

Original paper

## Changes in chemical attributes of soil treated with tannery sludge in Amazonia

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### Abstract

Application of residuals to soil can favor the development of nutrient-poor agricultural areas. The objective of this study was to evaluate changes in the chemical attributes of soil after application of tannery sludge. The applied treatments were 1) Mineral control: 100 kg N ha<sup>-1</sup>, applied in different stages (25% at planting and 75% when plant maize was in the 1.4 development stage); 2) tannery sludge: 50 kg ha<sup>-1</sup>; 100 kg ha<sup>-1</sup>; 200 kg ha<sup>-1</sup>; 400 kg ha<sup>-1</sup>; and 600 kg ha<sup>-1</sup> of organic-N. All plots were treated with fertilizer (75 kg ha<sup>-1</sup> P<sub>2</sub>O<sub>5</sub> and 50 kg ha<sup>-1</sup> K<sub>2</sub>O). In the mineral control, nitrogen was applied in ammonium sulphate form. Soil samples were analyzed to determinate pH, calcium, magnesium and aluminum in 1M KCl solution, potential acidity (hydrogen + aluminum in a calcium acetate solution pH 7), and potassium and sodium in a Mehlich 1 solution. The application of tannery sludge modified the chemical attributes of the soil, increasing pH and Na<sup>+</sup>, Ca<sup>+2</sup>, and Mg<sup>+2</sup> contents.

**Key-words:** Amazon, Disturbed areas, Fertilization, Soil pollution

### Introduction

The transformation of natural systems into agricultural areas in tropical regions is an important source of CO<sub>2</sub> emissions, associated with changes in climate on a global scale (Cerri et al., 2007). Cultivated pastures are the predominant land use in the Brazilian Amazon: the region contains at least 120,000 km<sup>2</sup> of pasture in varying states of degradation. One possible solution for minimizing environmental damage from traditional Amazonian pasture management is the recuperation of degraded pastures, generally by applying fertilizers or residues (Lavres Jr. et al., 2003).

Using fertilizers has greatly increased agricultural productivity in tropical regions. An increase in the use of organic and inorganic fertilizers, in conjunction with other complementary measures, may help reduce environmental problems by increasing the productivity of cultivated land and concurrently reducing pressure on marginal lands more susceptible to desertification and erosion (Fageria and Stone, 2006; Teixeira et al., 2007). In this context, the use of residuals may be a viable alternative for sustainable development of agricultural soils.

Urban or industrial organic waste applications in degraded areas can help solve the problem of waste disposal and the high organic content of

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residues helps to recuperate degraded areas. Soil organic matter can perform multiple functions such as increasing water retention, changing soil pH, and increasing soil fertility. In relation to soil fertility, organic matter is responsible to increasing cation exchange capacity in tropical soil, which has a strong influence on soil nutrient balance (Bohn et al., 1985).

Tannery sludge is a residue from leather processing, which is rich in organic matter, however Martines et al. (2006) state that technical criteria for agricultural use of tannery sludge are necessary. Inappropriate use of this material can contribute to high soil pH, high levels of soluble salts (Silva, 2008) and heavy metal pollution (Chandra et al., 2009), which can compromise future agricultural use of these areas.

In addition to recovering degraded areas, the agricultural use of tannery sludge may be an alternative to reduce production costs, making it a viable alternative for sustainable development of nutrient-poor agricultural areas. Therefore, the objective of this study was to evaluate soil chemistry after application of tannery sludge on soil samples from the southwestern Amazon.

## Material and methods

Ultisol samples were collected on the surface layer (0-20 cm) from soil located in the Amazonian region - AC, Brazil. Soil samples were air-dried and sieved (2 mm) to fill pots (7 kg capacity) in a greenhouse at the Agroforestry Research Center of Acre (Embrapa).

