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# Heavy metals and yield of cowpea cultivated under composted tannery sludge amendment

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**ABSTRACT.** The study aimed to evaluate the phytoavailability of heavy metals (Cr, Cd, Ni and Pb) concentrations in leaves and grains, and yield of cowpea (*Vigna unguiculata* L) grown in soil amended with composted tannery sludge (CTS) for two consecutive years. The experiments were carried out in 2009 and 2010 in soil amended with CTS at 0, 5, 10, 20, and 40 Mg ha<sup>-1</sup>. The CTS amendment rates applied were above 10 Mg ha<sup>-1</sup>, increased Cr concentrations in cowpea leaves. There were not increases in the heavy metals concentrations in cowpea grains after two years. In 2009, the application of CTS amendment did not promote increase in plant yield. However, in 2010, CTS amendment at 10 and 20 Mg ha<sup>-1</sup> increased cowpea yield. The amendment of composted tannery sludge linearly increased linearly the concentration of Cr in the leaves of cowpea after two years. Composted tannery sludge promoted increases in cowpea yield. **Keywords:** *Vigna unguiculata*, organic residues, trace elements.

## Metais pesados e produtividade de caupi cultivado sob aplicações de lodo de curtume compostado

**RESUMO.** O estudo objetivou avaliar a fitodisponibilidade de metais pesados (Cr, Cd, Ni e Pb) em folhas e grãos, e produtividade em caupi (*Vigna unguiculata* L) em solo após a adição de lodo de curtume compostado (LCC) por dois anos consecutivos. Os experimentos foram realizados em 2009 e 2010 em solo com adição de LCC a doses de 0, 5, 10, 20 e 40 Mg ha<sup>-1</sup>. A adição de LCC em doses acima de 10 Mg ha<sup>-1</sup>, por dois anos consecutivos, aumentou a concentração de Cr nas folhas do caupi. Não houve aumento na concentração de metais no grão de caupi após dois anos de aplicação. Em 2009, a aplicação de LCC não aumentou a produtividade da planta. Entretanto, em 2010, o LCC nas doses de 10 e 20 Mg ha<sup>-1</sup> aumentou a produtividade do caupi. A aplicação de lodo de curtume compostado aumentou linearmente a concentração de Cr nas folhas do caupi após dois anos. O lodo de curtume compostado promoveu aumento na produtividade de grãos.

Palavras-chave: Vigna unguiculata, resíduo orgânico, elementos traço.

#### Introduction

Tannery industries occupy an important place in the Brazilian economy with assets of 21 billion dollars per year (SILVA et al., 2010). However, these industries annually release 1 million tons of tannery sludge, 3% of which are solids (SANTOS et al., 2011). In Brazil, there is no established method for tannery sludge disposal, and landfilling is commonly used as a current method. Alternatively, land application has been suggested as a suitable method (COSTA et al., 2007). However, both methods bring a series of economic, social and environmental problems. Therefore, it is necessary to find new methods for tannery sludge recycling as alternative to landfilling and land application. In Brazil, the agricultural use of tannery sludge has been studied in several crops (ARAÚJO et al., 2006; MELO et al, 2007; SILVA et al., 2006; TEIXEIRA et al., 2006). These studies focused on untreated tannery sludge and reported that the main problem is chromium (Cr) content in the sludge. For example, Silva et al. (2006) evaluated tannery sludge as an organic fertilizer for maize crops and observed lower plant growth compared to cattle manure amendment, mainly due to the high quantity of Cr in tannery sludge. However, Teixeira et al. (2006) found increases in cowpea biomass after tannery sludge amendment with results similar to those observed with chemical fertilization.

Heavy metals are usually present in tannery sludge, particularly trivalent chromium  $(Cr^{3+})$ .

Once present in soil, air or water, whether by natural occurrence or by sludge amendment, this heavy metal can enter the food chain. When it reaches high concentration in plants, chromium can cause toxicity problems, such as decreases in plant yield and diseases in animals or humans (GONÇALVES JR. et al., 2011). Alternatively, composting has been suggested as a suitable method for tannery sludge treatment before agricultural use (SANTOS et al., 2011; SILVA et al., 2010). This method has been used to process sludge of different origins, such as sewage sludge (BERNAL et al., 1998) and textile sludge (ARAÚJO et al., 2007; ARAÚJO; MONTEIRO, 2006).

