RETENTION AND LEACHING OF COPPER AND ZINC IN "TABULEIRO" SOILS AS INFLUENCED BY NUTRIENT CARRIER[1]

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ABSTRACT. – The "tabuleiro" soils, due to their topography and physical properties, would be advantageous for agricultural development. However, they are sandy, highly leached and extremely infertile. Deficiencies reported include those of copper and zinc. Nutrient carriers which are not readily leached, but which will gradually release available forms for uptake by the crop would be most suitable. Determinations of the retention and leaching of copper and zinc, as related to carrier, were made on samples taken from 0–20 and 20–40 cm depths of Red Yellow Podzolic and Hydromorfic Podzol soils from the State of Pernambuco. The 0–20 cm layer of the Blodgett soil of Western Montana was included for comparison. Both elements were readily retained by the top soils, and to a greater extent than for subsoils. The Red Yellow Podzolic soil retained more copper and zinc than Hydromorfic Podzol soil at comparable depths. The organic fractions retained much more copper and zinc than mineral fractions of the same soil. The Blodgett soil retained more copper than the corresponding depth of Brazilian soils, however zinc was retained almost equally.

The sulphate forms of copper and zinc were leached less readily than resin adsorbed or chelated forms. Up to 100 percent of the copper or zinc added in these latter two forms was leached from the soil. Effects of adding peat to the soil or removing soil organic matter were variable with respect to copper or zinc retention. Results suggest that salt forms of copper and zinc may be very efficient for combatting deficiencies.

Index terms: leaching of micronutrient; micronutrient cations in "tabuleiro" soil.

INTRODUCTION

The "tabuleiro" soils of Northeastern Brazil cover a large part of the coastal area of that region. These soils occupy level areas and are well suited physically for agricultural development. The rainfall in most of the area is reliable and adequate for crop production. The soils are deep, but so infertile that crop production is impossible without the application of fertilizers. The soils are naturally acid and deficient in most plant nutrients, including deficiencies of copper and zinc. Where fertility was improved, excellent yields have been obtained. However, due to high rainfall and the permeability of "tabuleiro" soils, excessive leaching occurs, carrying soluble nutrients to soil depths beyond crop roots. To overcome this problem nutrient carriers which will gradually release available forms for uptake by the crop would be most suitable. Considering the nature of these problems, studies were conducted to determine the retention and leaching of two micronutrients, copper and zinc, as influenced by the type of carrier.

MATERIAL AND METHODS

Two soil samples were taken from the "tabuleiro" soils in the State of Pernambuco. One sample was taken from a Hydromorfic Podzol (HP) of the Engenho Ubu, southeast of the city of Igaraçu and the other from a Red Yellow Podzolic medium texture latosolic (P.V.) of the Engenho São José, north of the city of Recife. According to the 1970 "Soil Taxonomy", they are respectively included in Tropehumod and Palendult Great Groups. Both soils were sampled at two depths, 0–20 cm and 20–40 cm. These soils are characterized by low pH, from 4,0 to 5,5, have sand texture, and are highly leached.

A soil collected from the Bitterroot Valley of Montana, U.S.A., was included in this study so that comparisons could be made between the Brazilian soils and a Montana soil of low fertility. This soil is classified as Blodgett gravelly coarse sand loam. It belongs to the Chestnut Great Soil Group, and according to the 1970 "Soil Taxonomy", is included in the Typic Haploboroll Great Group.

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Soil characterization

Texture estimates were made for all soil samples and a mechanical analysis was done for the 0–20 cm layer of Red Yellow Podzolic soil. The sample was sieved to 2.0 mm opening, dialysed with Na_2CO_3, pH 9.5, and dispersed with ultrasonic vibrations. The procedure of Jackson (1956) was employed to separate the fractions. The soil texture was "sand", having 96.2% silt and 1.2% clay.

Soils were analyzed according to the Montana State University soil Testing Laboratory procedure. Their data are given in Table 1. The pH values for the four Brazilian soil samples are higher than those found under field conditions. This is a result of steam sterilization treatment of these samples upon admittance through United States of America customs. Other soil test data may have been influenced by this treatment also, and interpretation of results must be made with this fact in mind.

A mineralogical analysis of the Brazilian soils was made by x-ray diffraction. Since no specific pattern was shown by the clay, it would appear that the type of clay developed in the soil is amorphous, probably allophane.

