Immobilization of copper in contaminated sandy soils using calcium water treatment residue

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ABSTRACT

Chemical remediation has attracted increasing attention for heavy metal contaminated soils because of its relatively low cost and high efficiency. In this study laboratory incubation and column leaching experiments were conducted to understand the mechanisms of copper (Cu) immobilization by calcium water treatment residue (Ca-WTR) and to estimate the optimal rate for remediating Cu-contaminated soils. The results showed that Ca-WTR amendment significantly raised soil pH and decreased water soluble and exchangeable Cu by 62–90% in the contaminated soils. Most of the bioavailable Cu was converted into more stable Cu fractions, i.e. oxides-bound and residual Cu. The cumulative amount of Cu in the leachate after 10 leaching events was reduced by 80% and 73%, respectively for the two tested soils at the Ca-WTR rate of $20\,g\,kg^{-1}$ for Alfisol and $100\,g\,kg^{-1}$ for Spodosol. These results indicate that Ca-WTR is effective in raising soil pH and converting labile Cu to more stable forms in the contaminated soils. A pH value of 6.5 was found to be critical for lowering Cu availability in the soils. Based on this criterion and pH response curve to Ca-WTR application, the optimal rates of Ca-WTR can be estimated for different Cu-contaminated soils.

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1. Introduction

Copper contamination to agricultural soils is of great concern due to its wide and repeated use in agriculture and horticulture as fertilizers and fungicides [1]. Florida has a long history of citrus production [2]. In the last two decades, increased amounts of Cu-containing fungicides have been used to fight against canker and other diseases in citrus [3].

Soil contamination by Cu causes soil degradation, phytotoxicity, and enhanced Cu transport from land to surface and ground waters [4]. High Cu concentration is toxic to soil organisms, which are the driving forces of nutrient cycling and availability. For example, soil Cu concentration above $400\,mg\,kg^{-1}$ can significantly inhibit the activities of microorganisms, enzymes, and earthworms [5]. Mehlich 3 extractable soil Cu higher than $200\,mg\,kg^{-1}$ has been reported to cause leaf chlorosis (symptom of Cu toxicity) and reduce root and shoot growth of young Hamlin orange trees on Swingle rootstock [2]. Excessive soil Cu led to stippling fruit [6]. Total Cu as high as $300\,mg\,kg^{-1}$ was measured in the sediment from St. Lucie River, South Florida, which is 20–60 times greater than the background Cu levels ($5–15\,mg\,kg^{-1}$) [7,8].

Because of its persistent nature, remediation of Cu-contaminated soils is of great challenge. Physical methods such as scavenging or burial are effective but often too expensive for a large scale remediation. Phytoremediation is cost-effective, but requires a long time to accomplish desired results. Soil amendment that induces chemical stabilization of metals is often used to remediate agricultural soils. The amendments decrease Cu leachability and bioavailability via chemical processes: such as precipitation, adsorption, and/or chelation.

Amendment selection is often based on its affinity for the contaminants. In soils Cu is often associated with carbonates, phosphates, organic matter, oxides, clays and other silicate minerals [4]. Its stability in soil is strongly pH-dependent. Copper is mobile under both acidic and highly alkaline conditions, but its mobility is usually the lowest at neutral to slightly alkaline pH [9,10]. A range of amendments have been tested for Cu immobilization, including fly ash, clay minerals, compost, sewage sludge, peat, phosphates, and lime [11–20]. These materials reduce the mobility and toxicity of Cu to biota by raising soil pH and chemisobing or precipitating Cu in soils [21].

Application of industrial byproducts to agricultural soils to enhance plant growth has been reported extensively [11]. Water treatment residue (WTR) is a byproduct of water purification process, which radically differs from wastewater treatment biosolids in that it contains minimal amounts of contaminants and is eco-
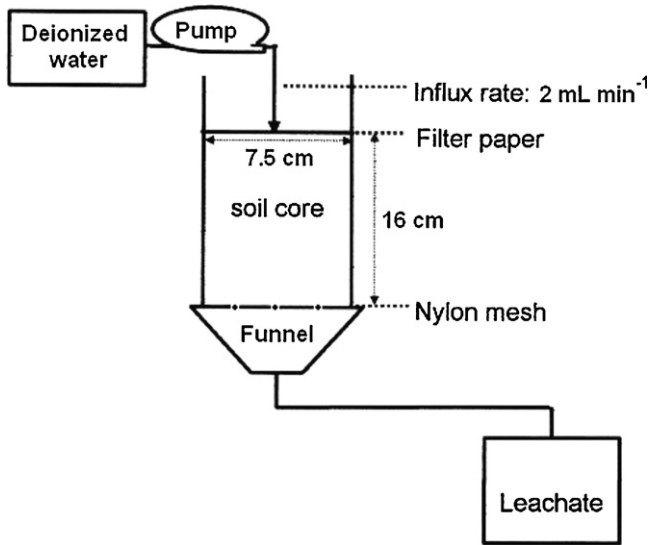
Fig. 1. Schematic diagram of leaching apparatus used in the column leaching study.
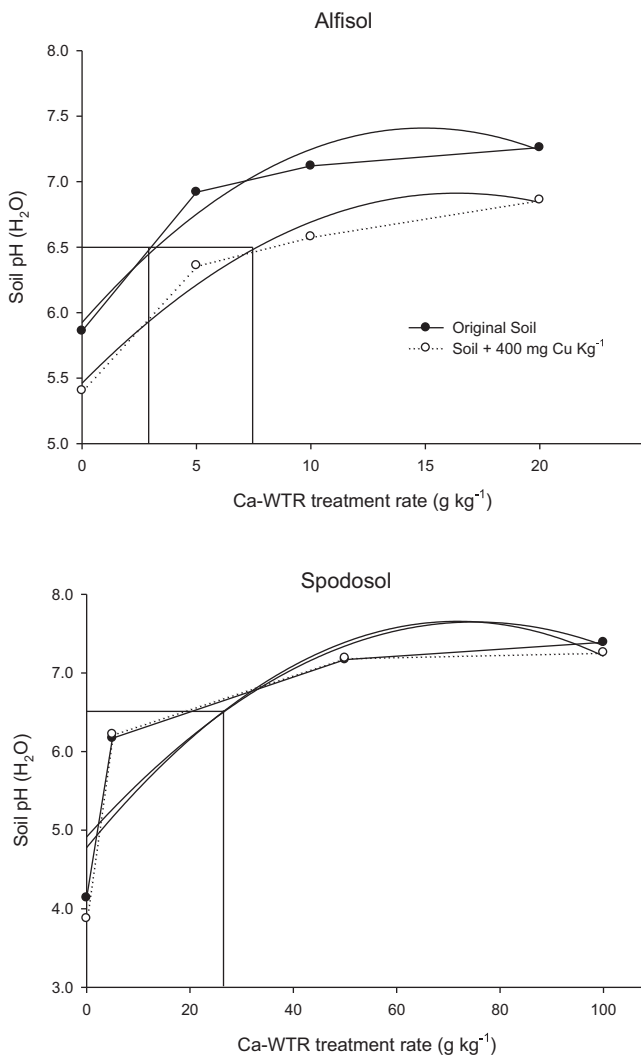
Fig. 2. Relationship between soil pH and Ca-WTR treatment rates.

