] and 11269-2 [14] methods with modifications. Seeds of the 16 plant species (a total of 23 plant varieties) were sterilized and

Table 1
Plants tested for As sensitivity.

Family	Species (Latin name)	Variety (Cultivar name)
Brassicaceae	Pakchoi (*Brassica chinensis* L.)	Fallwinter pakchoi (Shanghai Green)
		Spring pakchoi (Xinguan)
		Summer pakchoi (Baicai 17)
	Radish (*Raphanus sativus* L.)	White radish (Short Leaves 13)
		Red radish (Manshenghong)
	Chinese cabbage (*Brassica pekinensis* Rupr.)	Chinese cabbage (Jinfen)
	Leaf mustard (*Brassica juncea* Coss.)	Leaf mustard (Xuelihong)
	Cauliflower (*Brassica oleracea* L. var. *botrytis*)	Cauliflower (Yuxue)
	Kohlrabi (*Brassica oleracea* L. var. *capitata*)	Kohlrabi (Jingfeng 1)
Gramineae	Rice (*Oryza sativa* L.)	Early season rice (Jinshandu 1)
		Middle season rice (Teyou 627)
		Late rice1 (D Qibaoyou 527)
		Late rice2 (II You 153)
Solanaceae	Tomato (*Lycopersicon esculentum* Mill.)	Tomato (Cooperation 903)
	Eggplant (*Solanum melongena* L.)	Eggplant (Zhefengqie 1)
	Pepper (*Capsicum annuum* L.)	Pepper (Huajiao 17)
Compositae	Lettuce (*Lactuca sativa* L.)	Leaf lettuce (Four Seasons 268)
		Stem lettuce (Emperor)
Amarantaceae	Edible amaranth (*Amaranthus mangostanus* L.)	Red edible amaranth (Big Leaf)
Convolvulaceae	Water spinach (*Lpomoea aquatica* Forsk.)	Water spinach (Thailand Willow)
Leguminosae	Cowpea (*Vigna unguiculata* L.)	Red cowpea (Taiwan's Four Seasons)
Umbelliferae	Celery (*Apium graveolens*)	Celery (Jinnan 1)
Cucurbitaceae	Cucumber (*Cucumis sativus* L.)	Cucumber (Jinyou 36)

germinated in darkness in an artificial climate chamber (HP400GS; 22 ± 2 °C, 45% ± 7% relative humidity). Seedlings with two expanded leaves were transplanted and grown in ¼ strength Hoagland nutrient solution for 7 d before grown in nutrient solutions with As levels of 0, 0.1, 1.0, 5.0, 10.0, 20.0, 50.0, 100.0, and 200.0 mg L^{-1} (pH 5.8) under natural sunlight at 22 ± 2 °C. The nutrient solutions were aerated for 10 min every day and renewed every three days. The 14-d experiment was conducted in triplicates [13,14], and in each pot, two plants were grown. The root length, shoot height, and biomass of each plant were recorded [27].

Based on USEPA methods [5–12], the GEAEs chosen for ecological risk assessment included plant growth indices (e.g., root elongation, plant height, biomass, and mortality) and plant physiological indices (e.g., fibrous root growth, root and leaf color, and leaf abscission). As plants differ in their phytotoxicity thresholds, the plant species most sensitive to As toxicity was chosen for As phytotoxicity test.

2.2. Responses of rice to As toxicity in different soils

Rice (*Oryza sativa* L. CV. Diqibaoyou 527) was found to be the most As-sensitive plant species in the hydroponic experiment. The surface (A horizon) soil samples of nine representative soil types were collected from Fujian Province in South China (Table S1). The soil physical and chemical properties and As background values are presented in Table S2.

