Soil amendment to remediate copper contaminated soils

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Abstract

Copper contamination to agricultural soils has been accelerated due to its wide and repeated use in agriculture and horticulture as fertilizers or fungicides to protect vines, citrus trees, and other fruit crops against fungus diseases. Laboratory incubation and field survey were conducted to understand the mechanisms of Cu inactivation by Ca-water plant residuals (Ca-WTRs containing mainly $CaCO_3$ and minor CaO) and to estimate the optimal rate of Ca-WTRs for remediation of Cu-contaminated soils. The results indicate that Ca-WTRs can effectively raise soil pH and convert water soluble and exchangeable Cu to more stable oxides-bound and residual Cu fractions in the soils. A pH value of 6.5 was found to divide the high (pH<6.5) and low (pH>6.5) availability of Cu in the soils. Based on this criterion and the response curve of pH to Ca-WTRs application rate, the optimal rates of Ca-WTRs can be estimated for different Cu-contaminated soils.

Key Words

Acidic soils, chemical remediation, heavy metal contamination, Cu transformation.

Introduction

Copper contamination to agricultural soils has been accelerated due to its wide and repeated use in agriculture and horticulture as fertilizers or fungicides to protect vines, citrus trees, and other fruit crops against fungus diseases (He *et al.* 2005). In Florida, due to a long history of citrus production, Cu has accumulated in the soils (Alva 1993). A large proportion of soils under citrus production contains total Cu content above 85 mg/kg, the critical level for ecosystem health (Schuler and Hoang 2008). Soil contamination with Cu causes soil degradation, Cu phytotoxicity, and increased transport of Cu to surface and ground waters. Total Cu as high as 300 mg/kg was measured in the sediment from St. Lucie River, South Florida, which is 20-60 times greater than background levels (5—15 mg/kg) (Ma *et al.* 1997; Zhang *et al.* 2003). Because of the persistent nature of heavy metals, remediation of Cu-contaminated soils has become a great challenge. Physical approaches such as scavenging or burial of the contaminated surface soil or 'washing out' of Cu from the contaminated field with or without electrical dialysis are effective but often too expensive for a large scale remediation. Phytoremediation is cost-effective, but requires a longer time to accomplish desired results as compared to other approaches. Therefore, chemical approaches are frequently adopted for the remediation of agricultural soils. Soil amendment is one of the best management practices in Florida for reducing nutrient losses from agricultural production systems on sandy soils. Amendment of Ca-water plant residues (Ca-WTRs, pH 9.1, containing mainly $CaCO_3$ and minor CaO) to acidic sandy soils can effectively reduce Cu loading in surface runoff water based on our field observation, but the mechanisms of the effects are not clear. In this study laboratory incubation experiments were conducted to understand the mechanisms of Cu inactivation by Ca-WTRs and to estimate the optimal rate of Ca-WTRs for remediation of Cu-contaminated soils.

Materials and methods

Eighteen representative soils were collected at the 0-15 cm depth from commercial citrus groves in the Indian River area, South Florida, of which two typical soils were selected for incubation study (Table 1). The soil samples were air-dried, ground, and passed through a 2-mm sieve prior to the incubation study and physical and chemical analyses. The Ca-WTR was collected from the Fort Pierce Utility Authority facility with the following properties: pH 9.05, electrical conductivity (EC) 659 µS/cm, and total recoverable Cu 0.4 mg/kg. pH and EC of soil and Ca-WTRs were measured using a pH/ion/conductivity meter (DIM 200, Denver Instrument, Denver, CO). 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 and soil extractable Cu by the Mehlich-3 method (Mehlich 1984). Copper concentration in the digested solution or Mehlich-3 extracts was determined using inductively coupled plasma optical emission spectrometry (ICP-OES, Ultima, J. Y. Horiba, Edison, NJ, USA) following USEPA method 200.7.

Table1. Relevant properties of the soils

Soils	Soil classification	Cropping history*	Org. C (g/kg)	pH (H_2O)	Recoverable Cu (mg/kg)	M-3 Extr. Cu (mg/kg)
Alfisol	Fine loamy siliceous hyperthermic Typic Glossaqualfs	Red GF/1988	3.29	5.83	63.2	39.9
Spodosol	Sandy siliceous hyperthermic Alfic Haplaquods	Red GF/1979	7.24	4.18	114	72.3

*GF=grapefruit

Incubation study

Soils (each 1-kg oven dried basis) were amended with Ca-WTRs at the rates of 0, 5, 10, and 20 g/kg for the Alfisol and 0, 5, 50, and 100 g/kg for the Spodosol. There were two levels of Cu for each soil: with or without being enriched with 400 g/kg Cu in the form of $Cu(NO_3)_2$. The amended soils were then incubated at room temperature for 70 d and soil moisture was maintained at 70% of water holding capacity (WHC) during the incubation. At the end of incubation, subsamples of the soils were collected for the determination of pH, Mehlich-3 extractable Cu, and Cu fractionation into water soluble and exchangeable, carbonate-bound, organic- bound, oxide-bound, and residual fraction following the procedure modified from that of Amacher (1996).

