

Chemistry

Chemistry and Ecology

ISSN: 0275-7540 (Print) 1029-0370 (Online) Journal homepage: http://www.tandfonline.com/loi/gche20

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To cite this article: Lei Xu, Hongbiao Cui, Xiangyu Xing, Zhimin Du, Jiani Liang, Xuebo Zheng, Lunguang Yao & Jing Zhou (2018): Long-term stability and risk assessment of copper and cadmium in a smelter-impacted soil treated by four amendments, Chemistry and Ecology, DOI: 10.1080/02757540.2018.1501478

To link to this article: <u>https://doi.org/10.1080/02757540.2018.1501478</u>



Published online: 10 Aug 2018.

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RESEARCH ARTICLE



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Long-term stability and risk assessment of copper and cadmium in a smelter-impacted soil treated by four amendments

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ABSTRACT

In an effort to address public concerns of the long-term stability and ecological risk reduction of Cu and Cd in a farmland located at the Guixi, Jiangxi Province, China, containing $\sim 800 \text{ mg kg}^{-1}$ Cu and 0.8 mg kg⁻¹ Cd soil, were treated *in situ* by attapulgite, apatite, montmorillonite and lime at the rate: 10, 10, 10 and 4 g kg⁻¹ soil, respectively. Field experiment consisted of 2×3 -m plots arranged in a randomised complete block design with each treatment. Soil and plant samples were collected in sixth years post-treatments and analysed for Cu and Cd bioaccessibility, chemical fraction and Cu, Cd concentration in plant tissue. The results indicated that the apatite and lime treatments significantly reduced bioaccessible and exchangeable fractions Cu and Cd in the soil at sixth years post the treatments. Cu and Cd concentration in plant tissue was positively related to the bioaccessibility of Cu and Cd. The treatment used 10 g apatite kg⁻¹ soil appeared to be most effective for overall risk reduction. The Cu and Cd stabilisation and risk reduction by the apatite treatments were accomplished by the induced transformation of labile Cu and Cu species to relatively insoluble forms. This study illustrated that in situ Cu and Cd stabilisation by apatite would be long-term and ecologically safe, which could safeguard human health and ecosystem from Cu and Cd contamination in mining areas.

ARTICLE HISTORY

Received 10 February 2018 Final Version Received 3 July 2018

KEYWORDS

Copper; cadmium; contamination; *in situ* remediation; risk assessment; sustainability

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1. Introduction

Soil contamination with heavy metals is a growing worldwide problem due to intensive urbanisation and industrialisation, many manufacturing and agricultural activities and improper waste disposal [1–3]. Different from organic contaminants, heavy metals cannot be degraded under natural conditions and thus accumulate in soils, posing a great negative impact on the environment [4,5]. The pollution state of Cu and Cd in soil is serious around the world. According to statistics, there are about 470,000 hectares of farmland soil contaminated by heavy metals in Japan, and the heavy metal Cd is responsible for the most serious contamination of agricultural land [6]. In Europe, 2.55 million sites have risk of contamination, and heavy metals such as Cu and Cd are the major contaminated in all of the pollution situation is even more severe, 16.1% soils have been contaminated in all of the contamination [8]. Heavy-metal contamination in soils is of concern in agricultural production due to its adverse effects on food quality, crop growth and environmental health. Therefore, numerous physical, chemical and biological remediation techniques have been developed to minimise the risk of heavy-metal contamination [9].

In situ soil treatments using chemical amendments have been proven to be one of the cheapest and most effective methods to reduce the human and ecological risks associated with soil Cu and Cd, and thus safeguarding humans and ecosystems from contamination [10]. The researches have showed that phosphate, lime, organic matter (OM) and some other natural clay minerals such as montmorillonite and attapulgite have good effect on reducing heavy-metal activity and the risk of pollutants transferring to other media [11–14]. In recent years, Chinese researchers have carried out different scale remediation of Cu- and Cd-contaminated farmland in Huanjiang, Guangxi, Guixi, Jiangxi and Xiangjiang Basin, Hunan which have achieved good stabilisation effect [15-18]. Despite the verified effectiveness of those amendments for reducing the human and ecological risks associated with soil Cu and Cd, the long-term treatment efficacy and the long-term stability of Cu and Cd in contaminated mill waste are largely unknown. Under field conditions, the stability and bioaccessibility of Cu and Cd after treatment not only can be largely affected by plant roots and physicochemical or biological processes in soil, but also can be influenced by atmospheric acid deposition [19,20]. Evaluation of the long-term Cu and Cd stability is critical for assessing the success of the in situ treatment using amendments and its capacity to protect human health and the environment.