However, consecutive amendments with composted wastes may promote the concentration of heavy metals in soils and plants (MCBRIDE et al., 2004), and heavy metals may cause negative or positive effects on plant growth and yield. Some studies reported positive, negative or neutral plant responses to heavy metal accumulation in soil (MARTINS et al., 2003; MERLINO et al., 2010; SANTOS et al., 2011). In plants, heavy metal accumulation varies between different parts of the plant or among different plant species. In maize, Zn accumulates in the leaves, while Cr and Pb accumulate in the grains and shoots, respectively (PIERRISNARD, 1996). The cowpea is an important crop in Northeast Brazil, and there are no studies evaluating heavy metal accumulation in plant tissues due to composted tannery sludge amendment. Therefore, the aim of this study was to evaluate the phytoavailability of Cr, Cd, Ni and Pb in leaves and grains and the yield of cowpea (Vigna unguiculata) after two years of composted tannery sludge amendment.

#### Material and methods

The experiments were carried out under field conditions at the 'Long-Term Experimental Field' at the Agricultural Science Center, Teresina, Piauí State (05° 05' S; 42° 48' W, 75 m). The regional climate is dry tropical (Köppen), and it is characterized by two distinct seasons, rainy summer and dry winter, with annual average temperatures of 30°C and rainfall of 1,200 mm. The rainy season extends from January to April when 90% of total annual rainfall occurs. The soil is classified as Fluvic Neosol (10% clay, 28% silt and 62% sand). The values of chemical properties (EMBRAPA, 1997) in the 0-20 cm depth were as follows: pH (water) – 6.7; organic matter - 12.2 g kg<sup>-1</sup>; P - 8.04 mg dm<sup>-3</sup>; exchangeable K - 0.06 cmol<sub>c</sub> dm<sup>-3</sup>; Ca - 1.76 cmol<sub>c</sub> dm<sup>-3</sup>;  $Mg - 0.37 \text{ cmol}_{c} \text{ dm}^{-3}$ ; CTC - 3.92 cmol\_{c} dm^{-3};

 $Cr - 0.6 \text{ mg kg}^{-1}$ ; Ni – 0.04 mg kg $^{-1}$ ; Cd – 0.07 mg kg $^{-1}$ ; Pb –0.94 mg kg $^{-1}$ . The Cr, Ni, Cd and Pb levels were determined according to Usepa (1996). The physical properties are (EMBRAPA, 1997): soil density – 1.81 kg dm $^{-3}$ ; particles density – 2.62 kg dm $^{-3}$ ; soil porosity – 0.29 m $^3$  m $^{-3}$ . The soil is composed basically of caulinite and ilite and shows the presence of quartz.

The composted tannery sludge (CTS) was produced from tannery sludge mixed with sugarcane straw and cattle manure (ratio 1:3:1; v:v:v). The composting process was carried out using the aerated-pile method for 85 days (USDA, 1980). The size of pile was 2 m long, 1 m wide and 1.5 m high. The pile was turned twice a week during the first 30 days. Afterwards, it was turned twice a month for 55 more days. At the end of the composting process, twenty subsamples were randomly collected from the CTS to produce a composite sample. N, P and K content were evaluated by Kjeldahl, colorimetry and photometry, respectively. The other trace elements (trivalent Cr, Cd, Ni and Pb) were evaluated by spectrophotometry with atomic absorption according to Usepa (1996). The CTS basic characterization data are presented in Table 1.

**Table 1.** Chemical properties of composted tannery sludge(CTS).

| Properties                             | CTS    | CTS    | Limits of heavy metal  |
|----------------------------------------|--------|--------|------------------------|
|                                        | (2009) | (2010) | permitted <sup>1</sup> |
| pН                                     | 7.8    | 7.2    | -                      |
| C <sub>org</sub> (g kg <sup>-1</sup> ) | 187.5  | 195.3  | -                      |
| N (g kg <sup>-1</sup> )                | 1.28   | 1.39   | -                      |
| P (g kg <sup>-1</sup> )                | 4.02   | 3.83   | -                      |
| K (g kg <sup>-1</sup> )                | 3.25   | 3.51   | -                      |
| Ca (g kg <sup>-1</sup> )               | 95.33  | 84.28  | -                      |
| Mg (g kg <sup>-1</sup> )               | 6.80   | 5.71   | -                      |
| S (g kg <sup>-1</sup> )                | 9.39   | 8.43   | -                      |
| Cu (mg kg <sup>-1</sup> )              | 17.80  | 19.51  | 4300                   |
| Fe (mg kg <sup>-1</sup> )              | 5171   | 4932   | -                      |
| Mn (mg kg <sup>-1</sup> )              | 1848   | 1958   | -                      |
| Zn (mg kg <sup>-1</sup> )              | 141.67 | 128.31 | 7500                   |
| Mo (mg kg <sup>-1</sup> )              | 9.28   | 14.87  | -                      |
| Ni (mg kg <sup>-1</sup> )              | 21.92  | 28.61  | 420                    |
| Cd (mg kg <sup>-1</sup> )              | 2.87   | 3.93   | 85                     |
| Cr (mg kg <sup>-1</sup> )              | 2255   | 2581   | 3000                   |
| Pb (mg kg <sup>-1</sup> )              | 42.67  | 38.54  | 75                     |

The experiments were conducted in 2009 and 2010 with six treatments: 0 (no CTS), 5, 10, 20 and 40 ton ha<sup>-1</sup> of CTS (dry basis). The experiment was arranged in a completely randomized block design with four replications. The plots were marked (20 m<sup>2</sup> each and 12 m<sup>2</sup> of useful area for soil and plant sampling), including rows spaced 1.0 m apart.

