

## Chemical Assessment of Heavy Metal Contamination in Soil

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### Abstract

Current methods of evaluating soil contamination by heavy metals rely on analyzing samples for total contents of metals or quantities recovered in various chemical extracting solutions. Results from these approaches provide only an index for evaluation because these methodologies yield values not directly related to bioavailability of soil-borne metals. In addition, even though concentrations of metals may be less than those required to cause toxic effects to biota, they may cause substantial effects on soil chemical parameters that determine soil quality and sustainable productivity. The objective of this research was to characterize effects of Cu or Cd additions on soil solution chemistry of soil quality indices, such as pH, EC, nutrient cation distribution and quantity/intensity relations (buffer capacity). Metals were added at rates ranging from 0 to 400 mg/kg of soil. Soil solution was sequentially extracted from saturated pastes using vacuum. Concentrations of Cu or Cd remaining in soil solutions were very low as compared to those added to the soils, warranting that most of the added metals were recovered as nonavailable (strongly adsorbed) fractions. Adsorption of the added metals released cations into soil solution causing increases of soluble cation contents and thus ionic strength of soil solution. At metal additions of 200~400 mg/kg, EC of soil solution increased to as much as 2~4 dS/m; salinity levels considered high enough to cause detrimental effects on plant production. More divalent cations (Ca+Mg) than monovalent cations (K+Na) were exchanged by Cu or Cd adsorption. The loss of exchangeable nutrient cations decreased long-term nutrient supplying capacity of each soil. At 100 mg/kg of metal loading, the buffering capacity was decreased by 60%. pH of soil solution decreased linearly with increasing metal loading rates, with a decrement of up to 1.3 units at 400 mg Cu/kg addition. Influences of Cu on each of these soil quality parameters were consistently greater than those of Cd. These effects were of a detrimental nature and large enough in most cases to significantly impact soil productivity. It is clear that new protocols are needed for evaluating potential effects of heavy metal loading of soils.

### Introduction

Soil accumulations of some heavy metals continue to increase due to inputs from a variety of point- and non-point sources. Heavy metal contamination may cause toxicity to plants and other soil biota, as well as creating an avenue for metal entrance into the human food chain. To date, no simple, uniform protocols have been developed for assessing heavy metal impacts on soils. Current assessment is based on measurement of total contents or metal extractability using specific chemicals. Although these values may serve as indices for pollution, they do not describe metal bioavailability, biotoxicity, transport, or fate in the soil.

These processes are regulated by specific physicochemical forms (chemical species) and their soil reactions, rather than total or extractable concentrations. Methodologies showing promise to better evaluate soil contamination effects include chemical speciation, fractionation, direct determination of plant-uptake relations, and modeling.

Adequate assessment of soil quality must include consideration of the soil as a multi-functional body involving physical, chemical and biological processes. Important chemical indicators of soil function include a variety of nutrient availability parameters, such as pH, cation exchange capacity, electrical conductivity, and nutrient contents and their distribution in solid and liquid phases. Few studies have been reported to characterize heavy metal effects on these soil properties, and how they may alter biological productivity.

Objectives of this research were to investigate how Cu or Cd contamination of soils may change basic soil chemistry indices that relate to soil quality and productivity.

## **Materials and Methods**

Three non-contaminated soil samples were collected from the 0-30cm depth. Soils were contaminated with Cu or Cd (0 to 400 mg/kg) by adding predetermined amounts of Cu or Cd solutions to make saturated pastes. Pastes were equilibrated at 25°C for 24 hours. After 24 hr, soil solution was vacuum extracted with a dual stage pump. Extracted solutions were re-filtered through a 0.45  $\mu$ m membrane filter paper and their volume, pH, and EC were immediately measured. Solutions were analyzed for soluble cations (K, Na, Ca and Mg) and heavy metals (Cu and Cd) by AAS. Extracted soils were re-saturated by adding an aliquot of water equivalent to the volume of soil solution extracted. These pastes were re-equilibrated at 25°C for 24 hours and the same process repeated as described above until five cycles had been completed. At each cycle, about 5 g of soil subsamples were taken to analyze extractable (1M NH<sub>4</sub>OAc, pH 7.0) cations (K, Na, Ca and Mg) and DTPA-TEA extractable Cu or Cd by AAS. A separate sample of silt loam soil was experimentally contaminated with 100 mg Cu or Cd /kg and equilibrated at 25°C for 5 days. The soil paste was air-dried and sequentially extracted to determine water soluble, exchangeable, Mn-oxide bound, Fe-oxide bound, organically bound, and residual fractions. The regression model was used to evaluate changes of soil chemical parameters in the solution phase over the five-extraction series as a function of heavy metal concentration. Changes in soil buffer capacity from addition of heavy metals were evaluated from the relationship between exchangeable cations and those cations in soil solution.

## **Results and Discussions**

### **1. Soil Solution**

Concentrations of Cu or Cd remaining in the soil solution were very low as compared to amounts added to each of the three soils, indicating that most of these metals were adsorbed onto the solid phase. Solution concentrations did, however, increase with increasing rate of metal addition. Less Cu than Cd remained in solution at equal rates of addition, indicating higher specificity of soils for adsorbing Cu. No Cu was detected in soil solutions where the rate of application was less than 80 mg Cu/kg, and only 0.4 to 5% of Cu quantities above 200mg/kg were recovered in soil solution. As much as 26 % of Cd added at the highest rates was present in soil solution.