The soil samples were air-dried and passed through a 2-mm sieve. In each PVC pot (diameter: 12 cm, height: 10 cm), 0.5 kg soil was mixed with KH_2PO_4 and urea at rates of 100 mg N kg^{-1} soil, 80 mg P_2O_5 kg^{-1} soil, and 100 mg K_2O kg^{-1} soil. After 7 d of equilibrium, the soils were spiked with Na_2HAsO_4 solution at 0, 3.0, 5.0, 10.0, 20.0, 40.0, 80.0, 160.0, and 320.0 mg As kg^{-1} soil. Triplicates were set up for each treatment. The soils were moistened to 60% field holding capacity (FHC), covered with polymer films, and incubated at 25–35 °C. Water was added as needed to maintain soil moisture at 60% FHC during the incubation period. After 20 d of incubation, more water was added until saturation, and the soils were incubated for another 10 d.

Then, the pots were placed under natural sunlight at 22 ± 2 °C. According to the ISO 11269-2 method [14], germinated rice seeds were sown in the soils. After emergence, the rice seedlings were thinned to 6 per pot. The soils were watered to FHC. Three weeks after emergence, rice plants were harvested and the shoot height of each plant was recorded.

2.3. Soil and plant analyses

Total As concentration in soil was determined using hydride generation atomic fluorescence spectrometry (AFS 930, Beijing Jitian Instrument Co., China) following method GB/T 17134-1997 [30]. Since soil redox potential affects As availability, fresh soil was used for As extraction with NaH_2PO_4, and available As was quantified according to method DB35/T 859–2008 [31]. Briefly, 5 g of fresh soil, equivalent to approximately 3 g of oven-dried soil, was extracted with 45 mL of 0.5 mol L^{-1} NaH_2PO_4. The suspension was shaken at 250 r min^{-1} and 25 ± 1 °C for 120 min and filtered, and As concentration in the filtrate was determined using an atomic fluorescence spectrometer (AFS 930, Beijing Jitian Instrument Co., China)

Soil physio-chemical properties were determined according to Zeng et al. [32] and NATESC [33]. Soil texture was determined using

Table 2
Regression analysis between As tolerance index (y) of shoot fresh biomass and height and arsenic concentration (x) ($n = 9$).

Crop No.	Crop	Shoot fresh biomass		Shoot height	
		Regression equation	r^2	Regression equation	r^2
1	Fallwinter Pakchoi	$y = 3E\text{-}05\ x^2 - 0.010x + 0.841$	0.944**	$y = 1E\text{-}05x^2 - 0.005x + 0.986$	0.934**
2	Spring Pakchoi	$y = 0.893e^{-0.0065x}$	0.739*	$y = 0.951e^{-0.002x}$	0.694*
3	Summer Pakchoi	$y = 0.893e^{-0.0053x}$	0.860**	$y = 0.944e^{-0.0028x}$	0.932**
4	White Radish	$y = -0.082\ln x + 0.989$	0.835**	$y = -0.056\ln x + 0.997$	0.837**
5	Red Radish	$y = -0.146\ln x + 1.217$	0.912**	$y = -0.042\ln x + 0.946$	0.862**
6	Chinese Cabbage	$y = 0.911e^{-0.0155x}$	0.803**	$y = 1.056e^{-0.0075x}$	0.891**
7	Leaf Mustard	$y = 1.142e^{-0.0083x}$	0.937**	$y = 1.051e^{-0.0035x}$	0.928**
8	Cauliflower	$y = 4E\text{-}05\ x^2 - 0.013x + 1.053$	0.976**	$y = 2E\text{-}05x^2 - 0.008x + 1.048$	0.975**
9	Kohlrabi	$y = 4E\text{-}05\ x^2 - 0.012x + 0.854$	0.912**	$y = 3E\text{-}05x^2 - 0.008x + 1.018$	0.971**
10	Early Season Rice	$y = -0.073\ln x + 0.694$	0.863**	$y = -0.056\ln x + 0.818$	0.893**
11	Middle Season Rice	$y = -0.106\ln x + 0.827$	0.973**	$y = -0.0781\ln x + 0.874$	0.965**
12	Late Rice1	$y = -0.083\ln x + 0.696$	0.802**	$y = -0.051\ln x + 0.856$	0.861**
13	Late Rice2	$y = -0.116\ln x + 0.996$	0.806**	$y = -0.069\ln x + 0.887$	0.827**
14	Tomato	$y = 1.054e^{-0.0183x}$	0.859**	$y = 1.067e^{-0.009x}$	0.821**
15	Eggplant	$y = -0.152\ln x + 0.852$	0.929**	$y = -0.093\ln x + 0.880$	0.892**
16	Pepper	$y = -0.078\ln x + 0.674$	0.912**	$y = -0.040\ln x + 0.893$	0.897**
17	Leaf Lettuce	$y = 4E\text{-}05\ x^2 - 0.011x + 0.887$	0.962**	$y = 2E\text{-}05x^2 - 0.006x + 1.055$	0.959**
18	Stem Lettuce	$y = 3E\text{-}05\ x^2 - 0.011x + 0.989$	0.954**	$y = 1E\text{-}05x^2 - 0.005x + 1.026$	0.969**
19	Edible Amaranth	$y = 0.002\ x^2 - 0.064x + 1.020$	0.899**	$y = 0.002x^2 - 0.055x + 1.116$	0.763*
20	Water Spinach	$y = 1.155e^{-0.0327x}$	0.965**	$y = 0.975e^{-0.0209x}$	0.954**
21	Red Cowpea	$y = 0.0001\ x^2 - 0.022x + 0.908$	0.911**	$y = 5E\text{-}05x^2 - 0.011x + 0.874$	0.779*
22	Celery	$y = 2E\text{-}05\ x^2 - 0.007x + 0.889$	0.785*	$y = 7E\text{-}06x^2 - 0.002x + 0.942$	0.720*
23	Cucumber	$y = -0.177\ln x + 1.058$	0.779*	$y = -0.075\ln x + 1.172$	0.726*