The aim of the present study was to evaluate the long-term stability and risk of onetime application of attapulgite, apatite, montmorillonite and lime with *Elsholtzia splendens* in the remediation of heavy-metal-contaminated soils from 2009 to 2015 in the content of (1) the changes of bioaccessibility of copper (Cu) and cadmium (Cd) (CaCl₂-extractable) and soil pH, (2) the variations of soil Cu and Cd chemical fractions, and (3) the biomass and heavy-metal accumulation in *E. splendens*.

2. Materials and methods

2.1. Experimental procedures

The experimental site is located in Guixi, Jiangxi Province, China. A subtropical monsoon climate dominates this area, with an annual average precipitation of 1808 mm. Owing to

farmers using wastewater containing heavy metals discharged by a local copper smelter for irrigation and due to atmospheric metal depositions and waste residue accumulation, more than 130 hm² of surrounding farmland is suffering from issues with heavy-metal pollution (mainly Cu and Cd), resulting in Cd levels in rice exceeding the acceptable level [18]. The concentrations of lead (Pb), zinc (Zn) and arsenic (As) were also determined before the start of the field experiment, and it was found that the concentrations of all of these were below the second grade of soil environmental quality standards in China (GB 15618-1995). The soil texture is sandy loam; the primary pollutants in the soil are Cu and Cd, with concentrations of 797 and 0.843 mg kg⁻¹, respectively. Moreover, the site soil is very acidic (pH = 4.64), having soil organic carbon (SOC) content, available N, available P and available K of 30.8 mg kg⁻¹, 163 mg kg⁻¹, 63.7 mg kg⁻¹ and 66.2 mg kg⁻¹, respectively. CaCl₂ Cu and Cd in the soil were 106 mg kg⁻¹ and 146 µg kg⁻¹, respectively.

Field experiments were conducted in triplicate, and were designed with the land split into randomised blocks or plots. Each plot was 6 m² (3 m \times 2 m) and the plots were separated by plastic plates. The treatments applied were (1) 1% attapulgite (w/w according to the mass of surface 17 cm soil, 20.4 t h^{-1} , the same below), (2) 1% apatite (20.4 t h^{-1}), (3) 1% montmorillonite (20.4 t h^{-1}), (4) 0.4% lime (8.16 t h^{-1}) and (5) the control. The choice of the doses in the experiments was based on our previous experimental results, and the main properties of the materials are listed in Table 1. The soil and the materials were fully mixed with an agricultural harrow, and then irrigated with tap water after the application of the materials (500 t h⁻¹) on 1 December 2009. The seeds of ryegrass are spread evenly in the plot with the amount of $0.02 \text{ kg plot}^{-1}$ on 8 December 2009 with a compound fertiliser (N:P₂O₅:K₂O = 15:15:15) first applied before the plants were planted at a spreading of 0.833 t h^{-1} . No plants were no longer planted in the plots after reaping ryegrass in 16 April 2010, besides, during the study period 2009–2015, these materials were only applied at the start in 2009. E. splendens were planted with a spacing of $30 \text{ cm} \times$ 30 cm (70 plants $plot^{-1}$) in every plot on 26 April 2015, with a compound fertiliser (N: P_2O_5 :K_2O = 15:15:15) first applied before the plants were planted at a spreading of 0.833 t h^{-1} .

2.2. Analytical procedures

The *E. splendens* were harvested in 5 December 2015. Only the above-ground parts (shoots) of the plants were collected. The plant samples were washed with tap water and then rinsed with ultrapure water. Thereafter, the samples were dried to constant weight in an oven at 80°C and stored at room temperature before metal determination.

Amendments	Supplier	pН	Cu (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Particle size (mm)
Attapulgite	Nanjing Ya Dong Austrian Mining Co., Ltd. (Jiangsu, China)	8.02	31.9	0.39	0.11
Apatite	Nanzhang Li Hua Mineral Powder Factory (Hubei, China)	8.40	9.78	0.05	0.15
Montmorillonite	Zhejiang Feng Hong clay Chemical Co., Ltd. (Zhejiang, China)	7.42	2.19	0.09	0.10
Lime	Yingtan Building Materials Market (Jiangxi, China)	12.20	1.36	0.87	0.25

Table 1. Basic physico-chemical properties of the test amendments.

