Zinc and copper fractions in Oxisols of different textures fertilized with pig slurry

Frações de zinco e cobre em Oxisols de diferentes texturas adubados com dejeto suíno

Sulamirtes S. de A. Magalhães2* & Oscarlina L. dos S. Weber3

ABSTRACT: Disposal of pig slurry in the soil as a source of nutrients to plants, if improperly performed, can contribute to the contamination of ground and surface water and plants by the elements zinc (Zn) and copper (Cu). This study aimed to evaluate the zinc and copper fractions in Oxisols of different textures submitted to successive applications of pig slurry. Soil samples were collected in areas with and without pig slurry use, in the 0 - 0.10 and 0.10 - 0.20 m layers. The available and unavailable fractions of Zn and Cu were determined by sequential chemical fractionation, and the total and available Zn and Cu concentrations were evaluated. The Kruskal-Wallis test analyzed results. The areas with the longest pig slurry use showed the highest Zn concentrations in the most available forms. The soils in areas with and without pig slurry use showed a predominance of Cu in the not available form.

Key words: organic fertilization, heavy metals, agro-industrial residue, Cerrado

RESUMO: A disposição do dejeto suíno no solo, como fonte de nutrientes às plantas, se for realizada de maneira inadequada, pode contribuir para a contaminação de águas subterrâneas e superficiais e de plantas pelos elementos zinco (Zn) e cobre (Cu). Objetivou-se neste estudo avaliar as frações de Zn e Cu em Oxisols de diferentes texturas submetidos a sucessivas aplicações de dejeto líquido de suínos. Foram coletadas amostras de solos, em áreas com e sem histórico de uso com dejeto suíno, nas camadas de 0 a 0,10 e 0,10 a 0,20 m. Foram determinadas as frações disponíveis e não disponíveis de Zn e Cu pelo fracionamento químico sequencial e determinados os teores totais e disponíveis de Zn e Cu. Os resultados foram analisados pelo teste de Kruskal-Wallis. As áreas com maior tempo de uso de dejeto líquido de suínos apresentaram maiores teores de Zn nas formas mais disponíveis. Os solos das áreas com e sem uso de dejeto líquido de suínos apresentaram a predominância de Cu na forma não disponível.

Palavras-chave: adubação orgânica, metais pesados, resíduo agroindustrial, Cerrado

HIGHLIGHTS:
Higher concentrations of exchangeable Zn were found in areas with pig slurry application.
No higher concentrations of Cu were found in the exchangeable fraction in areas using pig slurry.
In all study areas, it was observed that more than 70% of Cu is in recalcitrant forms.
Introduction

The use of organic residues as a source of nutrients for crops has increased over the years, including pig slurry (PS) due to its biofertilizer potential. However, PS applications for long periods can contaminate soil and surface and subsurface waters due to the high concentration of trace elements, such as copper (Cu) and zinc (Zn) contained in the waste (Couto et al., 2015).

High Cu and Zn levels are present in the PS due to excessive amounts of these elements in the pigs' diets since approximately 85% of the Cu, and 98% of the Zn are excreted in the feed, quantities above the physiological requirement of this animal species (Smanhotto et al., 2010).

In the soil, Zn and Cu are found in different fractions (available and not available), its distribution in the soil compartments can be affected by the addition of PS (Ceretta et al., 2010). The Zn and Cu distribution estimation in different soil fractions is obtained by sequential extraction methods in which it is possible to separate the bioavailable (exchangeable), potentially bioavailable (linked to oxides, carbonates, and organic matter), and residual or not available (mineral structure) fractions. Although there is no standardization of sequential extraction schemes and several modifications are being carried out, the use of this method allows inferences about the form, flow, mobility, and transport of metals in soils (Tessier et al., 1979).

Understanding Zn and Cu accumulation forms in soils that received successive pig slurry applications is essential to know these elements' real contamination potential. This study aimed to evaluate Zn and Cu fractions in Oxisols of different textures submitted to successive pig slurry applications.

