Micronutrient cation relations of Tabuleiro soils of northeast Brazil
by Jose Pereira Leite

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Crop and Soil Science
Montana State University

Abstract:
This study was conducted with samples taken from two depths of two Brazilian soils from the "tabuleiro" of the state of Pernambuco, and the surface soil of Blodgett series of western, Montana. The tab uleiro soils are from very level areas which would be advantageous for agricultural development, but the soils are very sandy, highly leached and extremely infertile. Micronutrient cation deficiencies are common in these soils, and detailed studies had not been made to determine the chemistry and fertility relations of these elements in tabuleiro soils. The Blodgett soil represents a common soil from Western Montana, but one of relatively low fertility.

Determinations of the retention and leaching of copper and zinc, were conducted. Results indicated that both elements were readily retained by the top soils, and this retention was two to three times greater than that of subsoils. The Sao Jose soil retained more copper and zinc than the Ubu soil at comparable depths. The organic fractions retained five to ten times more copper and 'zinc than the mineral fractions of the same soil. The Blodgett soil retained 10 times more copper than the corresponding depth of Brazilian soils, however, zinc was retained almost equally.

The sulphate forms of copper and zinc were less subject to leaching than the resin adsorbed or chelated forms; these two forms leached up to 100 percent of the initial copper or zinc added.

Growth chamber experiments, using barley (Hordeum distichon L. variety Hypana) as a test crop, were conducted on these soils to identify micronutrient cation requirements, and obtain information to determine the most efficient source of copper, iron, manganese, and zinc to correct deficiencies.

It was found that copper appears to be the most limiting micro nutrient cation for plant growth on these Brazilian soils. The sulphate forms gave higher dry matter yields. Chelates failed to adequately supply the micronutrient cations required for optimum plant growth under the conditions of these experiments. Resin adsorbed micronutrient cations also were less -efficient, than sulfate salt forms. The Brazilian soils had been steam sterilized. The results must be interpreted by including the known influences of steam sterilization on micronutrient cation availability.

Results from the Blodgett soil from Montana suggest that only supplemental . nitrogen, phosphorus and potassium are required for barley growth under these experimental conditions.

MICRONUTRIENT CATION RELATIONS OF "TABULEIRO" SOILS OF NORTHEAST BRAZIL

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JOSÉ PEREIRA LEITE

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Crop and Soil Science

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To my wife, Odete, and daughter, Anamaria,

whose company, encouragement, and dedication

made this work possible

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ABSTRACT

This study was conducted with samples taken from two depths of two Brazilian soils from the "tabuleiro" of the state of Pernambuco, and the surface soil of Blodgett series of westenn Montana. The tabuleiro soils are from very leved areas which would be advantageous for agricultural development, but the soils are very sandy, highly leached and extremely infertile. Micronutrient cation deficiencies are common in these soils, and detailed studies had not been made to determine the chemistry and fertility relations of these elements in tabuleiro soils. The Blodgett soil represents a common soil from Western Montana, but one of relatively low fertility.

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INTRODUCTION

In Brazil, Columbia, and Venezuela, a large continuous area of Oxisol soils stretches from the Andes on the west to the coast on the east. Interspersed with the Oxisol soils are areas of hydromorphic soils, alfisols and entisols. Agricultural use of these soils has occurred mainly in southern and eastern Brazil and in northern Colombia and Venezuela. Very little agricultural development has occurred over extensive areas of the Amazon basin, although soils favorable for agricultural use have been surveyed there (106).

The Oxisol soils with inclusions of hydromorphic soil, alfisols, and entisols cover nearly 3,214 million hectares or nearly 25 percent of the land area of the world. The humid and wet-dry tropics and subtropics are covered mainly by these soils. The estimated potentially arable hectares come to 1,382 million of which today less than one fourth are under cultivation.

The minerals in the Oxisols are highly weathered. The soils have been subject to strong leaching with warmer water than in temperate regions.

With important local exceptions, most Oxisols are responsive to modern management system and can be highly productive for many food and industrial crops. Although practical ways have not yet been found for efficient farming on the most infertile Oxisols, such as some in Brazil, at a high level of productivity, research can be expected to find ways.

Many of the best undeveloped tropical soils are covered with heavy

tropical rain forests. These are the soils least understood of any. Judged by yields of earlier days, they were no more leached of plant nutrients than many of the currently most productive arable soils of the eastern part of the United States and of northwestern Europe. And they are higher in organic matter, although it is brown rather than black. An enormous potential exists within these soils, which could be highly developed with the science and technology of modern agriculture.

Travelers in the tropics commonly associate poor crops with "poor" soil, and are thus led to great errors. Even the most responsive soils give low yields with inadequate management (Kellogg 54).

Three types of coastal land forms may be observed along the east and northeast coast of Brazil; Lagoon sections; hilly lowlands; and the flat-topped mesa forms, with young sandstone cover (as in Espirito Santo) that reach the coast in cliffs 10-30 meters high, to which is given the name of "Tabuleiros". The latter two often occur together and erosion has reduced them to similar altitudes. They are distinctive both by their aspect and by their soils. The tabular forms contrast with rounded hills and the Tabuleiros carry leached, sandy infertile soils, while the hilly soils have weathered into reddish clays a difference that is very important to the farmers of this relatively densely populated coastal zone.

The northeast coastal area of Brazil has existed for centuries

on a sugar cane production economy. In spite of their topographical advantage, the Tabuleiros have not been used because of their low fertility. However, it has been impossible to mechanize care production on the hilly lands due to extreme slopes. The demand for more efficient methods of production has spurred interest in developing the level, but infertile Tabuleiros.

Northeastern Brazil covers an area of 1.5 million Km^2, 17.6 percent of the national area, and has a population of 28 million people, which represents 30.4 percent of the national, according to the 1970 census.

The area of humid brushland and associated grasslands of central and south central Brazil and "tabuleiros" of the northeast, covers approximately one-fourth the total area of Brazil. Most of the area is level and well suited physically for agricultural development. The soils are deep, sandy loams to clays and are composed mainly of kaolinitic clays and oxides of iron and aluminum. The rainfall in most of the area is adequate for crop production. The soils have so little fertility, that annual crops do not mature any seed without the application of fertilizers. Where fertility is improved, excellent yields have been obtained.

The area of the State of Pernambuco is 98,300 Km^2. The "Zona da Mata" of this state has an area of approximately 12,000 Km^2. The "tabuleiros" are located in this zone.

The soils are naturally acid and are deficient in both calcium and magnesium. Phosphorus is strongly deficient in all areas and nitrogen and sulphur are usually deficient. For some crops, zinc and boron addition are needed. Deficiencies of other trace elements may be observed in some areas.

It is to this latter problem that we have directed our attention. Objectives of this study were to investigate methods of determining which micronutrients are deficient for crop production, and, following verification of a specific deficiency, what materials could be used to satisfy requirements. The high rainfall (over 2,000 mm per year, see figure 2) and porous soils contribute to excessive leaching. Materials used should be maintained in the soil for long periods if crop needs are to be satisfied over several growing seasons.

BRAZIL

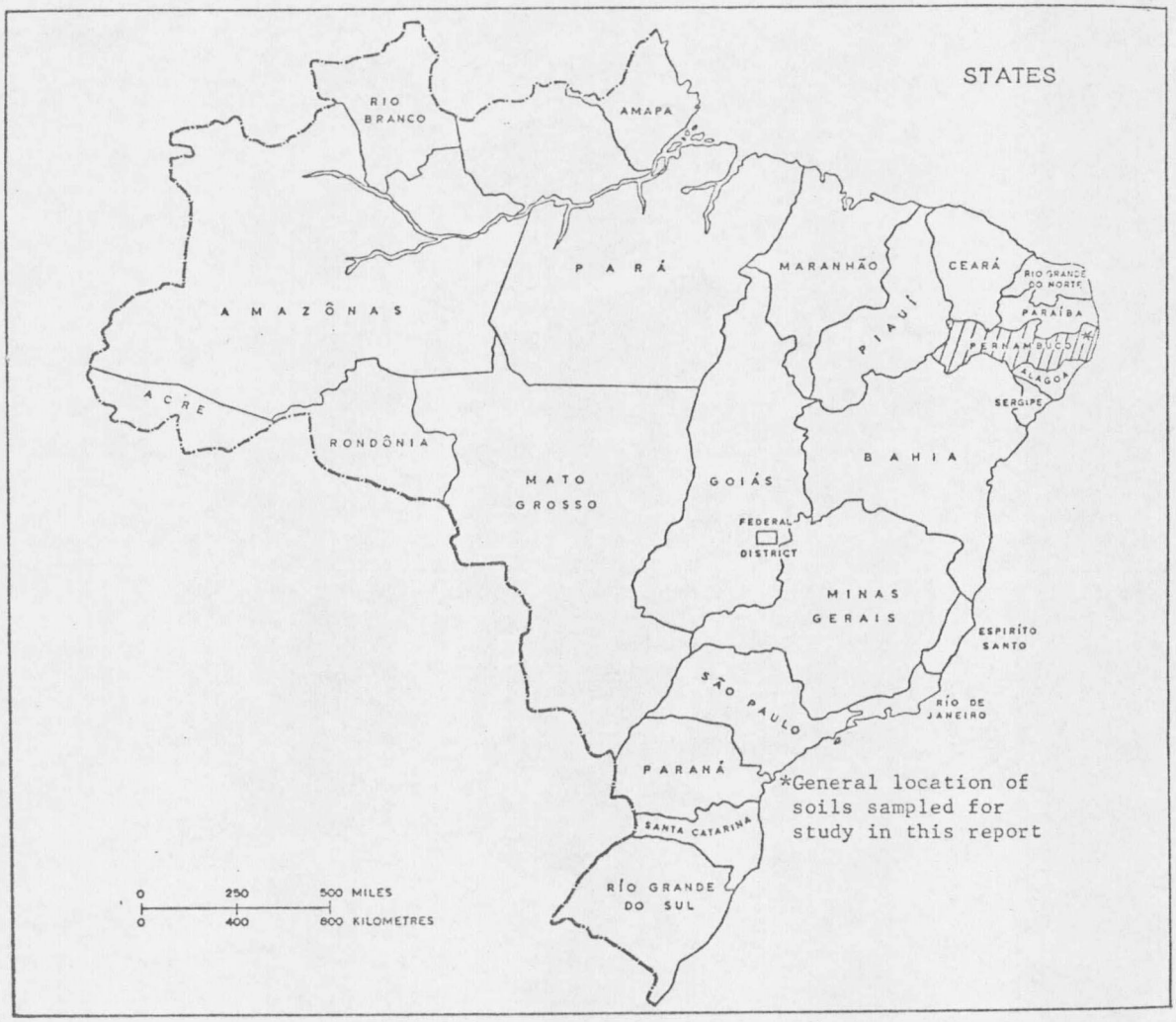

Figure.1. Map of Brazil showing its states. Soils in this study came from "Tabuleiro" soils of the coastal area of the State of Pernambuco (shaded).
(Taken from the following: Valverde, O. 1970. Brazil..pp. 88-125 World Atlas of Agriculture. Vol. III: Americas. I stituto Geografico De Agostini S. p. a. - Novara - Italy)

BRAZIL

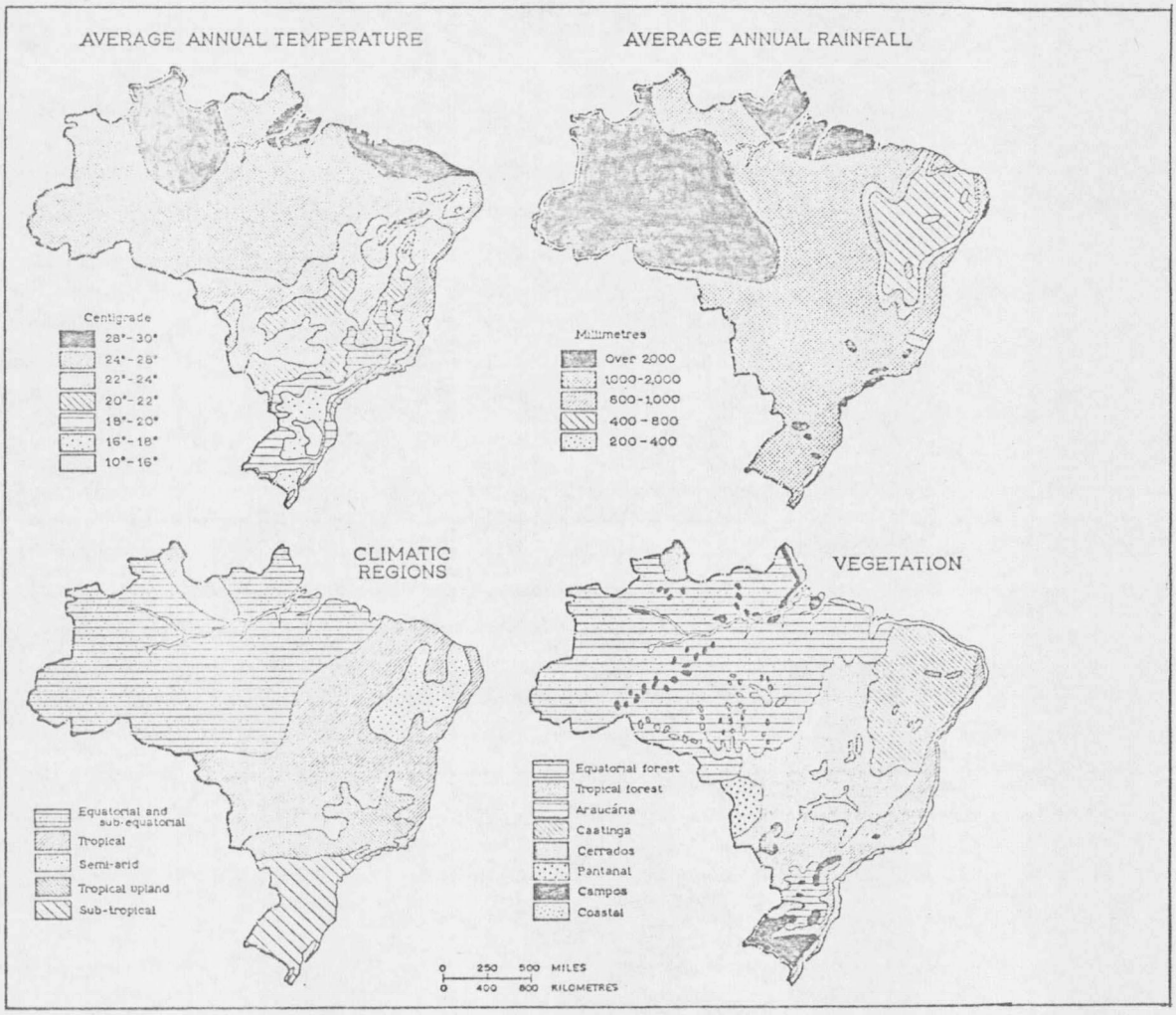

Figure 2. General climatic and vegetative zones of Brazil.
(Taken from the following: Valverde, O. 1970. Brazil. pp. 88-125
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LITERATURE REVIEW

Micronutrient cations

The term micronutrient is also referred to as microelement, minor element or trace element. The author prefers the term "micronutrient", but they will be used interchangeably throughout the literature survey to reflect the terminology used by authors cited. Furthermore, not all micronutrients are considered in this study, so discussion will be limited to those studied; iron, zinc, manganese and copper, the micronturient cations.

Geochemistry

Copper does not contribute appreciably to rock-forming silicate minerals and seems to occur in rocks mainly in the form of sulphides (23). Its abundance is 45 g/ton for the Earth's crust (about 50 ppm). Where copper is present in appreciable quantity in a rock magma it tends to associate with sulphur and iron and not with oxygen or silicon. The relatively few deposits of magmatic type copper are mainly of sulphides, particularly the several complex sulphides of iron and copper.

Iron is of high abundance in the Earth (23, 48), comprising five percent of the crust. In the crust as a whole, iron occurs in combination with oxygen and enters freely into silicate minerals. The Fe^{2+} ion cannot replace Ca^{2+} in feldspar for thermochemical reasons, but it is possible for Fe^{3+} to replace Al^{3+} in these minerals.

Manganese is the eighth most abundant metal (1000 g/ton or about 1100 ppm) in the Earth's crust (23). The element is essentially

cationic and the highly oxidized anions $MnO_4^{=}$ and MnO_4^{-} are unknown in nature. The ionic radius of Mn^{++} is 0.80 Å which is only slightly larger than Fe^{++}, which is 0.74 Å. Considerable interchange between the two ions in crystal lattices is therefore possible. Manganese is widely present in minerals, particularly silicates, as a trace element. Manganese bearing minerals of primary origin predominantly contain the Mn^{2+} ion and in the process of weathering, this passes into solution as $Mn(HCO_3)_2$. The Mn^{2+} ions from weathering processes remain mobile for greater distances than Fe^{2+} ions.

Manganese occurs in igneous rocks associated with iron (23,48). The ratio Fe/Mn in rocks is approximately 50. It is found in mineral structures in three degrees of oxidation: Mn^{2+}, Mn^{3+}, and Mn^{4+}. As with iron, manganese is found in hydrolysed residues formed from lateritic meteorization. Iron is first oxidized, mainly as $Fe(OH)_3$, however, manganese stays in solution until the greatest part of the iron has been precipitated. The most common and abundant manganese compound in nature is MnO_2. In sedimentary rocks manganese is found associated with zinc, cobalt, and molybdenum (40).

Zinc abundance in the Earth's crust is about 65g per ton (72 ppm)(23). In the weathering of rocks zinc passes into solution and subsequently is precipitated in various forms such as carbonates, silicates, phosphates, etc. However, most of these compounds are amenable to acid attack, for example, in soils.

Soil Relations

The total concentration of trace elements in whole soil is reported to be higher in well drained profiles (particularly for manganese)(26,46). There is a tendency for the total trace elements to increase with depth (46,113), irrespective of drainage status. It also was reported that in the surface horizons, the bulk of trace elements occur in the finer silt and clay fractions in both the well and poorly drained profiles (26).

One of the most important factors affecting the mobilization or immobilization of micronutrients in soil is drainage (46). The exchangeable or acid-soluble form of the element may be concentrated near the surface. This apparently holds true for well-drained soils, but for their poorly drained counterparts, even the extractable forms are concentrated in the lower horizons (100,102).

Soils vary along horizontal and vertical directions (68,75), and even apparently uniform layers differ in available nutrient content, the surface soil usually being the most fertile (75).

The total micronutrient content of a soil has little significance (32,107,108), because marked discrepancies between total content and availability have been noted (69,108). The availability of micronutrient cations generally is favored by acidity (107). The current trend in estimating availability of micronutrient cations is to extract the soil with more vigorous reagents in an attempt to establish the best

possible correlation of extractable cation with actual plant uptake (108). Soil testing for the micronutrients is particularly difficult because of our lack of knowledge of their behavior in the soil-plant system and our lack of dependable criteria for judging when a plant is suffering from a deficienty (110). The problem is one of making chemical and physiological reason out of the soil-plant system when so little is known about the physical chemistry of the micronutrients in the soil system and the plant's reaction to them (108).

One of the problems in testing soils for the micronutrient cations results from the differences in crop sensitivity to the supply of the elements. These differ among species, sometimes even among varieties in a species and are a manifestation of differences in the plant's ability to extract the nutrient from the soil and differences in the plant's requirement for metabolism. For each of the micronutrient cations there are plant species that are very susceptible to deficiency, species that are only moderately susceptible, and species that are resistant (110).

The availability of micronutrient cations is particularly sensitive to change in the environment (5,19,77,107,110). The availability of these elements increases with a decrease in soil pH. The pH of a soil does vary with soil management (5,110) and large pH fluctuations can occur. Manganese availability is very pH dependent. The Mn^{2+} content is higher in acid soil than in alkaline soils (48). At the same

time it has been reported that on some soils, copper availability is not affected by pH (110).

The chemistry of trace elements in soil is dominated by reactions that lead to the formation of inert and insoluble compounds or complexes (5). What to use as sources of micronutrients and what happens to their availability when they are mixed with other chemicals in fertilizer is a problem beset with the fact that chemists talk more than plants do (107), i.e., not much is known of these reactions.

Air, water, and soils are becoming increasingly contaminated in this highly industrialized age (19). The analysis of top-soils from urban areas in Scotland indicates that, in general, in such soils levels of Cu, Zn and B, are substantially enhanced by comparison with arable top-soils from rural areas (77).

Reactions of micronutrients with organic matter

Basically, four methods can be used to assess the contribution of organic matter to the chemistry of micronutrients in soils; a) the association of organic matter content with the distribution and availability of micronutrients in the soils; b) the effect of organic matter removal on the reactivity of soils with micronutrients; c) a direct attempt to assess the amount of an element present in the organic form, and d) characterization of organic matter and its reaction sites (46).

Removal of organic matter often results in a decrease in

reactivity of heavy metal in soils (45,46). Various studies of reactions that occur between organic matter and micronutrients reveal a relatively large capacity to combine very strongly with certain elements, notably copper (21,23,45,46). Carbonyl groups were in greatest abundance in the surface soil (121), while carboxyls, which concentrated strikingly in the subsoil, were the predominant form in the B_h horizon.

Micronutrient functions in plants

The micronutrients usually function in plants as components of enzyme systems (5,8,11,23,56,61,68,76,85,107). As an example of the catalytic importance of micronutrients it is said (107) that one ounce of molybdenum is tied to the fixation of 105 tons of CO_2. This indicates the importance of molydenum in enabling a plant to collect CO_2 and radiation to fix energy. Considering this ratio, molybdenum is functioning in the parts per billion range.

Copper exists at the active center of diphenol oxidases such as tyrosinase (8,21,56), cytochrome oxidase (56) and laccase (21). When the metal is removed, the activity of the enzyme is destroyed. Whether the terminal oxidase of a particular species is Cu-containing ascorbic acid oxidase or Fe-containing peroxidase or catalase appears to be the factor dominating the requirements of different species for these metals (11). Copper is also included in the formation and stabilization of chlorophyll, albumin, carbohydrate in nitrogen metabolism

and in the intensity of plant respiration (21,61).

Iron, both ferrous and ferric, is a co-factor of the cytochromes, peroxidase, catalases and ferrodoxin enzymes (56,84). The elaboration of chlorophyll requires the presence of iron (23,61,84), although the prosthetic group of the substance contains only magnesium.

Manganese is required for phosphotransferases and arginase activities (56). It is required in the process of photosynthesis, takes part in the regulation of oxido-reduction processes and raises the activity of the biochemical reactions which influence the carbohydrate and albumin metabolism in plants. Also, it is included in the chlorophyll molecule (61,74,97). Manganese replaces magnesium in some biological processes. It promotes the uptake of magnesium by plants, and is used for regulation and stabilization of oxido-reduction processes under conditions of excess moisture (61).

Zinc is known to be present in the granum protein of the chloroplasts (23, 85) and it acts as a co-factor of several enzymes (8,23, 56,61,85). Carbonic anhydrase contains zinc and catalyses the breakdown of carbonic acid to form carbon dioxide and water. Alcohol dehyogenase and carboxypeptidase also contain zinc. Zinc plays a great role in oxido-reduction processes in plants (61,76,85).

Considering the wide range of functions of the micronutrients it appears that the only thing they have in common is that plant and animal requirements for them are small (108). It is solely on this

basis that they have been arbitrarily grouped together and called "micronutrients".

Copper

Copper was first identified as being a constituent of plant tissue in 1916 (21); yet, it was not until 1931 that it was classified by Sommer as being an essential nutrient for all plant life (21,107). The analytical methodology available for this type of study had been inadequate in the interim period. The determination of copper today by atomic absorption is convenient and rapid. The method is accurate and free from interferences (3), thus greatly enhancing studies of this element.

