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Copper Concentration of Vineyard Soils as a Function of pH Variation and Addition of Poultry Litter

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ABSTRACT

Copper (Cu) concentration was evaluated as a function of pH variation and addition of poultry litter to a Dystrophic Lithic Udorthent and a Humic Dystrudept from the state of Rio Grande do Sul, Brazil, cultivated with vines treated with successive applications of Cu-based product. Samples were collected from the surface layer (0 to 10 cm). Soluble Cu concentration was determined using DTPA and Mehlich III as extractants, and exchangeable Cu was determined in $CaCl_2$. The availability of Cu was mainly affected by the soil pH. $CaCl_2$ extractant had the best correlation with Cu concentration in contaminated soils, according to treatments applied. The addition of poultry litter did not reduce Cu availability in these soils. Total soil Cu content varied between 1,300 and 1,400 mg kg^{-1} in both soils. Copper available fractions, extracted by DTPA, $CaCl_2$ and Mehlich III, averaged 35, 0.2 and 63%, respectively, of the total Cu present in the soil.

Key words: Vineyard soils, chemical extractors, pH and soil organic matter

INTRODUCTION

The continued use of some agricultural pesticides can lead to metals accumulation in the soil (López – Mosquera et al., 2000), contaminate the food chain and decrease crop yield (Obrador et al., 1997). Once heavy metals are persistent in the environment, they remain in the biosphere for long periods of time (Silveira et al., 2003). Deluisa et al. (1996), Flores Vélez (1996), Brun et al. (1998), and Pietrzak and McPhail (2004) described that the continuous use of Cu-based fungicides to control vine diseases resulted in Cu accumulation on the soil surface. A significant portion of the Cu reaching the soil remained in the upper layers, mainly bound to organic matter (OM) (Brun et al., 1998).

In a study with 25 soil samples from land cultivated with vines in France, Brun et al. (1998) observed total Cu contents varying from 30 to 250 mg kg^{-1}, depending on the age of the vines, type of soil, and regional climate. Comparing various extractors on these soils, they observed that Cu extractable with 0.01 mol L^{-1} $CaCl_2$ correlated well with the soil pH, (it decreased with increasing soil pH), that is an important property controlling the bioavailability of Cu, whereas Cu extractable by DTPA pH 7.3 correlated only with the CEC (it

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decreased with increasing soil CEC). Soil OM concentration was relatively low and none of the extractors used in the study correlated well with this attribute. Brun et al. (2001) cultivated maize in vineyard soils with high Cu content and observed that Cu concentration in the upper part of the maize plant had a high negative correlation with pH and a high positive correlation with soil OM, whereas CEC had a high positive correlation with Cu concentrations in the roots. $CaCl_2$ 0.01 mol L^{-1} had a better correlation with Cu in the upper parts of the plant than DTPA, but the opposite occurred with Cu in the roots.

Data for total Cu content in Brazilian soils are scarce (Abreu et al., 2001a). Jackson (1964) described that total content values within the range 5 to 40 mg kg^{-1} for soils in tropical and temperate regions were considered normal, although in some soils it was as low as 2 and in others higher than 100 mg kg^{-1}.

Mineral and organic soils can adsorb metals in differing intensities. OM, Fe and Al oxyhydroxides and clay minerals are the main components of soils that influence sorption reactions (Barry et al., 1995). According to Silveira and Alleoni (2003), the charge balance in the soil, influenced by the levels of OM and clay and the mineralogical characteristics, particularly the iron and aluminum oxide and hydroxide contents, were the most important factors controlling Cu adsorption reactions in acric soils. Even at low concentrations in the soil, they could coat sand and clay mineral surfaces, influencing adsorption reactions.

The availability of heavy metals is relatively low at pH 6.5 to 7 (Kabata–Pendias and Pendias, 1987). The mobility of the majority of heavy metals becomes limited as pH increases, due to the precipitation of insoluble forms as hydroxides, carbonates and organic complexes. As pH increases, the surface area of the negative charges on the colloid increases, enhancing the electrostatic attraction between the adsorbent and the metal (Sposito, 1989). As the CEC rises, the number of available adsorption sites on soil colloids increases to adsorb metallic cations.