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Soil samples (about 1 kg) were collected from the 0 to 17 cm depth at five representative locations per plot after harvest and then mixed together to form a composite sample. The soil samples were aired and ground for the physicochemical analysis.

Field immobilisation remediation was performed throughout the 3 years, surface soil (0–17 cm) was collected and passed through a 10-mesh sieve for determination of the basic properties and to assess the Cu and Cd concentrations. The Cu and Cd concentrations in the attapulgite (particle size 0.11 mm, Nanjing Ya Dong Austrian Mining Co., Ltd., Jiangsu, China) were 31.9 and 0.39 mg kg⁻¹, respectively; those in the apatite (particle size 0.15 mm, Nanzhang Lihua Mineral Powder Factory, Hubei, China) were 9.78 and 0.05 mg kg⁻¹, respectively; those in the montmorillonite (particle size 0.10 mm, Zhejiang Feng Hong Clay Chemical Co., Ltd., Zhejiang, China) were 2.19 and 0.09 mg kg⁻¹, respectively; while those in the lime (particle size 0.25 mm, Yingtan Building Materials Market, Jiangxi, China) were 1.36 and 0.87 mg kg⁻¹, respectively; the pH values of the attapulgite, apatite, montmorillonite and lime were 8.02, 8.40, 7.42 and 12.2, respectively.

2.3. Analytical method

The soil pH was measured with a glass electrode at a water:soil ratio of 2.5:1 (PHS-2CW-CN, Bante, Shanghai, China). The SOC was determined according to Walkley's method [21]. The soil available potassium(K) was measured in accordance with Zhang's method [22]. The soil available phosphate (P) and nitrogen (N) contents were measured in accordance with Bingham's method [23]. The total Cu and Cd contents in the whole soil and aggregates were digested with nitric acid (HNO₃), hydrofluoric acid (HF) and perchloric acid $(HClO_4)$ (5:10:5 mL) on an electric heating plate, then the solution content was determined using a fame or graphite furnace atomic absorption spectrophotometer (Model 240AA, Varian, CA, USA) [24]. In order to ensure the accuracy of the analysis results, replicate samples, blanks and a certified reference material (GBW07401, provided by the Institute of Geophysical and Geochemical Exploration, Langfang, Hebei Province, China) were included in all the analyses. The available heavy metals in soils were extracted with 0.01 mol L^{-1} CaCl₂ and measured according to Walker's method [25]. A sequential extraction procedure was used to fractionate Cu and Cd according to Cui's method [26], The metals were divided into five operationally defined fractions through the following steps:

- (1) Exchangeable fraction. 16 mL of 1 mol L⁻¹ MgCl₂ (pH 7.0) was added to a 50 mL centrifuge tube containing 2 ± 0.0001 g of soil. The extraction experiment was carried out under stirring at 120 rpm for 2 h at $25 \pm 1^{\circ}$ C, then the suspension was centrifuged for 10 min at 4000 rpm, and finally the supernatant was filtered with a 0.45 mm membrane and transferred into a 15 mL centrifuge tube and stored in refrigerator at 4°C.
- (2) Carbonate-bound fraction. 16 mL of 1 mol L^{-1} CH₃COONa (adjusted to pH 5.0 with CH₃COOH) was added to the residue soil from (1) and shaken in a reciprocating oscillating machine for 3 h at 25 ± 1°C.
- (3) Fe–Mn oxide-bound fraction. The residue from (2) was shaken with 40 mL of 0.04 mol L⁻¹ NH₂OH·HCl in 25% (v/v) CH₃COOH, followed with occasional agitation for 6 h at 96 \pm 3°C.