Various factors influence the degree to which soil copper is available to plants; these include: pH, organic matter, amount of clay, effect of other elements, carbonates, phosphates, and soil micro-organisms (69,98). Several investigators (31,67,78,82,104) have pointed out that, in spite of the fact that copper is less susceptible to changes in pH than zinc, and much less susceptible than manganese or molybdenum, copper availability decreases with increasing alkalinity of the soil. Copper deficiency apparently occurs most frequently on very sandy or gravelly soils (31).

For Oregon soils (120), a supply of 0.1 to 1.0 ppm of exchangeable copper is sufficient for normal growth, provided that a working margin of 0.5 ppm of available copper indicates roughly the boundary

between response and no response to copper additions.

In the U.S., 14 states have reported copper deficiencies (21). The beneficial influences of copper in plant growth are not due entirely to its essential function as a plant nutrient. It appears that copper can neutralize harmful conditions which exist in some soils. It is thought that copper can precipitate, or inactivate, certain toxic substances present in copper deficient organic soils. Soils having a low level of native copper are characteristically sandy soils having low organic matter contents and are, therefore, extremely susceptible to leaching (21).

Water-soluble copper was determined from the soils of the podzol region of eastern Canada, representing a range in textural classes from clay loam to fine sandy loam. Removal of the organic matter from the water-extract of soils increased the amount of copper considerably (two to four times)(34). Apparently, 50 to 80 percent of the copper in the direct water-extract of soil was complexed with the water-soluble organic matter.

Sixty four typical soils of Gujarat and Saurashtra in western India were analyzed for available and total copper contents (69). Available copper content varied from 0.03 to 1.93 ppm, with an average of 0.51 ppm. Total copper content varied from 11.0 to 175 ppm, with an average of 55.8 ppm, 100 times the average of the available copper content. A significant positive correlation was found between available

and total copper contents, a significant negative correlation between pH and available copper content, and a significant positive correlation between soil texture and total contents. No correlation was found to exist between available copper and organic matter and the calcium carbonate contents of the soils.

In Denmark (98) copper deficiency is mainly found in jutland, especially in sandy soils rich in humus, and in peat soils. It is, however, also widely found in sandy soil with normal humus contents of 2 or 4 percent in the same area.

The difficulties of determining available copper in the soil are very great. Extremely small quantities of copper are contained in the soil, and there is a strong tendency for the cupric ions to form slightly soluble complex compounds. These extraordinary difficulties exist both for definition of copper forms present and their quantitative analysis (98).

Steinbjerg and Boken (98) also report that copper may occur in the cuprous state in the crystal lattice of coarser particles of the soil. Due regard must be paid to this source of copper when chemical methods for the determination of copper deficiency of the soil are worked out. They suggest that the chemical nature of soil copper is unknown and the definition of available copper is based on empirical observations. Much recent work has eliminated uncertainties concerning the chemical nature of soil copper, and more direct approaches can now

be employed.

Based on empirical relationships, several soil extractants have been used for copper analysis. Gupta and Mackay (35) used four different reagents: 0.2 M ammonium oxalate (pH 3.0), 0.1 N HCl, 0.1 N NaOH, and 2 N citric acid solution as extractants for exchangeable copper on some of the podzol soils of eastern Canada. Ammonium oxalate gave maximum extraction of the element. Citric acid was poorest and HCl and NaOH were intermediate for copper extraction. It was concluded that 0.2 M ammonium oxalate (pH 3.0) was the best reagent for the determination of exchangeable copper. They reported also (36) that the water-soluble copper content ranged from 0.09 to 0.46 ppm. The total or exchangeable contents of nitrogen, phosphorus and potassium in soil seldom vary by 10-fold, but the amounts of exchangeable copper was found to vary up to 100-fold between individual samples. In addition, lower amounts of exchangeable copper were found in most of the sandy soils and were associated with higher leaching of the element.

Recently, the use of chelating agents for extraction of micronutreint cations has been studied by Lindsay and his associates (57, 58). The advantages and usefulness of these materials for extraction and their correlation with yield are discussed in the section on chelates, later in the literature review.

Copper is taken into the plant as the cupric (Cu^{2+}) ion. Once inside the root it is transported to all parts of the plant, a greater

amount tending to concentrate in the grain. The greatest plant requirement for copper is in the early growth period, prior to flowering. A lack of copper at this stage prevents normal seed development. Copper supplied after this period cannot overcome this condition (21).

In tests on peat soil, oats showed the greatest need for copper among field crops (70). An analysis of the peat soil on which these crops were grown revealed a content of 9.0 pounds per acre total copper and 0.015 pound per acre available copper as extracted with 0.1 N HCl. The copper fertilized plots were sampled during the growing season and found to contain 23.3 pounds per acre total copper and 4.5 pounds per acre available copper. The author reported there was very little correlation found between the 0.1 N HCl-soluble copper content of the soil and yield or copper content of the grain. No correlation was found between pH, copper content of the grain, or yield. The pH of these soils varied from 5.8 to 7.3.

In greenhouse experiments with barley and other crops (37), no significant yield response was obtained to applied copper. There was an increase in kernel yield of Hudson barley on three of the investigated podzol soils. Copper content of plant tissues, however, increased by 50% in Herta barley straw, and 400% in Hudson barley kernels, as a result of copper application.

After the harvest of the last crop, 85 to 94% of the applied copper was recovered from the plants as exchangeable copper in soils.

There was no apparent relationship between the exchangeable copper content of soils and the copper content of the crops. In spite of the coarse texture of the soil investigated, none of the crops except Hudson barley responded to applied copper.

Again under greenhouse conditions, Gupta and MacLeod (38), found that without applied copper, barley heads were delayed 14 days in emerging. For maximum yields under greenhouse conditions, the content of copper in plant tissues at the boot stage was 4.8 ppm for barley. A copper content of 2.0 ppm in barley kernels appeared to be sufficient. For straw, a copper content of 3 ppm for barley appeared to be adequate for optimum growth of the crop. The results indicated that exchangeable (oxalate-extractable) copper content of about 1.2 to 1.8 ppm in soil is indicative of copper deficiency for growing cereal crops under greenhouse conditions. An application of 0.5 ppm of copper to the soil increased the kernel yield of barley by 190%; more copper application did not increase the yield. Copper application slightly decreased the yield of barley straw. The same result was reported by Smild and Henkens (91) who attributed these effects to profuse tillering.

Interrelationships among copper, iron, manganese, and zinc are important. There is evidence that copper has a direct effect on phosphorus uptake, and low concentrations of copper have been reported to prevent the normal uptake of K by plants (3). Toxic levels of copper can reduce growth by depressing the activity of iron (21,24), and the

uptake of other heavy metals. Inhibitory effect of manganese on copper uptake by barley and rice were reported (24).

Iron

The necessity of iron for growing plants was shown by Gris of France in 1845 (84). In 1860, Sachs proved its essentiality for all plant life (107), but the correction of iron deficiency by soil application has frustrated research workers for years (84).

Despite years of research, the movement of iron from the soil to the plant and metabolism in the plant are not yet completely understood. Iron is found in adequate amounts in most agricultural soils but it is often in a form unavailable to the plant.

Iron exists in several forms in the soil; as a mineral, as an organic complex, inorganic compounds or precipitates, and as soluble compounds or ions dissolved in the soil solution. Iron exists as an electronically charged ion in solution in two forms; the ferrous or ferric form. The ferrous form is generally considered available to plants while the ferric form is not. Most iron in soils is in the ferric form. But by complexing the ferric form into an organic form, as a chelate, the unavailable ferric form, becomes available to plants.

Deficiency of iron is widespread and difficult to correct. The presence of calcium carbonate in soil ties up much of the iron present, reducing its availability to plants. Iron deficiency also occurs in acid soils.

Iron deficiency may be caused by one or more of the following conditions: 1) low supply of total iron (in acid soils), and 2) low supply of available iron because of: a) high soil pH and presence of calcium carbonate, b) erosion or land levelling exposing deficient parent material and removes organic matter which is the natural storehouse of organic iron in the soil, c) a high level of phosphate in the plants associated with band applications of fertilizers containing phosphorus, d) antagonistic interactions with other micronutrients (Mn and Cu) in the soil and plants, e) high soil moisture content and low soil temperatures before planting time, f) soil compaction associated with operating heavy land grading equipment in fields with high moisture conditions. This is a serious problem for soils low in organic matter or with a sandy texture. As a general rule, iron deficiency conditions in the field tend to diminish as the season progresses. This is due to the warming of the soil, reduction of the soil moisture and increased soil pore space (107).

Other factors mentioned for iron deficienty in plants that interfere with adsorption and translocation of the element are: low reducing capability of roots (13), micronutrient imbalance (15), iron inefficient plant species (30), high pH of the growth media (72), and the oxidation of Fe^{2+} to Fe^{3+}.

Factors employed to correct iron deficiency include the lowering of pH in growth media (17), genetic variants (16) and chelates (42).

Certain interactions with other micronutrient have been reported. Zinc interferred with translocation of iron from roots to above ground parts of soybean (Glycine max L.)(7). In barley plants manganese inhibited the adsorption of iron (24). The higher the concentration of manganese, the less was the adsorption of iron by plants. The inhibitory effect of manganese was very sharp at a higher concentration of Fe in the medium. At the concentration of 0.08 ppm Fe, the 0.08 ppm of manganese lowered Fe uptake to less than half of the control, which contained no Mn in the medium.

Manganese

Manganese was proven to be essential to all plant life by McHargue in 1922 (107).

Manganese deficiency is a serious nutritional problem of many crops and soils. More than 25 states have reported manganese deficiency for one or more crops, with deficiency of small grains and soybeans being recorded most frequently. Manganese deficiency has currently been estimated to be a major problem on at least 13 million acres in the U.S. and constitutes the largest single acreage for any of the micronutrients needed as soil amendments (97).

The main soil conditions under which manganese deficiency will occur are as follows: a) thin peaty soils overlying calcareous subsoils; b) alluvial soils and marsh soils derived from calcareous materials such as calcareous silt and clays; c) poorly drained cal-

careous soils with a high content of organic matter; d) calcareous black sands; e) calcareous soils recently taken out of long-term grassland programs; f) black horticultural soils where manure and lime have been applied regularly for many years; and g) very sandy, acid, mineral soils that are low in native manganese content.

A number of changes in soil management can reduce the level of available manganese in the soil. Raising the pH to above 6.5 favors the oxidation of manganeus manganese into manganic manganese. The latter is almost unavailable to plants.

Generally, the better drained the soil, the more highly oxidized is the manganese and the less available it is to the plant. Manganese deficiency is more prevalent in dry years than when moisture conditions are ample.

One of the factors determining the fraction of soil manganese extractable by alkaline pyrophosphate may be the organic matter content of the soil (41). Furthermore, manganese in alkaline pyrophosphate extracts of soil was found to be in the manganous form. It was concluded manganese deficiencies occur typically on soils high in organic matter content. It would appear that in these deficient soils the conditions may be such that all the divalent manganese is fixed by the organic matter in a form unavailable to the plants.

In tropical soils (96), it was found that lime reduced adsorption of manganese by legumes. In one soil the application of super-

phosphate increased manganese absorption.

Manganese transport into barley roots was reported to be metabolically mediated (60), however, in oat roots it was found to be non-metabolic (73).

There are conflicting reports on the chlorophyl content of manganese deficient plants (25). Manganese-deficiency interferes with synthesis of chlorophyll, thereby affecting carbon assimilation (9), however, manganese deficiency does not directly produce chlorosis. On a study of the effect of manganese deficiency on barley plants (81), it was found that the chlorophyll content of manganese deficient plants was more than double that of the control.

It is considered that the reduced photochemical activity of manganese deficient chloroplasts is directly related to the shortage of this element as a co-factor, rather than to changes in the submicroscopic structure of the grana. Manganese involved in these reactions is tightly bound in the chloroplast to photochemically active lamellae (74). The absence of this element leads to the formation of chloroplats in which the chlorophyll is distributed abnormally.

The addition of silicon to culture solutions has been shown by a number of workers (59,80,93), to result in an increase in plant yield, however, the beneficial effects obtained may well be due to secondary causes rather than to an essentiallity on the part of

silicon. Manganese was found to be toxic to barley plants when grown in Hoagland culture solution at concentrations from 0.5 to 5.00 ppm, but manganese becomes harmless when plants absorb silicon together with manganese (119). Silicon has no effect on the content of manganese in the leaf tissue. These results suggest that manganese forms complexes with silicon and is "inactivated". The same author found that calcium, magnesium and potassium also eliminate manganese toxicity by repressing the amount of manganese movement into the leaf. However, iron and hydrogen ions were found to be more effective (112) than calcium, magnesium and ammonium, in reducing manganese uptake by barley plants. It was explained that the depression of manganese absorption by these cations was the result of ionic competition.

A number of research workers have suggested that excess manganese in plant tissue oxidizes iron to the ferric state, in which condition it is precipitated and rendered biologically inactive, thus inducing iron deficiency (50,97). In this way, manganese depresses iron absorption in plants.

Manganese toxicity symptoms of rice plants were markedly reduced by increasing the concentration of zinc in the nutrient solution (50). It was concluded that the critical concentration of zinc resulting in zinc toxicity symptoms is highly influenced by manganese concentration in the nutrient solution. At 1 ppm level of zinc, zinc-content of the rice plants was generally reduced with increased

concentration of manganese in the solution. At 10 and 30 ppm zinc, the content of zinc in the roots was markedly reduced with inereased concentration of manganese in the nutrient solution. The results indicate a possible interaction between manganese and zinc in the growth of rice plants. The growth of rice plants depends not only on the content of manganese or zinc in tissues but also on the ratio of manganese to zinc in the tissues. Accordingly high yields will be expected even at high concentrations of manganese and zinc in tissue, if the Mn/Zn ratio is in the range of 0.1 to 10. These results suggest that manganese and zinc may interact to reduce the toxicity of each other in the tissue.

Manganese is not readily translocated between plant tissues (97). Manganese content of barley in the range of 0-12 ppm has been found to be deficient. At 13-18 ppm it is marginal, and at 19-100 ppm it is generally sufficient.

Most workers have found that manganese sulfate added to the soil generally gives most satisfactory results for correcting deficiencies. Manganese oxide and certain manganese-chelates are also satisfactory in many cases (97).

Zinc

In 1869, J. Rauling showed that zinc was indispensable for the growth of Aspergillus niger (109), but Sommer and Lipman (94) and Sommer (95) proved that zinc was indispensable for the growth of

barley and other higher plants in solution culture. This confirmed the earlier contention of Maze and Javinier that zinc was essential for green plants (65).

Zinc deficiency in crops now occurs in 32 states of the U.S., New Zealand, Australia, Africa, México and Brazil.

Zinc has a normal concentration range in plants of 15-60 ppm of dry weight. Seeds do not contain enough zinc to produce more than a small seedling, so plants must have an early and continuous supply from the soil. The zinc content of the plant reflects the supply available to it. Therefore, petioles and leaves are analyzed as a guide to zinc adequacy during plant growth. The determination of zinc and other elements in plants by atomic absorption spectrometry is at least as accurate and sensitive as other methods currently available, and is considered better in both rapidity and freedom from interference by extraneous elements (2,22). None of the elements present in plant digest interfere with the determination of zinc.

Zinc deficiency is most apt to occur in dry regions with neutral or alkaline soils or in warm and tropical climates with slightly acid soils. Deficiency symptoms are most frequent in areas with high light intensity. But Viets (109) reports that zinc deficiency is not related to type, texture, organic matter, mineralogy or total zinc content in soils. Zinc uptake by barley (and uptake of the

micronutrients elements as well) is reported to be metabolically mediated (83).

Barley belongs to the group of "insensitive plants" to zinc deficiency (85). The zinc content of barley is around 27 ppm and the grain about 17 ppm (109). The nature of resistance to zinc deficiency appears to be under genetic control (39).

Zinc interacts with manganese as was discussed in the manganese section (50). Zinc also interacted with iron decreasing its high level and corrected the deficiency. The results indicate that one characteristic of zinc deficient plants is high iron content.

The concentration of free zinc ions will decrease progressively as zinc is diluted by continuing growth (76).

Addition of a concentrated solution of $ZnSO_4$ to soil resulted in rapid absorption of zinc, about 75% of the total being accounted for on the cation exchange complex during the first minute. Subsequent rate of conversion from exchangeable to acid extractable forms varied widely among soils. The main factors that accounted for the extent of zinc retention were CEC and pH; there appeared to be no significant relation to available phosphorus (86).

Chelate Forms of Micronutrient Cations

Since the pioneer work of Stewart and Leonard in 1952 (99), use of chelated forms of micronutrient cations to correct deficiencies has gained in popularity. During the past two decades many

studies have been conducted concerning the nature of response and various interactions which they may cause. More recently they have been used as extracting agents for analysis of available micronutrients in soils.

Several chelate materials are being utilized, but in general they are chemically similar. The basic agents usually are organic acid molecules with molecular weights of 400-600. These bind or complex with the metal ion, preventing it from reacting in the soil to form highly insoluble compounds.

Because of the complex acids involved and their unwieldy names, the chelates are referred to by initials. The major ones used, their abbreviations and names are:

EDTA: Ethylenediamine tetracetate (dihydrate)

DTPA: Diethylenetriamine Pentaacetate

EDHPA: Ethylenediamine bis-(orthohydroxy-pentacetate acid)

EDDHA: Ethylenediamine di-(orthohydroxyphenylacetate)

These abbreviations will be used throughout the thesis.

The use of synthetic chelating agents to keep Fe soluble and available for plant growth has caused inquiries concerning the absorption of the chelating agents into the plants (14). As discussed by Chabarek and Martell (18), the introduction of the chelating agent into a plant may have serious and far-reaching implications with respect to the balance of essential trace metals maintained in the

growing plant system. If the deficient metal is carried into the system by the chelating agent and metabolized, the chelating agent may be liberated, and it may bind other trace elememts that are present. There is a possibility of not only creating secondary deficiencies, but also fundamentally altering the plant metabolism. The chelating agent itself may be metabolized.

It has been reported (101) that the chelating agent remained in the nutrient solution and that only the metal was absorbed. Earlier experiments with the Fe-EDTA, were interpreted as showing that the whole iron chelate molecule was absorbed by the roots (43, 114). More recently, however, it has been shown that plants are capable of selectively absorbing the iron from the very stable Fe-EDHPA, leaving the chelating agent in the culture solution (101).

Less definite conclusions were drawn by Hill and Jones (43), they reported that ion deficient plants absorbed iron rapidly and preferentially, absorption of the chelate itself being slower but continuous. Normal plants absorbed iron and chelate in equimolar amounts. Bicarbonate ions in the culture solution inhibited the preferential absorption of iron by iron deficient plants, equimolar amounts of iron and chelates being taken up in this case.

The recovery C^{14} from plants treated with C^{14} labelled chelates does not reflect the true extent of the breakdown that has taken place; with both EDTA and EDHPA less than half the C^{14} recovered

was as unchanged chelate, They also reported that the chelating action of the roots can be modified by the iron status of the plants, the roots having the greatest chelating power when the plant is most deficient in iron (43).

The relative availability of chelated ions vs exchangeable ions on the soil exchange complex has also been studied. Matsuda (63) reported that zinc absorbed by soil in chelated forms is more difficultly absorbed by plants than that in the exchangeable form. Amounts absorbed by plants in plots where chelate forms were added were lower than amounts absorbed in plants where both forms were used in spite of almost equal amounts of plant growth. If it is found that the order of absorption strengths of exchangeable and chelated zinc in soils corresponds with the difficulty of uptake of these forms of zinc by plants, the order of absorption strength should prove to be of great significance in the practice of agriculture (62).

Several factors influence the availability of metals supplied by chelates. Weinstein, et al., (118) suggest that in selecting a chelating agent for use in plant nutrition, a number of factors should be taken into consideration. The most important of these are the stability constant of the metal chelate and the pH of the medium in which it is to be used. The higher the stability constant, the less tendency there is for the complex to disassociate and yield metal ions. The stability constant for the Fe^{3+}-EDTA is greater than

that of EDTA chelates of other metal elements known to be essential in the nutrition of higher plants, and this holds true over a fairly wide pH range. Following Fe^{3+} in stability are Cu^{2+}, Zn^{2+}, Fe^{2+} and Mn^{2+}. It has been their experience that soil applications of Mn-EDTA to manganese deficient plants may result in a replacement of manganese in the chelate by iron in the soil.

Addition of chelated metal to soil is no guarantee that the added element will remain available to plants. Lindsay, et.al. (57) also reported that an added metal may be displaced from the chelate by other cations in the soil. This has been suggested as a reason for difference in effectiveness of different chelates on acid and alkaline soils. For example, Fe-EDTA has been reported as an effective iron fertilizer in acid soils, but it has been rather ineffective in alkaline soils. The relative effectiveness also is determined by the residual carryover, which is regulated by these same factors. Similar responses were reported from Fe-EDTA and Fe-DTPA on the first sorghum crop, but only Fe-DTPA had a beneficial residual effect on the second crop. In comparison to these forms, Fe-EDDHA was superior in its effects, both immediate and residual (57).

The relative amounts of chelates and metal ions also influences availability. Growth was reduced sharply in wheat, rye, corn, soybean, red kidney beans and okra, when the molar concentration of DTPA exceeded that of iron. Under such conditions, these plants were

unable to compete with the chelate agent for iron and developed iron chlorosis (12). Manganese concentrations increased in some plant species and then decreased in the more concentrated DTPA treatments. Iron and copper concentration in the plant material consistently decreased with increasing molar quantities of DTPA.

It has also been reported (115), that iron chelates applied to plants often induce manganese deficiencies. Iron chelates actually hinder the absorption of manganese. This can be a practical means overcoming manganese toxicity, as was successfully done in coffee (66).

Another interaction between micronutrient cations was reported by Ambler, et.al. (7). Zinc interferred with translocation of iron from roots to above ground parts of soybeans. Addition of iron as a ferric metal chelate (Fe-EDDHA), to the growth medium overcame the interference of zinc. In the root epidermis, potassium-ferricyanid formed as a precipitate (prussian blue) with Fe^{2+}, derived from the previously supplied Fe-chelate. The reduction of Fe^{3+} was suppressed by Zn^{2+}.

Studies on the relations between pH and chelate reactions were reported by Norvell and Lindsay (71). Chelates were reacted with suspensions of acid, neutral, and calcareous soils. Copper, iron, manganese and zinc were analyzed by atomic absorption spectrophotometry to determine what happened.

Fe-EDTA was stable in soil suspensions of pH 5.7 and 6.1,

moderately stable at pH 6.75, and unstable at pH 7.3 and 7.85. Zn-EDTA and Cu-EDTA were most stable in suspensions near neutrality.

In acid soils copper and zinc were increasingly displaced by calcium as pH increased.

The loss of Mn from Mn-EDTA was very rapid in all soils and was essentially complete in less than one day from suspensions of pH 6.1 to 7.85.

They concluded saying that 1) the availability of iron from Fe-EDTA is markedly reduced above pH 7, because iron is lost quite rapidly from the chelate, 2) in the most acid soil of pH 5.7, the great majority of both zinc and copper was displaced by iron, 3) Mn-EDTA was highly unstable in soils, and this unstability should seriously limit the usefulness of this chelate as a manganese fertilizer.

