



Metal Extractability Changes in Soils Under Thorny Amaranth

Abdul Kadir Salam*, Hery Novpriansyah, Henrie Bucharie

Department of Soil Science, Faculty of Agriculture, University of Lampung, Indonesia

ARTICLE INFO

Keywords:

Metal Analysis
Metal Extraction
Metal Forms
Tropical Soils

Article history

Submitted: 2022-09-19
Accepted: 2022-12-19
Available online: 2022-12-xx
Published regularly: Dec 2022

* Corresponding Author

Email address:

abdul.kadir@fp.unila.ac.id

ABSTRACT

The different forms of heavy metals may be significantly extracted from soils by plant roots. In a glasshouse experiment, the shifting of soil heavy metal forms under thorny amaranth was examined. To accomplish the research goal, thorny amaranth was planted for four weeks at field water content in soils with varying Cu and Zn contents. Copper and Zn levels in the soil were measured both before and after planting. High soil Cu and Zn levels reduced this plant's height and dry biomasses. Thorny amaranth considerably reduced the exchangeable and available Cu and Zn in the soil. The soil exchangeable and available Cu and Zn had a good correlation with the plant uptakes of these elements. Copper and Zn reductions by planting significantly lower than the available Cu and Zn. A significant portion of the soil exchangeable Cu and Zn shifted to stronger bonding during the incubation time. It was demonstrated that plants absorbed more Cu and Zn from forms different than the soil-exchangeable forms.

How to Cite: Salam, A K., Nopriansyah, H., Bucharie, H. (2022). Metal Extractability Changes in Soils Under Thorny Amaranth. Sains Tanah Journal of Soil Science and Agroclimatology, 19(2): 211-220. <https://dx.doi.org/10.20961/stjssa.v19i2.65456>

1. INTRODUCTION

Heavy metals in soils exist in various forms which determine their availability to plants (Abdu & Mohammed, 2016; Salam, 2017). The soluble metals that include free ions, complexes, and chelates are the most available to plants (Salam, 2017). The exchangeable forms of heavy metals are the soil solid-associated forms of heavy metal that are also available to plants after being released into the soil solution (El-Maghrabi & Mikhail, 2014; He et al., 2020; Salam, 2017). Other forms of heavy metals include the stronger adsorbed heavy metals, soil precipitates, or the secondary soil minerals and primary minerals that contain heavy metals with different solubility (Salam, 2017). These forms of heavy metals may release into the soil solution (soluble forms) and are available to plants regulated by the processes of adsorption-desorption and precipitation-dissolution depending on some determining factors like soil acidity which is controlled by plant root excretion (Chandra Shaha et al., 2012; El-Maghrabi & Mikhail, 2014; He et al., 2020; Salam, 2017; Salam & Helmke, 1998).

These various forms of heavy metals are related in an equilibrium system controlled by various soil chemical processes that include complexation-decomplexation, chelation-dechelation, adsorption-desorption, precipitation-

dissolution, and also oxidation-reduction in soils affected by water saturation (Abdu & Mohammed, 2016; El-Maghrabi & Mikhail, 2014; He et al., 2020; Salam et al., 2022; Salam, 2017; Salam & Sriyani, 2019; Ugwu et al., 2020; Xiao et al., 2017; Zhang et al., 2021). The disturbance on any part of the system may change the size of each form and the affecting chemical reaction. For instance, the uptake of heavy metals by plants may reduce the concentrations of heavy metals in the solution, which may cause the heavy metal precipitates to dissolve under the control of the associated soil mineral solubility product (Salam & Sriyani, 2019). Dissolution could advance until it reaches the solubility constant (Salam, 2017); (Xiao et al., 2017).

The presence of plant roots may probably absorb the available heavy metals that include parts of the soluble form, the exchangeable form, the precipitates, and also the primary minerals depending on the properties of the soil environment affected by plant roots (Dietz et al., 2020). For example, plant roots that effectively lower the soil pH through their excretion may effectively solubilize the precipitates and the primary soil minerals and, therefore, increase the soil heavy soil metals beyond those supplied by the soluble and the exchangeable forms (Bray et al., 2015; More et al., 2020; Ohta & Hiura,

2016; Wu et al., 2018; Yang et al., 2019; Zhang et al., 2021). Therefore, different plants may shift the sizes of soil heavy metal forms, including soil exchangeable form and total available heavy metals

The shifting of the soil heavy metal extractability is suggested to be more significant in the presence of phytoremediator plants that may extract greater amounts of heavy metals (Chen et al., 2019; Guerra Sierra et al., 2021; Ishii et al., 2015; Salam, 2022; A. K. Salam, M. A. Hidayatullah, et al., 2021; Silva et al., 2021; Sumiahadi & Acar, 2018; Sun et al., 2019). These plants may include several weeds like napier grass and several vegetables like lettuce, spinach, amaranth, broccoli, chickpea, sunflowers, cabbage, caisim, water spinach, and willows (Guerra Sierra et al., 2021; Ishii et al., 2015; Matthews-Amune & Kakulu, 2012; Naser et al., 2017). For example, our earlier investigation demonstrated that the absorption of Cu or Zn by napier grass was higher with the soil concentrations of Cu or Zn resulted by amendment with heavy metal-containing waste (A. K. Salam, M. A. Hidayatullah, et al., 2021). Knowledge on this phenomenon is scarce due to limited research, particularly those conducted in tropical soils of Indonesia.

In this research, the shifting of Cu and Zn extractability was investigated by measuring the changes in the soil exchangeable (extracted by dilute salts) and available Cu and Zn (extracted by dilute acids) in heavy metal polluted soils shortly planted with thorny amaranth. The soil exchangeable Cu and Zn was measured by employing 1 N NH₄OAc pH 7.0 and the soil available Cu and Zn by 1 N HNO₃ (A. K. Salam, A. F. Pakpahan, et al., 2021). Knowledge related to the shifting in the various forms of heavy metals in soils is of more importance in the midst of heavy metal contamination and pollution all over the world (Adejoh, 2016; Aksu, 2015; Aprile & De Bellis, 2020; Arif et al., 2016; Arshad et al., 2015; Asati et al., 2016; Ayari et al., 2010; Chibuike & Obiora, 2014; Fang et al., 2016; Febriansyah et al., 2021; Gaza & Kugara, 2018; Jamal et al., 2013; Jankowski et al., 2019; Juel et al., 2018; Khodijah et al., 2019; Kočevár Glavač et al., 2017; Nachana'a Timothy, 2019; A. K. Salam, A. F. Pakpahan, et al., 2021; Sun et al., 2019; Wang & Zhang, 2018).