The analysis of the soil chemical attributes revealed the following characteristics: pH = 4.75; P = 6.8 mg dm<sup>-3</sup>, K<sup>+</sup> = 0.053 cmol<sub>c</sub> dm<sup>-3</sup> and Na<sup>+</sup> = 0.017 cmol<sub>c</sub> dm<sup>-3</sup> (based on a Mehlich-1 solution), Ca<sup>+2</sup> = 0.967 cmol<sub>c</sub> dm<sup>-3</sup>, Mg<sup>+2</sup> = 0.683 cmol<sub>c</sub> dm<sup>-3</sup>, Al<sup>+3</sup> = 0.483 cmol<sub>c</sub> dm<sup>-3</sup> (KCl 1 mol L<sup>-1</sup>), H + Al (calcium acetate patch solution) = 3.63 cmol<sub>c</sub>.dm<sup>-3</sup> 'Base sum = 1.75 cmol<sub>c</sub>.dm<sup>-3</sup> 'Cation exchange capacity = 5.38 cmol<sub>c</sub>.dm<sup>-3</sup>, V = 32%; Organic carbon = 1.01 dag kg<sup>-1</sup> (via humid potassium dicromate); M.O = 1.74 dag kg<sup>-1</sup>.

A completely randomized experimental design was set up consisting of six treatments and six replicates. The treatments were: 1) mineral control application of 100 kg N ha<sup>-1</sup> (25% at planting and 75% when maize was in stage 1.5); 2) tannery

sludge application equivalent to 50 kg ha<sup>-1</sup> of N of organic N; 3) tannery sludge 100 Kg ha<sup>-1</sup> of organic N; 4) tannery sludge 200 Kg ha<sup>-1</sup> of organic N; 5) tannery sludge 400 Kg ha<sup>-1</sup> of organic N; 6) tannery sludge 600 Kg ha<sup>-1</sup> of organic N.

All treatments received a mineral supplement equivalent to 75 Kg ha<sup>-1</sup> P<sub>2</sub>O<sub>5</sub> and 50 Kg ha<sup>-1</sup> K<sub>2</sub>O, from single superphosphate and potassium chloride, respectively. For the mineral control the application of nitrogen was in the form of ammonium sulfate.

The applied tannery sludge consisted of a mixture of 50% primary sludge (wastes generated in first phase of treatment of leather with lime) and 50% sludge from the primary decanters (liquid effluent). Sludge was collected at the Curtume Bom Retiro company – AC, and represented a mixture of industrial sludge, which is disposed in agricultural areas and pastures of the region.

The tannery sludge was applied on the soil surface layer of pots for each experimental treatment. Deionized water was applied to 60 % of soil field capacity and then incubated for 8 days. Eight days after the application of the treatments, we planted commercial hybrid maize seeds. Forty-seven days after, sowing plants were collected of the soils and leaves and stalks were separated.

Fifty-five days after tannery sludge application, soil samples were separated (the pot's top and lower layer of soil) for subsequent chemical analysis. The soil samples were analyzed in relation to soil fertility where the following soil attributes were measured: soil pH in water; calcium, magnesium and aluminum exchangeable, in a 1M KCl solution; and potential acidity (H<sup>+</sup> = hydrogen + exchangeable aluminum, in a calcium acetate solution - pH 7). Finally, the levels of potassium and sodium exchangeable were analyzed in a Mehlich 1 solution (Embrapa, 1999).

Results were submitted to analysis of variance and regression curves were fitted between applied doses of tannery sludge and soil attributes.

## Results and discussion

### a) Exchangeable cations

Soil exchangeable Ca<sup>2+</sup> at the surface (0-10 cm depth) increased with tannery sludge application (Table 1). Tannery sludge has high concentrations of this element as hydroxide, sulfide and carbonate (Ferreira et al., 2003). No changes in Ca<sup>2+</sup> levels at the 10-20 cm depth.

Values of  $Mg^{2+}$  were not affected by addition of tannery sludge at the 0-10 cm depth. However, we observed changes at the 10-20 cm depth. These changes were unexpected due to the fact that tannery sludge has low  $Mg^{2+}$  levels. It is possible that the  $Ca^{+2}$  displaced  $Mg^{2+}$  from the soil surface layer to the subsurface layer.

**Table 1.** Exchangeable bases in soil treated with tannery sludge.

Attributes	Equations	R <sup>2</sup>	p-value	F
(cmol <sub>c</sub> dm <sup>-3</sup> ) -----0-10 cm-----				
Ca <sup>+2</sup>	Y=1.026 +0.001x	0.43**	0.000	24.891
Mg <sup>+2</sup>	Y= 0.75 + 3.5 10 <sup>-5</sup>	0.003ns	0.752	0.102
K <sup>+</sup>	Y= 0.57 -2.4 10 <sup>-5</sup> x	0.282**	0.001	12.957
Na <sup>+</sup>	Y= 0.036 + 0.001x	0.973**	0.000	1198.267
-----10-20 cm-----				
Ca <sup>+2</sup>	Y=0.966 -1.9 10 <sup>-8</sup> x <sup>2</sup>	0.0067ns	0.133	2.378
Mg <sup>+2</sup>	Y= 0.73 + 0.001	0.434 **	0.000	24.981
K <sup>+</sup>	Y= 0.054 – 2.19 x	0.161ns	0.017	6.337
Na <sup>+</sup>	Y=0.029 + 0.001x	0.715**	0.000	82.915

n<sup>s</sup>- not significant \*\* significant at 1%.