Chelates are organic compounds. It is not surprising that soil organic matter (O.M.) has large influences on the reactions of metal chelates added to the soil. Actually, many soil O.M. reactions are considered to be chelation reactions. For example, it is suggested that the chelation properties of organic matter are important in influencing the availability of certain ions in the soil. Soluble chelating agents have increased nutrient availability. Insoluble chelates may have the opposite effect. Stability constants might be expected to play an important role in determining the equilibrium

conditions of these nutrients in the soil since the insoluble chelate probably would not be absorbed by the plant (44).

Copper deficiency in plants is often found in organic soils (62), and is attributed to a decrease in the availability of copper caused by its complex formation with organic matter. But copper deficiency does not necessarily occur in every type of organic soil. It was also reported that the amounts of chelated zinc were greater in humic soils than in mineral soils. The absorption strength of zinc in soil humus is higher in chelated forms than in the exchangeable forms, but Tsutsumi, et al., observed that the absorption strength of copper was higher in humic soil than in mineral soil (105).

Himes and Barber (44) studied the O.M. factors which appear to be involved in soil chelating abilities. Removal of organic matter by oxidation with hydrogen peroxide destroyed the ability of the soil to chelate zinc. Humic and fulvic acids reacted with zinc in a matter similar to the untreated soil. Carboxyl groups did not appear to be important. The reaction between a chelating agent and the cation generally involves the anion forms of the chelating agent (64), therefore, the equilibrium of a chelation reaction is influenced by pH (as previously discussed).

Precautions must be taken when applying chelate materials to plant tissues or to the soil. It appears (114) that EDTA is at

least in part directly responsible for plant injury when excess quantities are applied. EDTA can be detected in plants after application to the soil. The content of EDTA within plant tissues confirms previous indirect evidence that EDTA was absorbed with iron by plants. These observations imply that it is quite possible that EDTA can effect translocation of iron in plants because of EDTA being at least partly stable within the plant. When using chelates, recommended rates and procedures should be followed.

Studies of various chelate reactions have led to studies concerning the use of chelates as extracting agents for micronutrient cation analysis of soils. Since most micronutrients will hydrolyze and precipitate at pH 6 if they are not carried as chelate compounds, the metal extracted with chelates could be a good test for their availability in a soil, if the quantity extracted is related to the quantity absorbed by the plant. This was suggested as a possible method in 1962 by Brown and Tiffin (14). This possibility has been investigated since that time by several scientists. A study by Wallace and Mueller (117) yielded some information in this respect. They reported that some plant species have greater ability than do others to absorb various nutrients. Adding DTPA to soils had less effect on yield than did EDTA. It tended to increase both Mn^{54} and total manganese in plants and it decreased the specific activities in corn at least with one soil type. This would indicate

that DTPA was making at least some of the easily reducible manganese of soil available to corn. The specific activity of manganese in the 10^{-3} M DTPA solution was essentially that of the easily reducible manganese, indicating that the technique of DTPA extraction could be used to monitor that portion of the soil manganese. The specific activities of both easily reducible manganese and that extracted by DTPA corresponded with those in bush bean plants.

Lindsay and his associates (27,57,71) have been quite active in this type of research. They found that DTPA could be used to predict availability of iron and zinc, simultaneously by soil test determination. They concluded from some of their earliest work that results indicated possible suitability of the techniques for manganese analysis also. In a later paper (71), it was shown that Mn-EDTA was highly instable in soils, and this instability could seriously limit the usefulness of this chelate as a manganese fertilizer.

In a greenhouse experiment (27), oats and corn were used to test the iron, manganese, and copper supplying power of Colorado soils as evaluated by the DTPA soil test. The results of the soil profile study with respect to available zinc, iron, manganese, and copper as measured by DTPA extraction may be summarized as follows: 1) The principle factors associated with available zinc in soil profiles were positively correlated with percent organic matter and

cation exchange capacity; 2) the principle factor associated with available iron in the soil profile was a negative correlation with soil pH; 3) the principle factors associated with available manganese in the soil profile were; a) positive correlations with percent organic matter, and b) negative correlations with both soil pH and lime content; and 4) the principle factors associated with available copper content were positive correlations with both total copper and clay content.

In general, the distribution patterns of available zinc, iron, manganese and copper indicate a decrease in availability with depth in the soil profile.

The DTPA soil test was sensitive to changes in the micronutrient cation content of soils resulting from application of micronutrient fertilizers.

Brown, et al. (10) recently conducted a study to compare chelate extractions with other methods for soil zinc analysis. They reported all four methods, (namely, DTPA, ammonium acetate-diphenylthiocarbazone (dithizone), 0.1 N HCl, Na_2EDTA) exhibited a high degree of correlation with each other; the highest correlation coefficient was obtained for the comparison of dithizone with DTPA. They also calculated predictive values for the methods which were 83,79,73,and 72%, respectively, for the 92 soils studied. On this basis the DTPA is preferable to the others and the critical level is

approximately 0.5 ppm Zn.

Resins

Adams and Holmes (1) first studied synthetic ion exchange materials in 1935. Since that time, several scientists have studied these materials as means to supply plant nutrients. In most cases, nutrient imbalances occurred and plant growth was very unsatisfactory. More recently, a different approach was used, with good results (87, 88,89). In these studies, the resins were considered as an exchanger phase present for the purpose of controlling the solution phase composition within a range known to be satisfactory for plant growth. Results demonstrated the utility of synthetic ion-exchange resin plant growth media for complete support of plant growth (89), for studies involving micronutrient variables (88), and as a substrate for ion variables added to soils (90).

Resin systems were employed by Japanese scientists to study antagonism between manganese and iron in barley (24). They also studied other micro-nutrient cation interactions. Their results indicated that in barley plants, manganese inhibited the absorption of iron. The higher the concentration of manganese, the less was the absorption of iron by plants. The inhibitory effect of manganese was very sharp at a higher concentration of iron in the medium. At the concentration of 0.08 ppm of iron, the 0.08 ppm of manganese lowered iron uptake to less than half of the control, which con-

tained no manganese in the medium. The effect of manganese on copper absorption was inhibitory in both rice and barley. But no correlation was obtained between the concentration of manganese and the extent of inhibitory effect as that found between manganese and iron absorption in barley plants. Iron showed neither inhibitory nor accelerating effect on copper absorption in the present experiment whereas copper apparently inhibited iron absorption.

Soil Sterilization

An additional factor must be considered as it relates to this study. The soils of major interest were imported from Brazil, necessitating customs clearance, sterilization, etc. In spite of definite instructions that dry heat sterilization be employed, steam sterilization was used. Undoubtedly, this had a definite influence on the micronutrient levels and reactions obtained. Results must be interpreted in consideration of this fact.

Sterilization of a soil has many undefined effects among them the increase in availability of micronutrients. Soil sterilization is known to increase available manganese (28,65,103) and increase Fe^{2+} in soils (49). A large and possibly harmful increase in soluble manganese often follows the heating of acid virgin loams (29). It also has been reported to increase available copper and zinc (18). Possible enzymes liberated during the sterilization process continue to degrade relatively complex organic compounds forming, among other

things, soluble complexing agents. An increase in pH due to steam sterilization has been noted (6).

Heat sterilization affects both organic and inorganic compounds. On the organic side the amount of water soluble matter is increased to an extent depending on the state of the organic matter.

On both the organic and inorganic sides, the effect of heat sterilization is to increase the amounts of soluble phosphate, potassium, manganese, zinc, iron, copper, boron, etc. It affects some of these elements more than others, and correspondingly higher concentrations of these elements are found in plants grown in sterilized soil. A degree of nutrient unbalance commonly results from the heating of soil.

Exactly what happens is far from clear but it seems that some of the products formed are harmful to plants. Microbial decomposition of organic complexing agents serves to stabilize reduced forms of iron and manganese, undoubtedly killing these microbes by sterilization provides an indirect means of promoting oxidation of the elements (46).

MATERIALS AND METHODS

Two soil samples were taken from the "tabulerios" of north-eastern Brazil in the state of Pernambuco. "Tabuleiros" are areas of flat land, with soils developed from sand and clay sediments of the "Serie Barreiras".

One sample was taken from the Engenho Ubu southeast of the city of Iguacu and the other from the Engenho Sao Jose northwest of the city of Recife. These soils are characterized by low pH, from 4.0 to 5.5, extremely leached due to high rain fall, sand texture, high bulk density of (1.5 g/cm^3) and low silt and clay contents.

Both soils were sampled at two depths, 0-20 cm and 20-40 cm. Four drums of the soils weighing around 1,000 kg each were shipped to the United States where they were sterilized according to U.S. customs requirements. A soil collected from the Bitterroot Valley of Montana was included in this study so that a general comparison could be made between the Brazilian soils and a typical Montana soil. The sampling site in Montana was in the N.E. ¼ of the S.W. ¼ of the Sec. 35, R 21 W, T 7N. This soil is classified as Blodgett gravelly course sandy loam. According to the 1939 Yearbook of Agriculture Soil Classification System it belongs to the Chestnut Great Soil Group, and according to the 1970 "Soil Taxonomy" it belongs to the Typic Haploboroll Great Group. A complete description of this soil follows (92):

Blodgett Series

The Blodgett soils are moderately dark colored, medium acid, and gravelly. They occur on the west side of the valley on the higher and older fans and slopes. They have developed from weathered granitic outwash, mostly gravel and cobblestones. The normal annual precipitation ranges from 12 to 15 inches. The vegetation was that of grassy parks or sparsely timbered areas. Slopes range from gentle to steep. Surface drainage is good. Except for local spots that may become seeped from over irrigation, underdrainage is good to excessive. The soils are only moderately productive and tend to be droughty.

The Blodgett soils have moderately thick, moderately dark colored surface soils, moderately thick weakly coherent subsoils, and substrata of loose weathered granitic material. The entire profile is medium to slightly acid.

Blodgett soils are permeable to moisture, roots, and air. Their capacity to hold moisture for plants is low. The erosion hazard is serious only on the steeper slopes. The soil is moderately high to low in fertility, but it will respond to liberal applications of barnyard manure, green manure, and commercial fertilizers.

Profile of Blodgett coarse sandy loam:

A_1-0 to 8 inches, grayish-brown (dry) to very dark gray (moist) friable coarse sandy loam; moderate fine crumb structure;

moderate organic matter content; medium acid.

B-8 to 15 inches, pale-brown (dry) to brown (moist), very friable coarse sandy loam.

C_1-15 to 28 inches, pale-brown (dry) to yellowish-brown (moist) loose gravelly coarse loamy sand; contains scattered weathered cobblestones.

C_2-28 to 42 inches, weathered loose loamy gravel and cobblestones derived from granite.

On smooth fans south of Bass Creek the parent material is underlain abruptly at depths of 3 to 4 feet by finer textured, less permeable material. In other areas the profile may be shallower and the substratum may be full of cobblestones. In some places cobblestones are scattered liberally on the surface.

BLODGETT GRAVELLY COARSE SANDY LOAM, GENTLY SLOPING

This soil occurs mostly on remnants of the original fan surfaces. Some areas are on narrow ridges but most are parts of broad, slightly convex slopes that dip toward the central valley. Slopes are generally between 2 to 5 percent, but a few small areas on slopes of less than 2 percent have been included. Most areas receive irrigation water from the side creeks. Only those farmers who have very early water rights get enough water for the full season. Those who hold later rights are likely to be short of late-season water in many years.

Under irrigation, this soil is used for both mixed hay and cultivated crops. Alfalfa is rarely grown because of the difficulty of maintaining stands. Truck crops and small fruits are grown to some extent, and a few apple orchards remain. Mixed hay is the main crop. Newly seeded meadows are mixtures of such plants as red clover, alsike clover, timothy, and orchard-grass. In older meadows, quackgrass, bluegrass, white-clover, and black medic may have invaded the hay stand. Usually the hay is cut once a year and the meadows are grazed in the fall. Small grain may be grown, either in planned rotations or at irregular intervals. Farmers whose water supply is short are likely to cultivate more often than those who can get ample water. Dryland areas are used only for pasture.

The Ubu soil was sampled in Goiana County, Pernambuco, Brazil. This county is located in the physiographic zone "Litoral-Mata" (rainy, wooded). The climate is hot and wet. It is located by the following coordinates: Latitude South 7° 33' 40' 'and Longitude west Gr 35° 00' 10''.

The soils are acid, the pH varies in the field from 5.0 to 5.3, and have low carbon and nitrogen contents. In general, they have sandy texture throughout the profile; the presence of A_2 horizon is clear, however, the B-horizon is broken into B_1, B_2 and B_3. Coarse sand predominates over fine sand throughout the profile.

Soil description:

The profile was opened in the Estacao Experimental de Italpirema, in Goiana county. It is located at sixty five meters of altitude and with a slight slope of 0.5 to 1%. Parent material is sandy clay sediments of Barreiras Series. The drainage is moderate to well drained. Sheet erosion is slight. The land is used mainly for fruit trees. Following are the general profile characteristics of a typical "Tabuleiro" Soil of this region:

Ap; 0-13 cm; dark gray brown (10 YR 4/2, wet); sandy loam; weak granular and sand single grains; abundant and medium pores; very friable; non plastic non sticky; plain and clear transition; pH 5.2

A_2; 13-34 cm; yellowish brown (10 YR 5/6, wet), loamy sand weak granular and sand single grains; abundant and medium pores; very friable;
non plastic non sticky; plain and gradual transition;
pH 5.1.

B_1; 34-56 cm; yellowish brown (10 YR 5/6, wet) sandy loam; weak granular; abundant medium and small pores; very friable; non plastic and slightly sticky; plain and diffuse transition; pH 5.0.

56-115 cm; brownish yellow (10 YR 6/6, wet); sandy clay loam; weak granular medium and coarse pores; friable;

plastic and sticky; irregular abrupt transition; pH 5.0

B_2 (ir); 93-95 cm; discontinuous irregular iron concretions, abrupt limits, dark brown (10 YR 3/3).

B_3; 95-140 cm; brownish yellow (10 YR 6/6, wet); mottled; 50 percent yellow (10 YR 7/8, wet); weak sandy clay; hard pan; common and medium pores; friable and firm; plastic and slightly sticky.

Observations: Abundant roots until the B_1, plentiful in the B_2 and few after the concretion zone.

The second soil sample was collected from similar material, about 30 km from the first from Engenho Sao Jose. Its general profile characteristics, landscape, and use are similar to that of the Ubu soil.

The manganese deficiency found in Zona da Mata, is due to the wet, hot climate. High rainfall and relatively acid pH of the soil are factors that favor its leaching as well as the leaching of other elements (48). Deficiencies of manganese and zinc have been demonstrated in these soils.[1/]

In the new Soil Taxonomy system the "tabuleiros" soils are included in the sub-border Acrustox.

Soil Characterization:

All four Brazilian soil samples were sand textured; and mech-

1/ Fernandes, C. S. and M. Grispon. 1968. Personal communication.

anical analysis was done only for the 0-20 cm layer of Sao Jose soil to obtain an idea of the specific quantities of sand, silt and clay present. The sample was sieved to 2.0 mm opening, and dialysed with Na_2CO_3, pH 9.5 and dispersed with ultrasonic vibrations. Jackson's (51) procedure was employed to separate the fractions. The soil texture was "sand", having 96.2% sand, 2.6% silt and 1.2% clay.

A standard soil test analysis was conducted according to procedures of the Montana State University Soil Testing Laboratory. The following results were obtained:

Table 1. Soil test results of five soils employed in studies.

Soil	pH	O.M. %	P. ppm	K ppm	Ca	Mg	Na	E.C.
					me./100g			mmhos/cm
Ubu; 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
Sao Jose; 0-20 cm	6.1	2.05	12.5	40.0	1.10	0.24	0.40	0.8
24-40 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

A mineralogical analysis of the Brazilian soils was done 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 an amorphous type, probably Allophane.

The micronutrients, copper, iron, manganese and zinc were

determined by the DTPA-TEA procedure of Lindsay, et al.[2/] All four micronutrients in soil were determined by this procedure in all experiments reported here. The analyses were made by Atomic Absorption Spectrophotometry. Ammonium acetate extractant also was used as a comparison with the soils. The procedure was the same as that used for DTPA-TEA extraction. Results are shown in Table 2.

Table 2. Analysis of soils. Means of ppm of Cu, Fe, Mn and Zn in soils as determined by DTPA-TEA or NH_4Ac methods

Soils	DTPA extractant Means, ppm of				NH_4Ac extractant			
	Cu	Fe	Mn	Zn	Cu	Fe	Mn	Zn
Ubu, 0-20 cm	ND	11.70bc	2.90b	3.76bc	ND	ND	4	0.8
Ubu, 20-40 cm	ND	3.50	.10	5.00a	ND	ND	ND	6.0
Sao Jose, 0-20 cm	ND	13.53b	2.50bc	3.67bc	ND	ND	4	3.2
Sao Jose, 20-40 cm	ND	10.00c	2.33bc	3.77b	ND	ND	2	1.2
Blodgett	.68	69.33a	21.33a	1.67				

Separation of Mineral and Organic Fractions:

For several studies it was desired to determine the influence of soil O.M. on specific micronutrient relations. Most of the O.M. of the two tabuleiro soils was not "humified". It appeared much like charcoal, but was primarily partially decomposed sugar cane residues. Upon addition of excess water to the soils, this organic debris would

2/ Lindsay, W. L. and A. Norvell. 1969. A micronturient soil test for Zn, Fe, Mn, and Cu. Agronomy abstracts pg 84.

float. This technique was used to separate the mineral and organic fractions of the four soil samples from Brazil. Specifically, the organic matter was separated from two kilogram 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 three times. As the separation was not complete, it was finished manually by several more extractions. Both organic matter and soil were air dried. Organic matter analysis of the soil following this separation showed that essentially all O.M. had been removed. A portion of the clay fraction likely was included in the organic fraction.

Copper Retention Studies:

Thirty gram portions of each soil were placed in 100 ml beakers. Seven ml of water or $CuSO_4$ solution with 5, 10, 50 or 100 ppm copper was added to each beaker. After four hours with intermittent shaking, the solutions were separated from soil by vacuum filtration. Each solution was analyzed for copper by atomic absorption anaylsis. After filtration, the soil was separated into mineral and organic fractions according to the previously described method. Each fraction was leached with 50 ml of 0.2% $SrCl_2$. The leachates were evaporated and the residues were dissolved in 10 ml of 2% HCl and analyzed for copper.

A second series of retention studies was run using more concentrated copper solutions. In this series, 10 ml of $CuSO_4$ solution was

used for each 30 g sample of soil, and the solutions contained 100, 250, 500 or 1000 ppm copper. The mineral and organic portions of the soil were not separated in this series. Instead, previously separated fractions (mineral or organic) were carried through the same procedure. Only one gram 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.

Zinc Retention Studies:

Zinc solutions were prepared from $ZnSO_4 \cdot 7H_2O$ at the following concentrations: 100, 200, 250, 500 and 1,000 ppm. Ten ml of these solutions were added to each beaker with 30 g of soil for four hours. Solutions were extracted from each soil using a Buchner funnel, and a test tube inside a suction flask. The same procedure was followed using the soil organic fraction or mineral fraction. Analyses of each solution for zinc was accomplished by atomic absorption analysis.

Soil Leaching Studies:

Portions of soil, each weighing 200 g, were mixed with $CuSO_4$, Cu-saturated exchange resin, Cu-chelate or peat. Treatments employed were the following, each designed to add equal amounts of copper, except 1:

1. Soil + 20 ppm of Cu-resin
2. Soil mineral fraction (O.M. removed) + 10 ppm of Cu-resin

3. Soil + 10 ppm of Cu-resin + 5% peat moss

4. Soil + 10 ppm of $CuSO_4$

5. Soil mineral fraction (O.M. removed) + 10 ppm of $CuSO_4$

6. Soil + 10 ppm of $CuSO_4$ + 5% peat moss

7. Soil + 10 ppm of Cu-resin

8. Soil + 10 ppm of Cu-EDTA

After thorough mixing, two 10 g portions were taken for Cu analysis. The remaining 180 g was 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 dionized 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 following:

1. Soil + 10 ppm of Zn-resin

2. Soil + 20 ppm of Zn-resin

3. Soil mineral fraction (O.M. removed) + 10 ppm Zn-resin

4. Soil + 10 ppm of Zn-resin + 5% peat moss

5. Soil + 10 ppm of $ZnSO_4.7H_2O$

6. Soil mineral fraction (O.M. removed) + 10 ppm of $ZnSO_4.7H_2O$

7. Soil + 10 ppm of $ZnSO_4.7H_2O$ + 5% peat moss

8. Soil + 10 ppm of Zn-EDTA

In both of these leaching studies the Blodgett soil was included for comparison. However, the treatments involving the soils mineral fraction only were not included for this soil.

Growth Chamber Experiments

Barley (Hordeum distichon L., variety Hypana) was grown in 500 ml plastic pots, containing 500 g of air dried soil. Ten seeds of barley were placed in a pot and after germination the plants were thinned to 5 when the height was 5 to 7 cm. The experiment was conducted in a growth chamber set for 10 hour dark and 14 hour light periods. The temperature was programmed to increase gradually from a dark period low of 13°C to light period high of 27°C. Water was added daily or as required. The experimental design was a randomized complete block with 10 treatments and four replications. The treatments were as follows:

1. Check

2. NPK

3. NPK + salts of Cu, Fe, Mn and Zn

4. NPK + resins of Cu, Fe, Mn, and Zn

5. NPK + Chelates of Cu, Fe, Mn and Zn

6. NPK + Chelates (- Cu)

7. NPK + Chelates (– Fe)

8. NPK + Chelates (– Mn)

9. NPK + Chelates (– Zn)

10. NPK + salts of Cu, Fe, Mn, and Zn + 5% peat moss

The nutrients were applied at the following manner:

KH_2PO_4 - 7.187 g/liter
NH_4NO_3 - 7.187 g/liter
} 20 ml/pot Equivalent to:

131 lb of P per 2 x 10^6 lb of soil

200 lb of N per 2 x 10^6 lb of soil

165 lb of K per 2 x 10^6 lb of soil

$MgSO_4$ (anhydrous) 0.227 g/pot

$CaSO_4.12H_2O$ 0.785 g/pot

Micronutrient materials and rates were as follows:

Element	Chelates		Resins	Salts*
	Kg/Ha	mg/pot	mg/pot	mg/pot
Copper	15	3.75	1.960	1.950
Iron	15	3.75	1.025	0.900
Manganese	12	3.00	1.678	1.440
Zinc	15	3.75	2.000	2.130

* Elemental basis.

After 59 days, the plants were harvested and placed in a drying oven at 65-70°C for four days. Dry weights were determined.

The five plants harvested were ground in a stainless steel Wiley mill and analyzed by the "wet ashing" procedure for copper, iron,

manganese, zinc and phosphorous. The micronturient analysis was done by the atomic absorption spectrophotometer and phosphorous by colorimetric vanadomolybdic method.

After completion of the experiment, soil samples were taken from each treatment for micronutrient determination by the DTPA-TEA extraction method.

RESULTS AND DISCUSSIONS

The results on Table 2 (page 48) demonstrate the effectiveness of DTPA-TEA, for extraction of micronutrients cations from soils, as compared with the amounts extracted by neutral normal ammonium acetate. Several workers have already testified to the efficiency of chelates as extractors of micronutrient cations from soils (14,71, 111,117). The failure of neutral normal ammonium acetate in extracting micronutrients has also been reported by several researchers (26,48,111). The results of Table 2, also support other results that the available forms of micronutrients generally occur in the top horizon(26,27,46). The large amounts of iron and manganese probably are due to the fact that they also are generally very abundant in total content in soil materials (23,48). In spite of the accuracy of the atomic absorption determinations of both copper (3) and zinc (2), the zinc sensitivity is much higher. The lower copper sensitivity appears to be the reason why copper was not detected.