2. MATERIALS AND METHODS

2.1 The Samples of Soils Polluted with Metals

This research was executed from June to September 2021. The glasshouse experiment was conducted in the College of Al-Madani and all laboratory works were done in the Soil

Science Laboratory the University of Lampung Bandar Lampung. Soil samples with different levels of heavy metals were employed to conduct this research. Composite soil samples were collected at an experimental field at 0-15 cm depth located at 5°20'14.1"S 105°14'39.2"E shown in Figure 1 (A. K. Salam, A. F. Pakpahan, et al., 2021). The experimental fields were set up in 1998 treated with industrial waste containing heavy metals at control level (0 Mg ha⁻¹), Low Heavy Metal (15 Mg ha⁻¹), and High Heavy Metal (60 Mg ha⁻¹) as reported by several researchers (Salam, 2000; A. K. Salam, A. F. Pakpahan, et al., 2021). For the glass-house experiment, soil was prepared as air-dried, ground to pass a 2-mm sieve, and thoroughly mixed sample. To establish oven-dry basis weighings, the water content of the soil sample was also determined. Table 1 contains a list of the soil samples' current properties. All of the soils were clay loam with a cation exchange capacity (CEC) of 9–11 cmol (+) kg⁻¹, a low organic C content, and a slightly low pH.

2.2 The Glass-House Test

As a growing medium, a 200 g of air-dry soil was used. Based on earlier studies, this amount of soil sample was deemed sufficient to support a 4-week growth and development of thorny amaranth. Before planting the thorny amaranth in the potting soil, the seed had been earlier prepared in a different medium and watered to 40%. (the related soil field-water capacity). For four weeks, thorny amaranth was grown in soil samples watered with capillary water provided by a water tank situated beneath the potting soil. Blank potted soil samples were made without any plants to assess the impact of thorny amaranth. Triplicates of each experimental unit were performed.

2.3 The Plant, Soil, and Data Analyses

Plant parts (shoots and roots) were analyzed for Cu and Zn uptakes. Therefore, plant parts were harvested and weighed for their wet-weight and oven-dry weight (after oven-drying at 60 °C for 3 x 24 hours) separately at the end of the planting period. The soil samples were also harvested for Cu and Zn determination by extraction using 1 N HNO₃. The iCE 3000 AAS was employed to measure the metal levels. The pH H₂O (1:2, pH electrode) of the soil, another significant aspect of the soil properties, was also measured. Analyses of the soil were performed both before and after planting. Soil analysis was also conducted on the blank soil without plants. Plant Cu and Zn were determined by the method as used by Silva et al. (2021).



Figure 1. The location of the experimental field

Table 1. Selected soil properties^{1,2}

Heavy Metal Levels	Soil Fractions			pH H ₂ O (1:2)	pH KCl (1:1)	CEC	Organic C
	Sand	Silt	Clay				
Control	33.35±2.46 a	34.54±0.33 a	31.10±2.79 a	5.99±0.06 a	4.76±0.08 b	8.59±1.40 a	15.86±7.01 a
Low	35.31±1.30 a	33.75±0.97 a	30.93±2.27 a	6.10±0.16 a	4.16±0.35 a	11.18±0.37 b	10.97±2.24 a
High	33.64±5.51 a	33.68±7.44 a	32.68±1.93 a	5.95±0.39 a	4.77±0.52 b	10.97±0.16 b	14.01±1.40 a

Remark: ¹Average of 3 replicates, ²Different characters in one column denote significant difference

Table 2. The dry biomasses of thorny amaranth planted in soils polluted with metals¹

Heavy Metal Level	Root	Shoot	Root + Shoot	Root/Shoot
Control	0.18 ± 0.16 ac	0.40 ± 0.26 ac	0.58 ± 0.41 ac	0.42 ± 0.09 b
Low	0.10 ± 0.04 bc	0.33 ± 0.06 bc	0.44 ± 0.09 bc	0.30 ± 0.07 ab
High	0.03 ± 0.01 a	0.13 ± 0.07 a	0.14 ± 0.07 a	0.23 ± 0.07 a

Remark: ¹Different characters in one column denote significant difference

The soil Cu and Zn analyses were conducted using two extractants i.e. 1 N NH₄OAc pH 7 to measure the soil exchangeable Cu and Zn and 1 N HNO₃ to measure the soil available Cu and Zn (A. Salam et al., 2021). The procedure was as followed, 10 g of oven-dry equivalent soil sample was weighed into an erlemeyer flask. After an addition of 20 ml 1 N NH₄OAc pH 7.0 (for measuring the soil exchangeable Cu and Zn) or 20 ml 1 N HNO₃ (for measuring the soil available Cu and Zn), the mixture was then shaken for 2 hours. The Cu and Zn concentration was determined using flame AAS after filtration.

The difference between treatment was evaluated using their standard deviation. The change in the soil exchangeable or the soil available heavy metals (Δ HM) was used to evaluate the changes in the soil exchangeable and available heavy metals by the presence of thorny amaranth. Eq. 1 and Eq. 2 were used to calculate Δ HM.

$$\Delta \text{ Exch. HM} = \text{Exch. HM (Before Planting)} - \text{Exch. HM (After Planting)} \quad [1]$$

$$\Delta \text{ Avail. HM} = \text{Avail. HM (Before Planting)} - \text{Avail. HM (After Planting)} \quad [2]$$

Regression analysis was employed to evaluate the relationship between two important variables, particularly between plant uptakes of heavy metals with the heavy metal availability in soils and also the soil heavy metal relationship with the soil pH. The values of R² were used to determine the variable relationship and the value of "a" (in the equation y = ax + b) to determine sensitivity.

3. RESULT

3.1 The Growth Characteristics of Thorny Amaranth

High heavy metal level (HHM) significantly inhibited the thorny amaranth growth. Low heavy metal (LHM) also slightly affected the plant growth (Figure 2 and Table 2). For example, after 4 weeks, the plant height and dry-weight biomasses of root and shoots slightly decreased by 5.75 and 24.1 % at LHM and significantly decreased by 43.7 and 75.9% at HHM. The waste addition at 15-60 Mg ha⁻¹ negatively affected the thorny amaranth growth currently planted after 23 years of

waste amendment. A similar trend was observed for both shoot and roots.

