Accumulation of zinc, copper and manganese in soil fertilized with pig manure and urea in Southern State of Santa Catarina (Brazil)

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Abstract
This study evaluates changes in the Zn, Cu and Mn contents of a typical red clay Ultisol in the municipality of Braço do Norte, SC, Brazil during a corn (*Zea mays*) and oat (*Avena sativa*) crop cycle for a no-tillage system. The soil was fertilised with pig slurry and mineral fertilizer (urea), and swine deep bedding, at two rates: using the recommended dose of N and twice for the corn crop. Six measurements were made at depths of 0-15, 15-30, 30-45 and 45-60 cm, during the corn crop cycle in the 2007 / 8 harvest. In general, increases in the Zn, Cu and Mn contents occurred in soil with applications of pig manure. During the corn cycle, higher Zn, Cu and Mn concentrations were found in the surface layer (0-15 cm), and these values decreased with depth. For the treatment using fertilization with the deep bedding system twice the N recommendation (BD2x) in the soil surface layer, the highest Zn, Cu and Mn concentrations were observed. Although the levels of these elements were higher in the surface layer, their levels are not considered critical for environmental toxicity risks.

Key Words
Micronutrients, organic manure, sustainability

Introduction
Soil contamination with heavy metals has been recognized as a major environmental problem. Increasing concentrations of these metals in the soil may lead to their increased availability to plants. This availability and its vertical movement in the soil profile is controlled by soil attributes, and the varying mobility of these elements will be determined by the types and amounts of clay, pH, cation exchange capacity (CTC), MO contents, among others, which will influence the adsorption / desorption , precipitation / dissolution, complexation and redox reactions (Santos *et al.* 1999). Prolonged and / or excessive use of pig manure as organic fertilizer can result in the accumulation of Zn, Cu and Mn in the soil, and, as a consequence, in significant changes in the microbial community and phytotoxicity to plants (Simioni 2001). This is due to the chemical characteristics of wastes that are related to the nutritional composition of diets for pigs, which among other nutrients are rich in N, P and K, and have high concentrations of micronutrients such as Zn and Cu. It is estimated that 92-96% of Zn, 72-80% of Cu, (Bonazzi *et al.* 1994) ingested by animals are excreted and found in their feces and urine. Therefore, knowing the dynamics of these elements in soils is essential for assessing the environmental impact caused by the use of manure, since the extent of this impact is directly related to the ability of soils to retain these metals. This study aims to evaluate the leaching of Zn, Cu and Mn in Ultisol fertilized with deep bedding manure, pig slurry and chemical fertilizer in SPD in the municipality of Braço do Norte, Santa Catarina, Brazil.

Methods
The experiment was installed in the year of 2002 in an Ultisol, cultivated under a system of no-tillage with the succession oats / maize without the use of pesticides, in a rural property located at the Cachorrinhos Watershed River, in the city of Braço do Norte, at the coordinates 28º 15 'S and 49 º 15' W. The climate of the city is a Cfa type, according to the classification of Köppen (Epagri 2000). The treatments were applied in experimental units (parcels) 4.5 x 6.0 m (27 m^2) in size, as follows: control with no fertilization (T), fertilization with swine bedding (BD), fertilization with pig slurry (PS), soluble nitrogen with urea application (AS). All the fertilization treatments were applied with doses related to one (1x) and two (2x) times the N recommended for cultures of oats and maize. The applied values were calculated based on the Chemical Commission and Soil Fertility (CQFS RS / SC 2004). The amount of N recommended for the cultures (30 kg/ha for oats and 90 kg/ha for maize) was based on soil analysis and expected productivity of maize. The swine deep bedding was manually applied on the soil surface, five days before planting the maize. The application of liquid swine manure and soluble fertilizer (urea) was according to the

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recommendation of the CQFS RS / SC (2004). The Zn, Cu and Mn contents during the course of the experiment were assessed at four depths (0-15, 15-30, 30-45 and 45-60 cm), 0, 7, 35, 53, 73 and 142 days after application of the deep bedding litter and the first application of pig slurry and urea. In each plot, 6 soil sub-samples were taken, with the help of a Dutch auger to form a composite sample. The material was transported to the laboratory, dried and then harrowed, thereby obtaining an air-dried soil sample. Measurements of Zn, Cu and Mn were done according to the method described by Tedesco *et al.* (1995), with extractions using KCl 1 mol/L and determined by atomic absorption spectrophotometry, performed at the Epagri Laboratory of Soils - Chapecó. The results in each soil layer and at different sampling dates were submitted to analysis of variance and the means were compared by the Tukey test at 5% of significance level.