Material and Methods

Soil samples belonging to the Oxisols class, with different textures and pig slurry use history, were collected in Campo Verde and Nova Mutum municipalities, one of the pigs farming industrial poles from the Mato Grosso state, Brazil. The coordinates, identification, use, and application time of PS are shown in Table 1.

The climate classification of Campo Verde and Nova Mutum is Aw-type by the Köppen classification. The rainfall regime is well defined, with a dry period, from May to September, and with a rainy period, from October to April. In Campo Verde, the average annual precipitation is 1726 mm, and the mean annual temperature is 22.3 °C. In Nova Mutum, the annual precipitation is 1934 mm, and the mean annual temperature is 24.6 °C.

In each municipality, areas were chosen with different PS application times. Next, five mini trenches were opened in those areas to collect, with a shovel, deformed samples in 0-0.10 and 0.10-0.20 m layers. The samples were packed in polyethylene bags, identified, and transported for analysis.

The soil samples were dried in a forced-air circulation oven at 60 ºC. Once dry, they were removed, sieved in a 2.00 mm mesh, and properly packed. The soil chemical and particle-size characteristics were determined according to the methodologies described in Teixeira et al. (2017) and are shown in Table 2.

The determination of total Zn and Cu was carried out according to adaptations of McGrath & Cunliffe (1985) methodology. Approximately 0.20 g of air-dried fine soil (ADFS), 6.0 mL of 12 mol L⁻¹ HCl, and 2.0 mL of concentrated HNO₃ (65%) were added to digestion tubes. The samples were successively digested in digester block: 2 hours at 60 °C, 1 hour at 105 °C and 140 °C until 0.5 to 1.0 mL of the extract remain in the tubes. After digestion, the extracts were filtered and diluted in 25 mL volumetric flasks, and the total Zn and Cu contents were determined by flame atomic absorption spectrometry.

The available Zn and Cu were extracted with the Mehlich-1 extractor based on Tedesco et al. (1995) methodology. In 50 mL flasks, 3.0 g of ADFS, and 30 mL of the extracting solution were weighed, the samples were shaken for 5 min on a horizontal shaker, and afterward, they were filtered on quantitative filter paper. The Zn and Cu were determined by atomic flame absorption spectrometry.

The determinations of Zn and Cu in the soil fractions (sequential extraction) were performed based on the methodology described by Seganfredo (2013), Silveira et al. (2006), and Ahnstrom & Parker (1999), with some

Table 1. Coordinates and identification of the study areas

<table>
<thead>
<tr>
<th>Area</th>
<th>Municipality</th>
<th>Location</th>
<th>Soil use</th>
<th>Time of pig slurry use</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV-0</td>
<td>Campo Verde</td>
<td>S 15° 34’ 21.03”</td>
<td>Soybean/corn</td>
<td>Without slurry</td>
</tr>
<tr>
<td>CV-3</td>
<td>Campo Verde</td>
<td>S 15° 34’ 22.11”</td>
<td>Soybean/corn</td>
<td>Three years</td>
</tr>
<tr>
<td>CV-5</td>
<td>Campo Verde</td>
<td>S 15° 34’ 24.87”</td>
<td>Soybean/corn</td>
<td>Five years</td>
</tr>
<tr>
<td>CV-7</td>
<td>Campo Verde</td>
<td>S 15° 33’ 57.72”</td>
<td>Soybean/corn</td>
<td>Seven years</td>
</tr>
<tr>
<td>NM-0.0</td>
<td>Nova Mutum</td>
<td>S 13° 44’ 36.91”</td>
<td>Pasteure</td>
<td>Without slurry</td>
</tr>
<tr>
<td>NM-3</td>
<td>Nova Mutum</td>
<td>S 13° 44’ 38.75”</td>
<td>Pasteure</td>
<td>Three years</td>
</tr>
<tr>
<td>NM-00</td>
<td>Nova Mutum</td>
<td>S 13° 44’ 38.49”</td>
<td>Pasteure</td>
<td>Without slurry</td>
</tr>
<tr>
<td>NM-5</td>
<td>Nova Mutum</td>
<td>S 13° 44’ 39.83”</td>
<td>Soybean/corn</td>
<td>Five years</td>
</tr>
<tr>
<td>CV-7</td>
<td>Campo Verde</td>
<td>S 15° 33’ 57.72”</td>
<td>Soybean/corn</td>
<td>Seven years</td>
</tr>
<tr>
<td>NM-0.0</td>
<td>Nova Mutum</td>
<td>S 13° 44’ 38.75”</td>
<td>Pasteure</td>
<td>Without slurry</td>
</tr>
<tr>
<td>NM-5</td>
<td>Nova Mutum</td>
<td>S 13° 44’ 39.83”</td>
<td>Soybean/corn</td>
<td>Five years</td>
</tr>
</tbody>
</table>