Organometallic associations can occur in both solid and liquid phases of the soil. Copper complexes can be formed by dissolved organic carbon (DOC), increasing the risk of leaching of the metal in the profile (Moolenaar and Beltrami, 1998). Humus and other organic compounds can chelate metals and form stable molecules altering their bioavailability.

The objective of this study was to assess the availability of Cu as a function of variation in pH and organic matter (OM) concentration in soils with high Cu content, assuming that available Cu concentration could increase as soil pH dropped and decreased as soil OM content increased.

MATERIAL AND METHODS

The study was carried out with samples from the surface layer (0 to 10 cm) of a typical dystrophic Lithic Udorthent (LU) and a Humic Dystrudept (HD), collected from the farms located in Pinto Bandeira (29º06'S and 51º27'W) and Bento Gonçalves (29º10'S and 51º31'W), in the Rio Grande do Sul highlands, Brazil. These soils had been cultivated for more than 15 years with vines (Isabel cultivar), receiving continuous applications of Cu-based phytosanitary products, mainly "calda bordaleza" (Bordeaux mixture) (approximately ten applications per year - approximately 65 kg ha^{-1} of Cu per year). The chemical properties of LU and HD soils were: pH in $CaCl_2$ 0.01 mol L^{-1} of 6.9 e 6.4; OM of 85 and 94 g kg^{-1}; 140 and 170 $mmol_c$ dm^{-3} of Ca; 35 and 39 $mmol_c$ dm^{-3} of Mg; 5.4 and 8.0 $mmol_c$ dm^{-3} of K; and 193.4 and 230.0 $mmol_c$ dm^{-3} for CEC. These soils had a high soluble Cu concentration in DTPA pH 7.3 (522 and 475 mg kg^{-1} for LU and HD, respectively).

Two experiments were conducted under laboratory conditions: a) Variation in soil pH values – 50, 100, 200, 300 and 400 mmol kg^{-1} of HNO_3 were applied to reduce pH values, since the pH for these soils was higher than 6.0. Samples were incubated close to the maximum water retention capacity, until the pH remained stable; b) Variation in soil OM concentration – rates equivalent to 10, 20, 40 and 80 t ha^{-1} of poultry litter (dry basis) were applied; this material was frequently used by farmers. Samples (1.0 kg) were incubated for three months, with humidity close to the maximum water retention capacity. Poultry litter had a C/N ratio of 15:1, 609 $g.kg^{-1}$ compostable OM, and total Cu content of 518 mg kg^{-1}. The two experiments were set up in a randomized block design with four replications. After incubation, samples were dried at 45°C and passed through a 2.0 mm sieve.

Sample pH was measured in $CaCl_2$ 0.01 mol L^{-1} (1:2.5 soil:solution). Organic carbon concentration was determined after oxidation with potassium dichromate, in the presence of suphuric acid, and titration of excess dichromate with ammonium ferrous sulfate (Cantarella et al., 2001). Cu concentration was determined in DTPA pH 7.3 (Abreu et al., 2001b), exchangeable Cu in $CaCl_2$ 0.01 mol L^{-1} (Brun et al., 1998), and exchangeable Cu by Mehlich III (Mehlich, 1984). Total Cu was determined according to the US-EPA 3052 method, with microwave-assisted digestion with HNO_3 + HF + deionized water (United States, 1996).

Analysis of variance was used to evaluate the significance of the effects of treatments effects on soluble and exchangeable Cu. Pairwise comparison methods was used to separate the extractor’s means.

RESULTS AND DISCUSSION

Variations in soil pH and OM contents

Under uncultivated conditions (natural soil), Lithic Udorthents of the vine-growing region of the Serra Gaúcha were moderately acid (pH around 5.6 in water), whereas the Humic Dystrudepts were extremely acid (pH around 4.1) (Flores et al., 1999). In such regions, lime was of common use, and pH was expected to increase up to 6.0. However, pH could be either reduced by the use of nitrogen-enriched fertilizers, such as ammonium sulfate, or it could be raised by the reapplication of lime, as cultivation progresses. The pH values dropped linearly from 7.0 to 3.8 as HNO_3 doses were added around (Fig. 1). However, the doses of HNO_3 did not alter the OM content (data not shown). Thus, the variation in Cu concentration was only due to pH variation.