Table 1
Physicochemical properties of the soils used in this study.

Soils	Cropping history	pH (H_2O)	EC ($\mu S\,cm^{-1}$)	Sand (>0.05 mm) (g kg^{-1})	Silt (>0.002 and <0.05 mm) (g kg^{-1})	Clay (<0.002 mm) (g kg^{-1})	Organic matter (g kg^{-1})	CEC (cmol$_c$/kg)	Recoverable Cu (mg kg^{-1})	Mehlich 3 extractable Cu (mg kg^{-1})
Alfisol	Red GF[a]/1988	5.83±0.14[b]	132±11	986±5	3±1	11±1	3.29±0.97	4.6±0.7	63.2±12.34	39.9±7.86
Spodosol	Red GF/1994	4.18±0.16	194±18	928±8	52±1	20±2	7.24±1.77	11.0±0.4	114±19.41	72.3±5.04
Ca-WTR		9.06±0.01	659±24	12±4	136±5	852±5	–	–	0.40±0.05	0.32±0.05

[a] GF = grapefruit.
[b] Mean ± SE (n = 3).

Fig. 3. Changes of Mehlich 3 extractable Cu in soils with incubation time as affected by Ca–WTR application rates. (A) Alfisol; (B) spodosol; (C) alfisol + 400 mg Cu kg^{-1} soil; (D) spodosol + 400 mg Cu kg^{-1} soil.

friendly. A number of studies have examined the effect of various WTRs on plant growth and nutrient uptake, with few focusing on its use for the remediation of contaminated soils, especially the mechanisms of heavy metal immobilization [22–25].
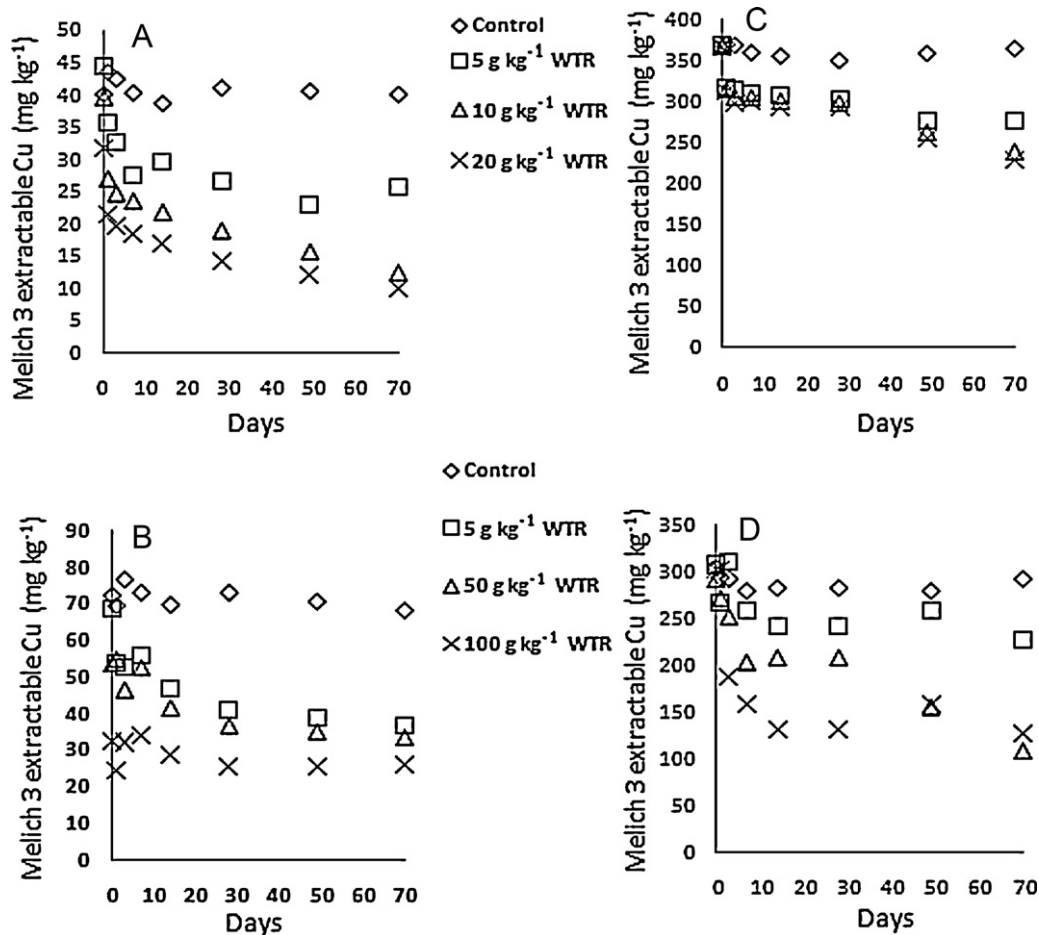
Calcium water treatment residue (Ca–WTR), containing mainly CaCO$_3$ and minor CaO, has potential for reducing Cu loading in surface runoff water in Florida soils due to its strong acid-neutralizing capacity based on our field observations [26]; however, the mechanisms involved are not well understood. In this study, laboratory incubation and column leaching experiments were conducted to understand the mechanisms of Cu immobilization by Ca–WTR and to estimate the optimal rates of Ca–WTR for remediating Cu-contaminated soils.

2. Materials and methods

2.1. Sampling and characterization

Alfisol and Spodosol are the dominant soils under citrus production in the Indian River area, South Florida, which received increased amounts of Cu-based fungicides [27]. The soils used in this study were: Riviera fine sand (Loamy, siliceous, active, hyperthermic Arenic Glossaqualfs) and Wabasso sand (sandy, siliceous, hyperthermic alfic alaquods). Soil samples were randomly collected at 0–15 cm depth from existing citrus groves. For each soil, 10 cores of soil (approximately 2 kg each) were composited to obtain one representative sample. After collection, the soil samples were air-dried, homogenized, and screened through a 2-mm sieve prior

to use. The Ca–WTR used in this study is a byproduct of drinking water purification collected from Utility Authority facility in Fort Pierce, FL.

The pH and EC of soil and Ca–WTR were measured in deionized water at the soil: water ratio of 1:1 and 1:2 using a pH/ion/conductivity meter (DIM 200, Denver Instrument, Denver, CO). Their physical and chemical properties are presented in Table 1. Cation exchange capacity was detected by an ammonium acetate method [28]. Effective calcium carbonate (ECC) of the Ca–WTR was determined by a titration method [29].