- (4) Organic matter-bound fraction. 6 mL of 0.02 mol L⁻¹ HNO₃ and 10 mL of 30% H₂O₂ (adjusted to pH 2.0 with HNO₃) were added to the residue from (3), and the mixture was heated at 85 ± 3°C for 2 h in a water bath. Then, 6 mL of 30% H₂O₂ (adjusted to pH 2.0 with HNO₃) was added to the mixture, and the mixture was heated again at 85 ± 3°C for 3 h. After cooling, 10 mL of 3.2 mol L⁻¹ CH₃COONH₄ in 20% (v/v) HNO₃ was added and the mixture was continuously agitated for 30 min at 25 ± 1°C.
- (5) Residual fraction. The residue from (4) was digested with nitric acid (HNO₃), hydrofluoric acid (HF) and perchloric acid (HClO₄) (5:10:5 mL) on an electric heating plate.

2.4. Statistical analysis

All the treatments were carried out in triplicate. The means and standard deviations of each treatment were calculated and presented. Differences between the means of treatments were estimated using one-way ANOVA at a significance level of .05 using SPSS 20.0 (IBM SPSS, Somers, NY, USA) when necessary. All the graphics were using Sigmaplot 12.5.

3. Results and discussion

3.1. Bioaccessibility

Bioaccessible Cu and Cd measurements in the soil presented in Table 2 demonstrated that the amendments treatments of apatite and lime resulted in a significant reduction of Cu and Cd bioaccessibility after 6 years treatments (P < .05). In comparison with the untreated plots (control), average of the reductions were 62.4% and 48.6% for Cu, 11.5% and 5.73% for Cd, respectively, where soil pH was 4.45-5.28. However, the treatments of attapulgite and montmorillonite had little effect on the bioaccessibility of Cu and Cd, and the soil pH after 6 years. Considering the vital role of the soil pH in controlling the soil solubility, mobility and bioavailability of heavy metals [27,28], the treatments of apatite and lime might through strengthening the soil pH, lead to a lowering of the heavy-metal bioavailability. Previous studies showed that all of these four amendments could significantly increase the soil pH and reduce the concentration of bioaccessible Cu and Cd after 1 year of application. This result indicated that the treatment effect of apatite and lime on the reduction of Cu and Cd bioaccessibility was long term, and the Cu and Cd transformation from labile species to relatively insoluble forms as induced by the treatment was maintained 6 years post-treatment. However, the other two amendments had a poor durability which suggested that the persistence of the two materials were worse than apatite and lime. The possible reason is that

Treatment	рН	Total Cu	Total Cd	CaCl ₂ –Cu	CaCl ₂ –Cd
Control	3.96 ± 0.031c	728 ± 118a	638 ± 40.4a	111 ± 6.17ab	157 ± 5.99a
Attapulgite	$4.10 \pm 0.23c$	703 ± 18.7a	619 ± 40.6a	105 ± 3.51b	146 ± 4.10ab
Apatite	5.24 ± 0.049a	798 ± 62.9a	685 ± 87.0a	41.7 ± 8.25c	139 ± 2.36b
Montmorillonite	$4.09 \pm 0.14c$	802 ± 59.1a	754 ± 17.9a	123 ± 7.75a	156 ± 8.58a
Lime	$4.54 \pm 0.083b$	$814 \pm 65.7a$	736 ± 68.2a	57.1 ± 6.90c	148 ± 7.05ab

Different lowercase letters indicate significant differences between treatments after 6 years (n = 3, P < .05).

the immobilisation mechanism of montmorillonite and attapulgite was adsorption because of the large specific surface area as clay minerals [29,30]. At the same time, our experiment was located in a typical acid deposition area where the pH value of precipitation was between 3.62 and 4.98 [31]. A large number of H^+ enter the soil with precipitation, which lead to the competition between the H^+ and heavymetal ion to the active adsorption site of montmorillonite and attapulgite, thus the original adsorbed Cu^{2+} and Cd^{2+} were reactivated again. Some researchers also have noted that heavy metals may release from the amendments and then return to the soil solution over time due to the variations of soil conditions such as pH, temperature and redox potential [32,33]. In addition, the total Cu and Cd concentrations were slightly increased in the repaired soils (Table 2). These results appeared to deviate from the remediation objective of soil remediation, which was to remove heavy metals. Previous studies mostly reported that the total heavy-metal concentration showed no significant difference or only a slight decrease compared to that of the control [12]. This was mainly because of the severe atmospheric deposition in this area, whereby heavy metals could continually enter the soil [34], while the surface runoff and leaching amount varied greatly among the different treatments. This could lead to an increased adsorption and retention capacity of Cu and Cd, and a strengthened immobilisation efficiency of Cu and Cd in the treated soil compared with those in the untreated soil [35,36]. Even so, apatite and lime could still reduce the bioaccessibility of Cu and Cd in the soil. Reduced Cu and Cd bioaccessibility implied that soil Cu and Cd had less probability to be dissolved in the GI tract and absorbed into the bloodstream through oral ingestion, which would potentially lower the human Cu and Cd exposure risk [37].