Results and discussion

Soil pH and extractable Cu

Amendment of Ca-WTRs effectively raised soil pH (Figure 1). At the rate of 5 g/kg soil pH was increased from 5.4-5.8 to 6.4-7.0 for the Alfisol and from 3.9-4.2 to 6.2 for the Spodosol. Copper loading at 400 mg/kg decreased soil pH by 0.45 and 0.26 units, respectively for the Alfisol and Spodosol, indicating that Cu contamination may result in secondary acidification. As a consequence, more Ca-WTRs were required to raise pH to the same level for Cu polluted soils. Extractable Cu decreased with increasing pH (Figure 2). Amendment of Ca-WTRs at the rate of 5 g/kg reduced M3-extractable Cu by 24-36% in the Alfisol and 22-47% in the Spodosol. Based on a linear model of the M-3 extractable Cu vs. soil pH, increasing soil pH by one unit decreased M-3 extractable Cu by 12-90 mg/kg, depending on soil type and Cu level in the soil. At pH 6.5, M3 extractable Cu was dropped by 28-30% in the Alfisol and by 42-44% in the Spodosol. These results indicate that Ca-WTRs amendment can effectively convert labile Cu to stable Cu.

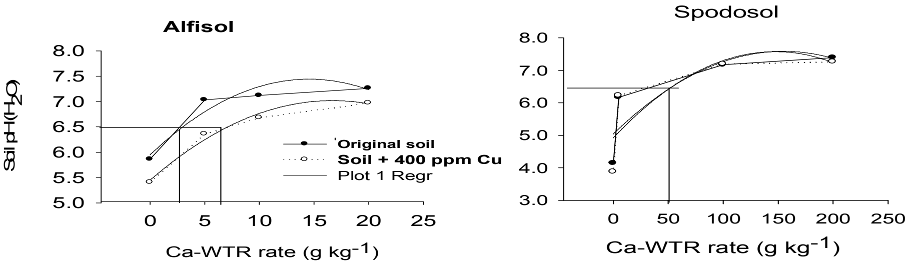

Figure 1. Response of soil pH to application rates of Ca-Water plant residuals in an Alfisol and a Spodosol with and without Cu enrichment at 40 mg/kg.

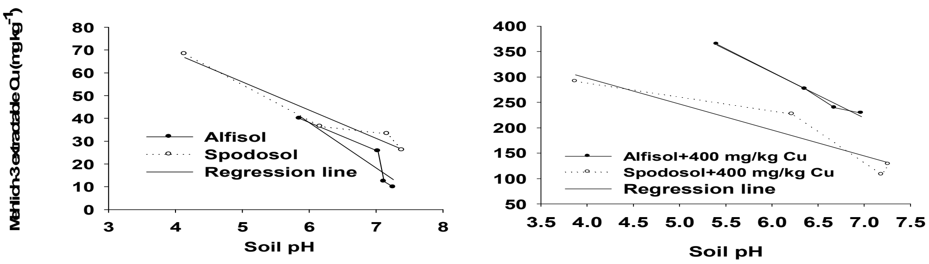

Figure 2. Relationship between Mehlich 3-extractable Cu and soil pH: Alfisol, y = 157-19.8x, r = 0.85; Sopdosol, y = 118-12.3x, r = 0.96; Alfisol + 400 mg/kg Cu, y = 854-90.3x, r = 0.99 ; Spodosol + 400 mg/kg Cu, y = 501-51x, r = 0.99.