* and ** indicate significance at $P < 0.05$ and $P < 0.01$, respectively.

the hydrometer method. Soil CEC was analyzed by the ammonium acetate method. Potassium dichromate and sulphuric acid were used to determine soil OM content. Determination of free iron oxide followed the dithionite-citrate-bicarbonate (DCB) extraction method. Exchangeable calcium (Ca) and magnesium (Mg) were extracted with ammonium acetate solution and quantified using an atomic absorption spectrometer (AA-6300C, Shimadzu, Kyoto, Japan).

The harvested rice plants were washed in sequence with 0.2% HCl solution, tap water, and deionized water, blotted dry, separated into roots and shoots, and dried in an oven at 70 °C for 48 h. The fresh and dry biomasses of roots and shoots were recorded.

2.4. Statistical analysis

Plant tolerance index (PTI) [34], defined as the ratio of plant growth parameter in the treatment to that in the control, was used to evaluate plant tolerance to As toxicity. Regression analysis between PTI and As concentration was performed with the SPSS 19.0 and Maple 17.0 softwares (Maple soft). Correlation analysis between soil properties and EC*x* was also performed using SPSS 19.0, and the significance level was set at $P < 0.05$.

3. Results

3.1. Plant response to As toxicity

The growth of all 16 plant species was evidently inhibited by As, and the PTI values of shoot fresh biomass and shoot height were significantly negatively related to As level ($P < 0.05$ and 0.01, respectively) (Table 2). The shoots were affected by As in a more intensive and consistent manner than the roots. There were significant differences in response to As toxicity among the plant species ($P < 0.05$). EC_{20}, the As concentration at which plant growth, e.g., shoot fresh biomass and shoot height, is inhibited by 20%, was computed based on the regression model to estimate plant sensitivity to As toxicity. Subsequently, the most As-sensitive plant species was screened as the ecological receptor for the toxicity test.