CV - Campo Verde, NM - Nova Mutum; CV-7 - Area with seven years of pig slurry use; CV-5 - Area with five years of pig slurry use; CV-3 - Area with three years of pig slurry use; CV-0 - Area without pig slurry use; NM-3 - Area with three years of pig slurry use; NM-0.0 - Area without pig slurry use, sandy texture; NM-5 - Area with five years of pig slurry use; NM-00 - Area without pig slurry use, clay texture
modifications. The sequential extraction started weighing 2.0 g of ADFS in centrifuge tubes. Then, the following extractions were performed:

1) Exchangeable fraction (EF): 15 mL of strontium nitrate (Sr(NO₃)₂ 0.10 mol L⁻¹ was added to the samples, followed by 2 hours on a horizontal shaker at 120 oscillations min⁻¹, centrifuged at 6000 rpm for 10 min, filtered on quantitative filter paper and stored in flasks with a lid.

2) Fraction linked to organic matter (OMF): in the EF residues, 25 mL of sodium hypochlorite (NaClO) 5% with pH adjusted to 8.5 with concentrated HCl were added, heating in a water bath at 90-95 °C for 1 hour. The suspension was stirred manually at 15 and 40 min of heating. After cooling, the extracts were stirred for 2 hours on a horizontal shaker at 120 oscillations min⁻¹, centrifuged at 6000 rpm for 10 min, filtered on quantitative filter paper, and stored in flasks with a lid.

3) Fraction linked to poorly crystallized iron oxides (FoFePc): in the OMF residues, 20 mL of the 0.20 mol L⁻¹ ammonium oxalate solution + 0.20 mol L⁻¹ oxalic acid with pH adjusted to 3.0 (with ammonium oxalate or oxalic acid). In this stage, the centrifuge tubes were covered with aluminum foil. The suspension was stirred for 2 hours on a horizontal shaker at 120 oscillations min⁻¹, centrifuged at 6000 rpm for 10 min, filtered on quantitative filter paper, and stored in flasks with a lid.

4) Fraction linked to crystalline iron oxides (FoFec): 40 mL of the 6 mol L⁻¹ HCl solution were added to the residues of the FoFePc fraction, stirring for 24 hours at 120 oscillations min⁻¹, centrifuged at 6000 rpm for 10 min, filtered on quantitative filter paper, and stored in flasks with a lid.

5) Residual fraction (RF): the residue (soil) was dried in an oven. From this dry mass, 0.2 g was weighed and transferred to digestion tubes, and then 6.0 mL of the solution of HCl 12 mol L⁻¹ and 2.0 mL of concentrated HNO₃ (65%) were added. Then they were placed in a digesting block for digestion for 2 hours at 60 °C, 1 hour at 105 °C, and 140 °C until between 0.5 and 1.0 mL of the extract remained in the tubes. After digestion, the extracts were filtered and diluted in 25 mL volumetric flasks.