3.2 The Uptakes of Cu and Zn

Plant uptake of Cu and Zn increased significantly with waste level over four weeks (Table 3). While HHM significantly increased Cu and Zn accumulation by 225 and 141%, LHM only slightly increased Cu and Zn accumulation by 31 and 71% compared to control treatment. Shown by Figure 3 that the Cu and Zn accumulation correlates well with the soil exchangeable and available Cu and Zn. The correlation coefficient of uptake Cu and available Cu or exchangeable Cu (0.707 and 0.626) was higher than those of Zn (0.343 and 0.294). Most of the absorbed Cu and Zn was accumulated in roots as indicated by TF for Cu and Zn < 1,00 (Table 3). The TF for Cu was 0.03-0.05 and for Zn was 0.03-0.06. Thorny amaranth was then classified as phyto-stabilizer.

3.3 The Changes in Soil Exchangeable and Available Cu and Zn

Thorny amaranth significantly lowered the soil exchangeable and available Cu and Zn. The soil exchangeable Cu and Zn decreased by 35.3 and 59.1% at Control, by 50.2 and 86.9 % at LHM, and by 56.1 and 44.5% at HHM (Table 4). Copper and Zn availability in the soil decreased by 40.7 and 51.2% at Control, 45.5 and 47.8% at LHM, and 30.1 and 28.4% at HHM, respectively (Table 5). These values exceeded the declines in soil by thorny amaranth (Table 4 and Table 5). As shown previously, the soil Cu and Zn after planting determine the plant Cu and Zn accumulations which correlated well with both the soil exchangeable and the soil available Cu and Zn (Figure 3). The soil exchangeable and available Cu and Zn negatively correlated with the soil pH, particularly for the soil available Cu and Zn (Figure 4 and Figure 5). The soil available Cu and Zn decreased with the increase in soil pH. The soil pH was shown to slightly decreased in the presence of thorny amaranth (Table 6). The correlation coefficients between the soil available Cu and the soil available Zn with the soil pH were 0.41 and 0.33, respectively. While those of the exchangeable Cu and exchangeable Zn were much lower, 0.03 and 0.09, respectively.

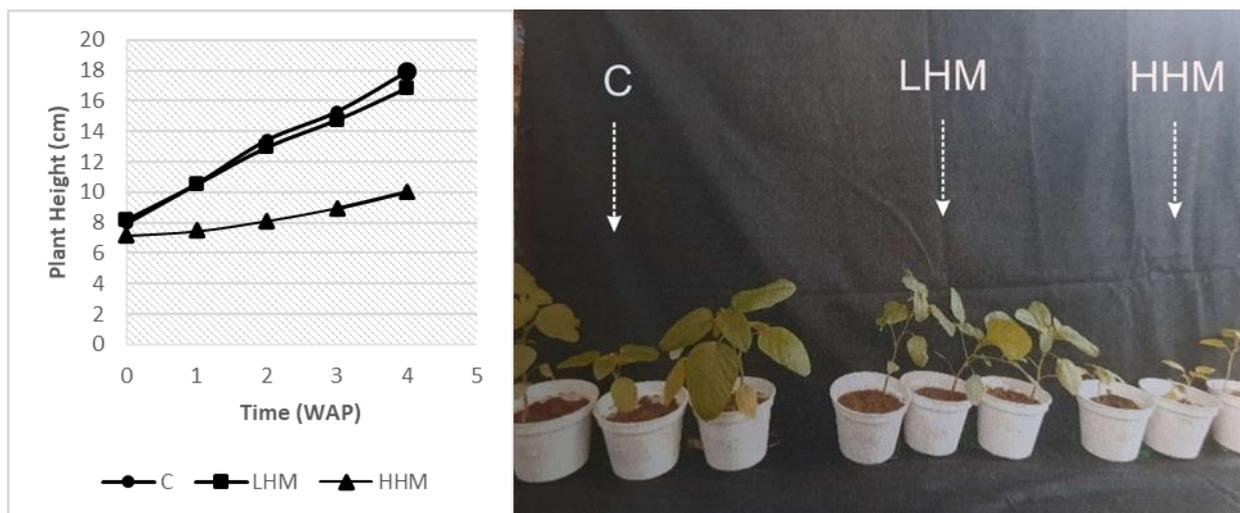


Figure 2. The thorny amaranth growth in the soils polluted with metals (C Control, LHM Low Heavy Metal, HHM High Heavy Metal)

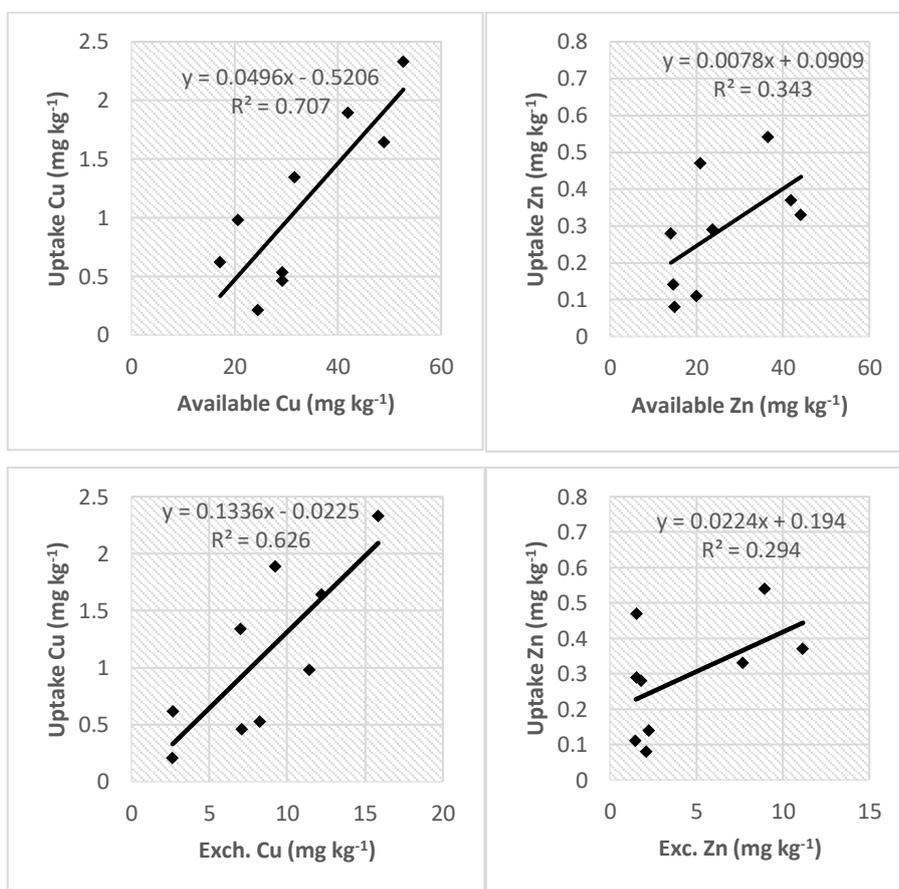


Figure 3. The plant uptake relationship with the soil Cu and Zn

Table 3. The Cu and Zn uptakes by thorny amaranth planted in soils polluted with metals¹