The EC_{20} values calculated based on the inhibition of shoot height and shoot fresh biomass for the 16 plant species were in the range of 1.38–104.4 mg L^{-1} (median value of 33.40 mg L^{-1}) and 0.24–42.87 mg L^{-1} (median value of 7.83 mg L^{-1}), respectively, showing 76- and 179-fold variations in As sensitivity among the tested plant species (Fig. 1). Shoot height and shoot fresh biomass responded similarly to As toxicity. The shoot fresh biomass toxicity endpoint for inorganic As was lower than shoot height, and the EC_{20} for shoot fresh biomass varied to a larger extent, indicating that shoot fresh biomass is more responsive or susceptible to As toxicity than shoot height. However, shoot height is a better parameter at the early growth stage when the biomass is small. Small biomass implies large standard deviations in measured values, making biomass an inappropriate parameter for As risk assessment. Moreover, rice root biomass, as a potential parameter, may also deviate greatly in measured values since it is not easy to separate the roots from soil without damaging the roots. Thus, shoot height inhibition was selected as an indicator of plant As toxicity.

Based on the EC_{20} and EC_{50} values, rice, pepper (*Capsicum annuum* L.), eggplant (*Solanum melongena* L.), and amaranth (*Amaranthus mangostanus* L.) were more sensitive to As toxicity than the other plant species (Fig. S1). These species can be used as receptor plants for establishing As baseline values. Rice is commonly recognized as an As-sensitive crop. The screening result of this study was consistent with those of other studies [35–39]. Therefore, rice was chosen as the ecological receptor for As TTV determination.

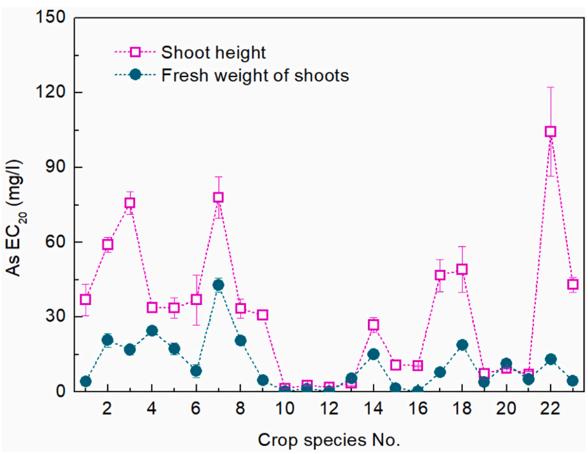

Fig. 1. Arsenic (As) EC_{20} of shoot height and fresh biomass of the 23 crop species. EC_{20} is defined as the concentration of As at which 20% of plant growth is inhibited due to As toxicity.

3.2. The toxic effects of As on rice growth in nine regional soils

Rice was identified as the most sensitive species to As toxicity among the 16 plant species and used as a toxicity receptor. Shoot height of the young rice seedlings was significantly negatively related to As dose ($P < 0.01$) (Fig. 2). When soil As concentration increased from 3.0 to 20.0 mg kg^{-1}, shoot height decreased slightly. However, when soil As concentration increased further from 20.0 to 320 mg kg^{-1}, shoot height decreased sharply. The inhibition of shoot height by As varied greatly among different soils. For example, at 80.0 mg As kg^{-1} soil, rice height was decreased by merely 9% in Fluvo-aquic soil but up to 61% in paddy soil. This suggests that soil type has a significant effect on plant response to As toxicity.

The EC_x ($x = 10$, 20, and 50) values of As in the nine soils were calculated based on the regression equations between the PTI values of seedlings and soil available As concentrations (Table 3). The results showed that the EC_{10}, EC_{20}, and EC_{50} values for rice plant height were 3.72–29.11, 7.12–45.60, and 18.89–76.25 mg kg^{-1}, with variable coefficients of 48%, 32%, and 58%, respectively, indicating that the different properties of different soils influence the availability and toxicity of heavy metals [15–19]. Multivariate regression analysis was performed to identify the key influencing factor of heavy metal phytotoxicity in soil.