In the wine-producing region of “Serra Gaúcha” the Inceptsols with humic characteristics were of common occurrence. These soils have an average organic carbon content (higher than 17.0 g kg^{-1}) up to a depth of 90 cm. On the other hand, Entisol, organic carbon content was lower (around 13.0 g kg^{-1}) (Flores et al., 1999). The application of residues including poultry litter has been a common practice to increase soil OM content, and improve the soil’s chemical and physical properties. The incubation with poultry litter resulted in a linear increase in OM concentration for both the soils, ranging from 85.3 (control) to 105.0 g kg^{-1} (after addition of 80 t ha^{-1} of poultry litter) in the LU, and from 94.6 (control) to 103.0 g kg^{-1} (after addition of 80 t ha^{-1} of poultry litter) in the HD (Fig. 1).

Effect of pH on soil copper concentrations

As expected, $CaCl_2$-Cu was higher at lower pH values (Fig. 2). There was a marked variation in Cu concentration at pH between 4 and 6, which was the predominant pH range of these soils when lime was not applied. Brun et al. (1998) observed a negative linear relationship between pH and concentration of Cu extracted with $CaCl_2$. Cu concentrations increase as the soil pH dropped due to the dissolution of Cu insoluble composts at pH lower than 5. At pH values higher than 6, Cu could be either adsorbed on the surfaces of Fe and Al oxides or precipitated in hydroxyl forms (Cu(OH)n). Under these conditions, the number of binding sites of Cu with OM could also increase, and the stability of the bonding consequently increases the quantity of adsorbed Cu (Sims and Patrick, 1978). There was no significant correlation between pH value and Mehlich III-Cu concentration.

The decrease in the concentration of Cu soluble in DTPA pH 7.3 after pH decrease was unexpected (Fig. 2). Camargo et al. (1982), worked with soils in the State of São Paulo, Brazil, and found a negative correlation between pH and DTPA-soluble Cu concentration, suggesting that Cu availability dropped as pH increased. It was possible that the observed drop in DTPA pH 7.3-extracted Cu concentration as a function of pH could have occurred due to the low efficiency of this extractor for these samples.

The stability of the DTPA boding to with Cu increased at pH higher than 7.0 (Norvell, 1991). Also, the pH of natural soil was 7.3, dropping to 5.8 at the highest dose of HNO_3. DTPA was developed to evaluate the availability of micronutrients in soils with low concentrations of these elements. Hence, when DTPA was used in contaminated soil, high amount of metals could saturate the extraction capacity of the DTPA solution. Brun et al. (1998) also observed no relationship between pH and DTPA-Cu.

The DTPA extractor, originally developed by Lindsay and Norvell (1978) to predict availability of Zn, Fe, Mn and Cu, and to identify soil deficiencies adversely affecting crop yield, is also used by many soil laboratories in Brazil. However, as suggested by Brun et al. (1998), under acidic conditions, DTPA might not be effective in assessing the bioavailability of Cu, since the buffer capacity of the extractor could exceed. This could be explain the behavior observed in regard to Cu concentration measured using DTPA.

Mehlich III-Cu concentration were on average approximately twice DTPA-Cu concentration figures, and 300 times those obtained using $CaCl_2$ in LU and HD soils (Fig. 2). This difference in extraction occurred because a significant part of the available Cu was chelated, and the extraction using a salt became more difficult (Stevenson, 1994). Comparing the Cu concentration found by Brun et al. (1998) in 25 vineyard soils, in the south of France, with that obtained in the two soils under investigation, it can be observed that the concentration values were much higher than those obtained in French vineyards, mainly at lower pH values, which was probably due to differences in the use of Cu-based products in the vineyards, as well as the chemical properties of the soils. Copper concentration at low pH values highlighted the importance of correcting soil acidity to attenuate the phytotoxic effect of Cu on plants, minimizing contamination in vine production systems.