Each year, the CTS was applied ten days before cowpea (*Vigna unguiculata*) sowing. It was spread on the soil surface and incorporated into the 20 cm layer with a harrow. Cowpeas were grown at a density of 5 plants m<sup>-1</sup> (approximately 62,000 plants ha<sup>-1</sup>). The data were collected 40 (flowering period) and 60 (harvest) days after plant emergence in both years. The leaves were collected from ten plants inside the plots. Plant yield was evaluated by sampling ten plants inside the plots, and grains were dried for 13% of humidity. In the first sampling, the Cr, Cd, Ni and Pb contents in leaves were evaluated. In the second sampling (60 days), the Cr, Cd, Ni and Pb in grains and the plant yield were evaluated. The Cr, Cd, Ni and Pb analyses in leaves and grains were performed according to methods described in Usepa (1986).

The data were subjected to the analysis of variance (ANOVA) and F test (5%). When F was significant, the data were adjusted to regression analyses as functions of rates of CTS amendment (SAS, 1996).

#### **Results and discussion**

The CTS enriched in heavy metals (Table 1), especially Cr, increased Cr concentration in soil (Figure 1). However, the Cr concentration values observed in the soil were below the limits permitted for agricultural soils according to Conama (2006) and Cetesb (2001), which are 150 and 300 mg kg<sup>-1</sup>, respectively. In addition, due to the low solubility of Cr in neutral or alkaline soils (SANTOS et al., 2011), only a small proportion of Cr is bio-available. This fact suggests that in agricultural soils with a neutral pH that are treated with tannery sludge relatively high in Cr, toxicity will rarely be observed (ALLOWAY, 1990).

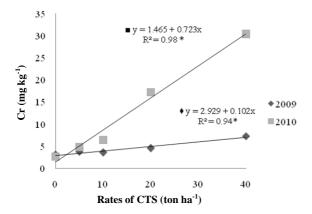
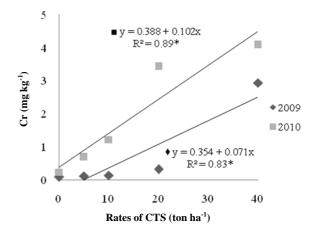


Figure 1. Pseudo total Cr concentration in the soil under different rates of composted tannery sludge - CTS in 2009 and 2010. \*-5% significance.

In the case of Cd, Ni and Pb in soil, CTS amendment did not promote significant (p < 0.05) increases in their concentrations. In this case, the

average Cd, Ni and Pb concentrations in soil found after two years of CTS amendment were 0.07, 1.68 and 2.4 mg kg<sup>-1</sup>, respectively. These concentrations are below the limits proposed by Conama (2006) and Cetesb (2001) for agricultural soils.

CTS amendment promoted a linear and significant increase in Cr concentration in cowpea leaves in 2009 and 2010 (Figure 2). Additionally, increases occurred between the first and second year for all CTS amendment rates. The values of Cr concentration in leaves found after two years of CTS amendment ranged between 0.09 and 4.08 mg kg<sup>-1</sup> for 0 and 40 ton ha<sup>-1</sup> CTS, respectively.



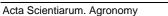
**Figure 2.** Total Cr concentration in cowpea leaves cultivated under different rates of composted tannery sludge - CTS in 2009 and 2010. **\***-5% significance.

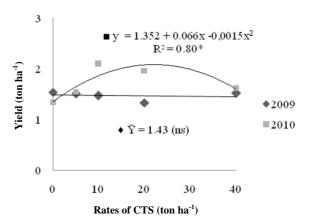
These increases in Cr concentrations are related to the high Cr concentration in the CTS (Table 1). Aquino Neto and Camargo (2000) also observed an increase in Cr concentration in lettuce leaves after application of tannery sludge as a direct response to the increase in tannery sludge rates. Thus, for some crops, Cr is translocated from the roots to the top parts of the plant and is influenced by plant species, although Cr is usually retained in the plant root system (DUDKA et al., 1991; PIOTROWSKA et al., 1991). For example, in soybean, Castilhos et al. (2001) observed that the increase in the Cr concentration in the plant root promoted an increase of Cr in the leaves. In cowpea, there is no information about Cr uptake after tannery sludge amendment, although some studies found a decrease in the plant dry weight as a direct response of tannery sludge with high Cr content (SANTOS et al., 2011; TEIXEIRA et al., 2006). After two years, the Cr concentrations in cowpea leaf tissue remained within the range considered normal, with levels ranging from 0.03 to 14 mg kg<sup>-1</sup> (KABATA-PENDIAS; PENDIAS, 2001).