Values of exchangeable K<sup>+</sup> decreased at both depths with tannery sludge application. Fonseca et al. (2007) also observed a decrease in K<sup>+</sup> values after application of effluent from sewage treatment with high Na levels. These authors state that the increase in Na favors desorption and leaching of K, which has a pronounced effect in tropical soils due to low CEC.

It was observed an increase in Na<sup>+</sup> levels at both depths. Tannery sludge has high concentrations of Na<sup>+</sup> due to use of sodium hydroxide in leather treatment. According to Richards (1954), when sodium dominates the soil exchange complex, it triggers dislocation of Ca and Mg which, consequently, precipitates these cations in the soil solution. As for physical characteristics, the large proportion of Na<sup>+</sup> in the exchange sites of clay minerals reduces the attraction between soil particles resulting in soil expansion and dispersion. Disperse soil particles move through the soil profile,

occupying porous spaces (Irvine and Reid, 2001) which results in deterioration of soil structure, reducing water infiltration and aeration properties - a serious problem in alkaline soils which affects vegetation growth (Raij, 1991).

Salinization risk from agricultural use of leather residuals is due to the high salt concentration, which can directly or indirectly cause toxic effects in plants, including nutritional imbalance. Various authors have detailed the salinization risk of tannery sludge application in agricultural areas due to high levels of exchangeable bases, mainly Na<sup>+</sup> (Costa et al., 2001; Aquino Neto and Camargo, 2000).

Tannery sludge application increased the base sum in the soil at both depths (y= 1.878 + 0.002x R<sup>2</sup>= 0.783\*\* at the 0-10 cm depth. y= 1.779 + 0.002 x R<sup>2</sup>= 0.783\*\* at the 10-20 cm depth).

The increase in the proportion of Na in relation to Ca and Mg was directly proportional to the increase in the amount of sludge applied. Therefore, increasing the quantity of tannery sludge results in a greater enrichment of Na than other alkaline cations, which can negatively affect soil fertility.

For the Na/K relationship it was found the same relationship at both depths. The increase in the Na/K ratio is due to both the increase in Na as well as a decrease of K<sup>+</sup> in soil solution. The increase in Na<sup>+</sup> concentrations dislocates K<sup>+</sup> the exchange complex by placing it in solution can then be easily leached (Fonseca et al. ,2007).

### b) Soil acidity

Soil acidity was neutralized by tannery sludge application. The soil pH increased in rates 300 - 400 g N kg<sup>-1</sup> at 0-10 cm. There was no change in soil pH at the 10-20cm depth. Other authors found an increase in soil pH after tannery sludge application (Ferreira et al., 2003; Gupta and Sinha, 2007; Konrad and Castilho, 2001). Observed changes in soil pH were restricted to the application layer. Even though tannery sludge is a microparticulate residue, chemical reactions occurred primarily at the application surface.

Levels of exchangeable H<sup>+</sup> and Al<sup>3+</sup> decreased after tannery sludge application. Al<sup>3+</sup> levels decreased at both depths; H<sup>+</sup> decreased at the 10-20 cm depth with the 300 g N/kg tannery sludge application (Table 2). Reductions in exchangeable

Al<sup>3+</sup> and H<sup>+</sup> levels were also observed in a greenhouse study that incorporated tannery sludge (Teixeira, 1981; Selah et al., 1991; Gianelo et al., 2011). Aluminum saturation (m value) also decreased at both depths.