Heavy Metal Level	Cu				Zn			
	Root	Shoot	Root+Shoot	TF	Root	Shoot	Root+Shoot	TF
Control	0.58 ± 0.38 a	0.03 ± 0.01 a	0.60 ± 0.39 a	0.05	0.16 ± 0.10 a	0.01 ± 0.00 a	0.17 ± 0.10a	0.06
Low	0.75 ± 0.48 a	0.03 ± 0.01 a	0.78 ± 0.49 a	0.04	0.28 ± 0.17ab	0.01 ± 0.00 a	0.29 ± 0.18 ab	0.04
High	1.90 ± 0.34 b	0.05 ± 0.02 a	1.95 ± 0.35 b	0.03	0.40 ± 0.11b	0.01 ± 0.00 a	0.41 ± 0.11 b	0.03

Remark: ¹Different characters in one column denote significant difference

3.4 The Shifting of Cu and Zn Extractability

In the presence of thorny amaranth, the decrease in the soil available Cu was significantly higher than that in the absence of plant, ranging from 14.30–25.08 mg kg⁻¹ compared to 1.43–4.88 mg kg⁻¹. On the other hand, the decrease in the soil exchangeable Cu was lower, 3.05–7.53 mg kg⁻¹ in the presence of thorny amaranth compared to 2.73–6.27 mg kg⁻¹ in the absence of plant (Table 7). These findings demonstrate that the soil exchangeable Cu decreased more noticeably than the soil available Cu in the presence of thorny amaranth. In contrast, the decline in the amount of available and exchangeable Cu in the absence of plant was noticeably less pronounced than it was in the presence of thorny amaranth. In the absence of thorny amaranth, the decrease in soil exchangeable and soil available Cu was roughly the same.

A similar phenomenon was demonstrated by soil Zn (Table 8). The decrease in the soil available Zn in soil without plant ranged from 3.79–4.50 mg kg⁻¹, about similar to soil exchangeable Zn ranging from 2.08–6.80 mg kg⁻¹. While the decreases in the soil available Zn in the presence of thorny amaranth ranged from 15.32–19.78 mg kg⁻¹ while that for the soil exchangeable Zn ranged lower from 3.21–10.15 mg kg⁻¹. This data show that in the presence of thorny amaranth, the soil available Zn decreased more significantly than the soil exchangeable Zn. Conversely, the decrease in the soil available Zn in soils without plant were relatively small, comparable to those of the soil exchangeable Zn.

4. DISCUSSION

As predicted based on some previous reports (Asati et al., 2016; Chibuiki & Obiora, 2014; Gill, 2014; Jamal et al., 2013; A. K. Salam, M. A. Hidayatullah, et al., 2021), the growth of thorny amaranth was significantly inhibited by the presence of high concentrations of heavy metals in soils. Similar data were also obtained in earlier studies using the same soil samples on caisim, lettuce, land spinach, napier grass, water spinach, and corn (Salam, 2022; A. K. Salam, M. A. Hidayatullah, et al., 2021; Silva et al., 2021). The high soil Cu and Zn concentrations are correlated with this. The Ni concentration in the waste-amended soils used in this study was quite high, according to our most recent analysis. At least these 3 heavy metals might have significantly lowered the plant height and biomasses including plant roots and shoots (Figure 2 and Table 2). Copper and Zn are actually micronutrients for plants but needed at low quantities. However, due to their high concentrations in soils, higher than the allowable concentrations, their presence was detrimental to this plant. Nickel was found at relatively high concentrations, which may have also inhibited plant growth, despite the fact that it is a trace element that is not a nutrient and is not harmful to plants at low concentrations. These 3 heavy metals were originated from the metal wares industrial waste amended in 1998 or 23 years ago. Heavy metals analysis before waste treatment into the experimented soils in 1998 revealed that the industrial waste was high in Cu and Zn, about 754 and 44.6 mg kg⁻¹, respectively (A. K. Salam, A. F. Pakpahan, et al., 2021). Current analysis of the control, low heavy metal (LHM) and high heavy metal (HHM) field plots show that the

concentration of soil Ni were 46.3, 49.1, and 80.6 mg kg⁻¹, respectively. Nickel was relatively high in HHM, similar to Cu and Zn. In order to give plants the right concentrations of heavy metals and prevent significant disruptions to plant growth, this level must be chemically lowered.

Although there are many different forms of heavy metals in soils, it is suggested that the most vulnerable forms to plant uptake are the soluble forms, the weakly held heavy metals on the soil solid surfaces, and the most soluble precipitates. Therefore, the soil exchangeable form of heavy metals (extracted by 1N NH₄OAc pH 7.00) and the available forms that include all soluble forms (free cations, chelates and complexes), the exchangeable form, and the soluble precipitates (extracted by 1N HNO₃) may greatly affect plant roots. Linear regression analysis with high correlation coefficients were found between the soil available Cu and Zn with the related plant uptake (R²= 0.707 for available Cu and R²=0.343 for available Zn). High correlations were also found for the soil exchangeable Cu and Zn with their uptakes (R²=0.626 for Cu and 0.294 for Zn) (Figure 3). This data show that the soil exchangeable and the soil available Cu and Zn both determine heavy metal effects on plant growth. The negative effects of heavy metals on plants were, therefore, governed by the amounts of metals absorbed by plant roots and shoots, which are determined by the soil available and the soil exchangeable forms.

The values of gradients (“a” in the linear regression of $y = ax + b$) which were higher for Cu than for Zn indicate that this plant was more responsive to Cu than to Zn, meaning that Cu was more detrimental to plants. As shown by Figure 3, the “a” values for Cu are 0.0496 and 0.1336 for the available and exchangeable form, respectively. These values are greater than those for Zn, which are 0.0078 and 0.0294 for the available and exchangeable form. According to some reports, Cu was more toxic than Zn. The values of TF << 1.00 indicate that the greater part of Cu and Zn were accumulated in roots rather than in shoots (Table 3). Therefore, these heavy metals could have destroyed roots more severely.