The Ca–WTR had an ECC of 95.4%, similar to high grade lime (CaCO$_3$), but its high pH (9.06) suggests that it may also contain a small amount of CaO. Other properties of the Ca–WTR included: electrical conductivity (EC) 659 μS cm^{-1}, Mehlich 3 extractable Ca 292 g kg^{-1}, Cu 0.32 mg kg^{-1} and total recoverable Cu 0.40 mg kg^{-1}, indicating that Ca was the major component and contaminants such as heavy metals were minimal in the Ca–WTR [26].

Particle composition of the soil sample was determined with the micropipette method [30]. Total organic carbon (C) was determined using a C/N analyzer (Vario Max, Elemental Analysensystem GmbH, Hanau, Germany). Total recoverable Cu in soil was determined following EPA method 3050B. Soil extractable Cu and nutrients were determined by Mehlich 3 extraction [31]. Copper concentrations in the digested solutions or extracts were determined using an inductively coupled plasma optical emission spectrometer (ICP–OES, Ultima; J.Y. Horiba Group., Edison, NJ, USA) following EPA method 200.7. The NELAC 2003 standards were followed for quality assurance and quality control of chemical analyses. For Cu analysis with
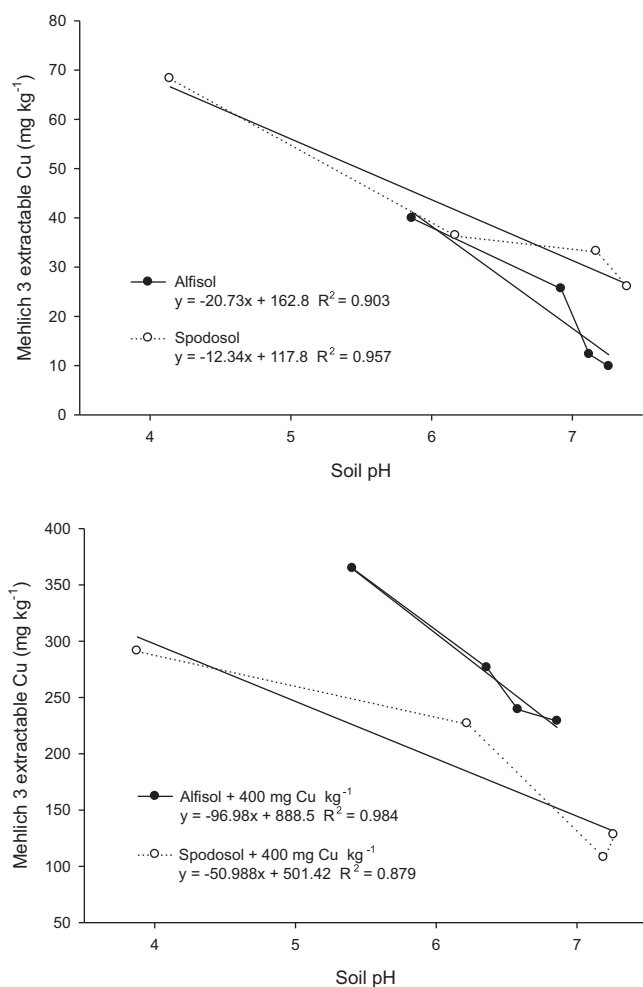
Fig. 4. Relationship between Mehlich 3 extractable Cu and soil pH.

ICP-OES, the detection limit was $0.8\,\mu g\,L^{-1}$ with the recovery of 90–110% for internal quality check and 95–105% for 2nd source QC samples.

2.2. Incubation study

The Spodosol had a lower pH but higher clay, organic matter content, and CEC value than the Alfisol (Table 1), and therefore, more amendment was required to inactivate Cu in the Spodosol than the Alfisol. For the incubation study, 2 kg of soil was mixed with different amounts of Ca-WTR: 0, 5, 10, and $20\,g\,kg^{-1}$ for the Alfisol and 0, 5, 50, and $100\,g\,kg^{-1}$ for the Spodosol. In addition to the original soil which were slightly contaminated, Cu-enriched soils were also used to represent moderately to severely contaminated soils in this area [32]. For preparation of Cu-enriched soil, $Cu(NO_3)_2$ dissolved in deionized water was applied to soil at the amount of $400\,mg\,Cu\,kg^{-1}$ by spraying and thoroughly mixing. The amended soil with moisture content being adjusted to 70% of water holding capacity (WHC) was left for equilibration for 48 h at room temperature (21–25 °C) before Ca-WTR was applied. The amended soils were then incubated at room temperature for 70 days with water content being maintained at 70% of WHC by weighing daily and adding the lost water. There were three replications for each treatment. At the intervals of 0, 1, 3, 7, 14, 28, 42, 70 days of incubation, subsamples were taken and analyzed for pH, and available Cu extracted by Mehlich 3 solution [1:10 ratio of soil/Mehlich 3 solution ($0.2\,M\,CH_3COOH + 0.25\,M$

$NH_4NO_3 + 0.015\,M\,NH_4F + 0.013\,M\,HNO_3 + 0.001\,M$ EDTA, pH 2.0); 5-min reaction time ([31]), including water soluble, exchangeable, part of $CaCO_3$–and organically bound Cu]. At the end of incubation, soil Cu was fractionated into water soluble and exchangeable, carbonate-bound, organic-bound, oxide-bound, and residual Cu fraction following the modified procedure of Amacher [33]. Soil samples (2.0 g) were sequentially extracted with 20 mL of 0.1 M $Mg(NO_3)_2$, 20 mL of 1 M NaOAc, 40 mL of 0.1 M $Na_4P_2O_7$, and 40 mL of 0.2 M ammonium oxalate + 0.2 M oxalic acid, and 0.1 M ascorbic acid (pH 3) for the water soluble and exchangeable, carbonate-bound, organically bound, and oxides-bound Cu fractions, respectively. Residual Cu was calculated by subtracting the sum of the above four fractions from their total recoverable soil Cu concentration.

2.3. Column leaching study

The column leaching experiment was conducted using a randomized complete block experimental design with three replicates for each treatment. A portion of the soil sample (1.0 kg) from the incubation study was packed into a PVC column (40 cm height by 7.5 cm diameter) to reach approximately 16 cm high (Fig. 1). The bulk density of the packed soil column was $1.40\,g\,cm^{-3}$. The bottom of the column consisted of a Plexiglas plate containing several 5-mm-wide holes. The plate was covered with a nylon cloth to prevent soil loss during leaching. The column was tightly closed to prevent the evaporation when leaching was not performed. Two disks of filter paper (Whatman #42) were placed on the top of soil to avoid soil surface disturbance by the influent droplets.