Results

The analysis of variance showed that the application of pig manure promoted significant accumulation of Cu, Zn and Mn in the soil. This accumulation results from the overdose of Zn, Cu and Mn in the diets used, since the requirement for pigs ranges from 5 to 10 mg/kg for Zn and from 6 to 10 mg/kg for Cu. Simioni (2001) found a relationship between the levels provided by diets and those found in manure, where diets rich in Zn and Cu resulted in higher Zn concentrations in the manure. Figure 1 shows that during the corn crop cycle, Zn had limited mobility within the soil layers up to 60 cm, with which higher concentrations in the surface layer (0 - 15 cm) for all treatments.

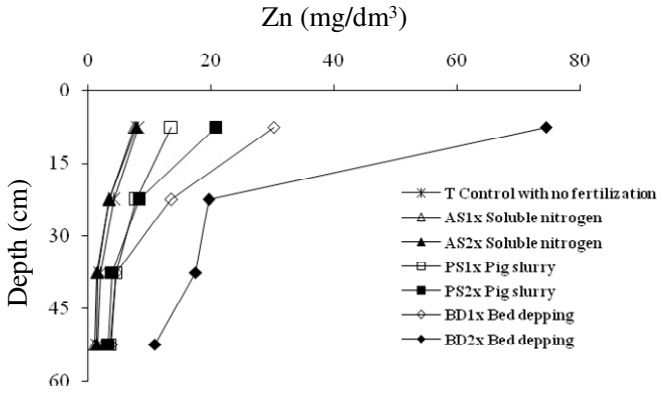

Figure 1. Zn concentration at depths of 0-15, 15-30, 30-45 and 45-60 cm.

The highest Zn concentration in the surface layer was for in the BD2x treatment, followed by BD1x, PS2x and PS1x, which significantly differ from each other. For all depths, the Zn concentrations for the treatments with mineral fertilizer showed no significant differences when compared to the control. The 15-30 cm layer also had the highest Zn levels for the treatment with BD and no differences were found for treatments with PS. In the 30-60 cm layer, the BD2x treatment differed from the others and there was no difference between the other treatments with organic fertilizers.

pH is one of the parameters with the greatest influence on the behavior of micronutrients in soils, because low values normally result in a higher availability, which may reach toxic levels. Araújo and Sobrinho (2000) studied Zn adsorption in several Brazilian soils and found a high correlation with organic carbon. Regarding the Cu contents in the soil (Figure 2), significant differences between treatments were also found. The highest Cu levels ($p < 0.05$) were observed for BD2x treatments in the surface layer, decreasing with depth. This Zn and Cu accumulation is consistent with data from L'Herroux *et al.* (1997), who also found increased levels and movement of these elements in the soil profile after four years of application of pig manure in France. These results differ from those found by Scherer and Nessi (2004) in the western state of Santa Catarina, on farms that had used pig manure for fertilization for 8 to 25 years. The authors observed higher Cu values in the 30 - 50 cm layer. According to the authors, this subsurface accumulation was due to the higher translocation capacity of this ion. For Zn, the highest contents were observed in the 0 - 10 cm layer.