The micronutrients, copper, iron, manganese, and zinc were determined by the DTPA–TEA procedure of Lindsay & Norvell (1969).

Separation of mineral and organic fractions

For these studies it was desired to determine the influence of soil organic matter (O.M.) on micronutrient retention. The O.M. was primarily partially decomposed sugar cane residues and upon addition of excess water to the soils, this organic debris would float. This phenomenon was used to separate the mineral and organic fractions of the four soil samples from Brazil. The organic matter was separated from two kilograms of each soil, first by shaking 200 g portions of soil with excess water for 10 minutes. The water carrying the O.M. was then decanted. This operation was repeated several times until the soil appeared to be free of O.M. Both organic matter and mineral fraction were air dried. Organic matter analysis of the "organic" fraction following this separation showed that the material was greater than 90% organic.

Analysis of the "mineral" fraction indicated that only traces of organic matter remained in it. Because the separation did not involve any chemical treatment, the two separated fractions were believed to represent their chemical properties as they were in the whole soil.

Copper retention studies

Thirty gram portions of each soil were placed in 100 ml beakers, and 10 ml of a $CuSO_4$ solution containing either 100, 250, 500 or 1000 ppm copper were added. After four hours with intermittent shaking, the solutions were extracted from the soil by vacuum filtration. These extracts were analysed for copper by atomic absorption analysis. Previously separated mineral and organic fractions were carried through the same procedure, but only 1 g of organic fraction was used in place of 30 g of mineral fraction. In addition, 0.5 g of charcoal was added prior to filtration of the organic fraction to prevent passage of dispersed materials through the filter.

TABLE 1. **Analytical data of the five soils studied**

Soils	Depths	pH	O.M.	P	K	Ca	Mg	Na	E.C.
			%	(– ppm –)		(– m.e./100 g solo –)			(mmhos/cm)
Hydromorfic Podzol	0–20 cm	6.2	2.16	10.0	40.0	1.44	0.33	0.30	0.9
	20–40 cm	6.2	1.47	15.0	20.0	0.60	0.16	0.30	1.1
Red-Yellow Podzolic	0–20 cm	6.1	2.05	12.5	40.0	1.10	0.24	0.40	0.8
	20–40 cm	6.0	1.59	10.0	40.0	0.04	0.16	0.30	1.5
Blodgett	0–20 cm	5.5	2.40	24.0	130.0	---	---	---	0.0

Zinc retention studies

Zinc solutions were prepared from $ZnSO_4.7H_2O$ at the same concentration in ppm as the copper solutions. The same procedure employed for copper also was followed for the study of zinc.

Soil leaching studies

Portions of $CuSO_4$ $5H_2O$, Cu-saturated exchange resin, or Cu-EDTA (cupric ethylenediamine tetraacetate, trihydrate) were mixed into 200 g portions of each soil to provide selected concentrations of copper. Peat was added to investigate its influence on copper retention.

The treatments and rates employed were as follows:

1. Soil + 20 ppm Cu from Cu-resin;
2. Soil mineral fraction (O.M. removed) + 10 ppm Cu from Cu-resin;
3. Soil + 10 ppm Cu from Cu-resin + 5% peat moss;
4. Soil + 10 ppm Cu from $CuSO_4$,
5. Soil mineral fraction (O.M. removed) + 10 ppm Cu from $CuSO_4$;
6. Soil + 10 ppm Cu from $CuSO_4$ + 5% peat moss;
7. Soil + 10 ppm Cu from Cu-resin;
8. Soil + 10 ppm Cu from Cu-EDTA.

After thorough mixing, two 10 g portions were taken for Cu analysis.

The remaining 180 g were divided into two 90 g portions and each was placed in an inverted 150 ml plastic bottle with its bottom removed. A rubber stopper fitted with glass tubing was placed in the neck of the inverted bottle as an outlet. Glass wool was placed in the neck to prevent soil escape.

Each soil assembly was leached with distilled deionized water daily at the rate of 1 ml of water per gram of soil. Each week, 10 g of soil were taken for copper analysis by the DTPA-TEA extraction procedure. The same steps used in the Cu leaching study were repeated for a study of zinc leaching. The treatments were the same as those listed above, using zinc in place of copper in each case.