The two Brazilian sandy soils had less of the four micronutrients determined, when compared with the Montana soil. Perhaps this is due to the influence of different soil forming factors at work in those two areas. It is known that sandy soil,subjected to high rainfall, even in temperate regions (36,113) is poor in micronutrients due to the leaching of mobile forms into deeper layers and certain amounts being fixed by iron and aluminum sesquioxides. The

influence of temperature hastening the development of the two Brazilian soils may account for some of the differences shown.

The data on copper retention shown in Table 3 indicate that surface soils have a tendency to retain more copper than the 20-40 cm depth layers. Ubu soil retained less copper than Sao Jose soil, considering the same depth and the Blodgett soil has a higher copper retention capacity than the two Brazilian soils. The copper retention capacity of each of these soil samples is directly related to the O.M. content (see table 1, page 47). This is expected since it has been definitely shown that copper is easily complexed with organic matter (21,34,45,46,69,98). The clay type in the Brazilian soil is probably allophane. The total clay content is very low and allophane probably has a fairly high exchange capacity; however, probably little copper "fixation" can be attributed to the clay fraction of these soils. Sesquioxides of iron and aluminum, which are known to fix micronutrients (113) may have contributed some to this reaction. The higher retention of copper in Blodgett soil probably is due to the higher contents of organic matter and clay.

Table 4 shows results of copper retention by the organic fraction separated from the Brazilian soils and by the mineral fraction of these soils. It seems clear that organic matter is highly responsible for the copper retention on those soils. Figures 3 to 5 show graphically the copper retention, by the soils and their fractions.

Table 3. Copper retention capacity of soils as measured by Cu remaining in solution after four hours of contact between soil and Cu solutions.

Cu Conc of solution used	Cu concentration (ppm) of solution after contact with soil				
	Ubu soil		Sao Jose soil		Blodgett soil
ppm	0-20cm	20-40cm	0-20cm	20-40cm	0-20cm
0	0.74	0.38	0.56	0.35	0.20
100	1.50	3.60	1.20	1.80	0.30
250	2.10	5.80	1.95	2.90	0.35
500	2.80	20.00	3.25	5.30	0.40
1000	9.50	20.00	11.20	20.00	2.50

Table 4. Copper retention capacities of organic and mineral fractions of soils as measured by Cu remaining in solution after four hours of contact between soil and Cu solutions

Cu conc of solution used ppm	Copper concentration (ppm) of solution after contact with soil							
	Ubu soil				Sao Jose soil			
	0-20cm		20-40cm		0-20cm		20-40cm	
	Organic fraction	Mineral fraction	Organic fraction	Mineral fraction	Organic fraction	Mineral fraction	Organic fraction	Mineral fraction
0	0	0.90	0.20	0	0.40	0.50	0.10	0.65
100	0	2.20	2.20	1.10	0.50	0.95	0.10	1.15
250	0.56	4.10	4.90	20.00	0.56	13.50	0.20	6.30
500	1.33	20.00	20.00	20.00	1.90	20.00	0.20	20.00
1000	3.00	20.00	20.00	20.00	7.20	20.00	2.80	20.00

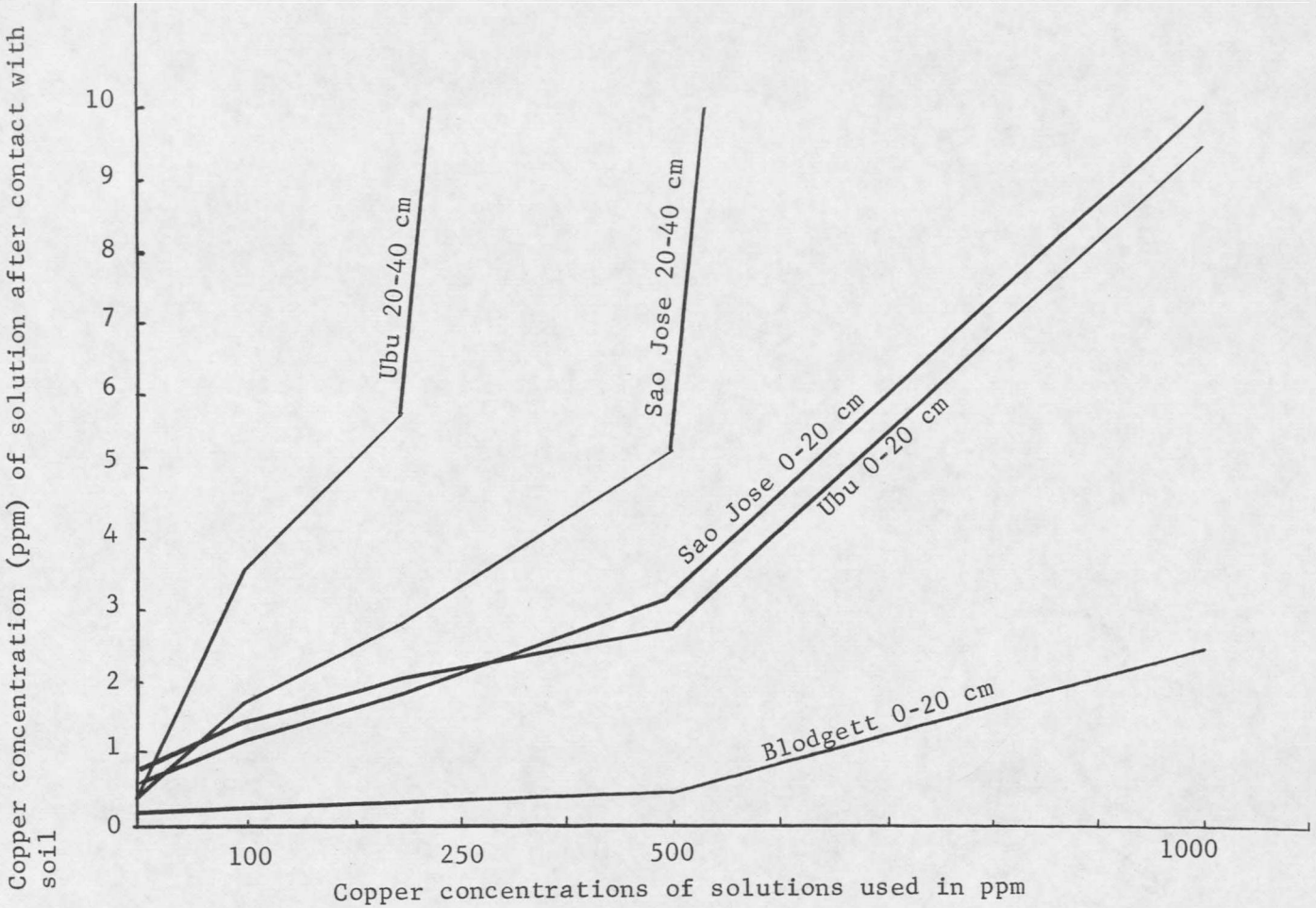


Figure 3. Copper retention capacity of whole soils as measured by Cu remaining in solution fater 4 hours of contact between soil and Cu solutions.

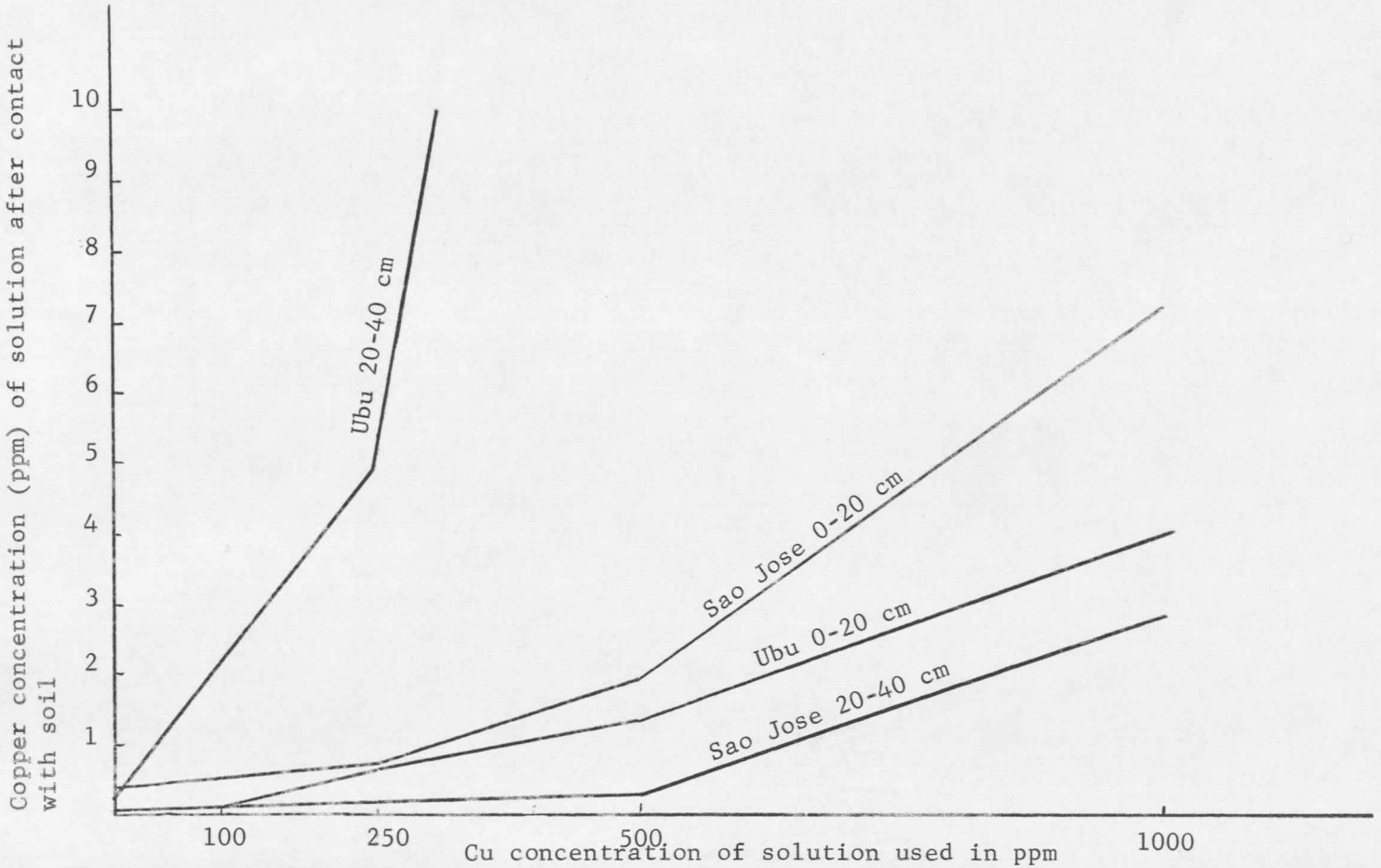


Figure 4. Copper retention capacity of soil, as measured by copper remaining in solution after 4 hours of contact between organic fractions and copper solutions.

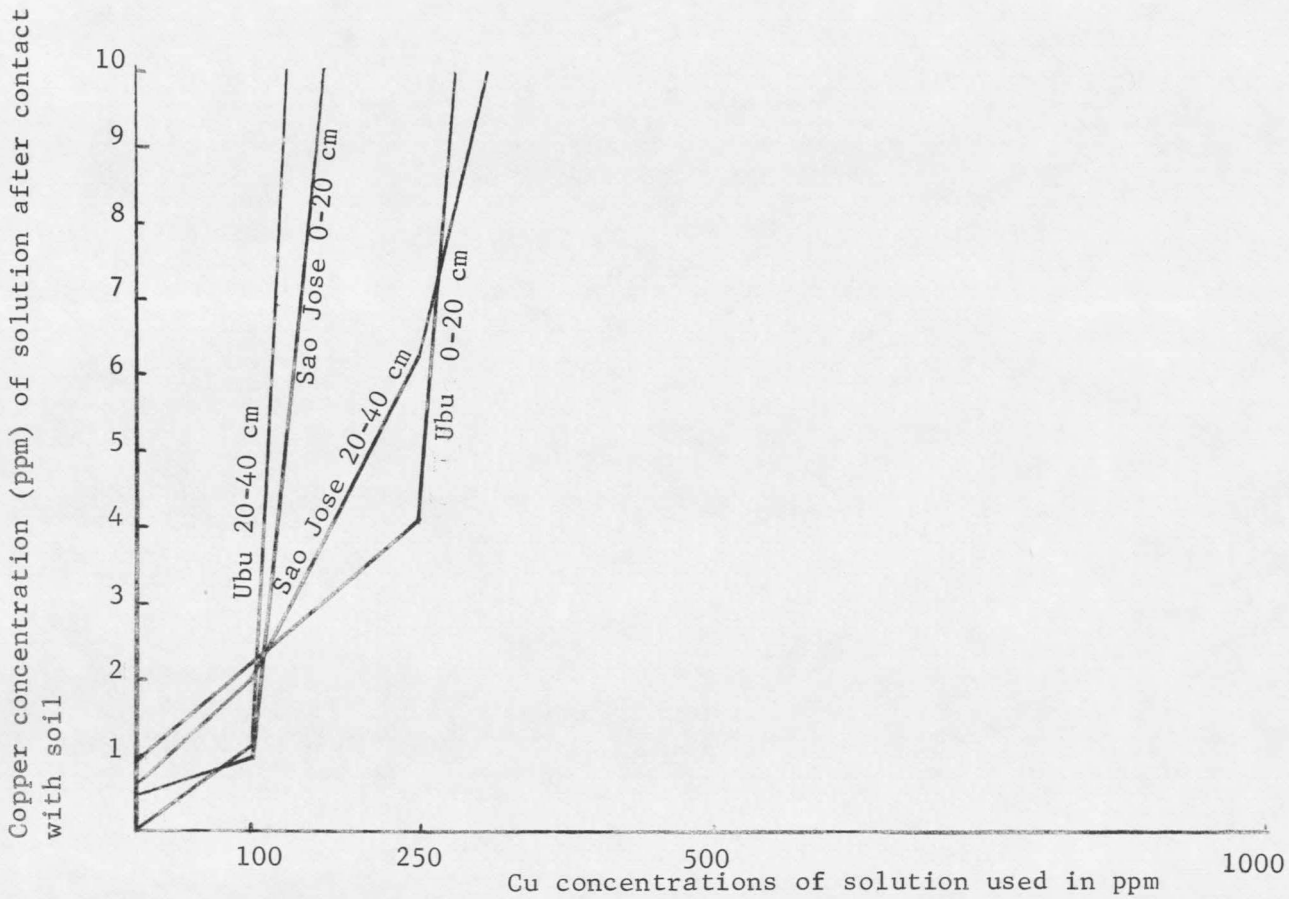


Figure 5. Copper retention capacity of soils as measured by copper remaining in solution after 4 hours of contact between the mineral fractions and copper solutions.

The results presented in Table 5 suggests the same trend for zinc retention as that found for oopper. Less zinc remained in solution from the first 20 cm depth in the two Brazilian soils than from the 20-40 cm depth. Again, the Blodgett soil retained more zinc than the two Brazilian soils. Retention of zinc by the five soils also appears to be associated with the organic matter present.

The data of Table 6 substantiate the influence of O.M. because without it retention of zinc was drastically decreased. In addition, type of clay, C E C., pH and phosphate anion may be responsible for some of the differences observed (53,86). Figures 6 to 8 show graphically the zinc retention by the soils and their fractions.

Results of the copper leaching study conducted on the two depths of the two Brazilian soils and the surface soil of a Montana soil are presented in Figures 9 through 13. In these studies, comparisons were made between salt, chelate and resin forms of copper added to this soils. In addition, the influence of organic material on copper leaching was studied by removing the organic matter from the soils (with the exception of the Blodgett soil) or adding and mixing peat into the soil. Dionized water was employed as the leaching agent.

Several important results can be observed. It is immediately apparent that both the chelate and resin forms of copper were rapidly leached from the four Brazilian soil samples. Generally, 80 to 90

Table 5. Zinc retention capacity of soils as measured by Zn remaining in solution after four hours of contact between soils and Zn solutions.

Zn Conc of solution used	Cu concentration (ppm) of solution after contact with soil				
	Ubu soil		Sao Jose soil		Blodgett soil
ppm	0-20 cm	20-40 cm	0-20 cm	20-40cm	0-20 cm
0	0.02	0.19	0.18	0.09	1.09
100	0.17	0.61	0.18	0.39	0.30
250	0.67	1.82	1.10	2.40	1.18
500	3.08	5.0	2.78	4.35	3.08
1000	5.0	5.0	5.0	5.0	5.0

Table 6. Zinc retention capacities of organic and mineral fractions of soils as measured by Zn remaining in solution after four hours of contact between soils and Zn solutions.

Zn conc of solution used	Zinc concentration (ppm) of solution after contact with soil							
	Ubu soil				Sao Jose soil			
	0-20 cm		20-40 cm		0-20 cm		20-40 cm	
ppm	Organic fraction	Mineral fraction	Organic fraction	Mineral fraction	Organic fraction	Mineral fraction	Organic fraction	Mineral fraction
0	0.05	0.12	0.18	0.66	0.08	1.32	0.15	0.08
100	.09	1.78	0.19	3.45	0.15	1.88	0.15	1.15
250	.24	4.45	0.48	4.40	0.44	4.80	1.35	4.80
500	1.45	5.0	2.32	5.0	1.90	5.0	1.75	5.0
1000	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0

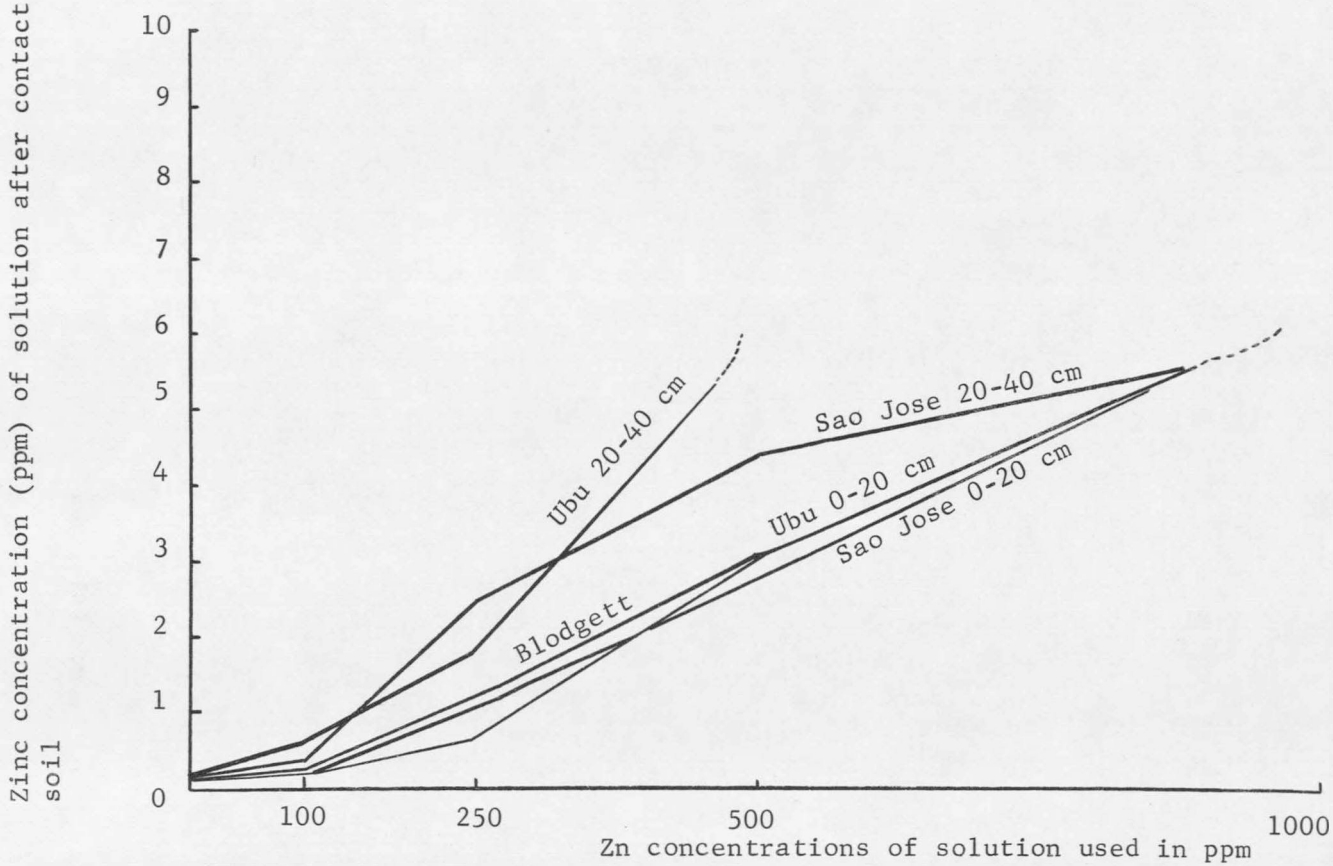


Figure 6. Zinc retention capacity of soils as measured by remaining in solution 4 hour of contact between soils and Zn solutions.

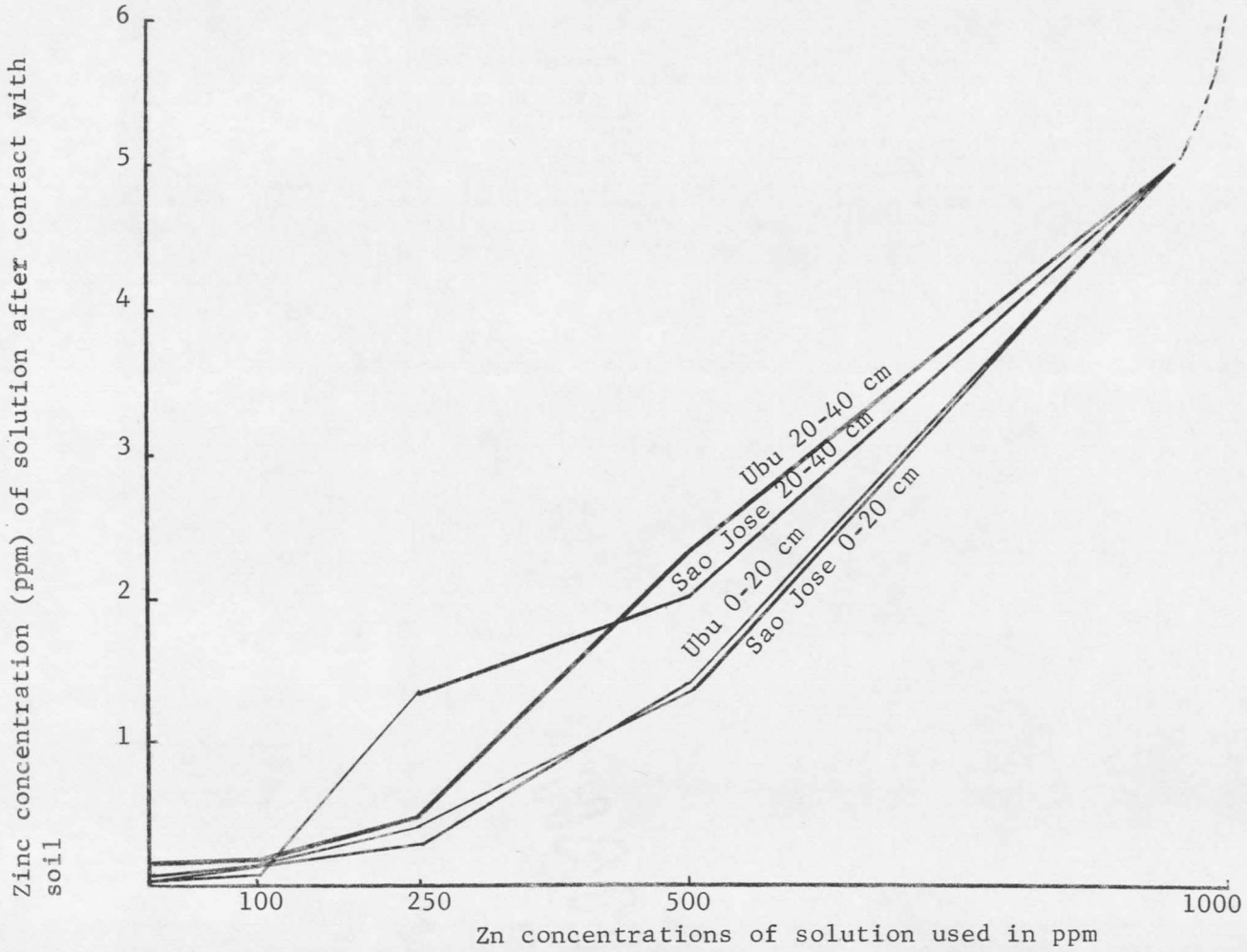


Figure 7. Zinc retention capacity of soils as measured by Zn remaining in solution after 4 hours of contact between soils organic fractions and Zn solutions.