3.3. Soil properties affect As threshold values

Univariate regression analysis was performed between soil available As concentration and soil properties (CEC, clay content, free iron oxide, pH, OM, and exchangeable Ca and Mg). The results showed that EC_x was positively correlated with free iron oxide ($P < 0.01$) (Fig. 3) and CEC ($P < 0.05$) (Fig. 4). Free iron oxide could explain 72%, 76%, and 83% of the variations in EC_{10}, EC_{20}, and EC_{50}, respectively, suggesting that free iron oxide content is the predominant soil property influencing the EC_x values of As in the acidic soils in South China.

Soil is a complex system, with multicollinearity existing among soil properties. Although univariate regression analysis can partially explain the relationships between variables, more factors should be included to quantify their contributions to As threshold values. The results of multivariate regression analysis between soil properties and EC_x showed that the correlation coefficients (r) between free iron oxide and EC_{10}, EC_{20}, and EC_{50} were 0.85, 0.87, and 0.91, respectively ($P < 0.01$) (Table 4). Free iron oxide was significantly ($P < 0.05$) correlated with soil properties such as CEC, clay, and exchangeable Mg, with r values of 0.74, 0.66, and 0.70, respectively. There was no significant correlation between EC_x and soil pH, which may be due to the narrow pH range (4.30–6.59) of the acidic soils collected from South China. pH has been reported to affect As sorption in different soils [40].

The results of regression analysis indicated that free iron oxide content is the major soil property that affects EC_x values of As in the nine acidic soils collected from South China. The regression equations between EC_x values (based on soil available As) and free iron oxide content are as follows:

$$[EC_{10}] = -1.45 + 1.16 \times [\text{free iron oxide}]\left(R^2 = 0.72, P = 0.004, n = 9\right) \tag{1}$$

$$[EC_{20}] = 1.66 + 1.79 \times [\text{free iron oxide}]\left(R^2 = 0.76, P = 0.002, n = 9\right) \tag{2}$$

$$[EC_{50}] = 16.37 + 2.72 \times [\text{free iron oxide}]\left(R^2 = 0.83, P < 0.001, n = 9\right) \tag{3}$$

Thus, As threshold concentrations of plants could be corrected for free iron oxide using the above models when applied to the different types of acidic soils in South China.

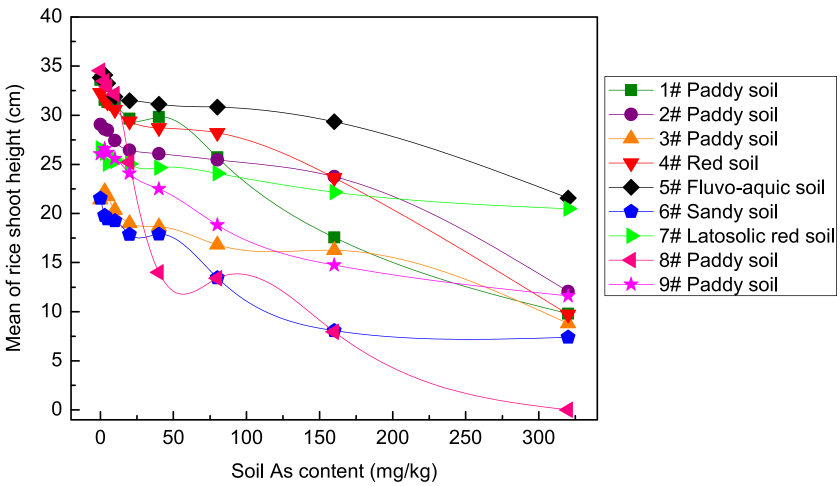

Fig. 2. Dose-response curves of rice shoot growth in nine soils.

Table 3
The regression models between plant tolerance index (y) and soil available As concentration (x) and the EC_{10}, EC_{20}, and EC_{50} values for the nine soils ($n = 9$).