In both of these leaching studies the Blodgett soil was included for comparison. However, the treatments involving the soil mineral fractions only were not included because it was not possible to remove the O.M. from this soil by the procedure employed.

RESULTS AND DISCUSSION

Results of micronutrients determinations are shown in Table 2. Surface soils retained more copper than did the 20–40 cm depth layers (Fig. 1A). Copper retention by Hydromorfic and Red Yellow Podzolic soils in the 0–20 cm layer were similar, but the Hydromorfic soil retained less copper than Red Yellow Podzolic soil at the 20–40 cm depth. The Blodgett soil retained more copper than the two Brazilian soils. The copper

TABLE 2. Analysis of soils. Means of ppm of Cu, Fe, Mn, and Zn in soils as determined by DTPA-TEA method

Soil	Depths	Means (ppm of)			
		Cu	Fe	Mn	Zn
Hydromorfic Podzol	0–20 cm	ND[a]	11.70cb	2.90b	3.76bc
	20–40 cm	ND	3.50	.10	5.00a
Red-Yellow Podzolic	0–20 cm	ND	13.53b	2.50bc	3.67bc
	20–40 cm	ND	10.00c	2.33bc	3.77b
Blodgett	0–20 cm	.68	69.33a	21.33a	1.67

[a] ND = not detectable

[b] Means followed by the same letter are not significantly different at the 5% level of probability by the Duncan Multiple Range Test.

retention capacity of each of these soil samples is directly related to the O.M. content (Table 1). This is expected since it has been definitely shown that copper is easily complexed with organic matter (Gupta & Mackay 1966, Hogdson 1963, Matsuda & Ikuta 1969, Neeklantan & Mehta 1961, and Steenbjerg Boken 1950). X-ray diffraction indicated that the clay type in Brazilian soils is probably allophane, which may have a relatively high exchange capacity. However, little copper "fixation" can be attributed to the clay fraction of these soils because of their extremely low (1–2%) clay content. The Blodgett soil probably retained more copper because of its organic matter and clay.

Organic matter was responsible for much of the copper retention on those soils (Fig. 1B). Only 1 g of organic fraction from these soils retained more copper than 30 g of whole soil. It is not known why the organic fractions of each soil sample retained different amounts of copper, but they did maintain the same position relative to each other as that recorded for the whole soil. The mineral fraction (Fig. 1C) retained relatively little copper, with only slight differences between soils.

Both "tabuleiro" soils retained more zinc than copper, while the Blodgett soil retained more copper than zinc. Zinc retention was closely related to the amount of O.M. When zinc retention was measured for the organic fraction of "tabuleiro" soils (Fig. 2B) differences between soils or sample depths were eliminated, indicating that on a unit basis, the organic fractions of these soils retained zinc equally well. Likewise, when the organic matter was no longer present (Fig. 2C), little difference in zinc retention could be observed. Several studies have demonstrated the involvement of O.M. in zinc retention or chelation, for example those of Himes & Barber (1957) and Matsuda & Ikuta (1969). It appears that this type of reaction may be responsible for much of the zinc retention in both the "tabuleiro" soils studied. The retention of copper by these soils however appears to involve more than a "chelation" mechanism, since the differences between soils could not be eliminated by studying the organic fraction separately. To help determine the ability of these soils to retain added copper or zinc against leaching, various treatments were established on each soil followed by exhaustive leaching. In these studies, comparisons made between salt, chelate and resin forms of added copper, and the influence of O.M. were studied.

Chelate and resin forms of copper were rapidly leached from the Hydromorfic and Red-Yellow Podzolic soil samples (Fig. 3). Essentially all of the DTPA extractable copper added to these soils was leached from the soil within three weeks. The copper sulfate salt form was much more resistant to leaching, with generally 25 percent or more of the original copper content still remaining after six weeks (42 soil volumes of water leached).

In the Blodgett soil the chelate and resin forms of copper resisted leaching as well or better than the copper sulfate form (Fig. 3C). The high rate of copper resin (20 ppm Cu) and the inclusion of peat with resin resulted in more rapid leaching than when 10 ppm of copper was supplied by resin alone. The reason for this influence is not clear at this time.