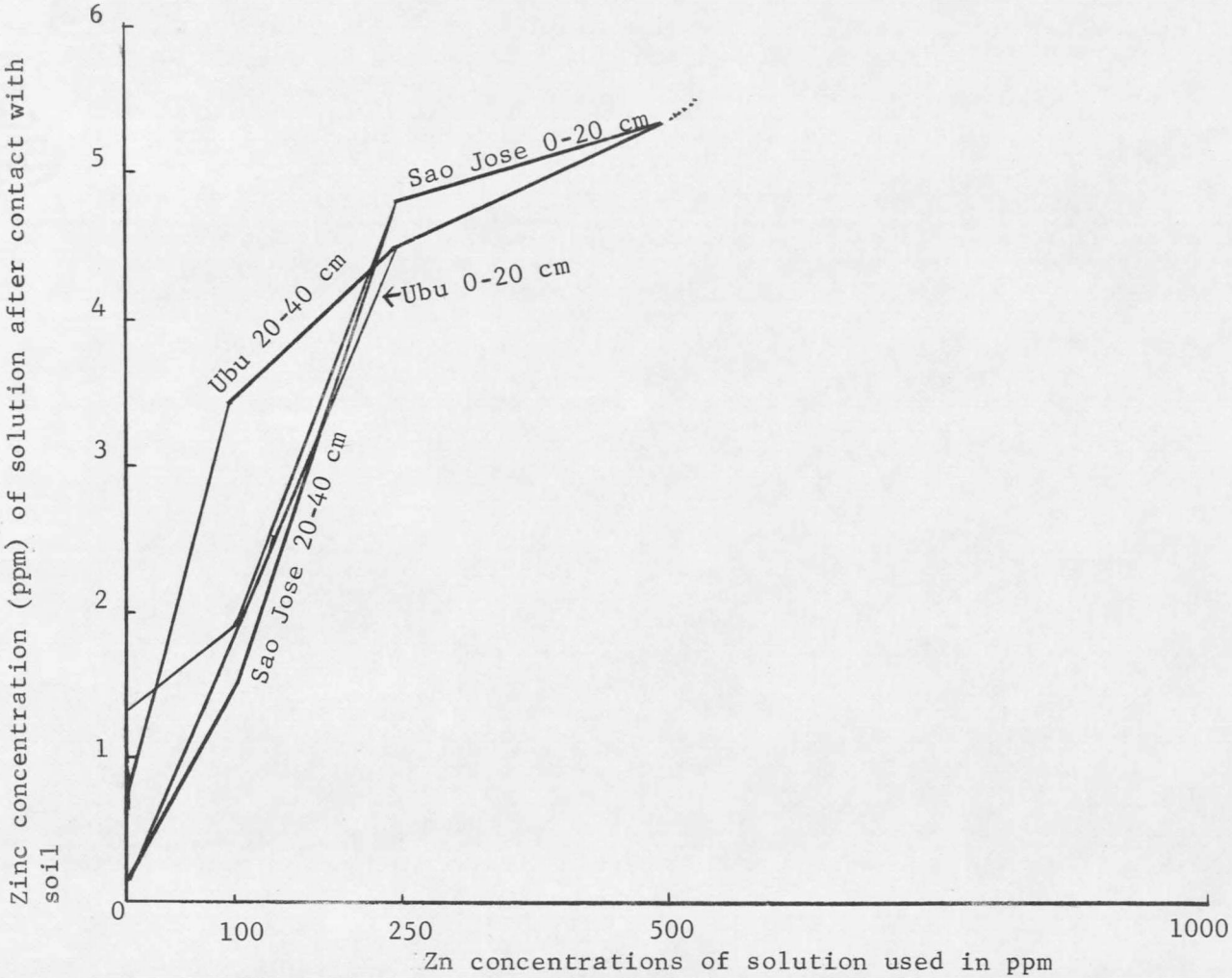


Figure 8. Zinc retention capacity of soils as measured by Zn remaining in solution after 4 hours of contact between soil mineral fractions and Zn solutions.

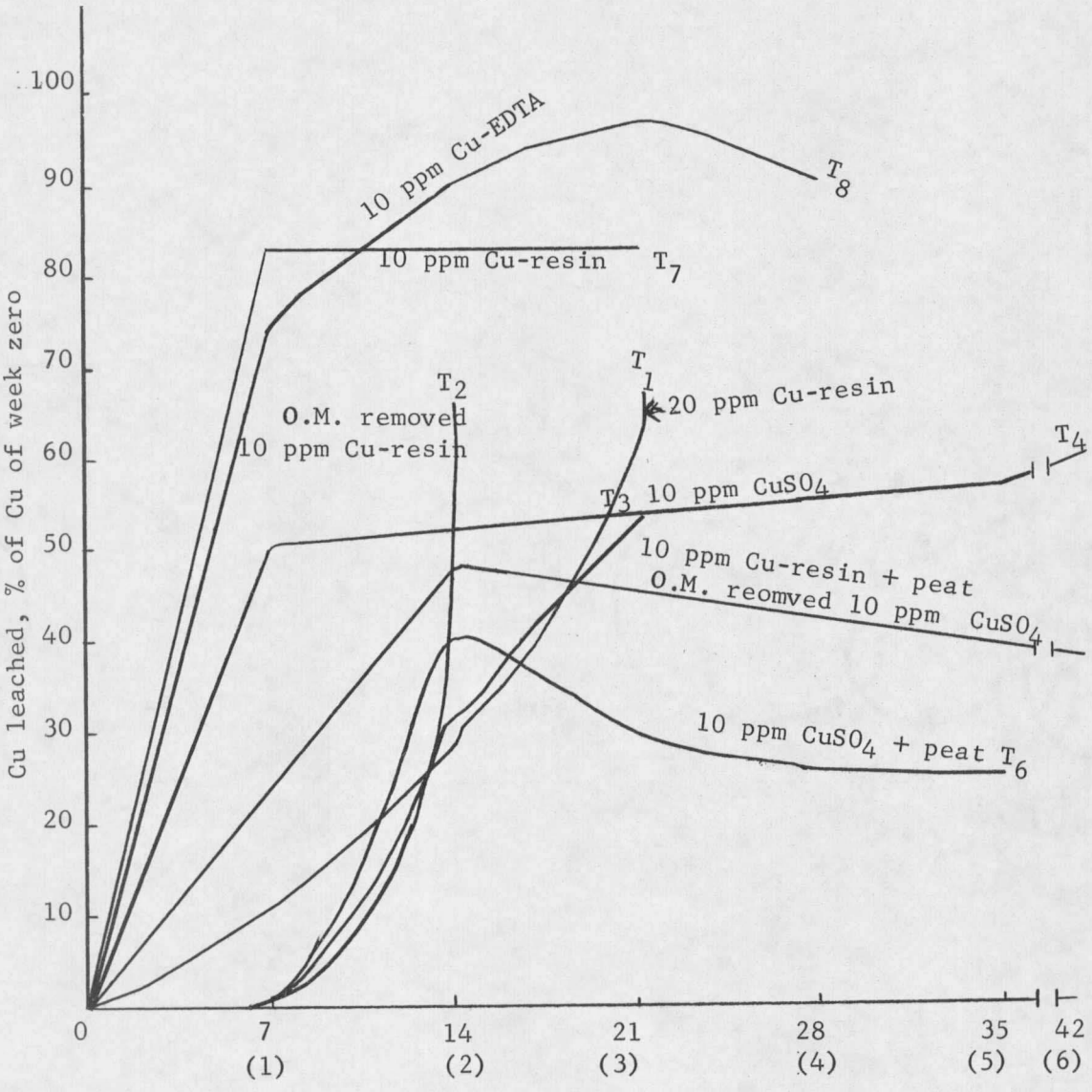


Figure 9. Percent of DTPA extractable copper leached from the soil as influenced by type of material added and amount of water leached over time.

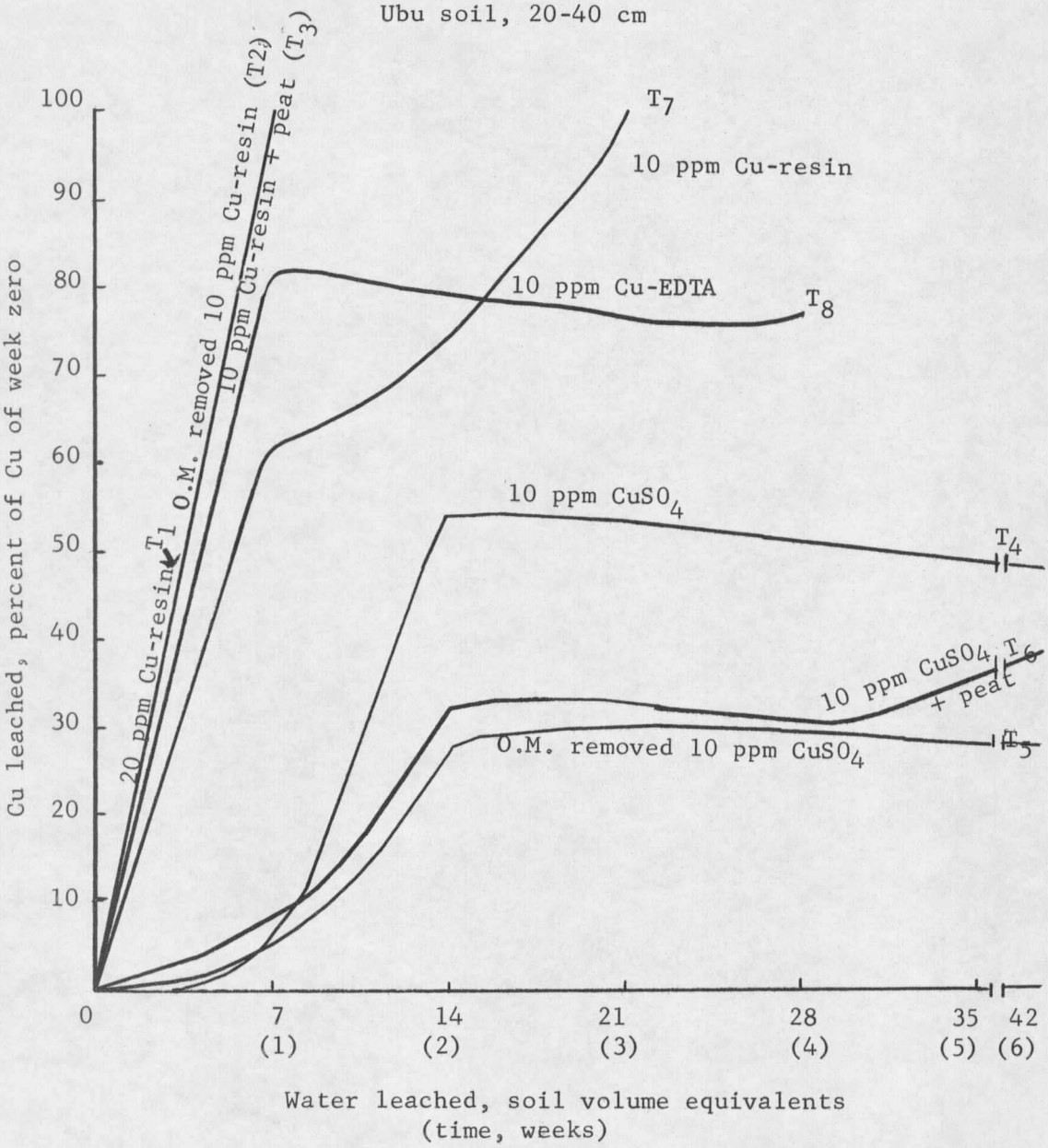


Figure 10. Percent of DTPA extractable Cu leached from the soil as influenced by type of material added and amount of water leached over time.

Sao Jose soil, 0-20 cm

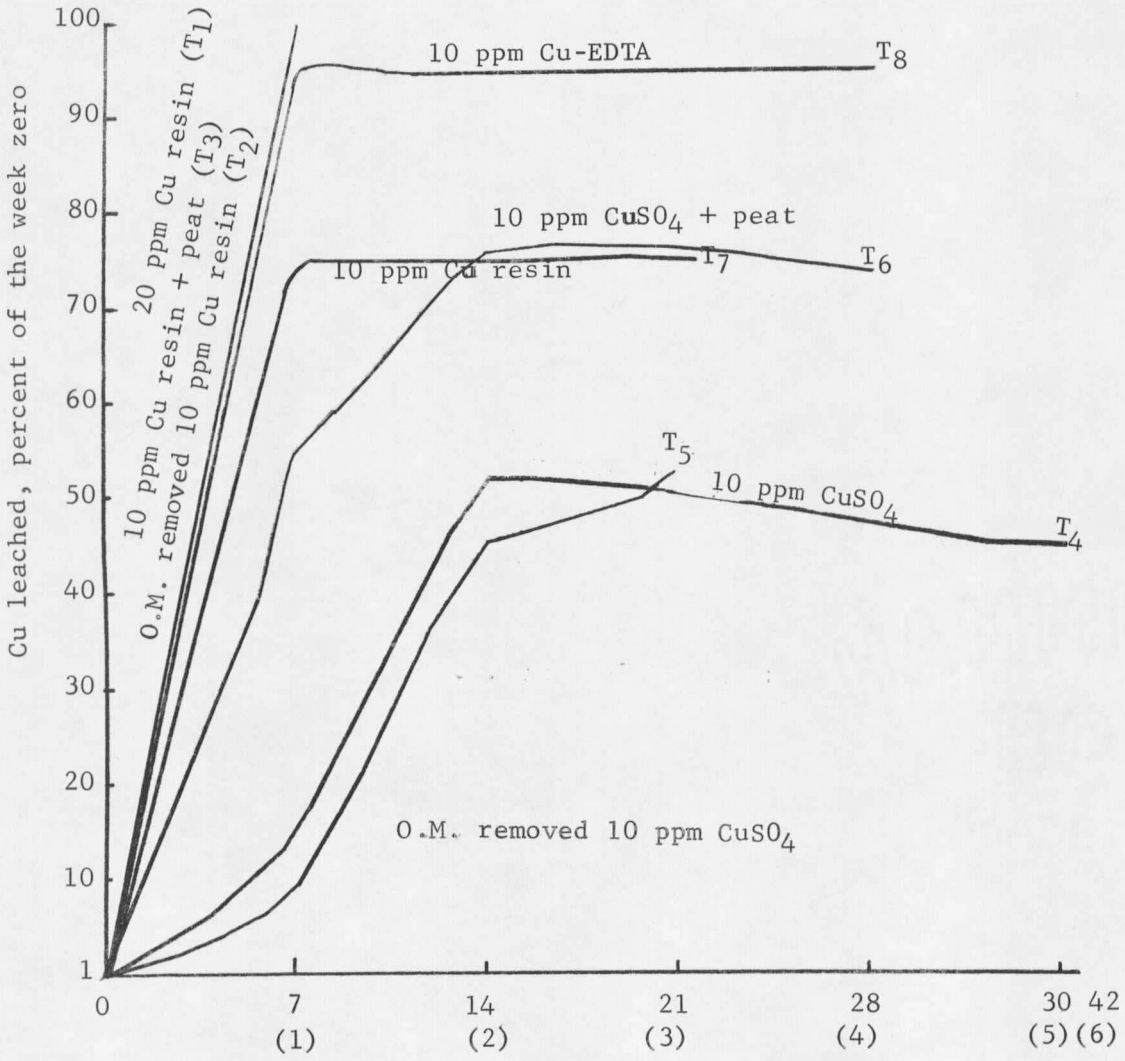


Figure 11. Percent of DTPA extractable Cu leached from the soil as influenced by type of material added and amount of water leached over time.

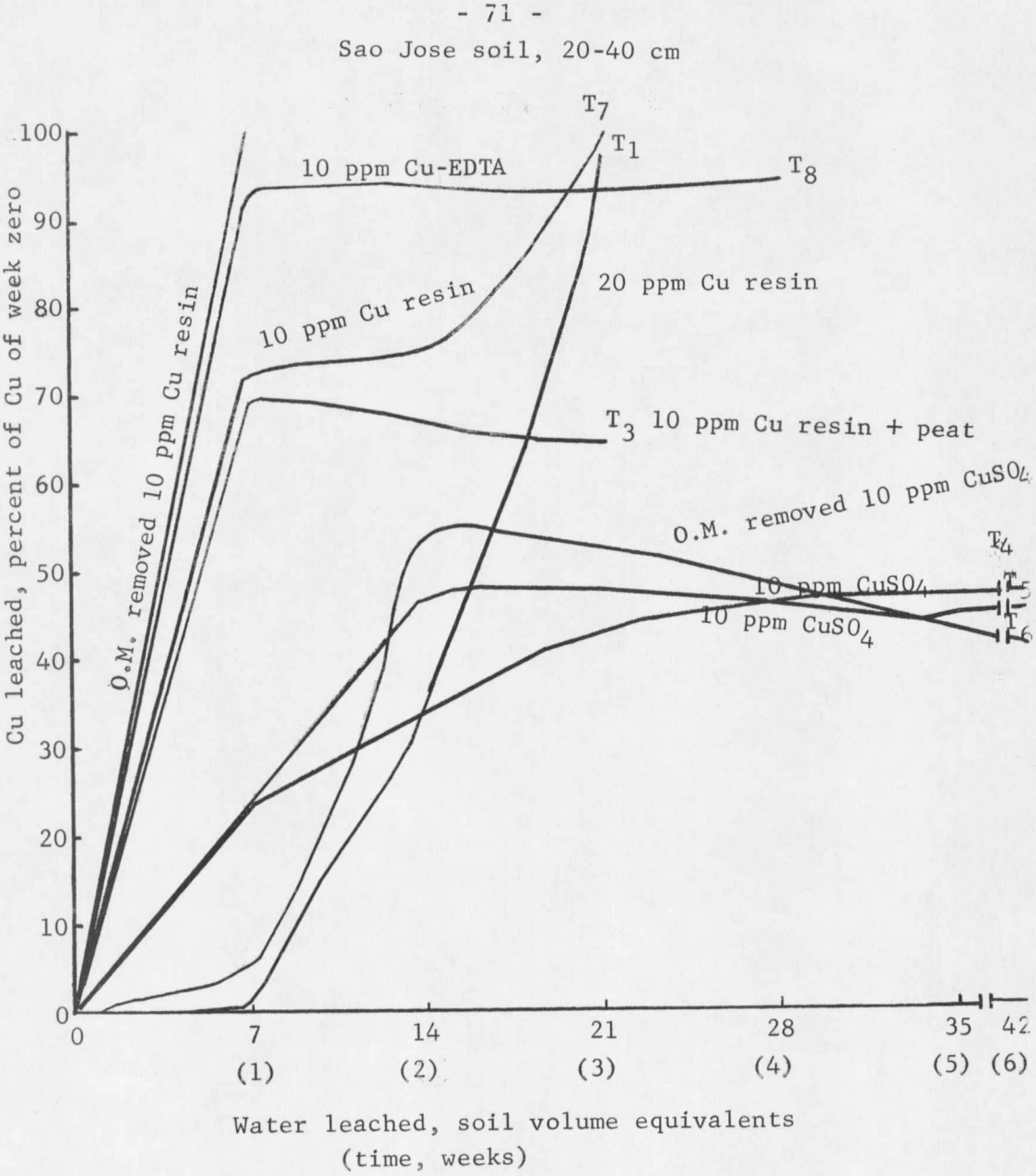


Figure 12. Percent of DTPA extractable Cu leached from the soil as influenced by type of material added and amount of water leached over time.

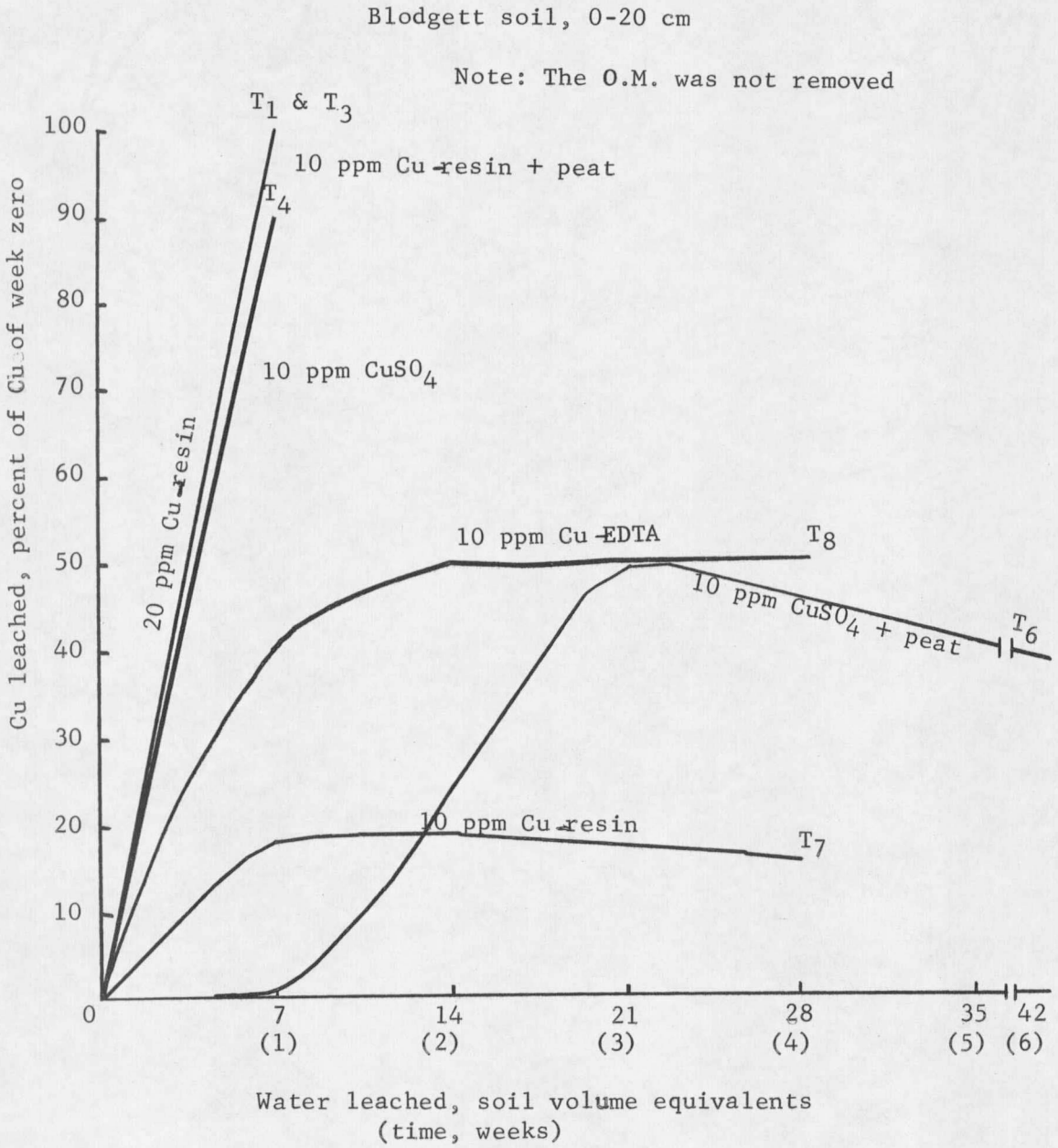


Figure 13. Percent of DTPA extractable Cu leached from the soil as influenced by type of material added and amount of water leached over time.

percent of the copper which was initially present in these soils after it was added as chelate or resin, was leached from the soil within three weeks. The copper sulfate salt form was much more resistant to leaching, with generally 50 percent or more of the original copper content still remaining after six weeks (42 soil volumes of water leachate).