Soil No.	Regression equation	r^2	EC_{10}	EC_{20}	EC_{50}
1	$y = -0.002\ x^2$ - $0.732\ x + 96.461$	0.987**	8.64	21.31	55.50
2	$y = -0.013\ x^2$ - $0.015\ x + 96.156$	0.958**	21.43	35.08	59.69
3	$y = -0.004\ x^2$ - $0.599\ x + 99.705$	0.928**	14.80	27.93	60.06
4	$y = -0.012\ x^2$ - $0.253\ x + 96.529$	0.986**	15.05	28.03	52.60
5	$y = -0.008\ x^2$ - $0.016\ x + 97.161$	0.880**	29.11	45.60	76.25
6	$y = -0.009\ x^2$ - $1.844\ x + 97.311$	0.966**	4.04	9.83	29.72
7	$y = -0.006\ x^2$ - $0.257\ x + 97.395$	0.951**	19.71	36.53	70.00
8	$y = -0.026\ x^2$ - $3.221\ x + 101.620$	0.951**	3.72	7.12	18.89
9	$y = -0.003\ x^2$ - $1.112\ x + 102.750$	0.994**	11.83	21.68	55.43

* and ** indicate significance at $P < 0.05$ and $P < 0.01$, respectively.

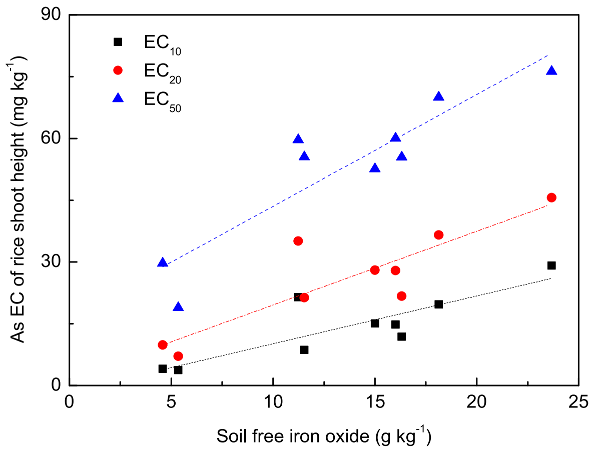

Fig. 3. Relationship between arsenic (As) EC_x ($x = 10, 20, 50$) of rice shoot height and free iron oxides in soils. EC_x is defined as the concentration of As at which x percent of plant growth is inhibited due to As toxicity.

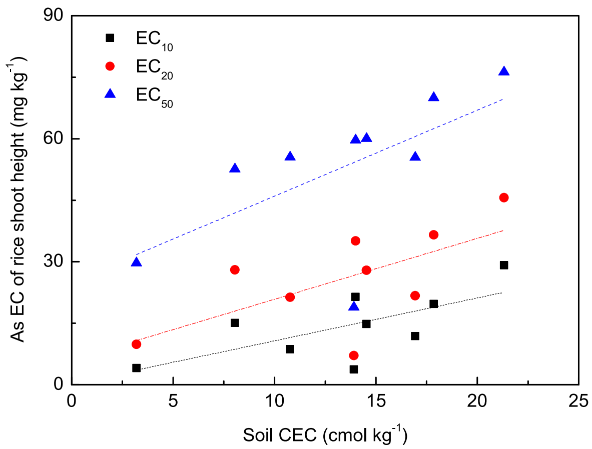

Fig. 4. Relationship between arsenic (As) EC_x ($x = 10, 20, 50$) of rice shoot height and soil cation exchange capacity (CEC). EC_x is defined as the concentration of As at which x percent of plant growth is inhibited due to As toxicity.

3.4. Toxicity threshold value of As in Fujian Province

Soil survey data of 409 samples collected from Fujian Province in South China showed that free iron oxide concentration in the soils ranged between 0.39 and 86.65 g kg^{-1}, with the median and mean values of 11.43 and 13.36 g kg^{-1}, respectively [41]. To establish the threshold values, 90% of the samples were included in the database, corresponding to a cutoff value of 5.62 g kg^{-1} for free iron oxide content (Fig. 5). For EC_x determination, this cutoff value was used for correction of the threshold values using Eqs. 1, 2, and 3 from the

Table 4
Correlation matrix between rice shoot height EC_x ($x = 10$, 20, and 50) based on available soil As extracted by NaH_2PO_4 and soil properties ($n = 9$).