**Table 2.** Components of soil acidity in soil treated with tannery sludge.

Components	Equations	R <sup>2</sup>	p-value	F
-----0-10 cm-----				
H <sup>+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	Y= 3.034 – 0.001x	0.285**	0.001	13.182
Al <sup>3+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	Y= 0.394 – 0.001x	0.677**	0.000	69.174
m (%)	Y= 17.14 – 0.0285x	0.692**	0.000	74.051
-----10-20 cm-----				
H <sup>+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	Y= 2.888- 1.4 10 <sup>-6</sup> x <sup>2</sup>	0.174ns	0.047	3.381
Al <sup>3+</sup> (cmol <sub>c</sub> dm <sup>-3</sup> )	Y= 0.437- 0.00x	0.374**	0.000	19.713
m (%)	Y=19.474 – 0.0023x	0.691**	0.000	30.186

n<sup>s</sup>- not significant. \*\* significant at 1%.

### c) Carbon, nitrogen and phosphorus

We have not detected changes in C and N levels after tannery sludge addition (Table 3). Based on Barajas-Aceves and Dendoveen (2001) N addition as ammonia and degradable organic substances accelerates mineralization of organic matter in soils with low C and N levels. Therefore, while tannery sludge has high C levels, this C was in the form of starch, sugars and simple acids. These compounds have a high oxidation rate. From the standpoint of disposing of the residue is interesting because, according with Gloria (1992) the high interest in using residuals on soil is based on the capacity to decompose organic material without significantly affecting the soil environment.

In a carbon mineralization study, Martines et al. (2006) found that the half-life of tannery sludge was only six days. This means that after the first ten days of incubation, more than half of the carbon was liberated as C-CO<sub>2</sub>, indicating a rapid mineralization phase followed by another slower and establishment/equalizing C-CO<sub>2</sub> fluxes. Konrad and Castilho (2001) found that microbial activity was

more pronounced until 50 days after tannery sludge application. Therefore, after those 55 days following the tannery sludge application the added C had been consumed by soil microbes/microbiota.

**Table 3.** Carbon, nitrogen, phosphorus and C/N ratio in soil treated with tannery sludge.

Components	Equations	R <sup>2</sup>	p-value	F
-----0-10 cm-----				
P (mg dm <sup>-3</sup> )	Y=7.741 + 0.19x – 2.6 10 <sup>-5</sup> x <sup>2</sup>	0.163ns	0.017	2.75
C (g kg <sup>-1</sup> )	Y= 9.887 + 0.006x – 1.0 10 <sup>-5</sup> x <sup>2</sup>	0.210 ns	0.644	0.217
N (g kg <sup>-1</sup> )	Y= 1.198 – 9 10 <sup>-7</sup> x <sup>2</sup>	0.183 ns	0.039	3.586
C/N	Y= 8.184 – 0.001 x	0.188 **	0.009	7.645
-----10-20 cm-----				
P (mg dm <sup>-3</sup> )	Y= 1.387 + 0.002x	0.233 **	0.003	10.046
C (g kg <sup>-1</sup> )	Y= 9.702 + 0.005 x – 7.2 10 <sup>-6</sup> x <sup>2</sup>	0.182 ns	0.069	3.563
N (g kg <sup>-1</sup> )	Y= 1.197 – 3.9 10 <sup>-7</sup> x <sup>2</sup>	0.017 ns	0.756	0.282
C/N	Y= 8.203 + 0.003x – 3.810 <sup>-6</sup> x <sup>2</sup>	0.062 ns	1.067	0.356

n<sup>s</sup>- not significant. \*\* significant at 1%.

The tannery sludge didn't affect the soil CEC (y = 5.261 + 0.001 x – 1.2 10<sup>-6</sup> x<sup>2</sup>. R<sup>2</sup> = 0.097<sup>ns</sup> at the 0-10 cm depth and y = 1.668 + 6.7 10<sup>-5</sup>. R<sup>2</sup> = 0.269\*\* at the 10-20 cm depth). Changes in CEC occurred primarily due to the addition of established C sources. Tannery sludge application combined with phosphate fertilizers did not influence soil P levels. It is likely that the low P levels in tannery sludge associated with elevated soil pH (Barajas- Aceves and Dendoveen, 2001) contributed to an increase in P and insoluble forms of calcium and hydroxyapatite.

### Conclusion

Applying tannery sludge to Ultisols changes the chemical soil attributes by increasing Na and Ca levels and soil pH, reductions of K and Mg availability. It is necessary to monitor tannery sludge

application, however, especially due to the risk of increasing soil salinity.

**Conflict of interest:** All authors declare no conflict of interest.

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