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# Solubility and Lability of Copper in a Copper-Mine Tailings Treated with Two Organic Amendments

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***Abstract*** **-** Copper-mine tailings contain considerable amounts of copper (Cu) that may be extracted biologically or by organic ligands and may then become available to plants. A laboratory incubation experiment was conducted to assess the effect of a commercial garden growth substratum (GGS) containing natural mycorrhizae (*Glomus intraradices*) and peat moss in combination with lemon peel waste (LPW) on the evolution of labile Cu pool with time in a slightly alkaline Cu-mine tailing containing calcite. There were eight treatments combining four rates (0, 12.4, 50 and 100 g GGS $kg^{-1}$ tailings) and two rates (0 and 100 g LPW $kg^{-1}$ tailings). The amendments were thoroughly mixed with air-dry tailings in plastic bags. Distilled water was added to maintain the substrate at field capacity throughout the 8-week incubation period. The amounts of labile Cu in tailings increased with incubation time. Extractable Cu fractions as labile Cu (DTPA, Mehlich-3) were significantly increased after adding GSS and LPW. The smallest amount of labile Cu was found in the unamended tailings and the highest amount in the GGS-amended tailings.

***Keywords*****:** lemon peel waste, peat moss, pH, calcite

## 1. Introduction

Copper (Cu) is an essential nutrient for growing green plants. Phytoreclamation of slightly alkaline Cu-mine tailing requires chemical or organic amendments. Organic amendments could increase mine tailings fertility level, and Cu solubility and availability to the plant [1]. Cu availability for plant absorption depends on the form of Cu in the soil and on other soil factors such as soil pH, soil texture, soil mineralogy, redox reactions, and calcium carbonate (CaCO3), organic matter and Fe-Mn oxides and hydroxides contents of soils [2], [3].

A chemical entity often responsible for lowered plant growth and nutrient availability in calcareous soils is the presence of CaCO3. Based on evidence from many experiments, Cu is strongly retained in calcareous soils [4] and has very low solubility in alkaline and calcareous soils [3], [5], [6]. Theoretically, if Cu-mine tailings contain calcite, the goal of phytoreclamation treatments should be to enhance Cu solubility and availability. However, few studies aimed to enhance Cu availability in slightly alkaline Cu-mine tailings treated with organic amendments. The use of certain organic amendments such as agro-wastes and garden growth substratum containing peat moss is important for in situ phytoremediation of Cu-mine tailings, since this practice can change tailings chemical properties and metal availability. Moreover, garden growth substratum containing mycorrhizal fungi may contribute to Cu and P plant nutrition [8], while mitigating the possible inhibition effects of Cu on colonization of soil by the arbuscular mycorrhizal fungus Glomus intraradices [9].

The objective of the study was to assess the effect of a commercial garden growth substratum containing natural arbuscular mycorrhizal fungus (Glomus intraradices) and peat moss in combination with lemon peel waste on the evolution of labile Cu pool with time in a slightly alkaline Cu-mine tailings containing calcite and originating from the Gaspé copper smelter at Murdochville, Quebec (Canada).

## 2. Methods and Results

### 2.1. Analytical methods

A commercial garden growth substratum (GGS) containing mycorrhizal fungus and peat moss were used alone or in combination with lemon peel waste (LPW) to assess the availability index of Cu in the Cu-mine tailings in controlled conditions. There were eight treatments combining four rates of GGS (0, 1.24%, 5% and 10%) and two rates of LPW (0 and 10%). The LPW and GGS were thoroughly mixed with 500 g air-dry tailings in plastic bags. Distilled water was added to bring and maintain the substrate at field capacity throughout the 8-week incubation period. The triplicated treatments were arranged in a completely randomized design. Samples were analyzed for pH-$CaCl_2$ (0.01 *M*) and two labile Cu fractions (readily and moderately labile Cu) at 2 periods, 24 h (1 day) and 8 weeks (56 days). A sequential extraction procedure was used to determine readily and moderately labile Cu. The two extractants were used sequentially: (i) DTPA-TEA-$CaCl_2$ adjusted to pH 7.3 [7], then (ii) Mehlich-3 [10].

Copper was determined using a Perkin Elmer atomic absorption spectrophotometer (AAnalyst 200). We assumed that extractable Cu represented the labile pool [11]. Hence, the first extractant (DTPA-TEA-$CaCl_2$ (step 1) measured readily labile Cu and the second one (Mehlich-3) (step 2) measured moderately labile Cu. Total labile Cu (readily + moderately) was estimated by summing the two measured extractable Cu as follows: $Cu_T = Cu_{DTPA} + Cu_{MehIII}$. Extraction using selected reagents is often used to provide an estimate of the level of available micronutrient, but as mentioned by Pickering [12], reagent selection can be somewhat arbitrary, with the efficiency often being a function of soil composition [12]. Statistical analysis was performed using the Analysis of Variance and Linear Models (Pearson correlation) procedures [13].

### 2.2. Tailing pH

The average pH values of amended tailings at day 1 varied from 7.21 (control) to 7.25 (GGS rates), 6.06 (10% LPW) and 5.98 (GGS+LPW treatment). At 56 days a general trend was established, with a marked increase in pH for tailings treated with LPW and GGS+LPW. Average pH of tailings treated with the two amendments followed the sequence of: 10% LPW (8.04) > (GGS+LPW) (7.90) > 10% GGS (7.49) > control (7.41).