The extracts of the EF, OMF, and FoFePc fractions were acidified with one drop of concentrated HNO₃. Determinations of the Zn and Cu contents for each fraction were performed by flame atomic absorption spectrometry. For each metal, the degree of recovery was calculated using Eq. 1 (Souza et al., 2012), using the sequential extraction results as a control criterion and stipulating the maximum tolerable difference in ± 15% of the total value of Zn and Cu.

\[
\text{Recovery} \% = \left( \frac{\sum (\text{Fractions})}{\text{Total Zn(Cu)}} \right) \times 100
\]

(1)

The mobility factor (MF) index proposed by Kabala & Singh (2001) was used to estimate Zn and Cu mobility in the soil. The metals linked to the OMF, FoFePc, FoFec, and RF fractions are less mobile in the soil, more strongly linked to the soil constituents than EF. Thus, this index was calculated by Eq. 2.

\[
\text{MF(\%)} = \left( \frac{\text{EF}}{\text{OMF + FoFePc + FoFec + RF}} \right) \times 100
\]

(2)

The Kruskal-Wallis test was performed in the data analysis to compare the study areas since an experimental design was not used.

### Results and Discussion

The total Zn levels ranged between 6.75 and 18.00 mg kg⁻¹ (Table 3); these values are below the prevention limit of 300 mg kg⁻¹ established by the Conama Resolution Nº. 420 (Brazil, 2009). The highest values were obtained in areas using pig slurry, but there was no statistical difference between the areas collected in Campo Verde, MT, Brazil. However, in Nova
Zinc and copper fractions in Oxisols of different textures fertilized with pig slurry

In Campo Verde and Nova Mutum, there was a difference between areas NM-5 and NM-00 (without PS).

It was found that the ZnA levels using the Mehlich-1 extractor (Table 3) were higher in areas with pig slurry use, with higher Zn contents in the 0-0.10 m layer. A difference was found between areas CV5 and CV0 and between areas NM5 and NM00 (layer 0-0.10 m), where the areas CV0 and NM00 do not use pig slurry.

Higher levels of Zn in areas with the application of manure are justified, as Zn is an important element for animal nutrition and present in the mineral complexes used in the formulation of feed (Basso et al., 2012). A higher concentration of Zn available in the 0-0.10 m layers can be attributed to the lack of/or little soil tillage in the study areas.

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In Campo Verde, there was a significant difference between the areas CV7 and CV0, with higher Zn levels in the area using pig slurry (CV7). In Nova Mutum, the difference was observed between areas of the same texture (NM3 and NM00), with higher Zn levels in the area using pig slurry. Tiecher et al. (2013) studied an Oxisol with a history of liquid waste application, showing increased Zn in the exchangeable fraction compared to the control (without waste). According to these authors, pig slurry is rapidly decomposed so that Zn can be released by increasing its amounts in the exchangeable soil fraction.

In the fraction linked to organic matter (OMF), in Campo Verde, the highest content of this fraction was found in the area without manure (CV0). In Nova Mutum, there was no difference between the study areas.

The highest Zn levels (Table 3) were obtained in the residual fraction in CV-5, CV-3, CV-0, NM-3, and NM-0.0 areas. In the CV-7, NM-5, and NM-00 areas, the highest Zn levels were in the poorly crystallized iron oxide fraction.

Tiecher et al. (2013), in studies using pig slurry, found that Zn was accumulated in the residual fraction in the soil without manure, and when pig slurry was applied, there was an increase in Zn in the mineral fraction.

The fractions with the lowest Zn content were exchangeable and those linked to organic matter. Thus, Zn has a greater affinity with the mineral phase than soil organic matter (Formentini et al., 2015).

Couto et al. (2015) also found higher Zn levels linked to the soil mineral fraction, which agrees with Zn and Cu electronic configuration differences. According to these authors, Zn is adsorbed to minerals and organic compounds in the soil, mainly in the form of precipitates. Zn is found in the exchangeable form in oxides and clays, and in the organic matter, it occurs both complexed to fulvic acids and in the exchangeable form. At low pH values, zinc is poorly adsorbed to soil components, which gives it greater mobility.

The recovery rate (R) of total Zn, which is the relationship between the sum of the Zn levels found in the fractionation stages and the values obtained using the aqua regia method, ranged between 55.75 and 92.12% (Campo Verde) and 63.12 and 91.91% (Nova Mutum), with the lowest recovery rate found in CV-0. According to Souza et al. (2012), the sequential extraction results are adopted as a control criterion in the recovery rate. The maximum tolerable difference is being stipulated at ± 15% of the total Zn value. Results of this study are within the limits of tolerable error in CV-7, CV-3, NM-3, and NM-5 areas (layer 0-0.10 m). In these areas, the sum of the six fractions is presented in agreement with the respective total concentration determined.