Parameter[a)]	CEC	Clay (<0.002 mm)	pH	Organic matter	Free Fe oxide	Exch. Ca	Exch. Mg	EC_{10}	EC_{20}	EC_{50}
CEC	1.000	0.675*	0.038	0.508	0.742*	0.633*	0.744*	0.683*	0.647*	0.627*
Clay		1.000	−0.256	0.377	0.658*	0.194	0.493	0.571	0.653*	0.728*
pH			1.000	−0.245	0.229	0.612	0.614	0.145	0.149	0.239
Organic matter				1.000	0.226	0.547	0.311	0.074	0.046	0.140
Free Fe oxide					1.000	0.583	0.698*	0.848**	0.874**	0.910**
Exch. Ca						1.000	0.862**	0.393	0.368	0.489
Exch. Mg							1.000	0.581	0.600	0.719*

* and ** indicate significance at $P < 0.05$ and $P < 0.01$, respectively.
[a] CEC = cation exchange capacity; Exch. Ca = exchangeable Ca; Exch. Mg = exchangeable Mg.

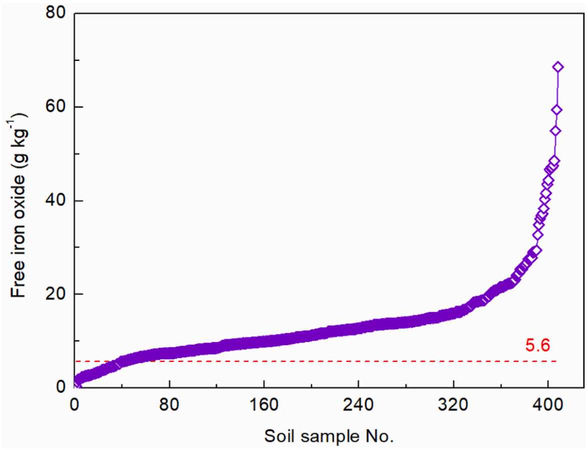

Fig. 5. Free iron oxide contents in the acidic soils of Fujian Province, South China ($n = 408$).

previous section. The EC_{10}, EC_{20}, and EC_{50} values of As for rice grown in Fujian Province were calculated to be 5.1, 10.1, and 41.4 mg kg^{-1}, respectively. These EC_x values can be used as a guideline for soil available As TTV in Fujian Province.

4. Discussion

The hydroponic experiment with 16 plant species showed that rice, pepper, eggplant, and edible amaranth were more sensitive to As toxicity than the other plant species. This finding was consistent with the finding of Rasheed et al. [35], who conducted an experiment to investigate the toxic effects of As on rice and wheat. Williams and coworkers showed that rice was more sensitive to As toxicity than upland crops. Plant sensitivity to heavy metals was related to heavy metal absorption kinetics, internal chelation, biotransformation, biochemical receptor and its regeneration, remediation efficiency, and other mechanisms [4]. For instance, the field experiment of Warren et al. [42] showed that beetroot, calabrese, cauliflower, lettuce, potato, radish, and spinach responded differently to the soil As contamination (748 mg As kg^{-1}). Studies have been limited on the sensitivities of different crop plants to As. Ecological receptor selection is key to establishing the threshold values of heavy metals in soil, because plants differ in their heavy metal absorption and tolerance mechanisms. Therefore, studying the sensitivities of different plants to As toxicity under the same conditions through dose-response experiments is important to screen plants that are highly sensitive to As toxicity as ecological receptors. This has important implications in the establishment of environmental quality criterion of soil As. Considering that rice is very important in feeding the world population and that paddy soil is subjected to alternating wetting and drying, rice has become one of the major crops for studying the pathways of redox-sensitive elements (e.g., As) from soil to human via the food chain [43]. Consequently, rice is commonly adopted as a plant receptor in studying soil As toxicity.