## **2. Adsorbed Fractions**

Water soluble and exchangeable ( $\text{NaNO}_3$ -extractable) fractions of Cu were not detectable. These are the forms considered available for plant uptake, suggesting that little or no Cu, when added to soils at this rate, would be bioavailable. Most (86%) of the added Cu was oxide- and organically-bound. Only about 11% of adsorbed forms of Cd were water soluble and exchangeable (available), with most of it being oxide-bound. Less than 10% as much Cd was tied up by organic matter as compared to Cu. These results further support the concept that Cd is more mobile, and potentially more toxic, than Cu.

## **3. Solution pH**

pHs were decreased in proportion to rate of Cu or Cd addition, due to proton release from soil colloids as more Cu or Cd were adsorbed. In each soil the pH decrement was greater from Cu than from Cd. This corresponds to the above results that indicated more adsorption of Cu than Cd. The 400 mg Cu/kg treatment is unusually high, and solution pHs decreased 0.55, 0.93 and 1.26 units in the SL, SiL and C soils, respectively. Linear models showed that the chemical concentrations of metal application required to decrease pH by 0.5 units ( $\text{pH}0.5$ ) were ranged from 118.8 to 351.7 mg/kg for Cu and from 95.2 to 530.6 mg/kg for Cd.

## **4. Distribution of Cations in Soil Solution**

The mass ( $\mu\text{mol}$ ) of each cation in solution (K, Ca, Mg and Na) were increased with increased rate of metal addition, illustrating the effects of metal salts on the process of cation exchange. More cations were exchanged by Cu than by Cd at the same level of treatment, and more divalent than monovalent cations were exchanged. The stoichiometric order of exchange was  $\text{Ca} > \text{Mg} > \text{K} > \text{Na}$  in all three soils. Higher Cu or Cd additions increased relative contents of divalent cations (Ca+Mg) in solution, but those of monovalent cations (K+Na) decreased. It is clear that, as divalent Cu or Cd were adsorbed on soil particles, they replaced mostly other divalent ions. Slight differences were observed between amounts of Ca vs Mg or K vs Na. As the number of extractions increased, total cation contents ( $\mu\text{mol}$ ) significantly decreased, with the greatest decrease occurring after the third extraction. Considering that most heavy metals in soils are very strongly adsorbed and immobile, assessment of soil chemical parameters that influence nutrient availability may be an appropriate approach to evaluate contamination consequences. Considering only potential toxicity may be misleading when evaluating long-term effects.

## **5. Electrical Conductivity of Soil Solution**

EC of soil solution increased in all soils in direct relation to rate of Cu or Cd addition. Again, Cu had a greater effect than did Cd. The increased EC can be attributed to increased cations in soil solution, along with associated anions required to maintain electrical neutrality. Soil salinity, as evaluated based on EC of saturated pastes may potentially influence the yield of very sensitive crops at a level of 2 mS/cm. If electrical conductivity is 4 mS/cm or more, yields of many crops are restricted. EC values of 2 to 4 mS/cm range were recorded for the SiL and SL soils at Cu addition of  $>200\text{mg/kg}$  and at  $400\text{ mgCd/kg}$ . These elevated salinity levels would likely have detrimental effects on most crops, even if metal toxicity was not a problem.

## 6. Quantity and Intensity Relationship (Buffering Capacity)

The buffer capacity of soil decreased as Cu or Cd application increased, due to adsorption of Cu or Cd and release of nutrient cations to soil solution. Buffer capacities decreased about 60% with application of 100 mg Cu or Cd/kg.

### Summary and Conclusions

When heavy metals are applied to soils, they may not be present in soil solution at concentrations strong enough to cause direct toxicity to plants or other organisms. Nevertheless, their presence may alter soil properties that are important for sustained productivity. Most of the added Cu was found to be in organically bound and residual forms, and most of the Cd was associated with Mn- and Fe-oxide fractions. Soil solution pH decreased as rate of Cu or Cd increased, with changes of as much as 1.26 units from the highest rate of Cu. This magnitude of pH change could have significant effects on the solubility and availability of several nutrients. The distribution of cation nutrients was also greatly influenced by heavy metal addition, with quantities of Ca and Mg in solution being directly related to rate of metal application. As the soils were sequentially extracted, nutrient cation concentrations in solution decreased to very low levels after metals had been added, particularly after the third extraction. The EC of soil saturated pastes increased to levels considered to be detrimental to crop yields when Cu was added at a rate of 100 mg/kg or Cd was added at 200 mg/kg. Soil buffer capacity for supplying cation nutrients was also decreased, with Cu having a greater effect than Cd. These results suggest that new protocols for assessing potential impacts of heavy metals in soils should be developed. Methods involving measurement of total or extractable metal concentrations do not provide the kinds of data that allow evaluation of indirect metal effects on soil characteristics that regulate sustainable productivity.