Soil Cu fractionation

The amendment of Ca-WTRs drastically reduced water soluble and exchangeable Cu but increased oxide-bound and residual Cu fractions (Figure 3). Carbonate-bound slightly increased at a low-medium rate of Ca-WTRs but decreased at a high rate whereas organic-bound Cu was slightly reduced. At the application rate of 5 g/kg, Ca-WTRs reduced water soluble and exchangeable Cu^{2+} by 63% in the original soils, and by 92% in the Cu-enriched soils regardless of soil type. Apparently Cu from the labile pool was largely adsorbed by some newly formed Fe and Al oxides/hydroxides due to increased pH, and converted into more stable forms. The carbonate-bound Cu was also at high Ca-WTR rates (>reduced by Ca-WTRs), which is unexpected as we thought that this Cu fraction would be increased due to the large input of CaCO$_3$/CaO from Ca-WTRs. This result probably indicates that the binding of Cu is stronger to oxides than carbonates.

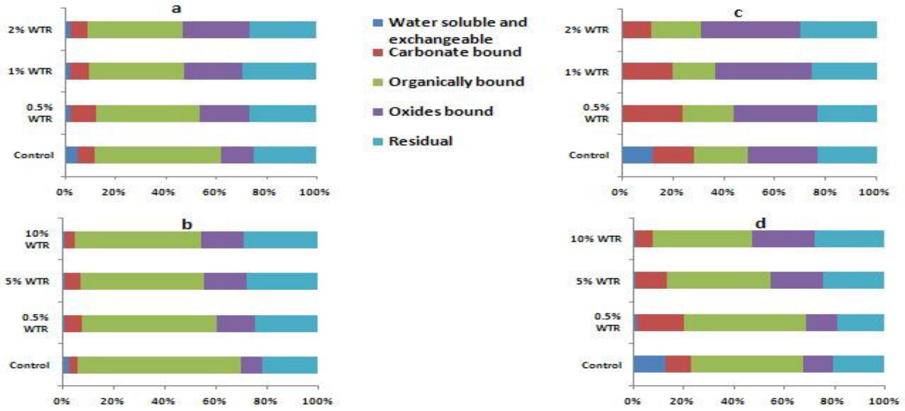

Figure 3. Cu Fractionation in soils amended with different Ca-WTRs rates: (a) Alfisol; (b) Spodosol; (c) Alfisol + 400mg Cu/kg soil; (d) Spodisol + 400mg Cu/kg soil.

Optimal rate of Ca-WTRs

A great challenge to chemical remediation of metal contaminated soil is to determine adequate rate of amendment, i.e. how much is the optimal. The results from our field survey indicate that the relationship between readily available Cu (as determined by CaCl$_2$ extraction) and total recoverable Cu is affected by soil pH, and a pH value of 6.5 divides the high (pH<6.5) and low (pH>6.5) availability status of Cu in the soils as reflected in the slope of available-total Cu relationship curve (Figure 4). This finding agrees with field observation that phytotoxicity symptoms often disappear in Cu contaminated soils at pH $\geq$ 6.5. Based on this criterion and the response curve of pH to Ca-WTRs application rate, it was calculated that the optimal rates of Ca-WTRs are 3, 6.5, and 50 g/kg, respectively for the Alfisol, Cu-enriched Alfisol, and Spodosol with or without Cu enrichment.

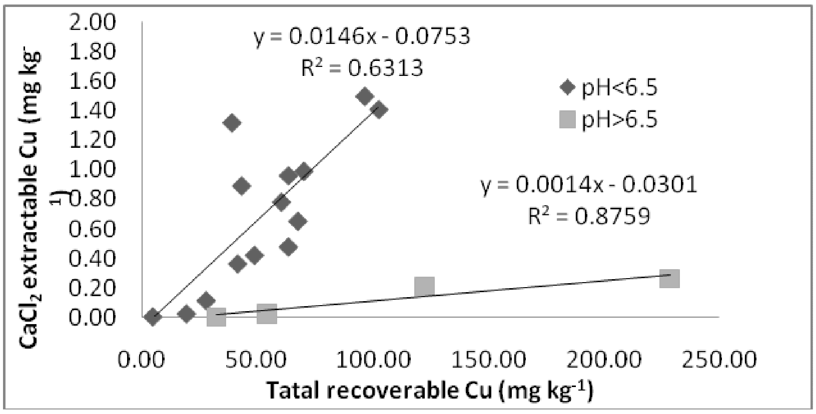

Figure 4. Relationship between CaCl$_2$extractable Cu and total recoverable Cu as affected by soil pH.

Conclusion

Amendment of Ca-WTRs can effectively raise soil pH and convert labile Cu into more stable oxides-bound and residual Cu fractions. Ca-WTRs, which can be obtained from a drinking water treatment facility at no cost and contain no detectable contaminants, thus have great application potential for remediation of Cu contaminated soils, particularly those acidic sandy soils under citrus production.

Acknowledgment

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