Differences greater than 15% verified in this study can be attributed to the operational difficulties in chemical Table 3. Fractions of zinc (Zn) in soil compartments without (0) and with pig slurry (PS) application, over time (3, 5, and 7 years), in Oxisols of different textures in Campo Verde (CV) and Nova Mutum (NM), MT, Brazil

<table>
<thead>
<tr>
<th>CV-0</th>
<th>CV-3</th>
<th>CV-5</th>
<th>CV-7</th>
<th>NM-0.0</th>
<th>NM-3</th>
<th>NM-00</th>
<th>NM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnT</td>
<td>ZnA</td>
<td>EF</td>
<td>OMF</td>
<td>FoFeMc</td>
<td>FoFec</td>
<td>RF</td>
<td>ZnTr</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(mg kg⁻¹)</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0-0.10 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-0.10 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10-0.20 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10-0.20 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10-0.20 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CV - Campo Verde; NM - Nova Mutum; CV - Campo Verde; NM - Nova Mutum; CV - Area with seven years of pig slurry use; CV-5 - Area with five years of pig slurry use; CV-3 - Area with three years of pig slurry use; NM-3 - Area with three years of pig slurry use; NM-0.0 - Area without pig slurry use, sandy texture; NM-5 - Area with five years of pig slurry use; NM-00 - Area without pig slurry use, clay texture; ZnT - Total zinc; ZnA - Mehlich-1 available zinc; EF - Zinc exchangeable fractions; OMF - Zinc linked to organic matter; FoFeMc - Zinc linked to poorly crystallized iron oxides; FoFec - Zinc linked to crystallized iron oxides; RF - Residual zinc; ZnTr - Total zinc recovered, the sum of fractions; R - Recovery rate; MF - Mobility factor; Means followed vertically by equal letters do not differ at p ≤ 0.05 by the Kruskal-Wallis test.

fractionation and the variation of attributes and origin of the samples.

Regarding the Zn mobility estimate (MF), regardless of the soil texture, the highest values were observed in areas with pig slurry. According to Ma & Rao (1997), high values for the mobility factor have been interpreted as indicative of the high availability of metals in soils.

The percentages of reactive (EF, OMF, and FOFePc) and recalcitrant (FoFec and RF) Zn forms were calculated. In addition to incorporating the fraction most readily available, the reactive form represents the forms potentially available during a cultivation cycle and those dissolvable to the environment (Hooda, 2010).

In the CV5, CV3, CV0, NM3, NM0, and NM0 areas, Zn’s predominant forms were recalcitrant. It is observed that regardless of the soil texture, in the CV7- and NM5 areas, the reactive form contents were higher with longer pig slurry use time.

The divergence between areas with and without pig slurry showed that the use of this residue as soil fertilizer could alter Zn forms in the soil. Areas with pig slurry application have increased percentages of Zn forms more easily available (reactive) since higher levels were observed there than in areas without pig slurry.

As for CuT (Table 4), the levels ranged between 19.5 and 6.45 mg kg⁻¹, values below the prevention limit, 60 mg kg⁻¹ established by the Conama Resolution No. 420 (Brazil, 2009).

A difference was observed between CV0 and CV7 / CV5 when comparing the CuT levels in the study areas. There was no difference in the same texture areas (CV3 and CV0 and CV7 and CV5) (layer 0-0.10 m, Campo Verde).