The soil columns were saturated with deionized water from the bottom for three days to reach field-holding capacity prior to leaching. Deionized water 350 mL (approximately 1 pore volume) was applied to the top of each soil column at a rate of $2\,mL\,min^{-1}$ every 3 days using a peristaltic pump. This application rate did not cause water ponding on the top of the column. This leaching was continued for 30 days and a total of 10 leachings were performed. For each leaching event, leachates were collected into a 1000-mL beaker below the soil columns and filtered through a 0.45-μm membrane filter for the analysis of pH, EC, DOC and Cu concentrations. At the end of the leaching experiment, soils were removed from the columns and mixed thoroughly. Subsamples (each 300 g) of the soils were air-dried and analyzed for 0.01 M $CaCl_2$ and Mehlich 3 extractable Cu.

2.4. Statistical analysis

All results were expressed as a mean of three replicates with a standard error, and treatment effects were determined by the analysis of variance according to the general linear model procedure of the Statistical Analysis System (version 8.2, SAS Institute, 2004). Differences among the treatment means were separated by the Least Significant Difference, at the 0.05 probability level.

3. Results and discussion

3.1. Addition of Ca-WTR increased soil pH and decreased extractable Cu

Both the Alfisol and Spodosol soil were acidic, sandy and low in organic matter. Addition of Ca-WTR significantly raised soil pH (Fig. 2), and at $5\,g\,kg^{-1}$, soil pH was elevated to 6.4–6.9 in the Alfisol and to 6.2 in the Spodosol soil.

Increasing Copper amount artificially up to $400\,mg\,kg^{-1}$ decreased soil pH by 0.26–0.45 units (Fig. 2). The mechanisms of pH decrease from external Cu loading or contamination are related

Table 2
Fractionation of Cu in the soils amended with different Ca-WTR rates after the ten leaching events.

Treatment Rates	Cu (mg kg^{-1})					Cu (%)				
	Exchangeable	Carbonate bound	Organically bound	Oxide bound	Residual	Exchangeable	Carbonate bound	Organically bound	Oxide bound	Residual
Original Alfisol (g kg^{-1})										
0	2.92	4.16	32.19	8.00	15.92	4.62	6.58	50.94	12.66	25.20
5	1.09	6.53	26.15	12.53	16.90	1.73	10.33	41.38	19.82	26.74
10	1.06	4.72	24.20	14.64	18.59	1.68	7.47	38.29	23.16	29.41
20	0.96	4.57	23.87	16.75	17.05	1.52	7.23	37.77	26.50	26.97
LSD$_{0.05}$	0.12	2.11	9.97	4.94	3.95					
Original Spodosol										
0	2.85	3.96	72.34	9.62	24.73	2.51	3.49	63.73	8.48	21.79
5	1.08	7.82	59.71	17.07	27.81	0.95	6.89	52.61	15.04	24.50
50	0.99	7.32	54.66	18.69	31.84	0.87	6.45	48.16	16.47	28.05
100	1.02	4.49	56.01	19.45	32.54	0.90	3.96	49.35	17.13	28.67
LSD$_{0.05}$	0.22	2.96	13.27	5.74	4.86					
Cu enriched Alfisol										
0	55.81	75.35	98.48	125.86	107.71	12.05	16.27	21.26	27.17	23.25
5	3.25	106.79	93.73	152.34	107.09	0.70	23.05	20.23	32.89	23.12
10	2.07	89.94	79.11	173.60	118.47	0.45	19.42	17.08	37.48	25.58
20	1.67	52.18	88.98	181.98	138.38	0.36	11.27	19.21	39.29	29.87
LSD$_{0.05}$	2.85	46.2	8.97	38.56	9.74					
Cu enriched Spodosol										
0	65.31	51.47	230.78	59.94	106.00	12.72	10.02	44.94	11.67	20.64
5	6.69	95.31	250.45	65.95	95.09	1.30	18.56	48.77	12.84	18.52
50	2.87	63.20	213.96	108.95	124.52	0.56	12.31	41.67	21.22	24.25
100	2.55	35.39	204.50	128.30	142.76	0.50	6.89	39.83	24.98	27.80
LSD$_{0.05}$	4.11	24.6	19.64	24.58	19.54					

to the replacement of exchangeable H$^+$/Al^{3+} on clay minerals and oxides. Similar results were reported by Yu et al. [34] in red soils, in which adsorption of one mole of Cu^{2+} resulted in the release of 1.1–2.6 mole of proton (H$^+$), depending on soil properties such

as contents of clay minerals and oxides and on Cu^{2+} adsorption mechanisms.

Higher application rates of Ca-WTR resulted in higher soil pH (Fig. 2). At 20 g kg^{-1} and 100 g kg^{-1} (equivalent to field application
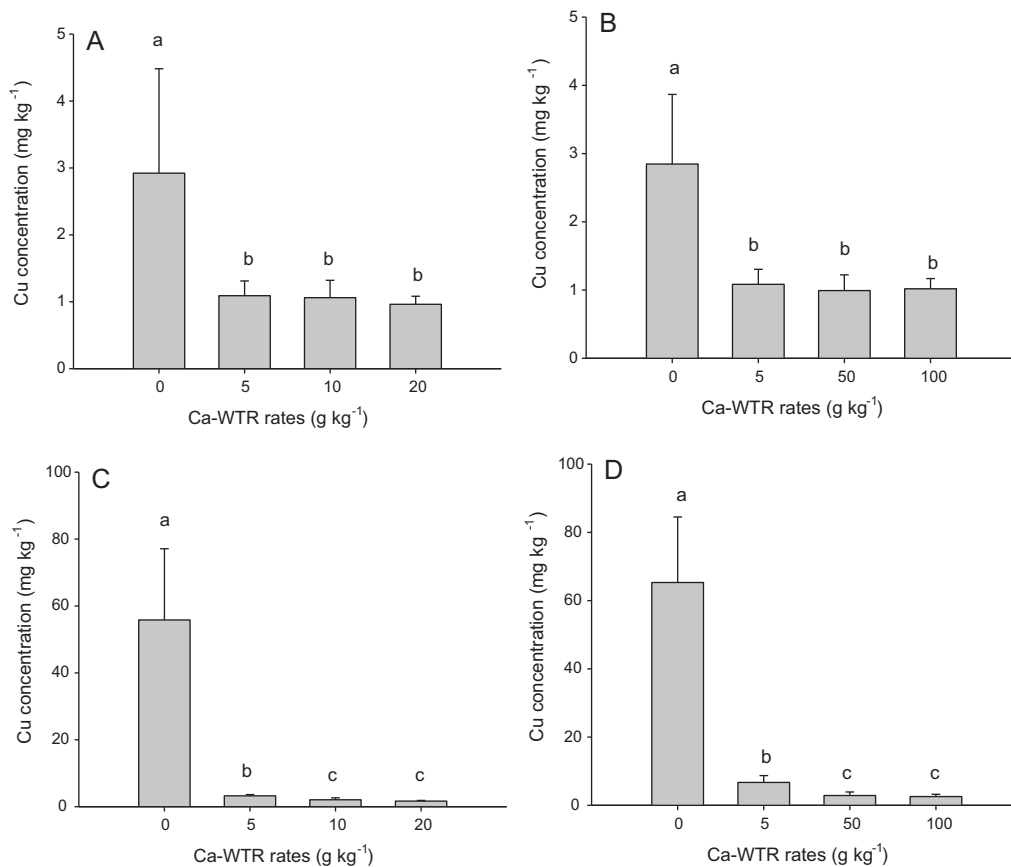