### 2.3. Labile Cu Pool

The amendments addition, compared with no amendments addition, enhanced Cu exchangeability. Total labile Cu ($Cu_T$) increased with increasing incubation time (Fig. 1).

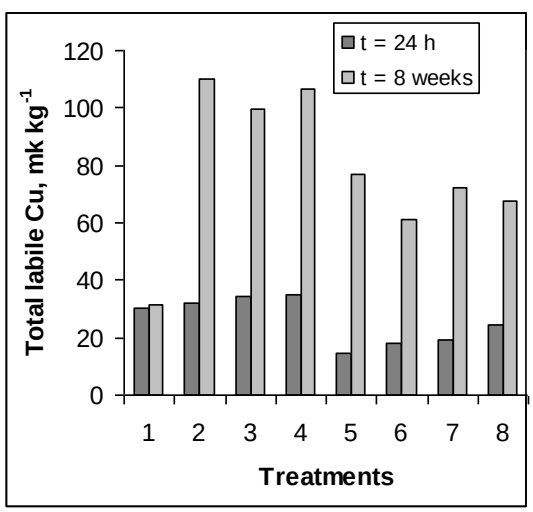


Fig. 1: Influence of lemon peel waste (LPW) and garden growth substratum (GGS) on the total labile Cu pool ($Cu_T$) in tailings. Treatments: 1= tailing without amendment; 2= 1.24% GGS; 3= 5% GGS; 4= 10% GGS; 5= 10% LPW; T6= 1.24% GGS+10% LPW ; 7= 5% GGS+10% LPW ; 8= 10% GGS+10% LPW.

Average CuT in GGS-amended tailings increased from 33.6 mg Cu kg-1 on day 1 (24 h) to 105.4 mg Cu kg-1 on day 56 (8 weeks), from 20.7 mg Cu kg-1 (on day 1) to 66.9 mg Cu kg-1 (on day 56) in the [GGS + LPW]-amended tailings, and from 14.5 (on day 1) to 76.8 mg Cu kg-1 (on day 56) in the LPW-amended tailings. The labile Cu fraction in the control was relatively stable from day 1 to the end of the experiment (Fig. 1). At day 1, CuT correlated positively with tailings pH (r= 0.859, P<0.001) and negatively with organic matter content of substrates (r=-0.926, P<0.001). Analysis of variance (Table 1) revealed a very highly significant effect (P<0.001) of LPW and GGS, and their interaction on CuT.

Table 1: Analysis of variance (F value) on the influence of lemon peel waste (LPW) and garden growth substratum (GGS) on the total labile Cu (CuT).

| Source of variation | d.f. | $Cu_T$ |
|---|---|---|
| LPW (A) | 1 | 107.6*** |
| GGS (B) | 3 | 91.4*** |
| Interaction (A x B) | 3 | 163.2*** |

*** Significant at *P*< 0.001.

## 3. Discussion

### 3.1. Tailing pH

The lower pH in the LPW-amended tailings at day 1 is attributable to the presence of residual organic acids including citric acid in LPW. After the neutralization of the available organic acids, tailing pH attained a value of 7.76 at 1-wk incubation. The increase in alkalinity of the LPW-amended tailings is significant and is a reflection of the degree of acid-neutralizing capacity of Cu-mine tailings containing calcite. De Coninck et al. [14] showed that the Cu-mine tailings and calcite mineral collected from the tailings site were well buffered against changes in pH. They concluded that the carbonate buffer system was the major factor controlling the ability of Cu-mine tailings system to withstand a large change in pH when acid was added.

### 3.2. Labile Cu Pool

As shown in Fig. 1, the lability of Cu increases with short term incubation due to the transformation of initially non available Cu fractions and sparingly soluble Cu compounds to available Cu-dissolved fractions and readily extractable Cu. According to his observation, Brandt et al. [15] found that Cu bioavailability relative to the total Cu concentration increased significantly with increasing Cu loading of manure and with increasing manure amendment to soils. In both cases, the immediate increase in bioavailability has been explained in part by increased Cu concentration in solution and in part by an increased bioavailability of dissolved Cu species. Almås et al. [16] reported that addition of organic matter (pig manure, Sus scrofa) increased the solubility of metals (Cd and Zn) in two mineral soils by the formation of organo-metallic complexes. Fig. 1 shows that the level of labile Cu pool was lower in the LPW treatment than in the GGS treatment. This result can be ascribed to the presence of more sorbent sites in LPW treatment. This might also result from a stronger binding affinity of Cu in the 10% LPW treatment. Lemon peels are characterized by the presence of pectin substances [17] which have adsorption capabilities for trace elements [18], [19]. Arslanoglu et al. [20] evaluated the metal sorption capacity of lemon peel and lemon resin. They found that lemon peel had a high affinity for Cu. It can also be deduced from Fig. 1 that the presence of peat (from GGS) in the [GGS + LPW]-amended tailings contributed more to the additional soluble Cu in amended tailings [21].

## 4. Conclusion

The effects of GGS and LPW on tailing acidification were limited due to the already-high pH and buffering capacity of the tailings. Extractable Cu fractions as labile Cu (DTPA, Mehlich-3) were significantly increased after adding GSS and LPW. The smallest amount of labile Cu was found in the unamended tailings and the highest amount in the GGS-amended tailings. The results indicated that extractable Cu in amended-tailings was incubation time- and amendment rate-dependent. The results show that it is possible to enhance the availability of tailings-copper by adding garden growth substratum in combination with lemon peels waste to Cu tailings.

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