Total Cu content varied between 1,355 ± 45 and 1,381 ± 31 mg kg^{-1} for LU and HD soils, respectively. These values were higher than the results obtained by Brun et al. (1998), who observed total Cu content ranging from 30 to 250 mg kg^{-1} in southern France. Also, Drouineau and Mazoyer (1962) and Flores Vélez (1996) showed values as high as 400 to 500 mg kg^{-1} total Cu in the vineyards of Alsace, Champagne and Burgundy, whereas Delas (1963) found up to 800 mg kg^{-1} total Cu total in areas of Bordeaux. In Australia, Pietrzak and McPhail (2004), evaluated 14 vineyards cultivated from 20 to older than 90 years, observed total Cu content between 10 and 250 mg kg^{-1}. The differences could be explained by climatic conditions in the Serra Gaúcha region, which required a higher number of applications of Cu-based products to control disease and for the high original concentration of Cu of these soils originated of the basalt. Total Cu content in the cultivated soils of Serra Gaúcha vineyards exceeded the maximum concentration currently permitted by the European Community (140 mg kg^{-1}) (CEC, 1986), which was worthy of attention owing to the possibility of contaminating the agricultural system. As expected, total Cu content was not affected by variations in soil pH.

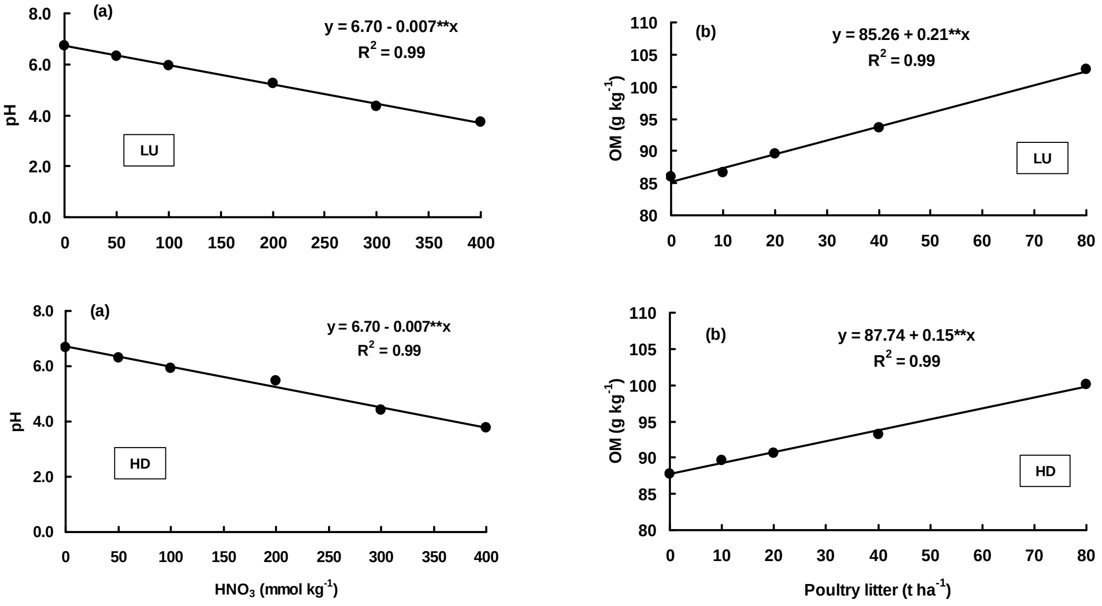

Figure 1 - Relationship between doses of HNO_3 and pH (a) and between doses of poultry litter and organic matter concentration (b) in a typical dystrophic Lithic Udorthent (LU) and a Humic Dystrudept (HD) in the Rio Grande do Sul highlands, Brazil