Fig. 5. Changes of water soluble/exchangeable Cu with Ca-WTR application rates: (A) Alfisol; (B) Spodosol; (C) Alfisol + 400 mg Cu kg^{-1}; (D) Spodosol + 400 mg Cu kg^{-1}. Vertical bars represent standard errors. Treatments with the same letter are not significantly different at $P < 0.05$.
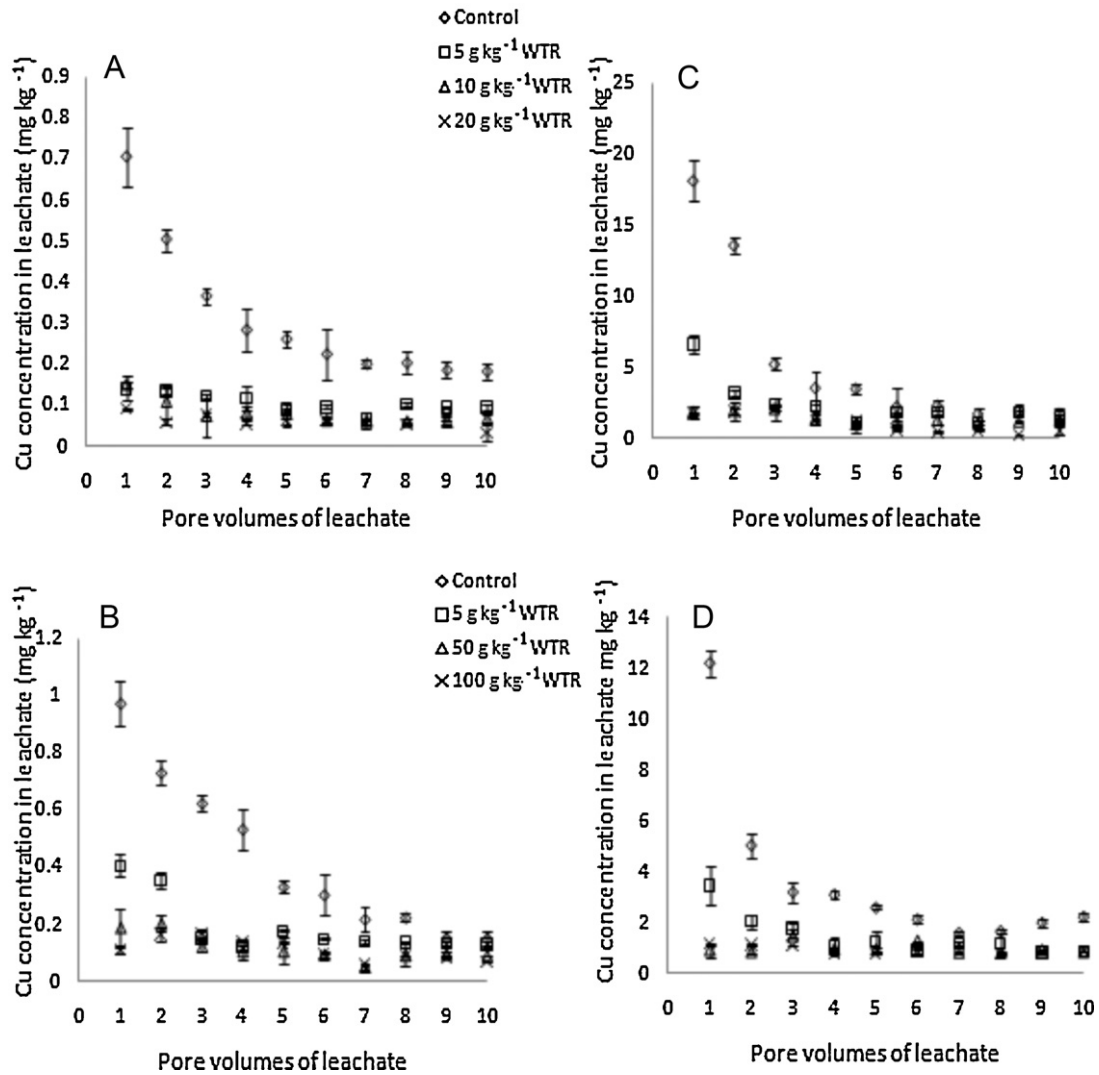
Fig. 6. The concentrations of Cu, in leachate from two soils in ten leaching events: (A) Alfisol; (B) Spodosol; (C) Alfisol + 400 mg kg^{-1} Cu; (D) Spodosol + 400 mg kg^{-1} Cu. Error bars indicate standard errors.

Table 3
Mehlich 3 and CaCl$_2$ extractable Cu (mg kg^{-1}) in the soils after the ten leaching events.

Treatment rates	Mehlich 3 extractable Cu (mg kg^{-1})		CaCl$_2$ extractable Cu (mg kg^{-1})	
	Original soil	Cu enriched soil	Original soil	Cu enriched soil
Alfisol (g kg^{-1})				
0	27.8a[a]	299.0a	0.063a	0.503a
5	21.4ab	225.6b	0.023b	0.432b
10	13.8b	213.8b	0.020b	0.263c
20	9.6b	198.1b	0.007c	0.244c
Spodosol				
0	60.2a	215.1a	0.035a	0.799a
5	33.8b	211.2a	0.026b	0.791a
50	30.1b	105.5b	0.020c	0.362b
100	21.9c	101.6b	0.016c	0.349b

[a] Means in the same treatment columns followed by the same letter were not significantly different at $P < 0.05$.

rates of ~44.8 and 224 Mg ha^{-1} incorporated into a soil depth of 15 cm), the soil pHs were increased to 6.7–7.2 in the Alfisol and 7.1–7.2 in the Spodosol. In general, high application rates should be avoided, as it may lead to negative effect on soil properties or crop yields [35]. Furthermore, Cu mobility in soils can increase at pH values above ~7.5 due to increased solubility of soil organic matter (SOM) and the formation of Cu-SOM complexes [36]. Application of coal fly ash (pH = 12.2) was effective in reducing Cu mobility,

however, increasing soil pH to above 8 (15% by weight) decreased its efficiency [37].

To determine the long-term effectiveness of Cu-immobilization by Ca-WTR, the soils were incubated for 70 days under 70% WHC. Melich 3 extractable Cu in the Ca-WTR amended soils decreased during the 70-days incubation (Fig. 3), indicating that a portion of Mehlich 3 extractable Cu (water soluble, exchangeable, part of CaCO$_3$- and organically bound Cu) [31] was converted into more

strongly bound fractions. The extractable Cu generally decreased with increasing WTR application rate (Fig. 3), which resulted in higher pH (Fig. 4). Amendment of Ca-WTR at $5\,g\,kg^{-1}$ reduced the extractable Cu by 24–36% in the Alfisol and 22–47% in the Spodosol. Based on a linear model of the extractable Cu vs. soil pH, increasing soil pH by one unit decreased extractable Cu by $12–90\,mg\,kg^{-1}$. At pH 6.5, the extractable Cu was reduced by 28–30% in the Alfisol and by 42–44% in the Spodosol.