Table 4. Fractions of copper (Cu) in soil compartments without (0) and with the application of pig slurry liquid manure (SLM), over time (3, 5, and 7 years), in Oxisols of different textures in Campo Verde and Nova Mutum (NM) municipalities, MT, Brazil

<table>
<thead>
<tr>
<th>Treatments</th>
<th>CuT</th>
<th>CuA</th>
<th>EF</th>
<th>OMF</th>
<th>FoFeMc</th>
<th>FoFec</th>
<th>RF</th>
<th>CuTr</th>
<th>R (%)</th>
<th>MF</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV0</td>
<td>11.45 a</td>
<td>2.25 a</td>
<td>0.36 a</td>
<td>0.65 a</td>
<td>0.68 a</td>
<td>2.72 a</td>
<td>6.25 a</td>
<td>10.86</td>
<td>94.89</td>
<td>3.42</td>
</tr>
<tr>
<td>CV3</td>
<td>10.12 ab</td>
<td>0.80 ab</td>
<td>0.09 b</td>
<td>0.63 ab</td>
<td>0.70 a</td>
<td>2.28 ab</td>
<td>5.50 ab</td>
<td>9.20</td>
<td>90.93</td>
<td>0.98</td>
</tr>
<tr>
<td>CV5</td>
<td>8.00 b</td>
<td>0.16 ab</td>
<td>0.07 b</td>
<td>0.15 b</td>
<td>0.66 a</td>
<td>2.2 ab</td>
<td>3.25 b</td>
<td>6.33</td>
<td>79.18</td>
<td>1.19</td>
</tr>
<tr>
<td>CV7</td>
<td>7.50 b</td>
<td>0.10 b</td>
<td>0.1 b</td>
<td>0.12 b</td>
<td>1.00 a</td>
<td>1.76 b</td>
<td>3.25 b</td>
<td>6.24</td>
<td>83.20</td>
<td>1.71</td>
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<td>NM0.0</td>
<td>15.50 ab</td>
<td>1.00 b</td>
<td>0.63 ab</td>
<td>0.46 a</td>
<td>1.34 a</td>
<td>3.36 ab</td>
<td>7.75 ab</td>
<td>13.54</td>
<td>87.38</td>
<td>4.87</td>
</tr>
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<td>13.75 b</td>
<td>1.00 b</td>
<td>0.51 b</td>
<td>0.40 a</td>
<td>1.10 a</td>
<td>3.04 ab</td>
<td>6.75 b</td>
<td>11.8</td>
<td>85.87</td>
<td>4.51</td>
</tr>
<tr>
<td>NM00</td>
<td>16.75 ab</td>
<td>1.00 b</td>
<td>0.93 a</td>
<td>0.46 a</td>
<td>1.86 a</td>
<td>1.6 b</td>
<td>9.75 a</td>
<td>14.6</td>
<td>87.19</td>
<td>6.8</td>
</tr>
<tr>
<td>NM5</td>
<td>19.50 a</td>
<td>4.22 a</td>
<td>0.85 a</td>
<td>0.31 a</td>
<td>1.58 a</td>
<td>4.12 a</td>
<td>8.75 ab</td>
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<td>13.75 a</td>
<td>1.00 a</td>
<td>0.70 ab</td>
<td>0.44 a</td>
<td>1.34 a</td>
<td>3.40 ab</td>
<td>7.5 ab</td>
<td>13.39</td>
<td>97.38</td>
<td>5.55</td>
</tr>
<tr>
<td>NM3</td>
<td>12.00 a</td>
<td>1.00 a</td>
<td>0.46 b</td>
<td>0.43 a</td>
<td>1.12 a</td>
<td>2.92 ab</td>
<td>6.75 b</td>
<td>11.69</td>
<td>97.43</td>
<td>4.14</td>
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<td>0.90 a</td>
<td>0.43 a</td>
<td>1.86 a</td>
<td>2.56 b</td>
<td>9.25 a</td>
<td>15.00</td>
<td>96.23</td>
<td>6.38</td>
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<tr>
<td>NM5</td>
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<td>2.20 a</td>
<td>0.81 a</td>
<td>0.34 a</td>
<td>1.62 a</td>
<td>3.68 a</td>
<td>9.00 a</td>
<td>15.45</td>
<td>96.59</td>
<td>5.53</td>
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</tbody>
</table>