Extensive leaching of copper when added as a chelate in the Brazilian soils is probably related to either 1. the instability of the copper chelate in these soils and the displacement of copper by a more strongly complexed metal ion and subsequent leaching of the copper ion; or 2. the actual leaching of the entire soluble chelate molecule, with its copper ion, from the soil. These soils are extremely sandy and have very little exchange capacity to prevent leaching of cations or soluble materials. Since the chelates are also highly soluble, there is apparently nothing in these soils that would prevent their rapid leaching by either of these two mechanisms.

The rapid leaching of the resin-adsorbed form of copper from the Brazilian soils is probably a result of copper displacement by other more strongly adsorbed ions and subsequent leaching of the released copper ion. The inclusion of peat may have provided a source of exchangeable ions, resulting in increased copper leaching when both resin adsorbed copper and peat were added to the soil. This was consistent for all three soils.

Removal of O.M. or the addition of peat did not influence leaching of copper from $CuSO_4$, except on the Blodgett soil where the addition of peat reduced leaching. There was no apparent disadvantage of removing the soil O.M. on the two "tabuleiro" soils when $CuSO_4$ was added. Different mechanisms of copper retention apparently are

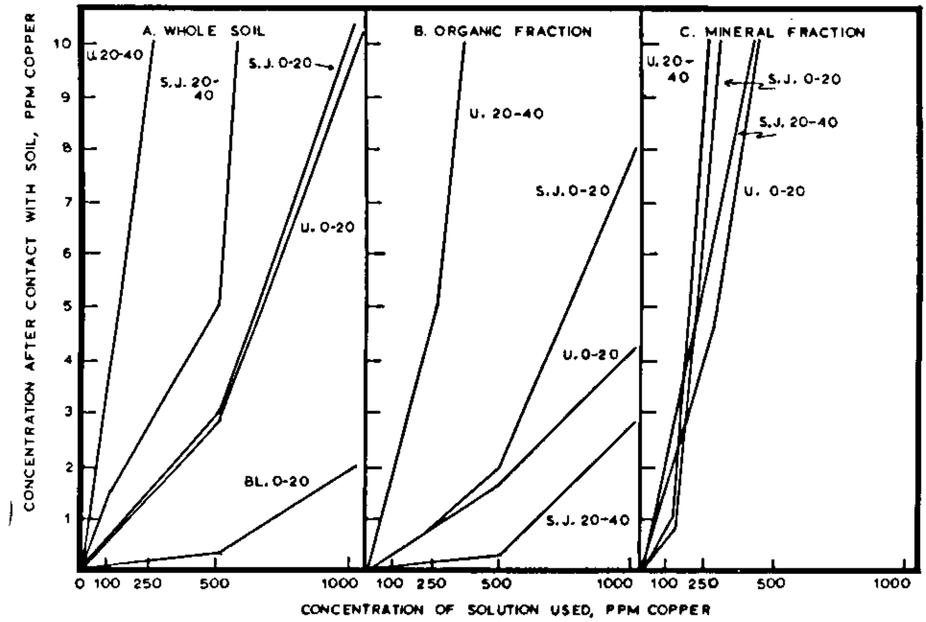

FIG. 1. Copper remaining in solutions of various initial concentrations after four contact with whole soil, organic fraction or mineral fraction of Hydromorfic Podzol (HP), Red-Yellow Podzolic (PV) or Blodgett (B1) soils.