The absorption of Cu and Zn lowered the soil exchangeable and available Cu and Zn (Table 4 and Table 5). Their concentrations also decreased in the absence of plant, probably due to the shifting of adsorbed heavy metal cations to high energy retention that make heavy metals more difficult to extract. However, these tables show that the decrease in Cu and Zn were much higher in soils also planted with thorny amaranth. Thorny amaranth definitely absorbed the soil Cu and Zn causing the lowering exchangeable and available Cu and Zn. This plant most probably also excretes some organic acid and soil enzymes causing the decrease in soil pH as shown in Table 6 (Bowles et al., 2014; Dietz et al., 2020; Meena & Rao, 2021; Wu et al., 2018). As suggested by some researchers the decrease in soil pH may solubilize the soil structural Cu and Zn and may increase their absorption. The negative relationship with soil pH, particularly of the soil available Cu and exchangeable Cu (Figure 4 and Figure 5) were in accordance with this suggestion (Salam & Helmke, 1998). These relationships may have caused the greater plant absorption and the decreases in the available and exchangeable Cu and Zn in soils planted with thorny amaranth.

Table 4. The changes in the soil exchangeable Cu and Zn by thorny amaranth¹

Time of Analysis	Level of Heavy Metal					
	Control		LHM ²		HHM ³	
	No Plant	With Plant	No Plant	With plant	No Plant	With Plant
..... mg kg ⁻¹						
<i>Cu</i>						
Before Planting	8.64 ± 0.00 b	8.64 ± 0.00 a	14.95 ± 0.00 b	14.95 ± 0.00 b	28.36 ± 0.00 b	28.36 ± 0.00 b
After Planting	5.91 ± 0.81 a	5.59 ± 5.07 a	8.68 ± 1.97 a	7.45 ± 0.70 a	16.27 ± 2.91 a	12.43 ± 3.31 a
<i>Zn</i>						
Before Planting	5.26 ± 0.00 b	5.26 ± 0.00 b	11.69 ± 0.00 b	11.69 ± 0.00 b	16.47 ± 0.00 b	16.47 ± 0.00 b
After Planting	3.18 ± 0.04 a	2.05 ± 0.23 a	6.76 ± 1.52 a	1.54 ± 0.03 a	9.67 ± 2.05 a	9.14 ± 1.94 a

Remark:¹Different characters in one column for each element denote significant difference, ²LHM Low Heavy Metals, ³HHM High Heavy Metal

Table 5. The changes in the soil available Cu and Zn by thorny amaranth¹

Time of Analysis	Level of Heavy Metal					
	Control		LHM ²		HHM ³	
	No Plant	With Plant	No Plant	With Plant	No Plant	With Plant
..... mg kg ⁻¹						
<i>Cu</i>						
Before Planting	35.10 ± 0.00 b	35.10 ± 0.00 b	55.15 ± 0.00 b	55.15 ± 0.00 b	68.50 ± 0.00 b	68.50 ± 0.00 b
After Planting	33.67 ± 0.76 a	20.80 ± 3.65 a	50.27 ± 2.25 a	30.07 ± 1.33 a	64.90 ± 1.75 a	47.86 ± 5.42 a
<i>Zn</i>						
Before Planting	29.92 ± 0.00 b	29.92 ± 0.00 b	41.35 ± 0.00 b	41.35 ± 0.00 b	57.13 ± 0.00 b	57.13 ± 0.00 b
After Planting	26.13 ± 1.82 a	14.60 ± 0.46 a	36.73 ± 0.67 a	21.57 ± 1.99 a	52.43 ± 3.23 a	40.90 ± 3.90 a

Remark: ¹Different characters in one column for each element denote significant difference, ²LHM Low Heavy Metals, ³HHM High Heavy Metal

Table 6. The changes in soil pH by thorny amaranth

Level of Heavy Metal	Planting Treatment	Before Planting	After Planting	ΔpH ¹
Control	No Plant	5.61	5.52	-0.09
	With Plant	5.61	5.59	- 0.02
Low	No Plant	5.66	5.55	-0.11
	With Plant	5.66	5.62	-0.04
High	No Plant	5.67	5.52	-0.15
	With Plant	5.67	5.57	-0.10

Remark: ¹ΔpH = Soil pH (After Planting) – Soil pH (Before Planting)

Table 7. The changes in the soil Cu extractability by thorny amaranth¹

Level of Heavy Metal	Plant Treatment	ΔCu ²			
		Available		Exchangeable	
	 mg kg ⁻¹ % mg kg ⁻¹ %
Control	No Plant	1.43 ± 0.74 a	4.1	2.73 ± 0.81 a	31.1
	With Plant	14.30 ± 3.69 c	40.7	3.05 ± 5.07 a	35.3
Low	No plant	4.88 ± 2.22 b	8.8	6.27 ± 1.98 b	41.9
	With Plant	25.08 ± 1.33 d	45.5	7.50 ± 0.70 b	50.2
High	No Plant	3.60 ± 2.91 ab	5.3	3.69 ± 2.91 a	18.5
	With Plant	20.64 ± 5.46 cd	30.1	7.53 ± 3.32 b	37.7

Remark: ¹Different characters in one column denote significant difference, ²ΔCu = Cu (Before Planting) – Cu (After Planting)

Table 8. The changes in the soil Zn extractability by thorny amaranth¹

Level of Heavy Metal	Plant Treatment	ΔZn ²			
		Available		Exchangeable	
	 mg kg ⁻¹ % mg kg ⁻¹ % ...
Control	No Plant	3.79 ± 1.82 a	12.7	2.08 ± 0.04 a	39.5
	With Plant	15.32 ± 0.44 b	51.2	3.21 ± 0.21 b	61.0
Low	No plant	4.62 ± 0.66 a	11.2	4.90 ± 1.52 bc	42.2
	With Plant	19.78 ± 1.95 c	47.8	10.15 ± 0.03 d	86.8
High	No Plant	4.70 ± 3.24 a	8.23	6.80 ± 2.05 c	41.3
	With Plant	16.23 ± 3.89 bc	28.4	7.33 ± 1.94 c	44.5

Remark: ¹Different characters in one column denote significant difference, ²ΔZn = Zn (Before Planting) – Zn (After Planting)