CTS amendment did not promote significant (p < 0.05) increases in the Ni, Cd and Pb concentrations in cowpea leaves due to the low Ni, Cd and Pb concentrations in CTS. The average Ni value found in cowpea leaves was 1.70 mg kg<sup>-1</sup>. This value is within the normal limits for plant tissue, which range from 0.1 to 5 mg kg<sup>-1</sup> (ADRIANO, 1986). The average values of Cd and Pb were 0.54 and 3.8 mg kg<sup>-1</sup>, respectively. These values are below the limits proposed by Kabata-Pendias and Pendias (2001), which range from 0.1 to 2.4 and 0.2 to 20 mg kg<sup>-1</sup> for Cd and Pb, respectively. These results are in accordance with Souza et al. (2005), which did not find significant effects of tannery sludge on Ni, Cd and Pb concentrations in maize leaves.

There were no significant (p < 0.05) increases in Cr, Ni, Cd and Pb concentrations in cowpea grains after two years of CTS amendment. According to Mortvedt (2001), some plants can absorb significant amounts of Cr, Ni, Cd and Pb, but these heavy metals generally are not translocated to grains. Leaves usually present higher heavy metal contents than seeds, nuts and fruits (OLIVEIRA et al., 2005). In an experiment with maize, these authors observed that after five years of sewage sludge amendment, the Cd, Zn, Cu and Ni contents were higher in leaves than in grains. The average Cr concentration in grains found after two years of CTS amendment was 1.42 mg kg<sup>-1</sup>. These results are in accordance with Anjos and Mattiazzo (2000) for Cr in grains of maize sowed in soils amended with sewage sludge for three years. These authors found values of Cr in grains varying between 1.27 and 1.85 mg kg<sup>-1</sup>. In the case of Pb, the average concentration in grains was 2.1 mg kg<sup>-1</sup>. Rangel et al. (2006) found values for Pb ranging from 2.3 to 3.3 mg kg<sup>-1</sup> in grains of maize after three years of sewage sludge amendment. However, the values of Pb concentrations in grains found by these authors and in our experiment are below the limit for grain proposed by Kabata-Pendias and Pendias (2001), which is 8.0 mg kg<sup>-1</sup>. The average concentrations of Cd and Ni were 0.16 and 2.35 mg kg<sup>-1</sup>, respectively. These values for Cd and Ni concentrations in grains are below the limits proposed by Kabata-Pendias and Pendias (2001), which are 1.2 and 4.5 mg kg<sup>-1</sup> for Cd and Ni, respectively.

In the first year, there were no differences between treatments for cowpea yield (Figure 3), where the average of yield was 1.43 ton ha<sup>-1</sup>, because the soil presented sufficient content of plant nutrients before installing the experiment. In addition, there was most likely no Cr toxicity when the CTS was applied the first time.





**Figure 3.** Cowpea yield cultivated under different rates of composted tannery sludge - CTS in 2009 and 2010. **\***-5% significance; ns – non-significant.

In the second year, there was a quadratic response of plant yield after CTS amendment. According to the equation of regression, the estimated maximum plant yield was 2,720 kg ha<sup>-1</sup> for an estimated CTS rate of 22 ton ha<sup>-1</sup>. This yield is almost two times higher than that found for control soil (0 ton ha<sup>-1</sup> CTS). Additionally, this plant yield is higher than reported by Ferreira et al. (2008) and Gualter et al. (2008) using chemical fertilization. It means that CTS has the potential to increase cowpea yield and may be an alternative for chemical fertilization. This quadratic response for plant yield conflicts with reports from Higgins (1994), which evaluated rates of sewage sludge during four years and found a linear response in maize. During high rates of CTS, the Cr content in soil likely may have had a toxic effect on cowpea, which most likely presents a lower tolerance to metals than maize.

#### Conclusion

Amendment with composted tannery sludge linearly increased the concentration of Cr in the leaves of cowpea after two years.

There were no changes in the concentrations of Cr, Cd, Ni and Pb in cowpea grains after two years of composted tannery sludge amendment.

After two years of amendment, composted tannery sludge promoted increases in cowpea yield.

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