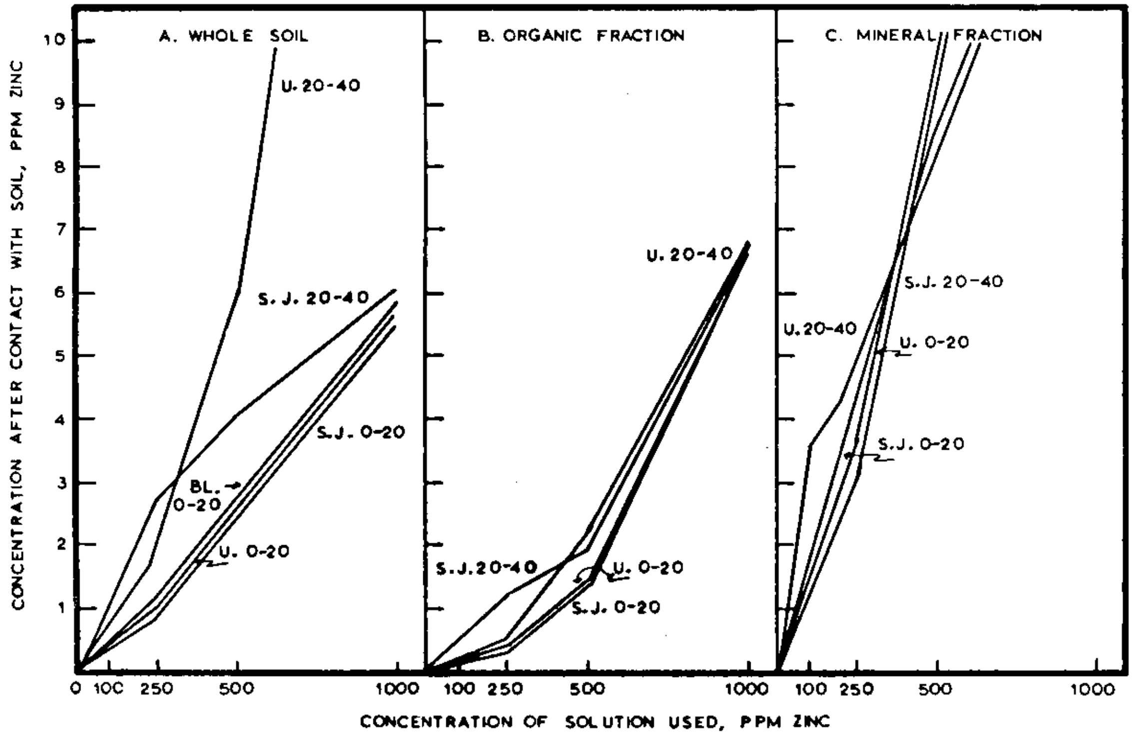

FIG. 2. Zinc remaining in solutions of various initial concentrations after four hours contact with whole soil, organic fraction or mineral fraction of Hydromorfic Podzol (HP), Red-Yellow Podzolic (PV) or Blodgett (B1) soils.

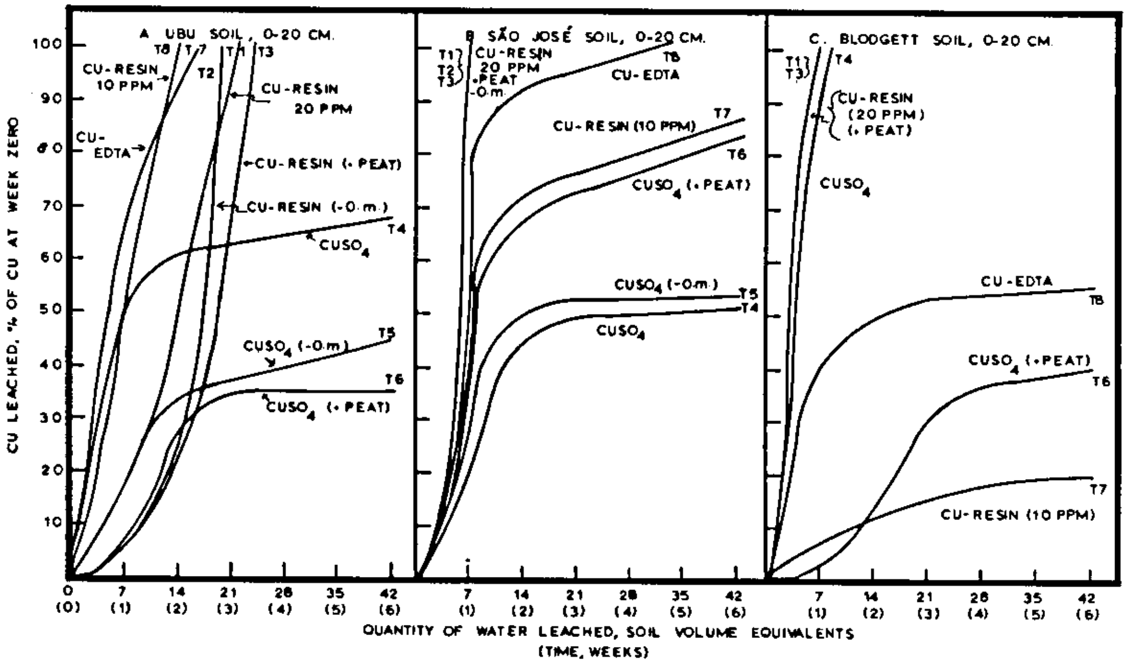

FIG. 3. Percent of initial DTPA extractable copper which leached from Hydromorfic Podzol (HP), Red-Yellow Podzolic (PV) or Blodgett woils as influenced by treatment and volume of leaching water over a six week period.