CV - Campo Verde; NM - Nova Mutum; CV - Campo Verde; NM - Nova Mutum; CV7 - Area with seven years of pig slurry use; CV5 - Area with five years of pig slurry use; CV3 - Area with three years of pig slurry use; NM3 - Area with three years of pig slurry use; NM0 - Area without pig slurry use, sandy texture; NM5 - Area with five years of pig slurry use; NM00 - Area without pig slurry use, clay texture; CuT - Total copper; CuA – Mehlich-1 available Copper; Cu in the fractions, exchangeable (EF), linked to organic matter (OMF), linked to poorly crystallized iron oxides (FoFePc), linked to crystallized iron oxides (FoFec), and residual (RF); CuTr - total recovered copper, the sum of fractions; R - Recovery rate; MF - Mobility factor; Means followed by equal letters in the rows do not differ statistically at p ≤ 0.05 by the Kruskal-Wallis test.
Regarding the available Cu (CuA), higher levels of CuA were found in the Campo Verde area, CV-0 (without pig slurry), which differed from the CV-7 area. This finding can be attributed to the lower Cu input to the soil in the study areas via PS, which depends on the residue metal concentration and dose, and application frequency (Couto et al., 2015). It was found that there was no difference between the areas of the same texture, NM-3 and NM-0.0, and NM-5 and NM0.0 (Nova Mutum). Thus, there was no difference between areas with and without pig slurry use.

The percentage of recovered Cu (R), considering the 0-0.10 m layer, ranged between 79.18 to 94.89% (Campo Verde) and from 80.08 to 87.38% (Nova Mutum). The results are below the tolerable error limits stipulated (± 15%) in CV-7, CV-5, and NM-5 areas. In the CV-3, CV-0, NM-3, NM-0.0, and NM-00 areas, where the error limit is within the tolerable error limits (± 15%), the sum of the six fractions agrees with the respective CuT concentration determined (Souza et al., 2012).

As with Zn recovery, Cu recovery values were below the values found by Souza et al. (2012), who studied areas with and without the use of sewage sludge. The recovery rates found by the authors were between 93 and 110%.

Cu was found to be associated with all soil fractions (Table 4). Regarding Cu in the exchangeable fraction (EF), the highest content of this fraction was found in CV-0 (without pig slurry), which differed from CV-5 and CV-3 areas. In Nova Mutum there was no difference between areas NM5 and NM00, and NM3 and NM0.0. Thus, no higher levels of Cu in EF were found in areas with the pig slurry use.

The highest Cu levels were determined in the residual fraction (RF), with more than 50% of Cu in more stable forms in all study areas (Table 4). The second fraction with the highest Cu content was the fraction linked to crystalline iron oxides (FoFec). The lowest levels of Cu were observed in EF and OMF. Seganfredo et al. (2013) also reported higher Cu levels in the residual fractions and linked to crystalline iron oxide in soils with and without pig slurry.

However, the higher Cu content in RF differs from the results found by Tiecher et al. (2013), who described higher Cu levels in the organic fraction (OMF) in soils fertilized with pig slurry. According to Croué et al. (2003), the electronic configuration of Cu provides high reactivity with the functional groups of organic matter in the soil; the carboxylic and phenolic functional groups present in humin compounds form negatively charged structures, which have a great affinity for Cu.

Thus, there may have been a saturation of the functional groups of organic matter in these study areas (Croué et al., 2003) since the second highest Cu percentage is in the mineral fraction, in which this metal may be especially linked to groups functionalities of Fe oxides and even Mn or phyllosilicates.

Besides, the higher the Cu accumulation in the residual fraction in superficial layers of the soil may indicate the greater presence of recalcitrant organic carbon. Still, in the deeper layers, the fact is explained by the presence of amorphous and clay mineral inorganic materials (Tessier et al., 1979).

The mobility factor (MF), regardless of the soil texture, was significantly higher in areas without the pig slurry use (CV-0, NM-0.0, and NM-00).

Regarding the reactive (EF, OMF, and FoFePc) and recalcitrant (FoFec and RF) forms of Cu in Oxisols of different textures in Campo Verde and Nova Mutum municipalities, MT, Brazil

Conclusions

1. The areas with the longest use of pig slurry showed the highest Zn concentrations in exchangeable form.
2. The soils in areas with and without pig slurry use showed a predominance of Cu in the residual form.

Literature Cited


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