3.2. Chemical fractionation

The soil heavy-metal forms can be classified into solid and solution phases, where heavy metals are generally more abundant in the solid phase [38]. Solid-phase heavy metals can be further divided into different fractions, whose solubility, mobility, bioavailability and potential environmental toxicity cannot be fully reflected by any single-step extraction method [39]. In the present study, a sequential extraction procedure was used to solve the problem. The different fractions of Cu and Cd in the soil are listed in Tables 3 and 4, respectively. The percentage distributions of the Cu and Cd fractions in the soil are shown in Figure 1(a) and (b), respectively.

Table 5. Effects of amendment application of Cu fractions.						
Treatment	EXC (mg kg ⁻¹)	CA (mg kg ^{-1)}	Fe-Mn (mg kg ⁻¹)	OM (mg kg ⁻¹)	RES (mg kg ⁻¹)	Total (mg kg ⁻¹)
Control	151 ± 21.0a	77.5 ± 8.58c	106 ± 17.8b	137 ± 24.8a	$220 \pm 42.7b$	$728 \pm 118a$
Attapulgite	140 ± 8.31a	104 ± 4.91b	112 ± 8.48ab	135 ± 12.1a	218 ± 5.40b	703 ± 18.8a
Apatite	62.3 ± 2.64b	130 ± 8.96a	134 ± 12.9ab	175 ± 7.61a	298 ± 18.5a	798 ± 63.0a
Montmorillonite	155 ± 15.0a	103 ± 4.92b	123 ± 4.42ab	155 ± 15.0a	248 ± 24.1b	802 ± 59.1a
Lime	70.3 ± 7.56b	114 ± 12.3ab	142 ± 14.3a	176 ± 24.0a	298 ± 17.1a	814 ± 65.7a

 Table 3. Effects of amendment application on Cu fractions.

EXC = exchangeable fraction, CA = carbonate-bound fraction, Fe–Mn = Fe–Mn oxide-bound fraction, OM = organic matterbound fraction, RES = residual fraction.

Different lowercase letters indicate significant differences between treatments after 6 years (n = 3, P < .05).

Treatment	EXC (μ g kg ⁻¹)	CA (µg kg ⁻¹)	Fe–Mn (µg kg ^{–1})	OM (μg kg ⁻¹)	RES (µg kg ⁻¹)	Total (µg kg ⁻¹)
Control	245 ± 7.23b	27.0 ± 2.16b	137 ± 3.22bc	46.9 ± 4.06b	169 ± 9.61c	627 ± 23.2b
Attapulgite	230 ± 9.76abc	15.1 ± 1.43c	127 ± 7.21c	47.1 ± 4.99b	198 ± 6.63bc	618 ± 27.2b
Apatite	209 ± 9.87c	36.0 ± 3.53ab	155 ± 13.0ab	43.4 ± 5.19b	244 ± 27.7ab	689 ± 57.8ab
Montmorillonite	294 ± 13.9a	41.0 ± 2.52a	149 ± 9.39abc	64.3 ± 5.17a	189 ± 9.25c	737 ± 34.9a
Lime	223 ± 8.83bc	44.5 ± 7.89a	160 ± 7.01a	60.3 ± 1.78a	246 ± 21.8a	735 ± 43.0a

Table 4. Effects of amendment application on Cd fractions.

EXC = exchangeable fraction, CA = carbonate-bound fraction, Fe–Mn = Fe–Mn oxide-bound fraction, OM = organic matterbound fraction, RES = residual fraction.

Different lowercase letters indicate significant differences between treatments after 6 years (n = 3, P < .05).



Figure 1. Effects of the amendment application on percentage of (a) Cu and (b) Cd fractions after 6 years. EXC = exchangeable fraction, CA = carbonate-bound fraction, Fe-Mn = Fe-Mn oxides-bound fraction, OM = organic matter-bound fraction, RES = residual fraction.