Ca-WTR amendment has a strong acid-neutralizing capacity. It is likely that less water soluble Cu compounds such as $Cu(OH)_2$ were formed at the raised soil pH. In addition, exchangeable Al^{3+} and Fe^{3+} were replaced by Ca^{2+} and precipitated as $Al(OH)_3$ and $Fe(OH)_3$ when soil pH is above 5.5 [38]. These newly formed oxides and hydroxides provide additional sites for sorbing Cu. As pH increased, there is an increase in negative surface charge or Cu^{2+} sorption on Fe, Al oxides, thus reducing Cu concentration in soil solution. In addition, some adsorbed Cu may be also occluded by the newly formed oxides and become inaccessible to chemical extraction [39,40].

3.2. Addition of Ca-WTR converted labile Cu to more stable Cu forms

Sequential fractionation was conducted to further distinguish different Cu forms in soil matrix. Among the five Cu fractions based on sequential extraction, water soluble and exchangeable Cu (WE-Cu) is more labile [41]. Addition of Ca-WTR drastically reduced WE-Cu and simultaneously increased oxide-bound and residual Cu fractions (Table 2). Although the best results were obtained at the highest dose, lower doses $(5–10\,g\,kg^{-1})$ were adequate for achieving significant reduction in WE-Cu fractions. At $5\,g\,kg^{-1}$, Ca-WTR reduced WE-Cu by 62% in the original soils, and by 90% in the Cu-enriched soils (Fig. 5). Ca-WTR introduced a significant amount of $CaCO_3/CaO$, which can control Cu mobility to a great extent by surface precipitation of $CuCO_3$ [38]. The retention of Cu through co-precipitation with carbonates is associated with the release of Ca^{2+}, Mg^{2+}, Na^+ and H^+ into the soil solution at equal molar ratios.

The precipitation of newly formed Cu phases in a soil represents an important mechanism of Cu immobilization in soils. These phases may include $Cu(OH)_2$, $CuCO_3/Cu_2(OH)_2CO_3$, CuO and various Cu-hydroxysulfates if sulfates are present [39,42–44]. The carbonate-bound Cu was reduced by Ca-WTR at the high application rates $(10–100\,g\,kg^{-1})$, probably because the binding of Cu is stronger to oxides than carbonates [45], as evidenced by the increase in the oxides-bound Cu fraction (Table 2). The conversion of labile Cu to more stable Cu forms was also supported by an increase in the residual Cu fraction.

3.3. Addition of Ca-WTR reduced leachable Cu in soil columns

The incubation studies provided an insight of Cu transformations as affected by Ca-WTR amendment, whereas column leaching studies were performed to determine Cu mobility, particularly downward movement in term of its environmental risks [46]. As expected, the highest leachable Cu concentrations occured in the first leaching event for all samples (Fig. 6). In the absence of Ca-WTR, higher Cu concentrations were leached out during the leaching period. At the beginning, $0.71–0.97\,mg\,L^{-1}$ Cu in the original soils, and $12.12–18.1\,mg\,L^{-1}$ Cu in the Cu-enriched soils were measured (Fig. 6). For the original soils, the decrease in leachable Cu concentration consisted of two phases: i.e. an initial rapid decrease, followed by a slow but consistent decrease (Fig. 6). In comparison, leachable Cu concentrations were constantly low in the amended soils, even at the lowest rate of $5\,g\,kg^{-1}$. For the unamended Cu-enriched soils, Cu concentrations in the leachate were above the U.S. EPA drinking water limit of $1.30\,mg\,L^{-1}$ [47]. In comparison,
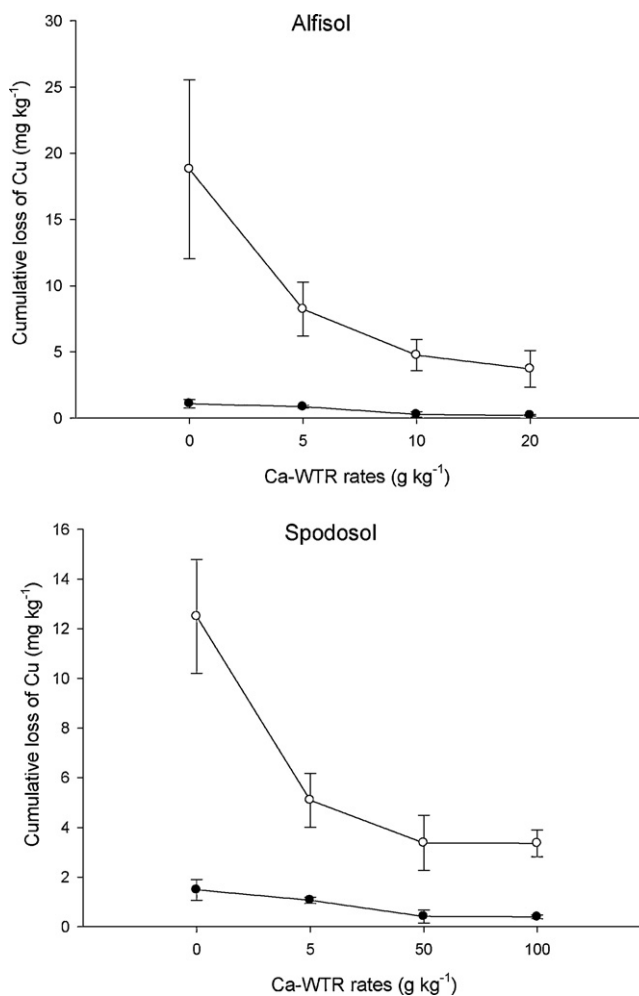

Fig. 7. Cumulative loss of Cu after 10 leaching events as a function of Ca-WTR treatment rates: error bars indicate standard errors.

Cu concentrations in the amended soils were below this limit at the end of the l0 leaching events even at the lowest treatment rates (Table 2).

After ten leaching events, the cumulative loss of Cu decreased with increasing Ca-WTR application rates for all soils (Fig. 7). Compared with the original soils, application of Ca-WTR at $5.0\,g\,kg^{-1}$ decreased Cu leaching loss by 56–66% in the original soils and by 55–59% in the Cu-enriched soils. In comparison, at the highest rates $(20\,g\,kg^{-1}$ for Alfisol and $100\,g\,kg^{-1}$ for Spodosol), the cumulative amount of Cu lost in the 10 leaching events decreased by 35% in the original soils and by 73–80% in the Cu-enriched soils. These results suggest that the amendment of Ca-WTR can significantly reduce Cu leaching losses from contaminated sandy soils. This agrees with the incubation studies results, indicating that a significant portion of labile Cu was converted to more stable forms in the amended soils (Fig. 4).