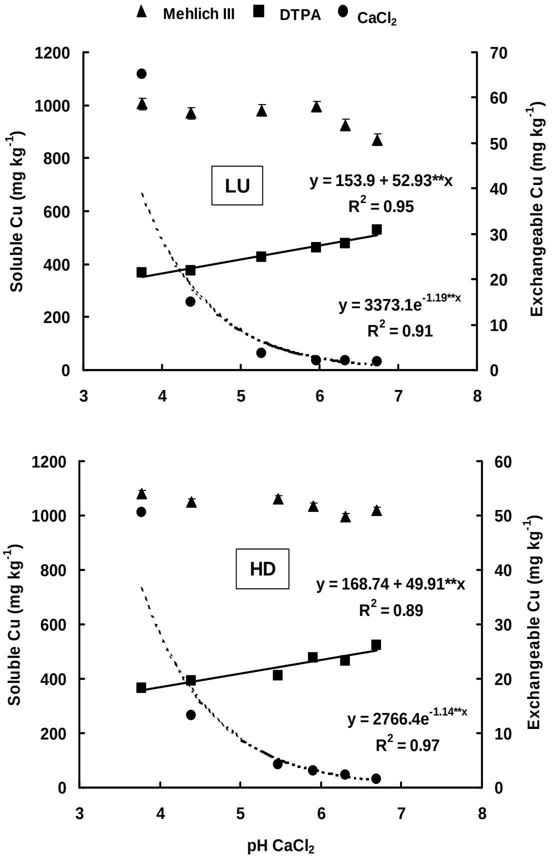

Figure 2 - Relationship between soil pH value in $CaCl_2$ and soluble Cu concentration, extracted by DTPA and Mehlich III, and exchangeable Cu concentration, extracted by $CaCl_2$, in a typical dystrophic Lithic Udorthent (LU) and a Humic Dystrudept (HD) in the Rio Grande do Sul highlands, Brazil

Effect of addition of poultry litter on soil copper concentrations

On average, Mehlich III-Cu concentration was around twice that of DTPA-Cu concentration, and 300 times higher than $CaCl_2$ Cu in LU and HD soils (Fig. 3), matching the proportions observed in the experiment assessing the effect of pH. Total Cu content ranged from 1,201 ± 17 and 1,274 ± 18 mg kg^{-1} respectively for LU and HD soils. Since clay minerals and OM are the main components involved in Cu retention in the soil, it is expected that soils rich in OM or receiving applications of organic residues may retain high quantities of this element, Cu forming stable complexes with humic and fulvic acids, mainly due to the high concentration of functional groups with oxygen, such as carboxyls and phenols (Stevenson and Ardakani, 1972).

The expected reduction in Cu concentration accompanying a rise in OM concentration was not observed for Cu extracted by DTPA pH 7.3 and Mehlich III (Fig. 3). This phenomenon indicated that the added OM was rapidly mineralized, adversely affecting the generation of organic complexes for the Cu retention. As these soils had a high OM concentration, it was probable that high proportions of total Cu were already retained in the soil's organic complexes, so that the small percentage of free Cu capable of retention by the organic matter did not alter the Cu concentration obtained using extractors. For vineyard soils with high OM concentration, the addition of organic residues probably did not contribute to reduce Cu availability. Conversely, for vineyard soils with low OM concentration, the addition of organic residues probably contributed to the higher retention of Cu came from the Cu-based phytosanitory products. $CaCl_2$-extracted Cu concentrations increased with the increase of OM concentration, which could be explained by the contribution of poultry litter in supplying Cu, since total Cu reached 518 mg kg^{-1}. Although there was a high bonding affinity between Cu and OM, the absence of a relationship between these two variables was also observed by Brun et al. (1998).

No significant linear relationship was observed between total Cu content and the concentration of Cu extracted by DTPA, Mehlich III and $CaCl_2$, as well as between the Cu concentrations for Mehlich III and $CaCl_2$ extraction for both soils (Table 1), which was justified by the different principles of the extractors used to obtain the soluble Cu concentrations. The Cu extracted by DTPA had a negative relationship with Cu extracted using Mehlich III and $CaCl_2$. Brun et al. (1998), working with 25 vineyard soils in France, observed significant linear correlation coefficients between total Cu and DTPA Cu, but did not obtain significant relationship between Total Cu and $CaCl_2$ Cu, and also for DTPA-Cu and $CaCl_2$-Cu.

Soil pH is the most important factor for Cu bioavailability (Gupta and Aten, 1993). Considering that the Cu concentration extracted by 0.01 mol L^{-1} $CaCl_2$ dropped suddenly with increased soil pH, and assuming that DTPA was not very effective in predicting Cu availability at low pH, 0.01 mol L^{-1} $CaCl_2$ seemed to be the most appropriate Cu extraction method for Cu contaminated soils.