Without any treatment (i.e. the control group), the residual (RES) fraction of Cu (220 mg kg⁻¹, 32.3%) was the most abundant, followed by the exchangeable (EXC) fraction (151 mg kg⁻¹, 21.7%), the OM fraction (137 mg kg⁻¹, 19.6%), the Fe–Mn fraction

(106 mg kg⁻¹, 15.2%) and the carbonate (CA) fraction (77.5 mg kg⁻¹, 11.2%). With the amendments application (apatite, lime), the EXC fractions were significantly reduced to 62.3 mg kg⁻¹ (7.95%), 70.3 mg kg⁻¹ (8.78%) in turn. However, the same as the bioaccessible Cu, attapulgite and montmorillonite had little effect on the EXC Cu. While the CA fractions were increased to 104 mg kg⁻¹ (14.7%), 130 mg kg⁻¹ (16.6%), 103 mg kg⁻¹ (13.2%) and 114 mg kg⁻¹ (14.2%) with the application of attapulgite, apatite, montmorillonite and lime, respectively. The Fe–Mn fractions were increased to 112 mg kg⁻¹ (15.8%), 134 mg kg⁻¹ (16.7%), 123 mg kg⁻¹ (15.8%) and 142 mg kg⁻¹ (17.7%). The RES fractions were significantly increased to 298 mg kg⁻¹ (16.7%), 298 mg kg⁻¹ (17.8%) with the application of apatite and lime, however, there was no significant difference between the attapulgite, montmorillonite treatment and the control. No significant differences in the OM factions were obtained as compared with the control.

In the untreated soil, the main form of Cd was the RES fraction (169 mg kg⁻¹, 27.0%), similar to the distribution of Cu. Additionally, the EXC fraction (245 mg kg⁻¹, 39.1%) was markedly greater than the CA fraction (27.0 mg kg⁻¹, 4.31%). With the amendment application (apatite and lime), the EXC fractions of Cd were significantly reduced to 209 mg kg⁻¹ (30.3%), 223 mg kg⁻¹ (30.3%), respectively, while the CA, Fe–Mn and RES fractions were markedly increased to 36.0 and 44.5 mg kg⁻¹ (5.22%, 6.05%), 155 and 160 mg kg⁻¹ (22.5%, 21.8%), 244 and 246 mg kg⁻¹ (35.4%, 33.5%), respectively. There was no significant reduction of the other two materials to EXC Cd, there was even a higher EXC Cd in the montmorillonite treatment than the control treatment.

The EXC fraction of heavy metals is considered the most easily mobile and available form, at the same time, it also has the greatest ecological risk [40,41]. Additionally, the carbonate-, Fe–Mn oxide- and OM-bound fractions of heavy metals are potentially available to plants and microorganisms, while the residual fraction was dominant among the five fractions. The EXC and CA-bound fractions of Cu are often present in uncontaminated soil at low concentrations (<10% of the total Cu) [42,43]. In the present study, the EXC and CA-bound fractions of Cu and Cd constituted 21.7% and 39.1% of the total Cu and Cd in the untreated soil, which made it inappropriate for agricultural use. We conjectured that the source of Cu and Cd was mainly artificial and introduced from exhaust gases, dust and wastewater from the nearby copper smelter.

Additionally, the exchangeable fraction can be used to evaluate the bioavailability and environmental toxicity of heavy metals [44,45]. In the current study, the concentrations of Cu and Cd were decreased in the exchangeable fraction but increased in the Fe–Mn oxidebound and RES fractions after the amendment application compared with that of the control. This result illustrated that all three kinds of amendments could significantly reduce the bioavailability of Cu and Cd in the contaminated soil, and thus were effective in remediating the soils contaminated with the two metals. The EXC fraction of Cd (39.1%) was greater than that of Cu (21.7%) in the untreated soil, indicating a higher mobility of Cd than that of Cu at this contaminated site. The EXC fraction (concentrations and percentages) of both Cd and Cu was significantly decreased after apatite and lime addition compared with the untreated soil. This demonstrated that apatite and lime could decrease the bioavailability of Cd and Cu even after 6 years, and thus was effective in remediating soils contaminated with the two metals.