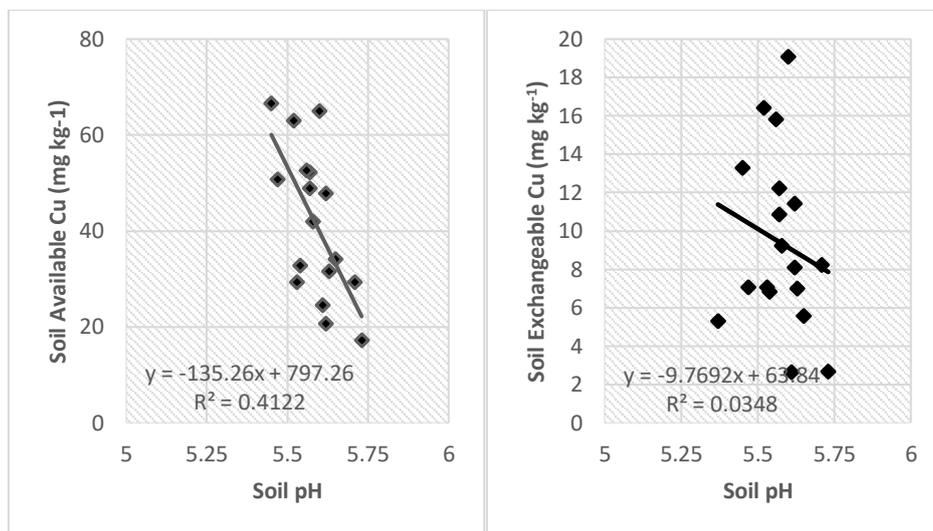


Figure 4. The soil Cu relationship with pH

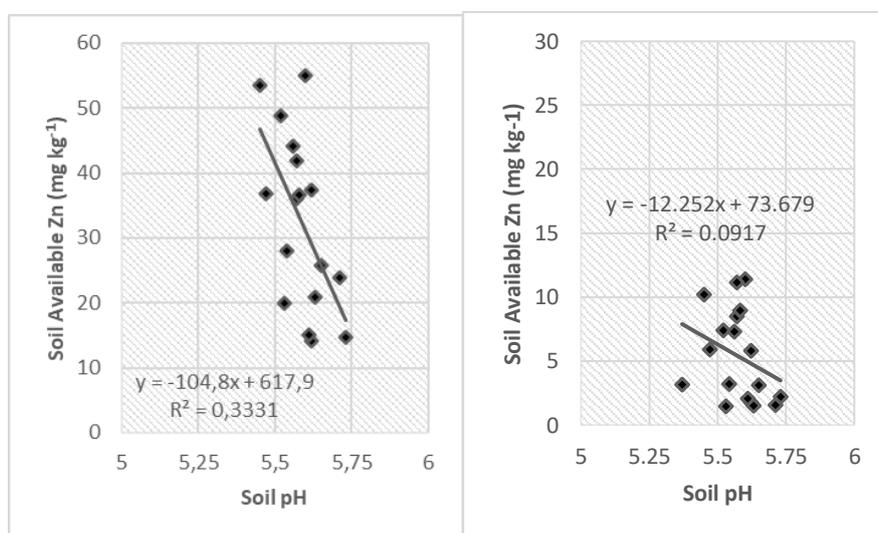


Figure 5. The soil Zn relationship with pH

The accumulated Cu and Zn in plant biomasses may have come from the soil exchangeable Cu and Zn or the soil available Cu and Zn which include the soluble forms, the exchangeable form, and soil precipitates. However, Tables 7 and 8 show that the decrease in soil available and exchangeable Cu and Zn in soils with plants was relatively comparable, whereas the decrease in soil available and exchangeable Cu and Zn in soils without plants was more pronounced. These observations indicate that the available heavy metal predominantly determines plant absorption. Heavy metals were absorbed by plant roots mostly from forms other than the soil exchangeable form. Part of the soil heavy metal precipitates most probably supplied the soil available form for plant absorption.

Therefore, in measuring the availability and also the mobility and toxicity of Cu and Zn and also other heavy metals, the use of dilute acids may give more accurate prediction than the use of dilute salt that measure the soil exchangeable heavy metals. Further research must be conducted to devise the suitable acid concentrations that may give better correlation with particular plant accumulation of heavy metals through correlation studies.

5. CONCLUSION

The growth of all plants as indicated by plant height and dry-biomasses was depressed by the presence of higher soil exchangeable and available Cu and Zn. Thorny amaranth considerably reduced the exchangeable and available Cu and Zn in the soil. The plant Cu and Zn uptakes correlate well with the soil exchangeable and available Cu and Zn. However, a significant part of the soil exchangeable Cu and Zn probably shifted to stronger bonding during the incubation time. It was demonstrated that plants absorbed more Cu and Zn from forms different than the soil-exchangeable forms.

Declaration of Competing Interest

The authors declare that no competing financial or personal interests that may appear and influence the work reported in this paper.

References

- Abdu, N., & Mohammed, I. (2016). Adsorption-solubility equilibria and speciation of Pb, Cd, and Zn in a savanna soil. *Spanish Journal of Soil Science: SJSS*, 6(3), 244-260.