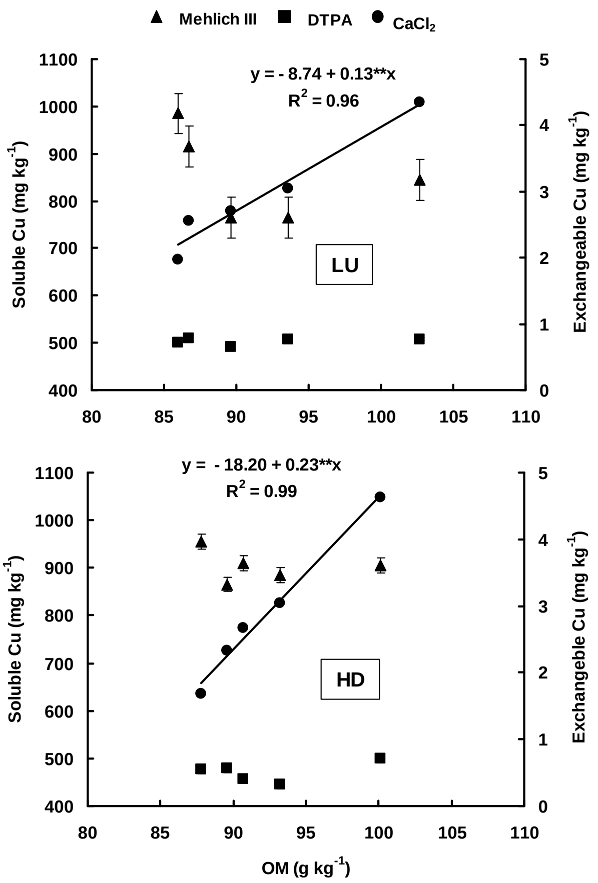

Figure 3 - Relationship between soil OM concentration and soluble Cu concentration, extracted by DTPA and Mehlich III, and exchangeable Cu concentration, extracted by $CaCl_2$, in a typical dystrophic Lithic Udorthent (LU) and a Humic Dystrudept(HD) in the Rio Grande do Sul highlands, Brazil

Table 1 - Linear correlation coefficients between total Cu and the different forms of Cu extractable from a typical dystrophic Lithic Udorthent (LU) and a Humic Dystrudept (HD) in the Rio Grande do Sul highlands, Brazil, as a function of variation in soil pH and OM.

	Cu_{DTPA}	$Cu_{Mehlich\ III}$	Cu_{CaCl_2}
Cu_{Total}	-0.18^{NS}	0.22^{NS}	-0.32^{NS}
Cu_{DTPA}		-0.57^{**}	-0.71^{**}
$Cu_{Mehlich\ III}$			0.38^{NS}

CONCLUSIONS

- **Cu** concentration was mainly affected by soil pH. 0.01 mol L^{-1} $CaCl_2$ solution was the extractor resulting the best correlation with Cu concentration in contaminated soils;
- Application of poultry litter in the soils did not reduce their Cu concentration;
- Total Cu content varied between 1,200 and 1,380 mg kg^{-1} in both soils, exceeding the maximum permitted concentration currently imposed by the European Community (140 mg kg^{-1});
- Available Cu fractions extracted by DTPA, $CaCl_2$ and Mehlich III represented, on average, 35, 0.20 and 63%, respectively of total Cu present in the soil, indicating that some Cu was present in other forms.

RESUMO

Avaliaram-se os teores de Cu em função da variação do pH e da adição de cama-de-frango de dois solos com elevados teores deste elemento. Foram coletadas amostras da camada superficial (0 a 10 cm) de um typical dystrophic Lithic Udorthent – LU (Neossolo Litólico distrófico típico) e de um Humic Dystrudept - HD (Cambissolo Húmico alumínico típico) da região da Serra do RS, cultivados com parreirais que receberam aplicações sucessivas de produtos à base de Cu. Foram determinados os teores de Cu solúvel em DTPA e pelo método Mehlich III, além do Cu trocável em $CaCl_2$. A disponibilidade de Cu foi afetada principalmente pelo pH do solo. O extrator $CaCl_2$ foi o que melhor se correlacionou com os teores de Cu em solos contaminados em função dos tratamentos aplicados. A adição de cama-de-frango não diminuiu a disponibilidade de Cu destes solos. Os teores de Cu total variaram entre 1.300 e 1.400 mg kg^{-1} nos dois solos. Considerando os teores totais de Cu nos solos, as frações “disponíveis”, extraídas por DTPA, por $CaCl_2$ e por Mehlich III representaram, em média, 35%, 0,20% e 63% do total de Cu presente no solo, respectivamente.

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