Results from the pot experiment with rice seedlings showed that free iron oxide was the most critical pedological factor that caused the differences in threshold values of soil As toxicity to plants (Table 4). The adsorption capacity of iron oxides can be up to 260 mg g^{-1} for As(III) and 200 mg g^{-1} for As(V), which are 10–15 times greater than those of montmorillonite and kaolinite [44]. Therefore, iron oxides are stronger adsorbents for As(III) and As(V) than clay minerals, controlling As bioavailability in iron oxide-rich acidic soils [36,44,45]. The large adsorption capacity of iron oxides for As is attributed to their high specific surface area and abundant active sites [23,46]. The iron plaque formed on the surface of rice roots is another important mechanism by which iron oxides protect rice plants from As toxicity [37]. Besides free iron oxide, CEC, clay content, and exchangeable Mg are important factors influencing As phytotoxicity in acidic soils. Research by other experts also showed that soil factors, such as OM, pH, CEC, and redox potential, play an important role in the adsorption and desorption processes of As and its speciation in soil. Consequently, these factors directly or indirectly influence the availability and toxicity of As to plants. Meanwhile, these soil factors are interrelated, and their interactions may also have an effect on As toxicity to plants [1,23]. These soil factors are significantly correlated with heavy metal availability and phytotoxicity [20,36,38,47–52]. However, application of toxicity thresholds in establishing soil environmental quality standards requires verification with important soil and environmental factors, including the extent of influence and the normalized relationships with toxicity threshold values, which are necessary to calibrate the determined toxicity thresholds for As and heavy metals. Related research has been conducted. Zhuang et al. [53] established a threshold inference model of soil cadmium based on rice intake in a village in Fuyang, Zhejiang Province, China. The differences in soil properties resulted in a large spatial variation in cadmium threshold, with soil pH being the most influential soil property. Atish et al. [1] reported that CEC and available Ca were the most significant soil properties affecting the plant toxicity threshold of nickel. Herman et al. [18] reported that soil pH and OM content were the best parameters for establishing a copper toxicity model, whereas pH and CEC were the best parameters for a zinc toxicity model. Soil CEC and exchangeable Ca were reported to be the best variables for predicting the threshold value of Co toxicity [2]. Since the key factors influencing plant toxicity thresholds vary with soil contaminants, their normalization relationships may differ from one to another. Therefore, research should be carried out on regional soils with similar transformation and mobility behavior of contaminants to determine the key soil factors that influence toxicity threshold values. A normalization relationship model can be developed and calibrated, and eventually, a regional soil environment benchmark can be established.

5. Conclusions

In the toxicity test of plant seedlings, although both shoot height and biomass can be used to effectively indicate the toxicity of As to crop plants, shoot height was chosen due to its higher measuring accuracy. Based on the test results of 16 plant species, rice, cucumber, red cowpea, edible amaranth, pepper, and eggplant were more sensitive to As toxicity and could be ecological receptors for determining the critical values of As phytotoxicity in soil. Rice is one of the staple foods and a commonly recognized As-sensitive crop. Plenty of research has been conducted on As toxicity to rice. Therefore, rice is a good ecological receptor for As TTV investigation.

The response of rice seedlings to As toxicity varied greatly with soil type. Stepwise regression analysis between the seven soil physio-chemical properties and EC_x showed that free iron oxide in soil is the key factor that affects the critical value of As toxicity to plants. According to the principle that 90% of the agricultural soils should be protected and the free iron oxide contents in agricultural soils of Fujian Province, the EC_{10} and EC_{20} values of As are 5.1 and 10.1 mg kg^{-1}, respectively, based on the regression models.

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Data availability statement

Data will be made available on request.

Authors' contributions

Fenghua Ding: Visualization, Formal analysis, Conceptualization, Writing – original draft. Guo Wang: Conceptualization, Funding acquisition, Project administration, Supervision, Methodology, Resources. Shuxin Liu: investigation, software, Formal analysis, Conceptualization, Writing – review & editing. Zhenli L. He: Formal analysis, Conceptualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2023.e19905.

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