These results were rather surprising. The type of response expected is more nearly represented by the data from the Bldogett soil (Figure 13). Here the chelate and resin forms of copper were equal to or superior to the copper sulfate treatment regarding resistance to leaching. This is what would be expected in most temperate region soils with normal organic matter and clay contents.

The failure of the chelate form of copper to prevent its leaching in the Brazilian soils is probably related to 1) the instability of the copper chelate in these soils and the displacement of copper by a more strongly complexed metal ion; or 2) the actual leaching of the entire 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.

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. In soils with more normal cation exchange capacities, this apparently does not occur as readily, as expressed by results from the Blodgett soil.

The influence of removing the organic matter from the Brazilian soils was not consistent relative to copper leaching. In general, it appears that the organic matter in these soils (much like a charcoal residue of sugar cane stalks) contributes very little to maintaining ions in the soil.

The addition of peat to these soils also had little measureable influence on copper leaching. Again, results varied considerably without apparent cause and effect relationships from soil to soil. The addition of peat to these soils with the desired benefit of decreased leaching would apparently require additional conditions. Perhaps a time interval during which the peat would further decompose and react with the soil would improve its beneficial use.

Figures 14 through 18 present results of a similar study on zinc leaching. The same general type of response was observed with zinc leaching as that discussed for copper. However, a few differences can be observed. Although the salt form of zinc again was generally the best, its distinct advantage was not as great as in the case of copper. The resin adsorbed form of zinc performed

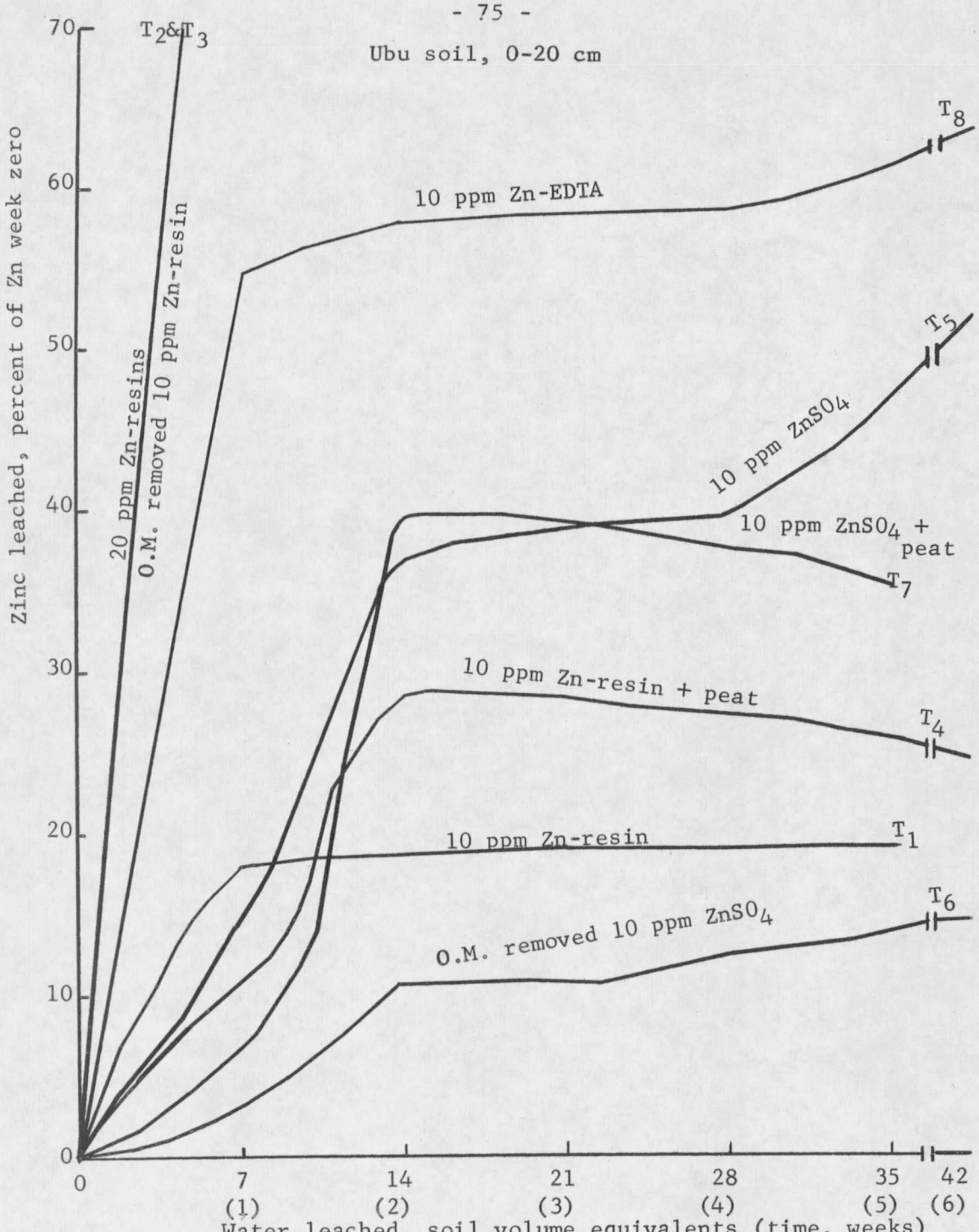


Figure 14. Percent of DTPA extreactable zinc leached from the soil as influenced by type of material added, and amount of water leached over time.

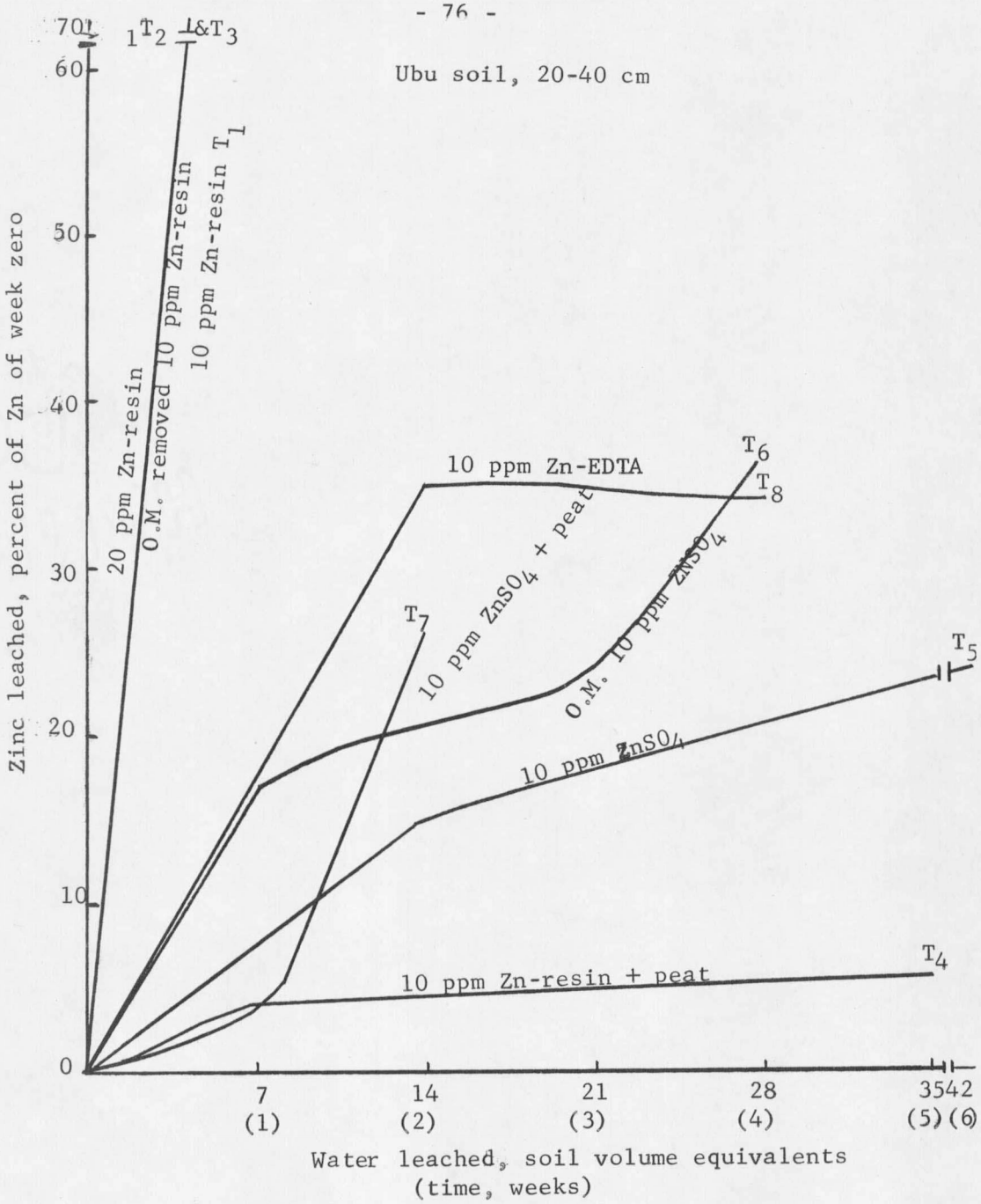


Figure 15. Percent of DTPA extractable zinc leached from the the soil as influenced by type of material added, and amount of water leached over time.

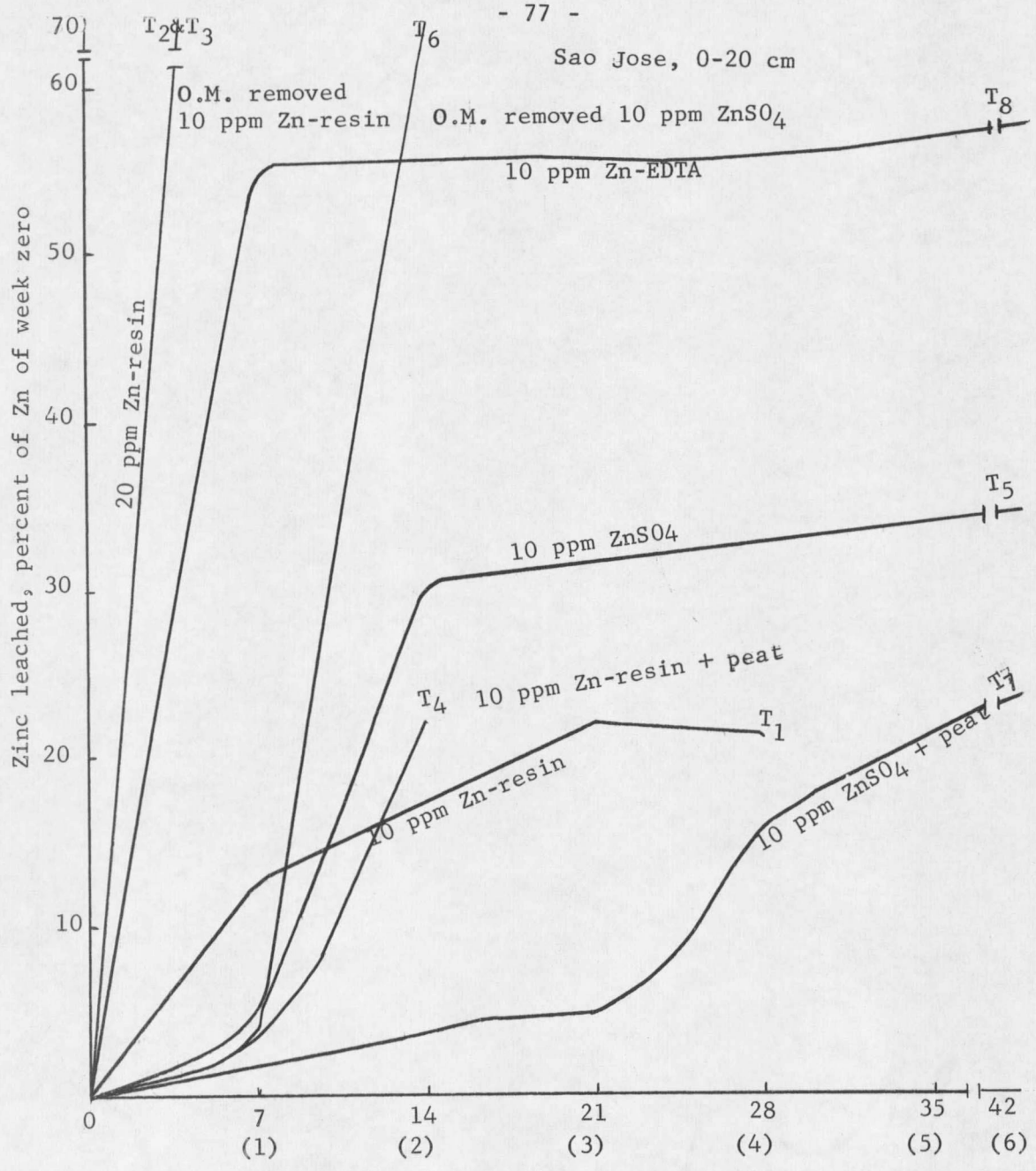


Figure 16. Percent of DTPA extractable zinc leached from the soil as influenced by type of material added and amount of water leached over time.

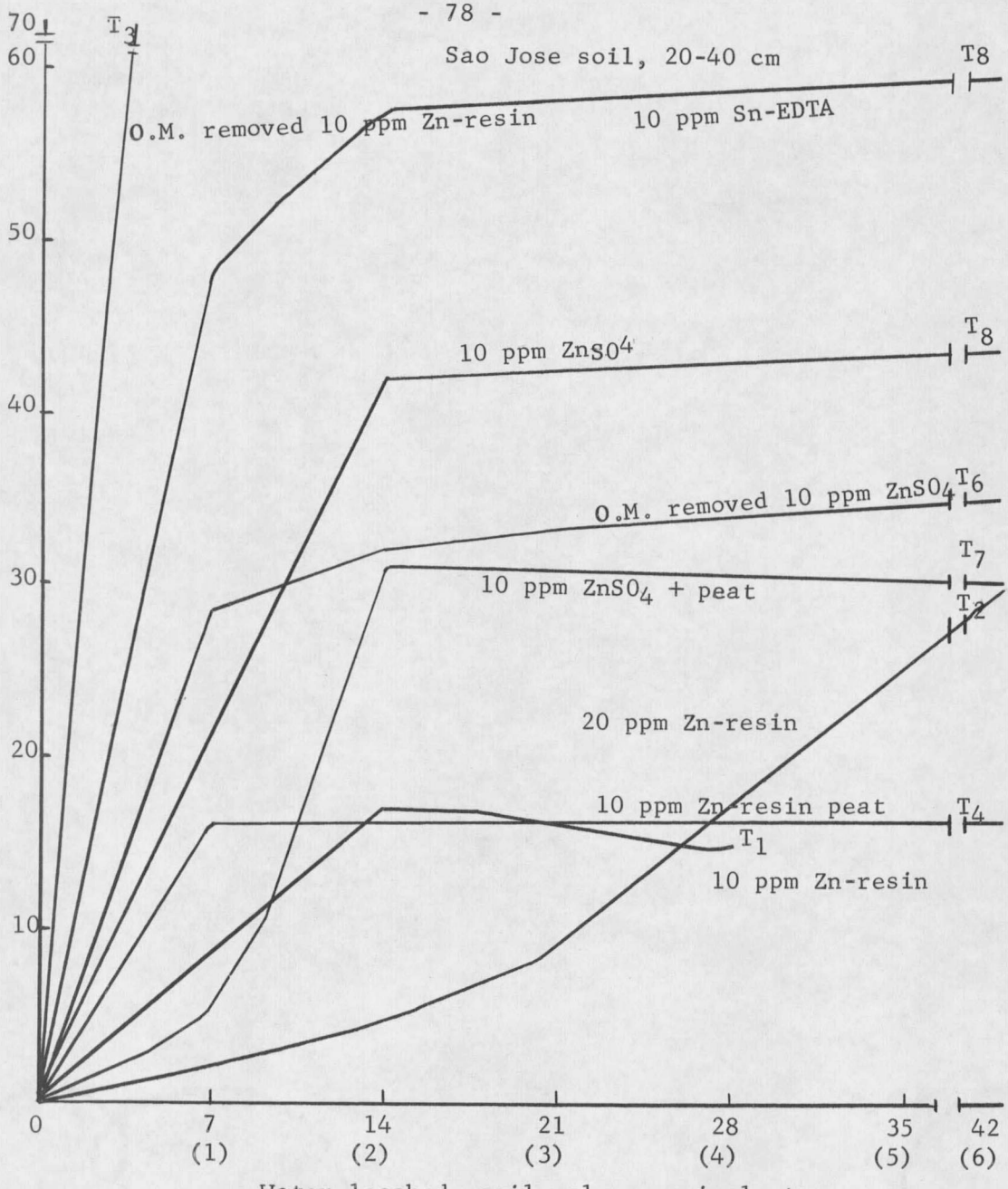


Figure 17. Percent of DTPA extractable zinc leached from the soil as influenced by type of material added and amount of water leached over time.

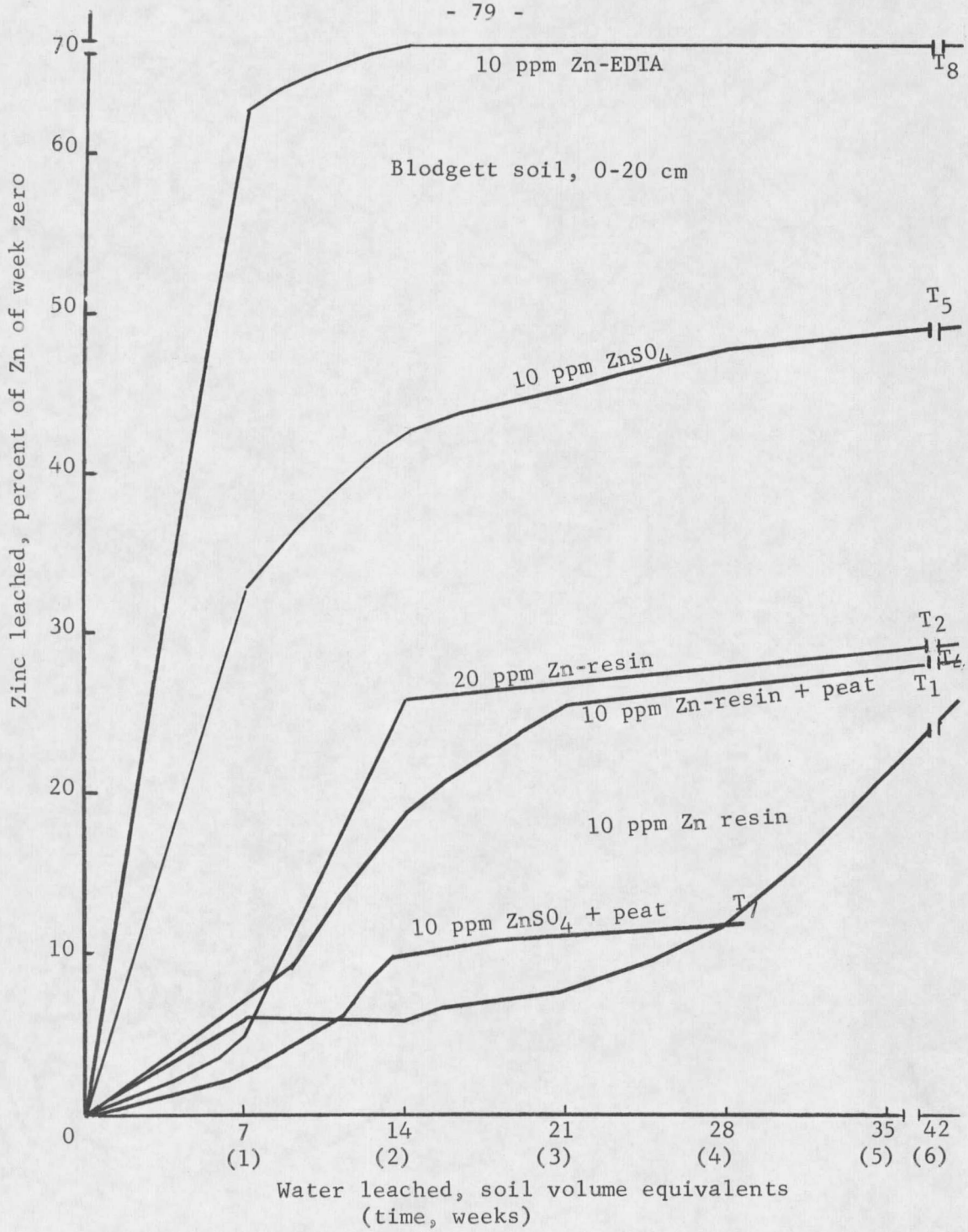


Figure 18. Percent of DTPA extractable zinc leached from the soil as influenced by type of material added and amount of water leached over time.

nearly as well as the zinc sulfate treatment, with a couple notable exceptions. The addition of peat also appeared to improve the retention of resin adsorbed zinc, while it had little or no influence on the other forms of zinc added, or on any of the forms of copper. As was observed for copper, it appears that chelated zinc would be a rather ineffective material with which to combat zinc deficiencies on these soils. Even in the Blodgett soil the chelate form of zinc was leached more readily than the other forms.

The behavior of both copper and zinc in these studies may have great agronomic significance in the area from which the soils were sampled. At this stage, it is very important to conduct further studies under field conditions to ascertain the validity of these laboratory studies. If similar results were obtained, it would mean that the inexpensive, readily available forms of these micronutrients would be the most effective materials with which to combat deficiencies in the field.

Growth Chamber Experiments

The dry weight of barley plants grown in two Brazilian soils, each from two different depths, and one Montana soil as influenced by fertility treatments are given in table 7. The data for the first 20 cm depth of Ubu soil indicate that no statistical differences were found among the means for treatments, 3, 5, 8, 9, and 10. Yield

Table 7. Dry weight yield of five barley plants per pot as influenced by fertility treatment on two soil layers of two Brazilian soils and the surface layer of Blodgett soil.