With increasing application rates the cumulative losses of Cu dramatically decreased, particularly for the Cu-enriched soils, but the decrease diminished with further increases in WTR (Fig. 7). This indicates that there was an optimal level of WTR application rate, above which the benefit may be limited. The cumulative losses of Cu in the Cu-enriched soils was greater in Alfisol than Spodosol, indicating higher Cu leaching potential in Alfisol soils because of its lower organic matter and clay contents for holding Cu (Table 1).

A great challenge to chemical remediation of metal-contaminated soils is to determine the optimal amendment rates [48]. The calculated Ca-WTR rate for achieving the lowest Cu

loss was ∼15 g kg^{-1} for the Alfisol and 75 g kg^{-1} for the Spodosol. However, high amendment rates are not recommended for economic consideration. In addition, high rates may lead to negative effects on soil quality and/or crop yield. The results from our field survey indicate that the relationship between readily available Cu (by CaCl$_2$ extraction) and total recoverable Cu is affected by soil pH, and a pH value of 6.5 is optimum for reducing Cu availability in soils [26]. Based on this criterion and the response curve of pH to Ca-WTR application rates (Fig. 2), the optimal rates of Ca-WTR were 3–8, and 30 g kg^{-1}, respectively for the Alfisol and Spodosol.

In addition to total Cu in the leachate, Mehlich 3 extractable Cu in the leached soils was also determined. It was found that Mehlich 3 extractable Cu generally decreased with increasing Ca-WTR application rates. Application of Ca-WTR at 20 g kg^{-1} to the Alfisol and 100 g kg^{-1} to the Spodosol decreased Mehlich 3 extractable Cu by 34–66% and 53–64%, respectively. For CaCl$_2$ extractable Cu, the reduction was 55–89% and 50–52%, respectively (Table 3). Both Mehlich 3 extractable Cu and CaCl$_2$ extractable Cu were significantly correlated with the leaching loss of Cu ($r = 0.86$ and 0.73, respectively). There was no significant difference in the proportion of extractable to the total Cu in the soils before and after the leaching (Fig. 3). These results suggest that leaching has a minimal effect on the overall Cu distribution in the soils and the amendment of Ca-WTR increases soil Cu holding capacity and establishes a relatively stable equilibrium of Cu in the contaminated soils.

4. Conclusions

Copper contamination to agricultural soils results in soil acidification and enhanced Cu loss into the environment. Application of Ca-WTR effectively raised soil pH and converted labile Cu into more stable forms. Ca-WTR amendment significantly reduced leachate Cu concentrations and the cumulative amounts of Cu loss. The cumulative loss of Cu as a function of Ca-WTR treatment rates can be described by a quadratic model. From the environmental and economic considerations, the optimal Ca-WTR application rates can be estimated based on soil pH of 6.5 for significant reduction of available Cu in the soil. As a by-product from drinking water treatment facility, Ca-WTR can be obtained at a minimum cost and eco-friendly, and therefore has a great potential for the remediation of Cu contaminated soils, particularly those acidic sandy soils.