- <https://www.frontierspartnerships.org/articles/10.3232/sjss.2016.v6.n3.06>.
- Adejoh, I. P. (2016). Assessment of heavy metal contamination of soil and cassava plants within the vicinity of a cement factory in north central, Nigeria. *Advances in Applied Science Research*, 7(3), 20-27.
- Aksu, A. (2015). Sources of metal pollution in the urban atmosphere (A case study: Tuzla, Istanbul). *Journal of Environmental Health Science and Engineering*, 13(1), 79. <https://doi.org/10.1186/s40201-015-0224-9>.
- Aprile, A., & De Bellis, L. (2020). Editorial for Special Issue "Heavy Metals Accumulation, Toxicity, and Detoxification in Plants". *International Journal of Molecular Sciences*, 21(11), 4103. <https://doi.org/10.3390/ijms21114103>.
- Arif, N., Yadav, V., Singh, S., Singh, S., Ahmad, P., Mishra, R. K., . . . Chauhan, D. K. (2016). Influence of High and Low Levels of Plant-Beneficial Heavy Metal Ions on Plant Growth and Development [Mini Review]. *Frontiers in Environmental Science*, 4. <https://doi.org/10.3389/fenvs.2016.00069>. English
- Arshad, N., Hamzah, Z., Wood, A. K., Saat, A., & Alias, M. (2015). Determination of heavy metals concentrations in airborne particulates matter (APM) from Manjung district, Perak using energy dispersive X-ray fluorescence (EDXRF) spectrometer. AIP Conference Proceedings, <https://doi.org/10.1063/1.4916878>
- Asati, A., Pichhode, M., & Kumar, N. (2016). Effect of heavy metals on plant growth: An overview. *International Journal of Application or Innovation in Engineering & Management (IJAIEM)*, 5, 79-101. <https://doi.org/10.13140/RG.2.2.27583.87204>.
- Ayari, F., Hamdi, H., Jedidi, N., Gharbi, N., & Kossai, R. (2010). Heavy metal distribution in soil and plant in municipal solid waste compost amended plots. *International Journal of Environmental Science & Technology*, 7(3), 465-472. <https://doi.org/10.1007/BF03326156>.
- Bowles, T. M., Acosta-Martínez, V., Calderón, F., & Jackson, L. E. (2014). Soil enzyme activities, microbial communities, and carbon and nitrogen availability in organic agroecosystems across an intensively-managed agricultural landscape. *Soil Biology and Biochemistry*, 68, 252-262. <https://doi.org/10.1016/j.soilbio.2013.10.004>.
- Bray, A. W., Oelkers, E. H., Bonneville, S., Wolff-Boenisch, D., Potts, N. J., Fones, G., & Benning, L. G. (2015). The effect of pH, grain size, and organic ligands on biotite weathering rates. *Geochimica et Cosmochimica Acta*, 164, 127-145. <https://doi.org/10.1016/j.gca.2015.04.048>.
- Chandra Shaha, S., Kashem, M., & Osman, K. T. (2012). Effect of lime and farmyard manure on the concentration of cadmium in water spinach (*Ipomoea aquatica*). *International Scholarly Research Notices*, 2012. <https://doi.org/10.5402/2012/719432>.
- Chen, X. C., Huang, L., Chang, T. H. A., Ong, B. L., Ong, S. L., & Hu, J. (2019). Plant Traits for Phytoremediation in the Tropics. *Engineering*, 5(5), 841-848. <https://doi.org/10.1016/j.eng.2019.07.019>.
- Chibuike, G. U., & Obiora, S. C. (2014). Heavy Metal Polluted Soils: Effect on Plants and Bioremediation Methods. *Applied and Environmental Soil Science*, 2014, 752708. <https://doi.org/10.1155/2014/752708>.
- Dietz, S., Herz, K., Gorzolka, K., Jandt, U., Bruelheide, H., & Scheel, D. (2020). Root exudate composition of grass and forb species in natural grasslands. *Scientific reports*, 10(1), 1-15. <https://doi.org/10.1038/s41598-019-54309-5>.
- El-Maghrabi, H. H., & Mikhail, S. (2014). Removal of heavy metals via adsorption using natural clay material. *Journal of Environment and Earth Science*, 4(19), 38-46. <https://www.iiste.org/Journals/index.php/JEES/article/view/16620>.
- Fang, H., Huang, L., Wang, J., He, G., & Reible, D. (2016). Environmental assessment of heavy metal transport and transformation in the Hangzhou Bay, China. *Journal of hazardous materials*, 302, 447-457. <https://doi.org/10.1016/j.jhazmat.2015.09.060>.
- Febriansyah, M. R., Septiana, L. M., Supriatin, S., & Salam, A. K. (2021). The patterns of lead and copper levels in the vicinity of heavy metal sources in Lampung, the southern part of Sumatra, Indonesia. IOP Conference Series: Earth and Environmental Science, <https://doi.org/10.1088/1755-1315/739/1/012001>
- Gaza, T., & Kugara, J. (2018). Study of heavy metal air pollution, using a moss (*Grimmia dissimulate*) biomonitoring technique. *Universal Journal of Chemistry*, 6(1), 1-13. <https://doi.org/10.13189/ujc.2018.060101>.
- Gill, M. (2014). Heavy metal stress in plants: a review. *International Journal of Advanced Research (IJAR)*, 2(6), 1043-1055. <https://www.journalijar.com/article/2142/heavy-metal-stress-in-plants-a-review/>.
- Guerra Sierra, B. E., Muñoz Guerrero, J., & Sokolski, S. (2021). Phytoremediation of heavy metals in tropical soils an overview. *Sustainability*, 13(5), 2574. <https://doi.org/10.3390/su13052574>.
- He, G., Zhang, Z., Wu, X., Cui, M., Zhang, J., & Huang, X. (2020). Adsorption of heavy metals on soil collected from Lixisol of typical karst areas in the presence of CaCO₃ and soil clay and their competition behavior. *Sustainability*, 12(18), 7315. <https://doi.org/10.3390/su12187315>.
- Ishii, Y., Hamano, K., Kang, D.-J., Idota, S., & Nishiwaki, A. (2015). Cadmium phytoremediation potential of napiergrass cultivated in Kyushu, Japan. *Applied and Environmental Soil Science*, 2015. <https://doi.org/10.1155/2015/756270>.
- Jamal, Q., Durani, P., Khan, K., Munir, S., Hussain, S., Munir, K., & Anees, M. (2013). Heavy metals accumulation and their toxic effects. *Journal of Bio-Molecular Sciences (JBMS)*, 1(1), 27-36.
- Jankowski, K., Malinowska, E., Ciepiela, G. A., Jankowska, J., Wiśniewska-Kadżajan, B., & Sosnowski, J. (2019). Lead and cadmium content in grass growing near an expressway. *Archives of environmental contamination*