Treatment	Plant height (cm)	Shoot biomass (kg plot ⁻¹)	Shoot Cu concentration (mg kg ⁻¹)	Shoot Cd concentration (µg kg ⁻¹)
Control	-	-	_	-
Attapulgite	-	-	-	-
Apatite	83.3 ± 1.53a	5.22 ± 0.286a	460 ± 35.9b	2.83×10 ³ ± 418b
Montmorillonite	-	-	-	-
Lime	80.7 ± 3.21a	4.77 ± 0.110a	507 ± 20.1a	4.30×10 ³ ± 264a

Table 5. Shoot biomass and Cu and Cd accumulation in each plant after 6 years of remediation.

Different lowercase letters indicate significant differences between treatments in the same year (n = 3, P < .05). – indicates no plant growth.

3.3. Plant uptake

In the present study, the *E. splendens* were able to grow normally in the apatite and lime treatments (Table 5). Although *E. splendens* could grow in treatments of control, attapulgite and montmorillonite at the beginning, the plants grew slowly and gradually withered within 2 months – a typical symptom of plants suffering from heavy-metal poisoning [14]. The *E. splendens* in apatite treatment had the larger biomass and reached 5.22 kg plot⁻¹ in 2015. Cu and Cd concentration in plant tissues indicates the potential risk of soil Cu and Cd to plant community. Data showed that Cu and Cd concentrations in above-ground tissues of *E. splendens* were 460, 507 mg kg⁻¹ and 2.83×10^3 , 4.30×10^3 µg kg⁻¹ for apatite and lime treatment, respectively. Both of Cu and Cd were significantly lower in the apatite treatment than which in the lime treatment. However, there was no significant difference in



Figure 2. Relationship between bioaccessible Cu and Cd in soil and Cu and Cd concentration in plant tissues.

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the effects of these two materials on the absorption of copper and cadmium in plants in 2010 [46], which showed that the persistence of lime was worse than that of apatite. Generally, apatite and lime could effectively maintain the bioavailability of heavy metals at lower level compared with attapulgite and montmorillonite. A number of mechanisms have been proposed to explain the decrease of heavy-metal bioavailability. First of all, the application of the amendments led to the increase of soil pH, which enhanced the negative charges of variably charged colloids in soils such as those in clays, OM, and Fe and Al oxides, and thus resulted in enhancing sorption of heavy metals by soils [47]. Moreover, lime can immobilise Cu and Cd by precipitating as carbonates or hydroxides during solid dissolution and ion exchange [48]. For apatite, the mechanisms for heavy-metal immobilisation included dissolution, ion exchange, complexation and coprecipitation of metals with Ca, and precipitation of some amorphous to poorly crystalline [42,49–51]. It has been reported that the formed metal phosphate was more stable and of higher acid buffering capacity than that of CaCO₃ [52].

The Cu and Cd concentration in tissue was found positively related to Cu and Cd bioaccessibility in the mill waste (Figure 2), with an R^2 of 0.9036 and 0.7251 for Cu and Cd, respectively. This could be accounted for by less amounts of dissolved Cu and Cd in the aqueous phase or less Cu and Cd availability for plant uptake, due to the Cu and Cd immobilisation or solubility reduction induced by the treatments.

4. Conclusions

This field study verified that the application of attapulgite, apatite, montmorillonite and lime to treat Cu and Cd-contaminated farmland could provide a better growth condition for ryegrass in the first year. However, only apatite and lime would result in a long-term reduction in Cu and Cd bioaccessibility, and phytoavailability, which significantly lowers the Cu and Cd hazards to human health and the environment. Meanwhile, apatite had the best durability. Cu and Cd phosphates formed post treatments were relatively insoluble and chemically stable under the surface soil conditions. The risk reductions by the apatite treatment are accomplished by inducing transformation from labile Cu and Cd species to relatively insoluble species through immobilisation or stabilisation reactions. The results demonstrated that the *in situ* farmland remediation treatment apatite and lime could be a long-term effective, environmentally-safe stabilisation technology to safe-guard humans and the environment from Cu and Cd contamination in smelting sites.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

The authors acknowledge the PhD special project of Nanyang Normal University (2018ZX018), Chinese Academy Of Agricultural Sciences (2015BAD05B01), National Natural Science Foundation of China (41571461, 41601340, 41701361), Scientific Research And Service Platform Fund Of Henan Province (2016151) and the fund of scientific and technological innovation team of water ecological security for water source region of mid-line of south-to-north diversion project Henan province (17454).

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