Acknowledgments

References

[1] Z.L. He, X.E. Yang, P.J. Stoffella, Trace elements in agroecosystems and impacts on the environment, J. Trace Elem. Med. Biol. 19 (2005) 125–140.
[2] A.K. Alva, Copper contamination of sandy soils and effects on young Hamlin orange trees, Bull. Environ. Contam. Toxicol. 51 (1993) 857–864.
[3] L.W. Timmer, S.E. Zitko, L.G. Albrigo, Split applications of copper fungicides improve control of melanose on grapefruit in Florida, Plant Dis. 82 (1998) 983–986.
[4] B.J. Alloway (Ed.), Heavy Metals in Soils, Blackie Academic and Professional, London, 1995.
[5] L. Van-Zwieten, M. Graham, M. Van-Zwieten, Review of impacts on soil biota caused by copper residues from fungicide application. 3rd Aust.-New Zeal, Soils Conf. Proc. (2004) 1–8.
[6] G.C. Schutte, K.V. Beeton, J.M. Kotze, Rind stippling on Valencia orange by copper fungicides used for control of citrus black spot in South Africa, Plant Dis. 81 (1997) 851–854.
[7] Z.L. He, M. Zhang, P.J. Stoffella, X.E. Yang, Vertical distribution and water solubility of phosphorus and heavy metals in sediments of the St. Lucie Estuary, South Florida, USA, Environ. Geol. 50 (2006) 250–260.
[8] M. Chen, L.Q. Ma, W. Harris, Baseline concentrations of 15 trace elements in Florida surface soils, J. Environ. Qual. 28 (1999) 1173–1181.
[9] F. Celardin, C. Trouillet, R. Tisiot, pH dependence of copper adsorption in vineyard soils of Geneva, Environ. Chem. Lett. 1 (2004) 225–227.
[10] S. Boudesocque, E. Guillon, M. Aplincourt, E. Marceau, L. Stievano, Sorption of Cu(II) onto vineyard soils: macroscopic and spectroscopic investigations, J. Colloid Interface Sci. 307 (2007) 40–49.
[11] B.P. Jackson, W.P. Miller, Soil solution chemistry of a fly ash-, poultry litter-, and sewage sludge-amended soil, J. Environ. Qual. 29 (2000) 430–436.
[12] J.W. Stuckey, A. Neaman, R. Ravella, S. Komarneni, C.E. Martinez, Highly charged swelling mica reduces free and extractable Cu levels in Cu-contaminated soils, Environ. Sci. Technol. 42 (2008) 9197–9202.
[13] E. Alvarez-Ayuso, A. Garcia-Sanchez, Palygorskite as a feasible amendment to stabilize heavy metal polluted soils, Environ. Pollut. 125 (2003) 337–344.
[14] A.K. Alva, T.J. Baugh, S. Paramasivam, K.D. Sajwan, Adsorption/desorption of copper by a sandy soil amended with various rates of manure, sewage sludge, and incinerated sewage sludge, J. Environ. Sci. Health B: Pestic. Food Contam. Agric. Wastes 40 (2005) 687–696.
[15] E. Besnard, C. Chenu, M. Robert, Influence of organic amendments on copper distribution among particle-size and density fractions in Champagne vineyard soils, Environ. Pollut. 112 (2001) 329–337.
[16] O. Kiikkila, T. Pennanen, J. Perkiomaki, J. Jerome, H. Fritze, Organic material as a copper immobilising agent: a microcosm study on remediation, Basic Appl. Ecol. 3 (2002) 245–253.
[17] S. Paramasivam, K.A. Richards, A.K. Alva, A.M. Richards, K.S. Sajwan, K. Jayaraman, A. Heanacho, J. Afolabi, Evaluation of poultry litter amendment to agricultural soils: leaching losses and partitioning of trace elements in collard greens, Water Air Soil Pollut. 202 (2009) 229–243.
[18] X.D. Cao, L.Q. Ma, D.R. Rhue, C.S. Appel, Mechanisms of lead, copper, and zinc retention by phosphate rock, Environ. Pollut. 131 (2004) 435–444.
[19] R.Q. Liu, D.Y. Zhao, In situ immobilization of Cu(II) in soils using a new class of iron phosphate nanoparticles, Chemosphere 68 (2007) 1867–1876.
[20] E.C. Nzegbule, Amelioration of copper toxicity in the soils of aged cocoa plantation in Bende District, Nigeria, Environ. Ecol. 25 (2007) 448–452.
[21] M.B. McBride, C.E. Martines, Copper phytotoxicity in a contaminated soil: remediation tests, with adsorptive materials, Environ. Sci. Technol. 34 (2000) 4386–4391.
[22] P. Rengasamy, J.M. Oades, T.W. Hancock, Improvement of soil structure and plant growth by addition of alum sludge, Commun. Soil Sci. Plant Anal. 11 (1980) 533–545.
[23] H.A. Elliott, B.A. Dempsey, Agronomic effects of land application of water treatment sludges, J. Am. Water Works Assoc. 84 (1991) 126–131.
[24] N.T. Basta, R.J. Zupancic, E.A. Dayton, Evaluating soil tests to predict bermudagrass growth in drinking water treatment residuals with phosphorus fertilizer, J. Environ. Qual. 29 (2000) 2007–2012.
[25] M.L. Silveira, M.K. Miyittah, O'Connor S G.A., Phosphorus release from a manure-impacted spodosol: effects of a water treatment residual, J. Environ. Qual. 35 (2006) 529–541.
[26] Z.L. He, J.H. Fan, W.R. Chen, J.Y. Yang, Y.G. Yang, Q. Lu, Y.B. Wang, D.J. Banks, P.J. Stoffella, D.V. Calvert, Soil Amendment to Reduce Nitrogen, Phosphorus, and Heavy Metals (Including Copper) in Surface Runoff from Citrus Groves in the Indian River Area. St. lucie river issues team-south Florida water management district project final report, 2009.
[27] Z.L. He, M.K. Zhang, D.V. Calvert, P.J. Stoffella, X.E. Yang, S. Yu, Transport of heavy metals in surface runoff from vegetable and citrus fields in Florida, USA, Soil Sci. Soc. Am. J. 68 (2004) 1662–1669.
[28] M.E. Sumner, W.P. Miller, Cation and exchange capacity and exchange coefficients. in: D.L. Sparks, (Ed.), Methods of Soil Analysis, Part 3: Chemical Methods. SSSA Book Series No 5, ASA-CSA-SSSA Inc. Madison, WI, 1996, pp. 1201–1231.
[29] R.H. Leoppert, G.L. Suarez, Carbonates and gypsum. In: D.L. Sparks (ed.), Methods of Soil Analysis, Part 3: Chemical Methods. SSSA Book Series No 5, ASA-CSA-SSSA Inc. Madison, WI, 1996, pp. 437–474.
[30] W.P. Miller, D.M. Miller, A micro-pipette method for soil mechanical analysis, Commun. Soil Sci. Plant Anal. 18 (1987) 1–15.
[31] A. Mehlich, Mehlich 3 soil test extractant: a modification of Mehlich 2 extractant, Commun. Soil Sci. Plant Nutr. 15 (1984) 1409–1416.
[32] W.N. Beyer, Evaluating soil contamination, US fish Wildl, Serv. Biol. Rep. 90 (1990) 1–25.
[33] M.C. Amacher, Nickel, cadmium, and lead. In: D.L. Sparks (Ed.), Methods of Soil Analysis, Part 3: Chemical Methods. SSSA Book Series No 5, ASA-CSA-SSSA Inc. Madison, WI, 1996, pp. 739–768.
[34] S. Yu, Z.L. He, C.Y. Huang, G.C. Chen, D.V. Calvert, Adsorption–desorption behavior of copper at contaminated levels in red soils from China, J. Environ. Qual. 31 (2002) 1129–1136.
[35] L.W. Titshall, J.C. Hughes, C.D. Morris, P.J.K. Zacharias, The disposal of a lime water treatment residue on soil and spoil material from a coalmine: a glasshouse investigation, J. Environ. Qual. 36 (2007) 568–579.
[36] D. Fernandez-Calvino, C. Perez-Novo, J.C. Novoa-Munoz, M. Arias-Estevez, Copper fractionation and release from soils devoted to different crops, J. Hazard. Mater. 167 (2009) 797–802.
[37] R. Ciccu, M. Ghiani, A. Serci, S. Fadda, R. Peretti, A. Zucca, Heavy metal immobilization in the mining-contaminated soils using various industrial wastes, Miner. Eng. 16 (2003) 187–192.
[38] W.L. Lindsay, Chemical equilibria in soils, New York–Chichester–Brisbane–Toronto, John Wiley & Sons, 1979.

[39] Y. Ma, E. Lombi, I.W. Oliver, A.L. Nolan, M.J. McLaughlin, Long-term aging of copper added to soils, Environ. Sci. Technol. 40 (2006) 6310–6317.

[40] S. Sayen, J. Mallet, E. Guillon, Aging effect on the copper sorption on a vineyard soil: column studies SEM-EDS analysis, J. Colloid Interface Sci. 331 (2009) 47–54.

[41] L.Q. Ma, G.N. Rao, Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils, J. Environ. Qual. 26 (1997) 259–264.

[42] A.A. Ponizovsky, H.E. Allen, A.J. Ackerman, Copper activity in soil solutions of calcareous soils, Environ. Pollut. 145 (2007) 1–6.

[43] M. Komarek, A. Vanek, V. Chrastny, J. Szakova, K. Kubova, P. Drahota, J. Balik, Retention of copper originating from different fungicides in contrasting soil types, J. Hazard. Mater. 166 (2009) 1395–1402.

[44] D.G. Strawn, L.L. Baker, Molecular characterization of copper in soils using X-ray absorption spectroscopy, Environ. Pollut. 157 (2009) 2813–2821.

[45] M. Jalali, Z.V. Khanlari, Effect of aging process on the fractionation of heavy metals in some calcareous soils of Iran, Geoderma 143 (2008) 26–40.

[46] L.D. Tyler, M.B. Mcbride, Mobility and extractability of cadmium, copper, nickel, and zinc in organic and mineral soil columns, Soil Sci. 134 (1982) 198–205.

[47] United States Environmental Protection Agency. Lead and Copper Rule: A Quick Reference Guide. EPA816-F-04-009 www.epa.gov/safewater 2004.

[48] J. Kumpiene, A. Lagerkvist, C. Maurice, Stabilization of Pb- and Cu-contaminated soil using coal fly ash and peat, Environ. Pollut. 145 (2007) 365–373.