Treatment	Ubu soil		Sao Jose soil		Blodgett
	0-20cm	20-40cm	0-20cm	20-40cm	0-20cm
	g/pot	g/pot	g/pot	g/pot	g/pot
1. Check	.21 e	.14 d	.22 d	.19 d	1.03 b
2. NPK	.65 cd	.56 c	.53 c	.86 bc	1.83a
3. NPK + salts of Cu,Fe,Mn and Zn	.91ab	.64 c	.83ab	.77 c	2.00a
4. NPK + resins of Cu,Fe,Mn and Zn	.78 bcd	.57 c	.63 bc	.92 bc	1.90a
5. NPK + Chelates of Cu,Fe,Mn and Zn	.88abc	.70 bc	.61 c	.97 bc	1.83a
6. NPK + Chelates (- Cu)	.62 d	.46 c	.67 bc	1.10abc	2.07a
7. NPK + Chelates (- Fe)	.79 bc	.62 c	.50 c	.97 bc	1.97a
8. NPK + Chelates (- Mn)	.89ab	.90 b	.68 bc	1.19ab	1.97a
9. NPK + Chelates (- Zn)	.94ab	.62 c	.92a	1.08abc	1.94a
10. NPK + salts of Cu,Fe,Mn,Zn + 5% peat moss	1.10a	1.02a	.98a	1.45a	2.26a

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

differences were found at the 5% level, from treatments, 1, 2, 4, 6, and 7. There was tendency for an increase in yield for those treatments which received all four micronutrients as salts (tmt 3) and mainly when they were mixed with peat (tmt 10). For this layer, there were no statistical differences among the means from the treatments minus iron, minus manganese and minus zinc, but the treatment that did not receive copper (tmt 6) was no better than the treatment which received no micronutrients (tmt 2). This suggests that the soil is deficient in copper, a result suspected from the appearance of sugar cane grown in the area from which the sample came. All treatments were significantly different from the check, indicating a definite requirement for the macronutrients.

In the same Ubu soil, but in the 20-40 cm layer, the treatment supplying micronutrients as salt plus 5% peat produced significantly more yield than all the other treatments. Again, the minus copper treatment tended to yield less than any treatment receiving copper, suggesting that the subsoil is also copper deficient. All treatments yielded significantly more than the check. Comparing the yields of equal treatments on these two soil depths, there was a tendency for the plow layer to give higher yields.

On the 0-20 cm layer of Sao Jose soil the highest yields were obtained when all nutrients were added as salts (with or without peat)

or when only zinc was omitted. All treatment yields were greater than that of the check. If a micronutrient cation deficiency is present in this soil, it appears to be a combination of Fe, Cu, and Mn in that order. As regarding the 20-40 cm layer of this soil, it can be observed that no statistical difference occurred among the dry matter productions from treatments 6, 8, 9, or 10, suggesting that iron may be most limiting of the micronutrients in this layer of soil. Surprisingly, the dry matter production from equal treatments on this layer, was generally more than that of the plow layer or 0-20 cm depth. Perhaps, development of a slight textural B horizon and entrapment of some leached ions has increased the fertility of this layer.

For the yields of plants grown on Montana soil, it was found that all treatments but the check, produced alike, with no statistical difference among them. All treatments were greater than the check, indicating that the NPK treatment was the primary requirement of these soils. Both Brazilian soils in general showed lower productivity when compared with Montana soil.

The results are graphically presented for each soil in Figure 19 through Figure 23. Figure 24a and 24b presents the comparisons among soils of each treatment effect.

Regarding the Brazilian soils, previous results reported copper,

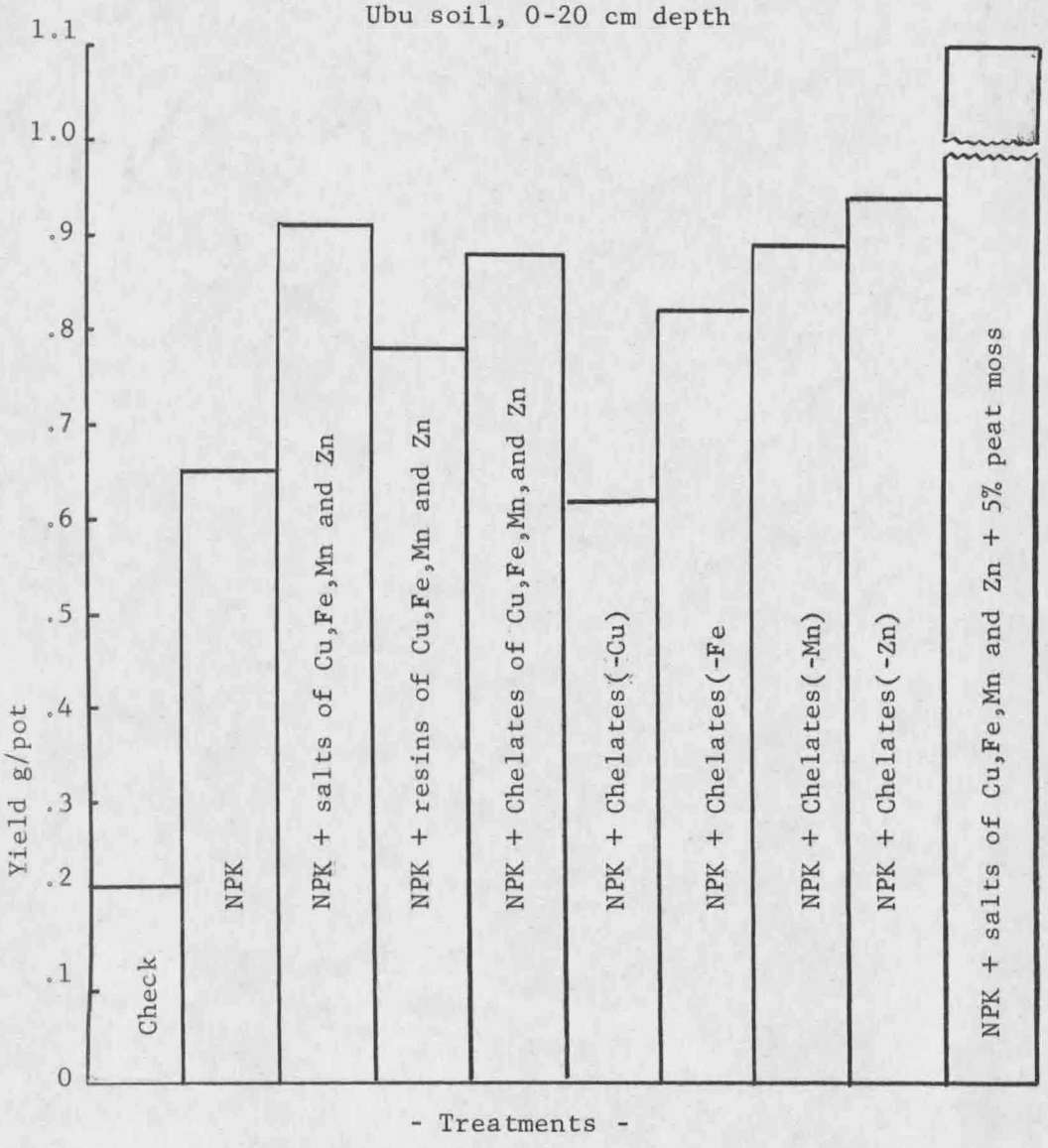


Figure 19. Yield of dry matter of barley on the 0-20 cm layer of Ubu soil as influenced by fertility treatment and source of micronutrients.

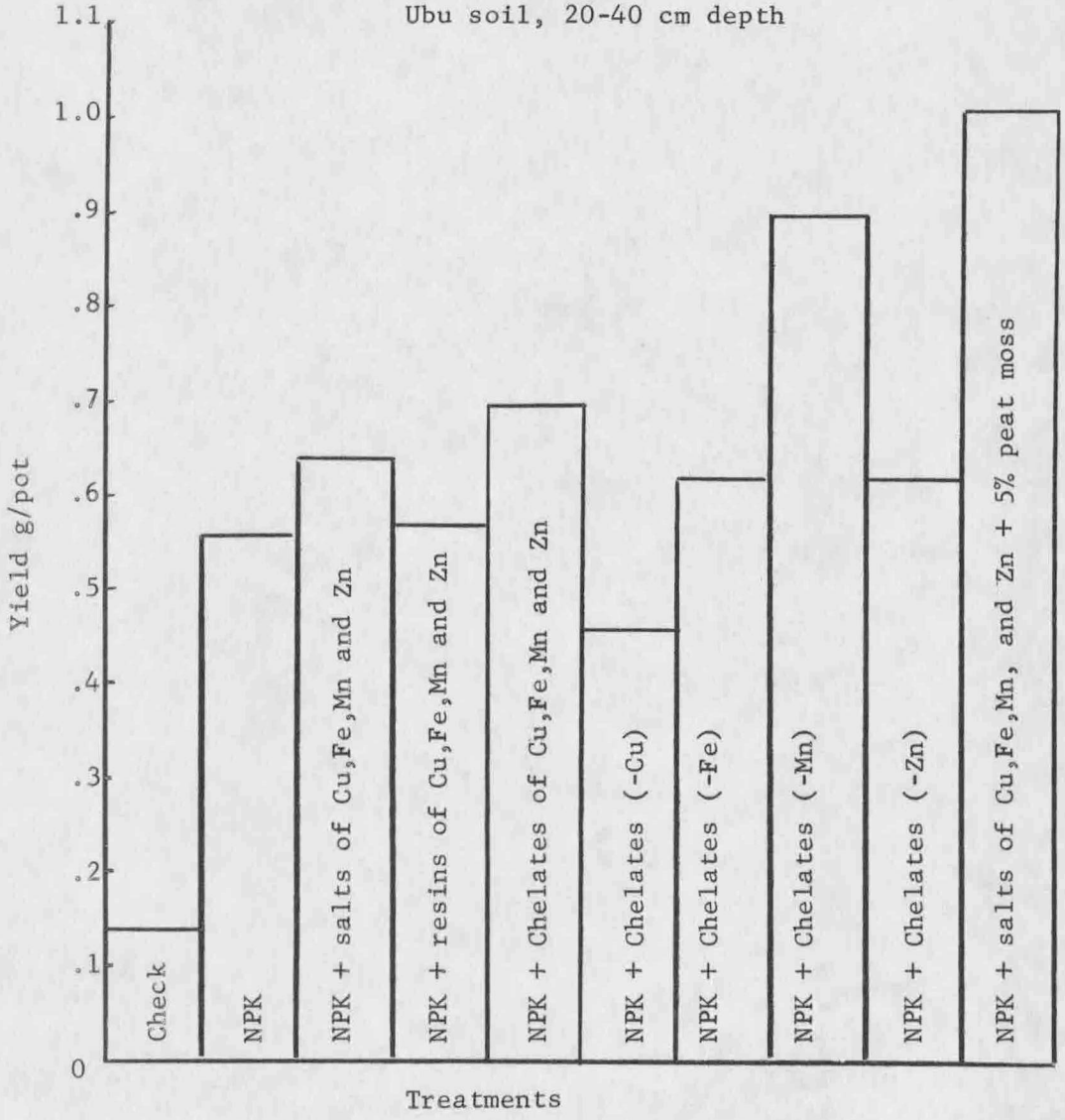


Figure 20. Yield of dry matter of barley on the 20-40 cm layer of Ubu soil as influenced by fertility treatment and source of micronutrients.

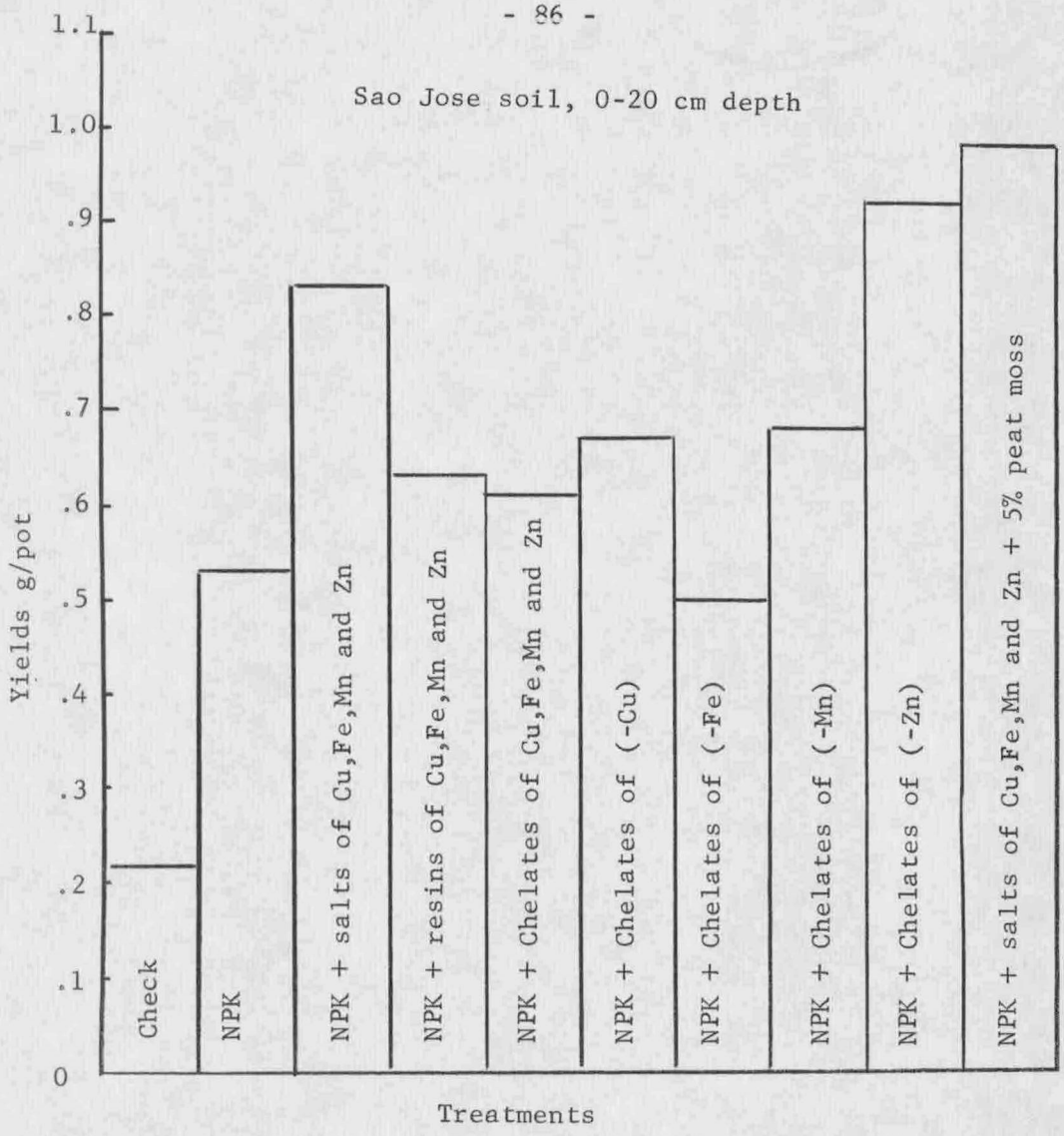


Figure 21. Yield of dry matter of barley on the 0-20 cm layer of Sao Jose soil influenced by fertility treatment and source of micronutrients.

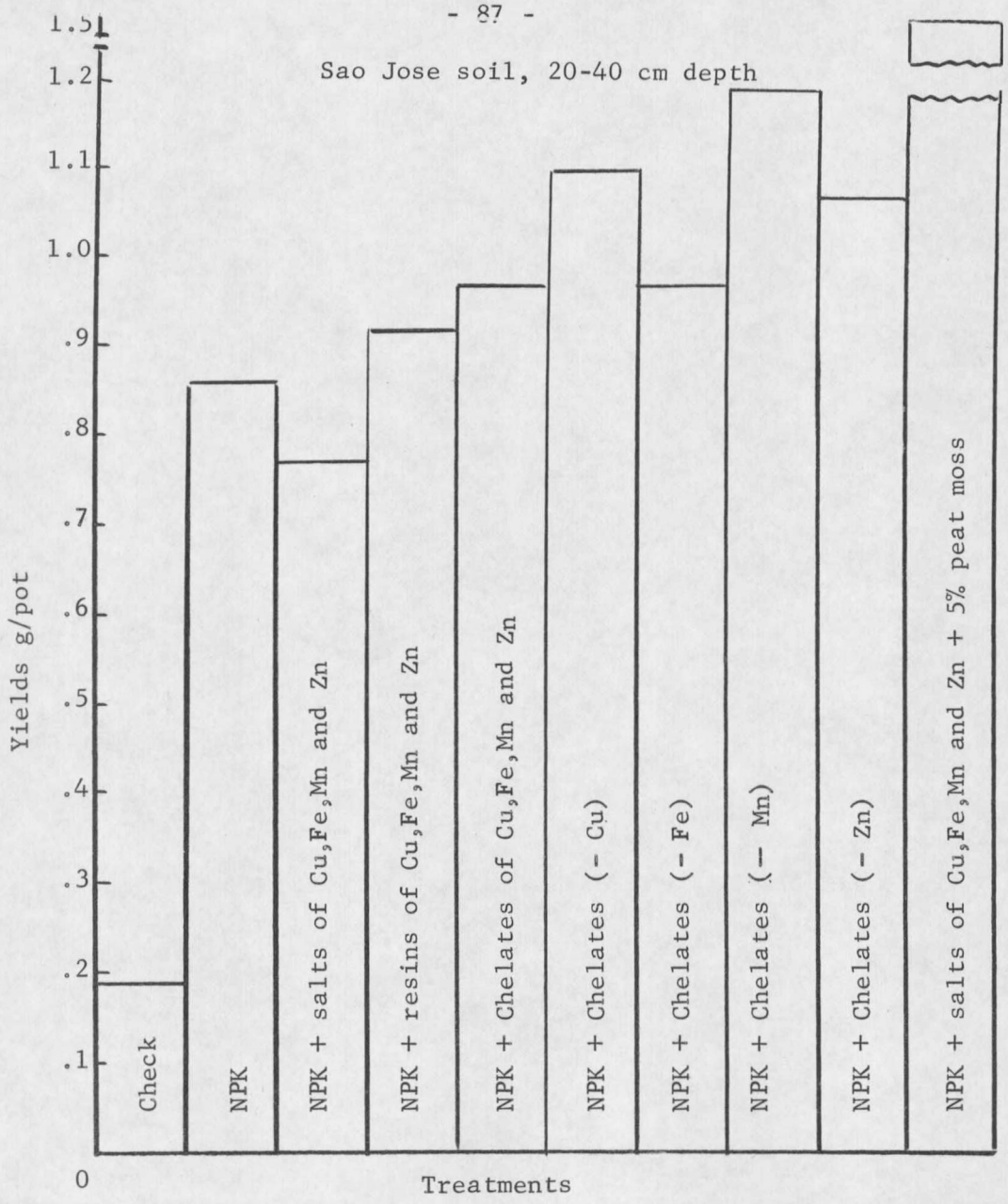


Figure 22. Yield of dry matter of barley on the 20-40 cm layer of Sao Jose soil as influenced by fertility treatment and source of micronutrients.