- and toxicology, 76(1), 66-75. <https://doi.org/10-1007/s00244-018-0565-3>.
- Juel, M. A. I., Dey, T. K., Akash, M. I. S., & Kumar, K. (2018). Heavy Metals Phytoremediation Potential of Napier Grass Cultivated in Tannery Sludge. 4th International Conference on Civil Engineering for Sustainable Development (ICCESD 2018),
- Khodijah, N. S., Suwignyo, R. A., Harun, M. U., & Robiartini, L. (2019). Phytoremediation potential of some grasses on lead heavy metal in tailing planting media of former tin mining. *Biodiversitas Journal of Biological Diversity*, 20(7). <https://doi.org/10.13057/biodiv/d200725>.
- Kočevar Glavač, N., Djogo, S., Ražić, S., Kreft, S., & Veber, M. (2017). Kopičenje težkih kovin iz tal v zdravilnih rastlinah. *Arhiv za higijenu rada i toksikologiju*, 68(3), 236-244. <https://doi.org/10.1515/aiht-2017-68-2990>.
- Matthews-Amune, O. C., & Kakulu, S. (2012). Determination of Heavy Metals in Forage Grasses (Carpet Grass (*Axonopus Ompressus*), Guinea Grass (*Panicum Maximum*) and Elephant Grass (*Pennisetum Purpureum*)) in the Vicinity of Itakpe Iron Ore Mine, Nigeria. *International Journal of Pure & Applied Sciences & Technology*, 13(2).
- Meena, A., & Rao, K. (2021). Assessment of soil microbial and enzyme activity in the rhizosphere zone under different land use/cover of a semiarid region, India. *Ecological Processes*, 10(1), 1-12. <https://doi.org/10.1186/s13717-021-00288-3>.
- More, S., Shinde, S., & Kasture, M. (2020). Root exudates a key factor for soil and plant: An overview. *Pharma Innov. J*, 8, 449-459. www.thepharmajournal.com.
- Nachana'a Timothy, E. T. W. (2019). Environmental pollution by heavy metal: an overview. *Chemistry*, 3(2), 72-82. <https://doi.org/10.11648/j.ijec.20190302.14>.
- Naser, H., Rahman, M., Sultana, S., Quddus, M., & Haoque, M. (2017). Remediation of heavy metal polluted soil through organic amendments. *Bangladesh Journal of Agricultural Research*, 42(4), 589-598. <https://doi.org/10.3329/bjar.v42i4.35786>.
- Ohta, T., & Hiura, T. (2016). Root exudation of low-molecular-mass-organic acids by six tree species alters the dynamics of calcium and magnesium in soil. *Canadian journal of soil science*, 96(2), 199-206. <https://doi.org/10.1139/cjss-2015-0063>.
- Salam, A., Milanti, M., Silva, G., Rachman, F., Santa, I., Rizki, D., . . . Sarno, S. (2021). The use of N HNO₃ to determine copper and zinc levels in heavy-metal polluted tropical soils. IOP Conference Series: Earth and Environmental Science, <https://doi.org/10.1088/1755-1315/905/1/012001>
- Salam, A., Rizki, D., Santa, I., Supriatin, S., Septiana, L., Sarno, S., & Niswati, A. (2022). The biochar-improved growth-characteristics of corn (*Zea mays* L.) in a 22-years old heavy-metal contaminated tropical soil. IOP Conference Series: Earth and Environmental Science, <https://doi.org/10.1088/1755-1315/1034/1/012045>
- Salam, A. K. (2000). A four year study on the effects of manipulated soil pH and organic matter contents on availabilities of industrial-waste-origin heavy-metals in tropical soils. *Journal of Tropical Soils*, 6(1), 31-46.
- Salam, A. K. (2017). *Management of heavy metals in tropical soil environment*. Global Madani Press.
- Salam, A. K. (2022). The Potential Roles of Biochar in Restoring Heavy Metal Polluted Tropical Soils and Plant Growth. <https://doi.org/10.5772/intechopen.105791>.
- Salam, A. K., & Helmke, P. A. (1998). The pH dependence of free ionic activities and total dissolved concentrations of copper and cadmium in soil solution. *Geoderma*, 83(3-4), 281-291. [https://doi.org/10.1016/S0016-7061\(98\)00004-4](https://doi.org/10.1016/S0016-7061(98)00004-4).
- Salam, A. K., Hidayatullah, M. A., Supriatin, S., & Yusnaini, S. (2021). The phytoextraction of Cu and Zn by elephant grass (*Pennisetum purpureum*) from tropical soil 21 years after amendment with industrial waste containing heavy metals. IOP Conference Series: Earth and Environmental Science, <https://doi.org/10.1088/1755-1315/637/1/012044>
- Salam, A. K., Pakpahan, A. F., Susilowati, G., Fernando, N., Sriyani, N., Sarno, S., . . . Dermiyati, D. (2021). The Residual Copper and Zinc in Tropical Soil over 21 Years after Amendment with Heavy Metal Containing Waste, Lime, and Compost. *Applied and Environmental Soil Science*, 2021. <https://doi.org/10.1155/2021/7596840>.
- Salam, A. K., & Sriyani, N. (2019). *The Chemistry and Fertility of Soils under Tropical Weeds*. Global Madani Press.
- Silva, G., Aini, S. N., Buchari, H., & Salam, A. K. (2021). The Phytoextraction of Copper from Tropical Soil 21 Years after Amendment with Heavy-Metal Containing Waste. *Journal of Tropical Soils*, 26(1), 11-18. <https://doi.org/10.5400/jts.2021.v26i1.11>.
- Sumiahadi, A., & Acar, R. (2018). A review of phytoremediation technology: heavy metals uptake by plants. IOP Conference Series: Earth and Environmental Science, <https://doi.org/10.1088/1755-1315/142/1/012023>
- Sun, L., Guo, D., Liu, K., Meng, H., Zheng, Y., Yuan, F., & Zhu, G. (2019). Levels, sources, and spatial distribution of heavy metals in soils from a typical coal industrial city of Tangshan, China. *Catena*, 175, 101-109. <https://doi.org/10.1016/j.catena.2018.12.014>.
- Ugwu, E., Tursunov, O., Kodirov, D., Shaker, L., Al-Amiery, A., Yangibaeva, I., & Shavkarov, F. (2020). Adsorption mechanisms for heavy metal removal using low cost adsorbents: A review. IOP Conference Series: Earth and Environmental Science, <https://doi.org/10.1088/1755-1315/614/1/012166>
- Wang, M., & Zhang, H. (2018). Accumulation of heavy metals in roadside soil in urban area and the related impacting factors. *International journal of environmental research and public health*, 15(6), 1064. <https://doi.org/10.3390/ijerph15061064>.
- Wu, L., Kobayashi, Y., Wasaki, J., & Koyama, H. (2018). Organic acid excretion from roots: a plant mechanism for enhancing phosphorus acquisition, enhancing aluminum tolerance, and recruiting beneficial rhizobacteria. *Soil Science and Plant Nutrition*, 64(6),

- 697-704.
<https://doi.org/10.1080/00380768.2018.1537093>.
- Xiao, R., Huang, Z., Li, X., Chen, W., Deng, Y., & Han, C. (2017). Lime and phosphate amendment can significantly reduce uptake of Cd and Pb by field-grown rice. *Sustainability*, 9(3), 430.
<https://doi.org/10.3390/su9030430>.
- Yang, Y., Yang, Z., Yu, S., & Chen, H. (2019). Organic acids exuded from roots increase the available potassium content in the rhizosphere soil: A rhizobag experiment in *Nicotiana tabacum*. *HortScience*, 54(1), 23-27.
<https://doi.org/10.21273/HORTSCI13569-18>.
- Zhang, D., Li, T., Wu, X., & Wang, Y. (2021). Effect of amendments (lime–zeolite–biochar) on the immobilization of Cd and Pb in a contaminated acidic soil. *IOP Conference Series: Earth and Environmental Science*, 742(1), 012016.
<https://doi.org/10.1088/1755-1315/742/1/012016>.