Borkert *et al.* (1998) determined critical toxicity limits of these elements for some cultures. In general, legumes were more susceptible to Zn, while grasses were more susceptible to Cu. The critical limits established for corn were 300 mg of Zn/kg and 17 mg of Cu kg/soil. That is, the BD2x treatment presented Cu values close to or larger than the critical limit for the corn crop, at the 0-15 cm layer. Taking into consideration the standards set for European countries, which allows reaching up to 140 mg of Cu kg/soil

and 300 mg of Zn kg/soil, the soil under study still con be used for the application of pig manure. However, scientific works conducted in various parts of the world have shown that concentrations much lower than the reported levels are able to negatively affect some components of the soil system. Baath *et al.* (1998) showed that 40 kg of Cu/ha (20 mg of Cu/kg soil) and 280 kg of Zn/ha (160 mg of Zn/kg soil) altered the biological diversity.

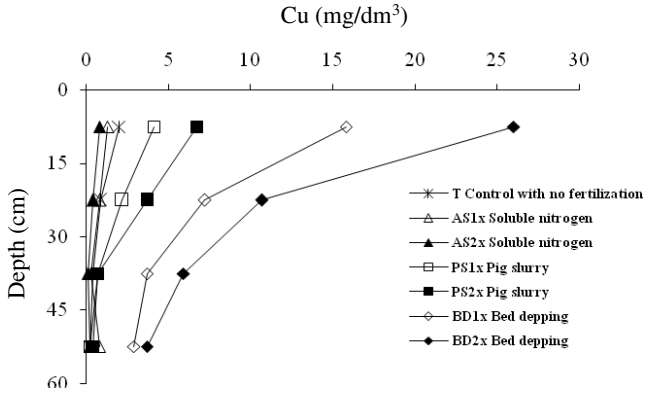

Figure 2. Cu concentration at depths of 0-15, 15-30, 30-45 and 45-60 cm.

For Mn, it was found that the BD2x treatment differed significantly from the others and promoted the accumulation of this element at the surface layer. In all treatments, decreased Mn contents at depth were observed (Figure 3). The largest accumulation at the surface layer is mainly due to the fact that Mn applied as fertilizer in a no-tillage system is retained in the organic fractions in a unavailable stable form (Moreira *et al.* 2006), which may also be related to a higher light incidence on the surface layers, increasing Mn solubility, which decreases in depth (Borkert *et al.* 2001).

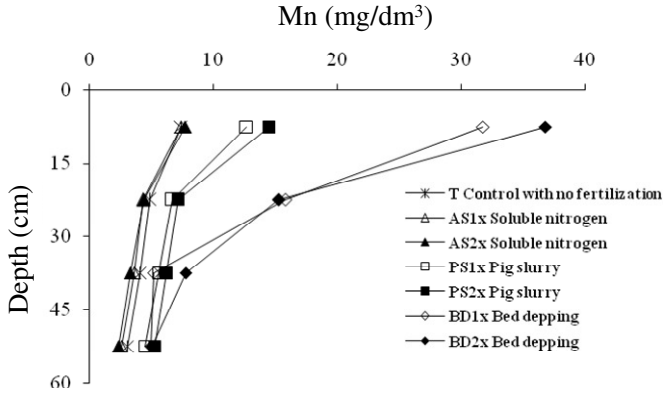

Figure 3. Mn concentration at depths of 0-15, 15-30, 30-45 and 45-60 cm.

Hargrove *et al.* (1982) observed higher Mn accumulation in weathered soil in southwestern USA under a no-tillage system when compared with a conventional system, attributing this difference to the deposition of plant residues. Brazil does not have legislation that determines the maximum Mn amount to be applied to soils. Sfredo *et al.* (2006), based on the Mehlich method, estimated Mn ranges in soil (Mg/dm^3) for the interpretation of their content in soils from the state of Paraná, and classified values above 30 as very high. Considering these rates, our research on fertilization with BD showed values that can be considered as very high. In a study conducted in the Rio Coruja / Bonito micro basin located at the municipality of Braço do Norte Mattias (2006), the authors observed that despite the large amounts of pig manure annually applied, the levels of heavy metals found were relatively low.

Conclusion

In general, increases in Zn, Cu and Mn levels were observed in the soil with pig manure applications, especially in the fertilization with swine bedding at a double dose, with the highest concentrations at the surface layer. The Zn, Cu and Mn contents added through pig manure were not considered critical to the environment.

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