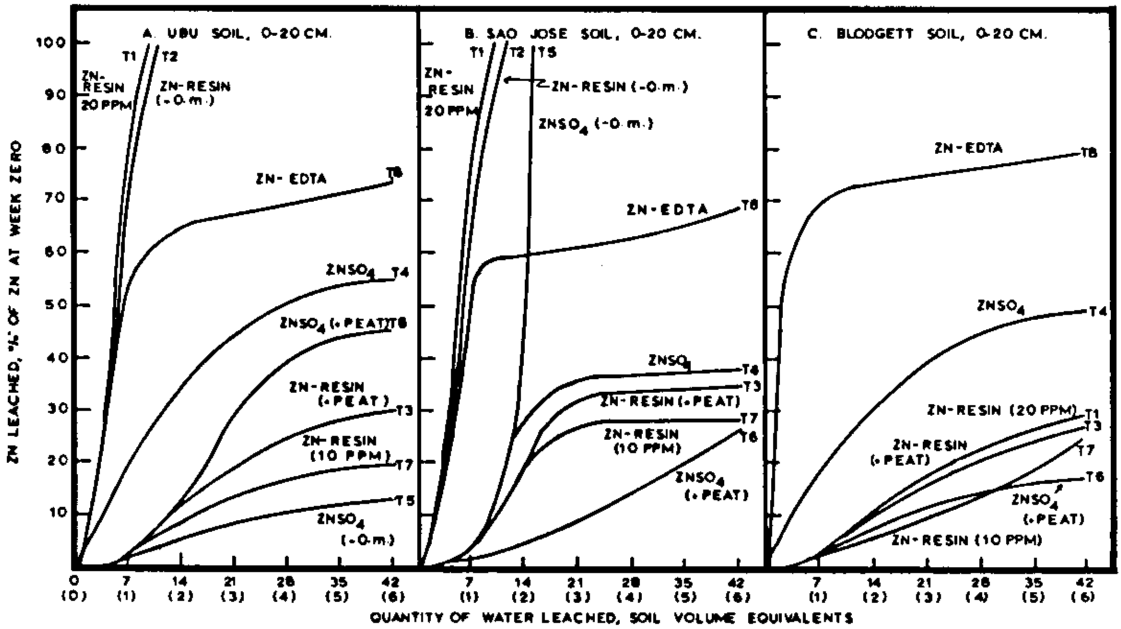

FIG. 4. Percent of initial DTPA extractable zinc which leached from Hydromorfic Podzol (HP), Red-Yellow Podzolic (PV) or Blodgett woils as influenced by treatment and volume of leaching water over a six-week period.

involved when copper is added as resin or chelate forms as compared to the sulfate form. In addition, the mechanisms of copper retention appear to be different in the Blodgett soil from those acting in the "tabuleiro" soils.

There was no distinct advantage from adding zinc in the sulfate form (Fig. 4), such as was the case for copper. The resin adsorbed form of zinc performed nearly as well as the $ZnSO_4$ treatment, except at the high rate of application or when soil O.M. was removed. The addition of peat along with resin adsorbed zinc did not have the detrimental effects which were observed with copper for this combination. The differences in leaching of copper and zinc under similar conditions suggest that different mechanisms of retention are active for these two ions. However, as was observed for copper, it appears that chelated zinc would be a rather ineffective material with which to combat zinc deficiencies in these soils. Even in the Blodgett soil the chelate form of zinc was leached more readily than the other forms of added zinc.

These studies were not designed to allow definition of types of retention mechanisms or reactions which may influence the usefulness of these plant nutrient carriers. However, one might speculate that the apparent stability of copper and zinc sulfates, which are highly water soluble, may be a result of rapid reversion of these materials to $Cu(OH)_2$ and $Zn(OH)_2$. These hydroxides are highly insoluble in water and they were found by Bingham *et al.* (1964) to form from soluble copper and zinc salts under favorable pH conditions. Further studies should be conducted with these soils in their natural state to determine if retention of sulfates remains high under the more acidic conditions occuring in the field, and to determine the influence of liming rates on copper and zinc retention. In addition, the efficiency of less soluble compounds, such as hydroxides, carbonates or sulfides, should be investigated.

Results of this study may have considerable agronomic significance in the area of "tabuleiro" soils. Studies under field conditions are necessary to ascertain the validity of these laboratory studies and to investigate associated problems. If similar results were obtained, it would mean that inexpensive, readily obtainable materials would be most effective in combatting copper or zinc deffficiencies in the field.

REFERENCES

BINGHAM F.T. PAGE A.L. & SIMS J.R. 1964. Retention of Cu and Zn by H-montmorillonite. Soil Sci. Soc. Am. Proc: 28: 351–354

GUPTA U.C. & MACKAY D.C. 1966. Procedure for the determmation of exchangeable copper and molybdenum in Podzol soils. Soil Sci. 101: 93–97.

HIMES F.L. & BARBER S.A. 1957. Chelating ability of soil organic mater. Soil Sci. Soc. Am. Proc. 21: 368–373.

HODGSON J.F. 1963. Chemistry of micronutrients in soil. Adv. in Agron. 15: 119–159.

JACKSON M.L. 1956. Soil chemical analysis. Advanced course. Chap 2. Published by the author. Madison, Wisconsin.

LINDSAY W.L. & NORVELL A. 1969. A micronutrient soil test for Zn, Fe, Mn, and Cu. Agronomy Abstract pg. 84.

MATSUDA K. & IKUTA M. 1969. Absorption strength of zinc for soil humus. I. Relationship between forms and adsorption strength of zinc added to soils and soil humus. Soil Sci. Plant Nutr. 15: 169–174.

NEEKLANTAN V. & MEHTA B.V. 1961. Copper status of soils of Western India. Soil Sci. 91: 251–256.

STEENBJERG P. & BOKEN E. 1950. Copper content and copper deficiency in Danish soil types. Plant and Soil 2: 195–221.

RESUMO. – RETENÇÃO E LIXIVIAMENTO DE COBRE E DE ZINCO, INFLUENCIADOS PELA FONTE NUTRIENTE, EM DOIS SOLOS DE "TABULEIRO".

Foram estudados 2 solos de "tabuleiro" de Pernambuco: um Podzólico Vermelho-Amarelo e outro Podzol Hidromórfico muito arenoso, ambos altamente lixiviados e extremamente inférteis; a capacidade de retenção e o grau de lixiviamento do cobre e do zinco, nas profundidades de 0–20 e 20–40 cm, usando-se como fontes de suprimento desses microelementos $CuSO_4 . 5H_2O$, $ZnSO_4, 7H_2O$, resina saturada em Cu e Zn e Cu (Zn) – EDTA, com ou sem adição de 5% de turfa. Foi incluído no experimento, para fins de comparação, um solo de baixa fertilidade coletado a 0–20 cm em Western Montana, U.S.A.

Os tratamentos incluíram amostras dos solos integrais e das respectivas frações minerais (removida a M.O.), a adição dos nutrientes em doses de 10 e 20 ppm, o lixiviamento intensivo durante 6 semanas e a coleta semanal de extratos de solos, que foram analisados por absorção atômica para determinação do teor de cobre e de zinco.

Os resultados obtidos mostraram que nos dois solos brasileiros a retenção de cobre e de zinco esteve diretamente relacionada com o teor de M.O. na amostra; assim, a retenção foi maior na camada superficial, mais rica em M.O. do que a de 20–40 cm, e 30 vezes maior na fração de M.O. do que no solo integral de 0–20 cm de profundidade; esses dois solos retiveram mais zinco do que cobre, e no solo vermelho-amarelo Podzólico a retenção dos dois elementos foi maior do que no solo Podzol Hydromórfico. O solo de Montana reteve mais cobre do que zinco e apresentou maior retenção de cobre do que os solos brasileiros, mas a retenção de zinco foi equivalente. Os sulfatos apresentaram menor lixiviamento do que as outras formas de adição desses nutrientes, indicando que a forma de sal é a mais eficiente para combater a deficiência desses elementos nos solos estudados.

Termos para indexação: lixiviação de nutrientes; micronutrientes nos solos de tabuleiros.