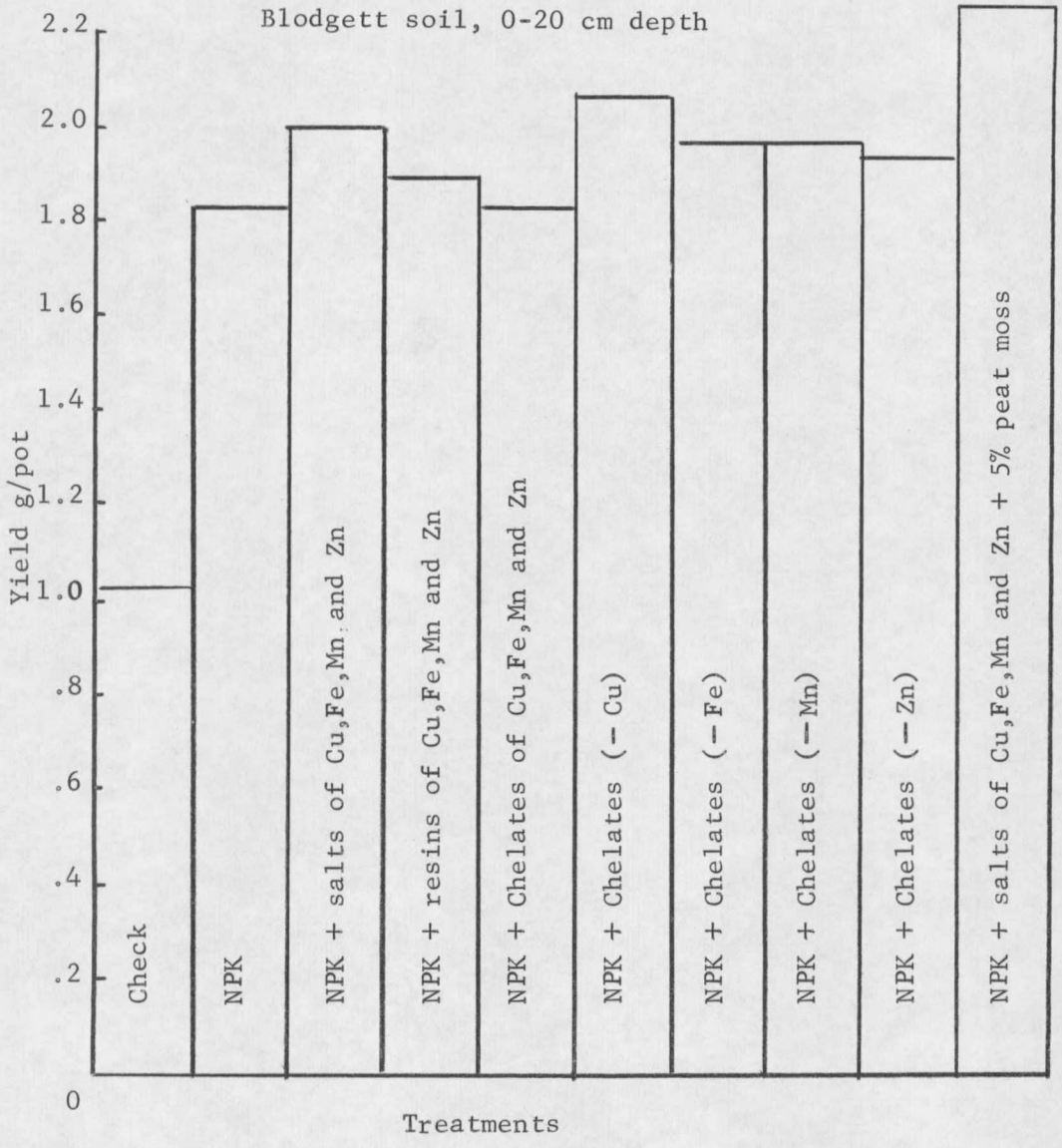
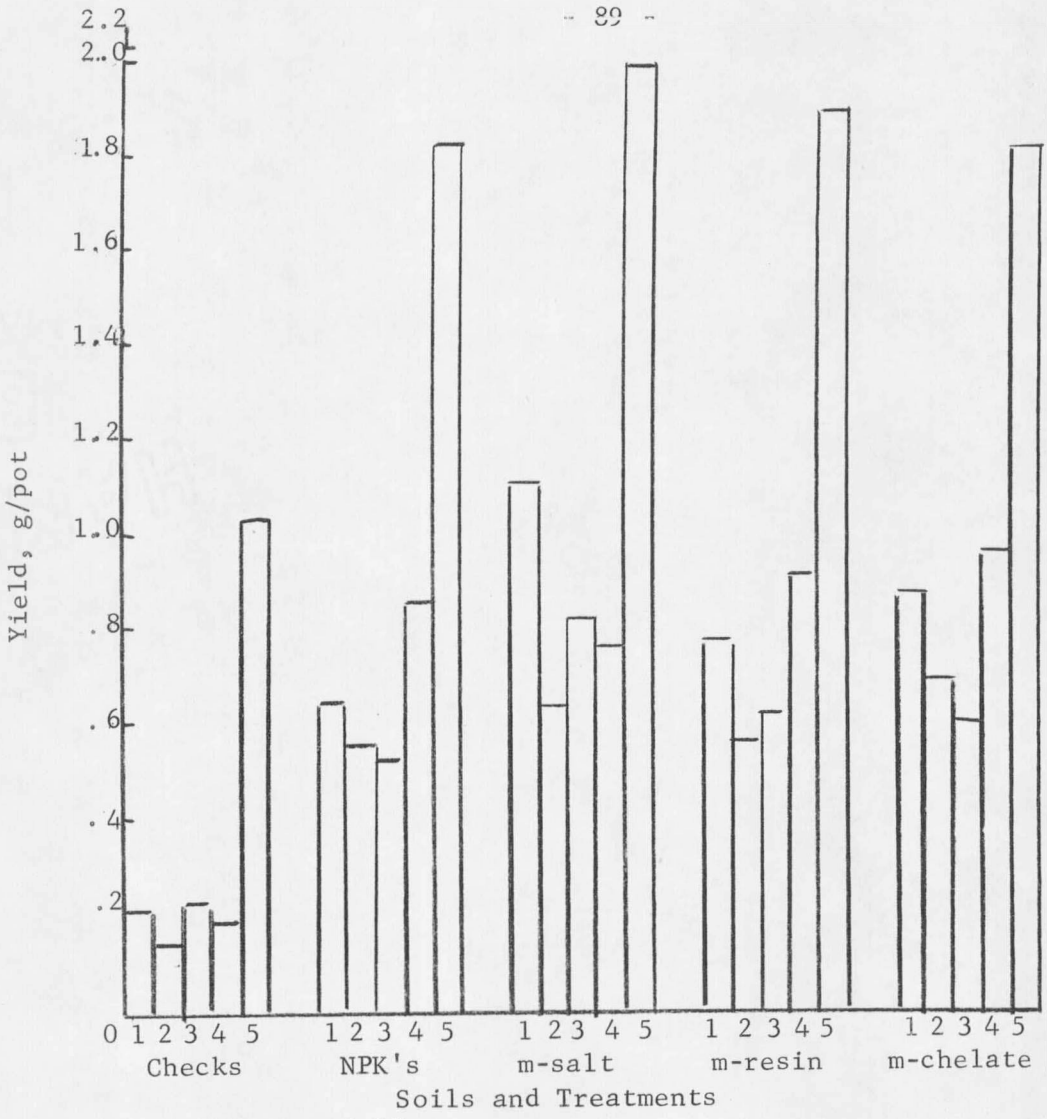
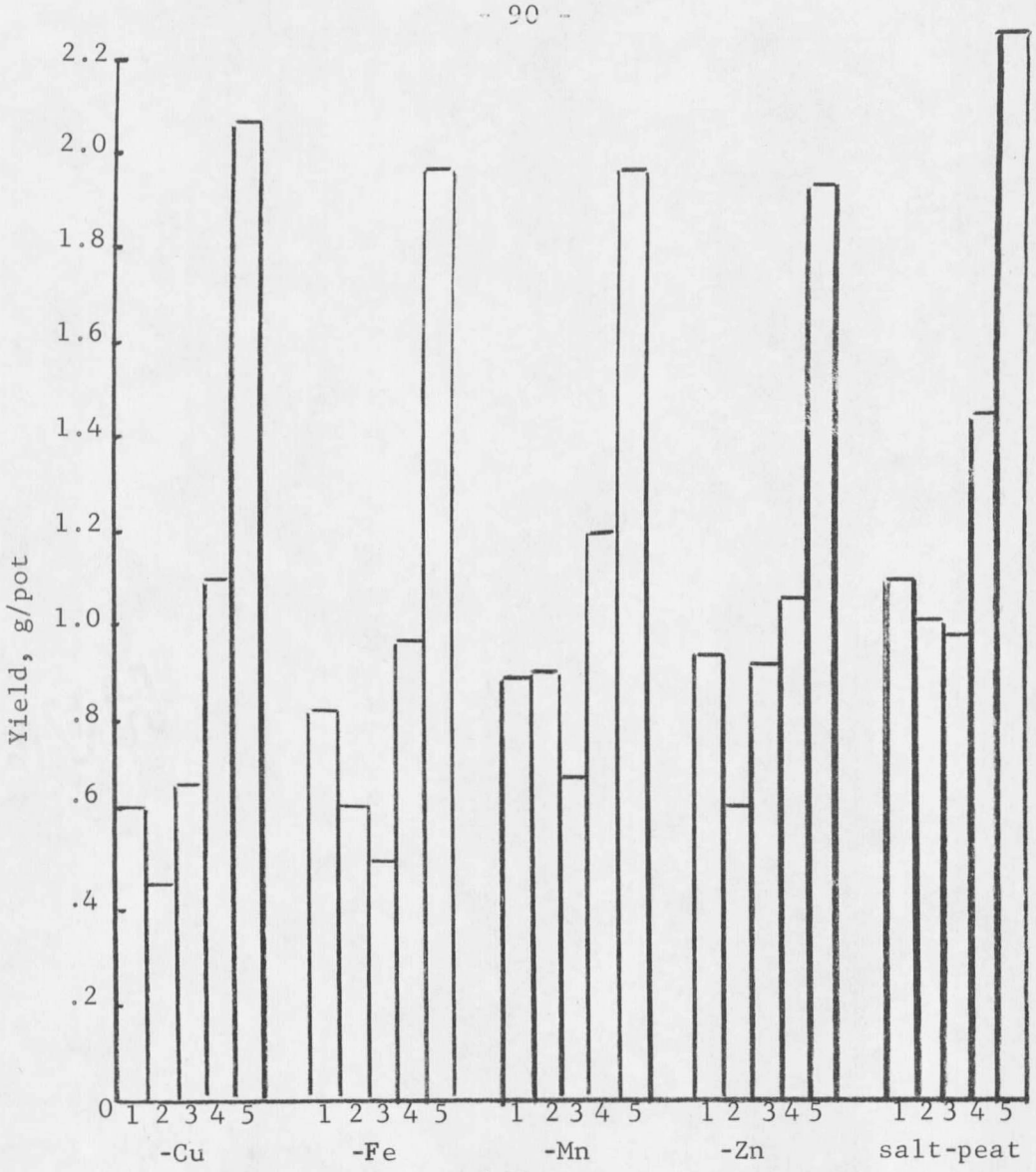


Figure 23. Yield of dry matter of barley on the 0-20 cm layer of Blodgett soil as influenced by fertility treatment and source of micronutrients.



Soil 1 = Ubu, 0-20 cm
Soil 2 = Ubu, 20-40 cm
Soil 3 = Sao Jose, 0-20 cm
Soil 4 = Sao Jose, 20-40 cm
Soil 5 = Blodgett, 0-20 cm

Figure 24a. Comparison of each treatment effect on each soil. Dry weight yields of barley as influenced by fertility level and micronutrient source.



Soil 1 = Ubu, 0-20 cm
Soil 2 = Ubu, 20-40 cm
Soil 3 = Sao Jose, 0-2- cm
Soil 4 = Sao Jose, 20-40 cm
Soil 5 = Blodgett 0-20 cm

Figure 24b. Comparison of each treatment effect on each soil. Dry weight yields of barley as influenced by fertility level and micronutrient source.

manganese and zinc deficiencies in soils at the same locations or in soils belonging to the same Great Soil Group (48).[3/] However, the results reported here must be considered from the standpoint of steam sterilization treatment on these soils. Failure to demonstrate specific deficiencies may be related to these effects (6,20,28,29,46, 49,65,103). Irregardless of this, it can be said that both soils are extremely low in fertility and that they respond to application of both macro and micronutrients. This ascertaion is verified by comparing their dry matter yields with the yields obtained in the Blodgett soil, a soil which is relatively low in fertility by comparison with other Montana soils.

These results do not completely confirm the comparable values of chelates as sources for micronutrients as others have reported (14,44,47,57,66,114,118). The yield from the complete micronutrient treatment added as chelates was less than when they were added as salts on the 0-20 cm layer of Sao Jose soil. Resins (24,87,88,89) and salts (31,32,37,38,52,96,120) appear to be equal as tools to study the availability of micronutrients for plant growth when the system is limited to one in which there is no leaching. Leaching conditions may alter this comparison in favor of the salt forms.

The addition of peat was generally beneficial in relation to yield of dry matter.

3/ Leite, J.P. 1967. Instituto de Pesquisas Agronomicas; Recife, Pernambuco, Brazil.

Table 8 presents the ppm of copper in soils determined after the barley plants had been harvested. As can be seen, copper was detected only in the treatments which received micronutrients as salt in each layer of the two Brazilian soils. However, in treatments receiving mincronutrients as chelate forms, copper was found in the second layer of Ubu soil and in both layers of Sao Jose soil. Copper was present at detectable levels in a few other soils after plant growth, but generally only when plant growth was low. Addition of peat to the soil increased copper in the plant considerably, but the result of peat analysis indicated that only 0.39 µg of copper were contributed by the peat. Apparently, the peat influenced the release of copper from the soil. It appears the amounts of copper added were not more than adequate, resulting in levels non-detectable at the termination of plant growth.

In the Blodgett soil, copper was extracted at detectable levels from all treatments, but the mean was statistically greater than that of other treatments only where the micronutrients were added as salts.

The ppm of iron in soils determined after the plants had been grown on them is found in table 9. As can be seen, only the means of ppm of iron from the micronutrients as salts plus peat, treatments (tmt 10) were statistically different from all the other means of the remaining treatments. This was true for both layers of both

Table 8. Means of DTPA extractable "Cu" in soils after the barley plants had been harvested

Treatment	Ubu soil		Sao Jose soil		Blodgett
	0-20cm	20-40cm	0-20cm	20-40cm	0-20cm
	ppm	ppm	ppm	ppm	ppm
1. Check	N.D.	N.D.	N.D.	N.D.	.39 ef*
2. NKP	N.D.	N.D.	N.D.	N.D.	.39 ef
3. NPK + salts of Cu,Fe,Mn and Zn	.41	.81	.50	.55	1.47a
4. NPK + resins of Cu,Fe,Mn and Zn	N.D.	N.D.	N.D.	N.D.	.34 f
5. NPK + Chelates of Cu,Fe,Mn and Zn	N.D.	.10	.10	.10	.61 bcd
6. NPK + Chelates (- Cu)	N.D.	N.D.	N.D.	N.D	.44 def
7. NPK + Chelates (- Fe)	N.D.	.17	N.D.	.17	.55 cde
8. NPK + Chelates (- Mn)	N.D.	.20	.10	.20	.67 bc
9. NPK + Chelates (- Zn)	N.D.	.20	.10	.20	.68 bc
10. NPK + salts of Cu,Fe,Mn,Zn + 5% peat moss	.58	.60	.55	.42	.77 b

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

Table 9. Means of DTPA extractable "Fe" in soils after the barley plants had been harvested.

Treatment	Ubu soil		Sao Jose soil		Blodgett
	0-20cm	20-40cm	0-20cm	20-40cm	0-20cm
	ppm	ppm	ppm	ppm	ppm
1. Check	15.10 b	10.60 b	12.53 b	7.90 b	70.67a
2. NPK	4.63 c	3.90 c	5.67 c	2.70 c	64.33 b
3. NPK + salts of Cu,Fe,Mn and Zn	6.27 c	4.60 c	6.00 c	3.90 c	64.00 b
4. NPK + resins of Cu,Fe,Mn and Zn	5.60 c	4.23 c	6.53 c	5.17 b	65.00a
5. NPK + Chelates of Cu,Fe,Mn and Zn	6.77 c	5.23 c	7.87 c	4.63 b	69.00a
6. NPK + Chelates (— Cu)	5.33 c	3.87 c	7.10 c	5.33 b	62.67 b
7. NPK + Chelates (— Fe)	6.40 c	4.27 c	6.53 c	4.63 b	65.33a
8. NPK + Chelates (— Mn)	7.77 c	5.00 c	9.53 bc	5.67 b	71.00a
9. NPK + Chelates (— Zn)	7.37 c	4.97 c	9.27 bc	6.27 b	70.33a
10. NPK + salts of Cu,Fe,Mn,Zn + 5% peat moss	24.00a	18.67a	24.00a	16.67a	67.33a

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

Brazilian soils. The check of Ubu soil in both depths was also different statistically from all the other means. In the 0-20 cm depth of Sao Jose soil, the check treatment did not differ statistically in extractable iron from that of treatments 8 and 9 (-Mn and -Zn), but the latter two treatments were not different from the remaining ones (2 through 7). The iron recovered from the check plot of the 20-40 cm depth of the Sao Jose soil was not different from the means of treatments 4 through 8. Treatments 2 and 3 had significantly less extractable iron than did treatments 4 through 8.

In the Blodgett soil, the means of treatments 2, 3, and 6 were equal but less than all the remaining means, which in turn were statistically equivalent. In general, these values are relatively low for the Brazilian soils, but high for the Blodgett. Lyndsay[4/] reports that soils with less than 5 ppm DTPA extractable Fe may be deficient for plant growth (sorghum). It appears that even in tropical soils, which are considered to be high in iron oxides, available iron may be inadequate for good crop yields. The higher iron extracted from the soils of check treatments is probably associated with decreased plant growth from these treatments as limited by N, P, and K. Most plants were dead at the harvest time on the check plots of the Brazilian soils.

Table 10 presents means of ppm of manganese in soils extracted

4/ Lyndsay, W. L., Letex on Nov. 20, 1969 to V. Haby about DTPA-TEA method.

Table 10. Means of DTPA extractable "Mn" in soils of the barley plants had been harvested.

Treatment	Ubu soil 0-20cm	Ubu soil 20-40cm	Sao Jose soil 0-20cm	Sao Jose soil 20-40cm	Blodgett 0-20cm
	ppm	ppm	ppm	ppm	ppm
1. Check	2.56 b	.55 b	1.79 bc	2.26 b	10.43a
2. NPK	1.53 c	.18 b	1.53 c	1.44 d	15.00a
3. NPK + salts of Cu,Fe,Mn and Zn	1.86 bc	.80	1.70 bc	1.79 c	14.30a
4. NPK + resins of Cu,Fe,Mn and Zn	1.52 c	.37 b	1.70 bc	1.68 c	22.23a
5. NPK + Chelates of Cu,Fe,Mn and Zn	1.61 c	.45 b	1.53 c	1.61 c	21.33a
6. NPK + Chelates (-Cu)	1.60 c	.72 b	1.70 bc	1.79 cd	18.10a
7. NPK + Chelates (—Fe)	1.37 c	.37 b	1.37 d	1.93 bc	19.97a
8. NPK + Chelates (—Mn)	1.44 c	.37 b	1.37 d	1.61 c	20.57a
9. NPK + Chelates (— Zn)	1.68 b	.72 b	1.96 b	1.77 c	20.77a
10. NPK + salts of Cu,Fe,Mn,Zn + 5% peat moss	4.20a	24.17a	4.10a	3.60a	31.77a

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

after the plants were harvested. It is obvious that for the two Brazilian soils and at both depths, treatments 10, (micronutrients as salt plus peat), had significantly more manganese than did soils from all other treatments. Manganese, like iron, is normally rather abundant in most tropical soils. The extractable manganese of these soils is probably adequate for all except the 20-40 cm layer of the Ubu soil. One ppm has been suggested as the "critical" value for DTPA extractable manganese[4/]. It must be remembered, too, that the levels of micronutrients found in this study may be artificially high because of the steam sterilization treatment of the soils.

No significant differences were found among the means of ppm of manganese extracted from the Blodgett soil. It appears that this soil has an adequate supply of this micronutrient.

Table 11, presents the means of ppm of zinc in soil following harvest. It can be seen that the Blodgett soil did not show any significance at all among the treatments. The same can be said regarding the 0-20 cm layer of Sao Jose soil. In the 0-20 cm layer of Ubu soil, treatment 10 (micronutrients as salts plus peat) was significantly greater than all remaining treatments. In the 20-40 cm layer, only the treatment receiving NPK without micronutrients (tmt 2) and that supplied with resin forms of micronutrients (tmt 4) were significantly less than all others. On the 20-40 cm layer of Sao Jose soil, it was evident that both check and micronutrients as salts plus peat treat-

Table 11. Means of DTPA extractable "Zn" in soils after the barley plants had been harvested.

Treatment	Ubu soil 0-20cm	Ubu soil 20-40cm	Sao Jose soil 0-20cm	Sao Jose soil 20-40cm	Blodgett 0-20cm
	ppm	ppm	ppm	ppm	ppm
1. Check	3.60 b	5.00a	3.57a	3.60a	1.84a
2. NPK	2.26 c	2.77 b	2.27a	1.91 c	1.67a
3. NPK + salts of Cu,Fe,Mn and Zn	2.57 bc	5.00a	3.21a	2.67 b	2.70a
4. NPK + resins of Cu,Fe,Mn and Zn	2.03 c	3.32 b	2.48a	2.22 c	1.87a
5. NPK + Chelates of Cu,Fe,Mn and Zn	2.26 c	5.00a	2.62a	2.18 c	2.04a
6. NPK + Chelates (−Cu)	2.18 c	5.00a	3.83a	2.54 b	1.99a
7. NPK + Chelates (−Fe)	2.03 c	4.30a	2.47a	2.16 c	2.24a
8. NPK + Chelates (−Mn)	3.10 bc	5.00a	3.05a	2.77 bc	1.93a
9. NPK + Chelates (−Zn)	2.24 c	4.43a	3.21a	2.20 c	1.90a
10. NPK + salts of Cu,Fe,Mn,Zn + 5% peat moss	5.00a	5.00a	5.00a	4.27a	3.10a

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

ments were not significantly different from each other, but they were greater than all the others. Available zinc determined on these soils, was relatively high, and it is doubtful that a zinc deficiency would occur at these levels. The "critical" level for zinc is suggested to be 0.8 ppm. More research is needed on these soils under field conditions to verify these levels obtained on sterilized samples. Many crops, especially citrus and corn, have exhibited visual zinc deficiency symptoms when grown on tabuleiro soils of N. E. Brazil.

Table 12 presents the data of manganese concentrations in barley plants grown in the growth chamber on these soils. The highest manganese concentrations were obtained from check treatments on the Brazilian soils. Undoubtedly, this is due to curtailed plant growth. It is interesting to note, also, that the manganese content of barley was least on the treatment in which it was not added (tmt 8) although it was not significantly less than in several other treatments on these four soils. On the Blodgett soil, plants from the check treatment had the least manganese. Adding only NPK; or everything except manganese resulted in lower manganese concentrations in barley than from all treatments in which manganese was added, regardless of the form used.

The manganese concentrations are generally within the adequate, but not excessive range. Chapman (19) reports that ample but not excessive levels commonly fall in the 20 to 500 ppm range. The lower plant concentrations of manganese from the minus manganese treatments

Table 12. Manganese concentrations of barley grown on five different soils as influenced by fertility treatment and form of micronutrient

Treatment	Ubu soil 0-20cm	Ubu soil 20-40cm	Sao Jose soil 0-20cm	Sao Jose soil 20-40cm	Blodgett 0-20cm
	ppm	ppm	ppm	ppm	ppm
1. Check	194.48a*	250.99a	87.59ab	105.54a	59.66 b
2. NPK	69.78 b	47.88 b	68.14abc	36.38 c	139.50ab
3. NPK + salts of Cu,Fe,Mn and Zn	63.09 b	59.73 b	60.01 bc	64.39 bc	170.50a
4. NPK + resins of Cu,Fe,Mn and Zn	74.79 b	26.39 b	64.48 bc	46.90 bcd	175.00a
5. NPK + Chelates of Cu,Fe,Mn and Zn	46.30 b	31.95 b	63.83 bc	45.63 cd	177.50a
6. NPK + Chelates (--Cu)	72.08 b	60.91 b	62.55 bc	47.03 bcd	181.80a
7. NPK + Chelates (--Fe)	66.77 b	43.63 b	69.36 bc	38.78 cd	159.67a
8. NPK + Chelates (--Mn)	34.70 b	29.38 b	42.31 c	33.50 d	130.33ab
9. NPK + Chelates (--Zn)	40.97 b	38.35 b	48.64 c	48.79b cd	165.00a
10. NPK + salts of Cu,Fe,Mn,Zn + 5% peat moss	63.32 b	70.12 b	93.98a	75.00 b	205.50a

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

on the Brazilian soils would be near the deficient levels.

Many literature references report the instability (71,116) of manganese chelates in soils and also that manganese may be replaced by iron in soil (118). These facts cannot be contested, but under the conditions of this experiment, the manganese chelate was equally as good as the salt form employed or when manganese was added as a resin-adsorbed cation. Under field conditions where leaching may be important, especially in such sandy soils, the chelate form may not be as effective. Results of the study on micronutrient cation leaching as influenced by these forms suggests that such may be the case.

Table 13 contains the data from the zinc determination in barley plants grown on the five soil samples of this study. The zinc concentrations of barley from the check treatments were significantly greater than those from all other treatment means for the Brazilian soils, except on the 0-20 cm layer of the Sao Jose soil where chelates were used (tmt 5) or where iron was omitted (tmt 7). No other distinct differences could be observed. The zinc content of the plants grown on the Blodgett soil, did not show any statistical significance when the means were compared by Duncan Multiple Range Test.

The high zinc content found in the plants grown on the check treatments should be interpreted as a result of poor plant growth due to macronutrient deficiencies. When other factors are no longer limiting for plant growth, zinc concentrations will decrease with

Table 13. Zinc concentrations of barley plants grown on five different soils as influenced by fertility treatment and form of micronutrient.

Treatment	Ubu soils		Sao Jose soil		Blodgett
	0-20 cm	20-40 cm	0-20 cm	20-40 cm	0-20 cm
	ppm	ppm	ppm	ppm	ppm
1. Check	97.13a*	161.75a	70.65a	135.01a	39.50a
2. NPK	40.44 b	71.82 c	47.34 c	85.88 b	44.50a
3. NPK + salts of Cu,Fe,Mn and Zn	38.69 b	70.17 c	48.12 c	47.29 b	48.00a
4. NPK + resins of Cu,Fe,Mn and Zn	36.94 b	72.29 c	37.99 c	41.06 b	48.50a
5. NPK + Chelates of Cu,Fe,Mn and Zn	45.73 b	88.49 c	65.36ab	50.02 b	34.50a
6. NPK + Chelates (- Cu)	55.37 b	97.84 bc	49.66 bc	85.79 b	43.50a
7. NPK + Chelates (- Fe)	64.26 b	96.72 bc	66.04ab	42.82 b	41.00a
8. NPK + Chelates (- Mn)	46.36 b	72.08 c	48.38 c	36.00 b	40.50a
9. NPK + Chelates (- Zn)	36.87 b	82.78 c	45.57 c	31.59 b	51.00a
10. NPK + salts of Cu,Fe,Mn,Zn + 5% peat moss	56.24 b	124.14 b	72.06a	44.00 b	40.83a

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

increased dry matter production. As stated by Price (76) "the concentration of free zinc ions will decrease progressively as zinc is diluted by continuing growth".

According to Chapman (19), deficiency levels of zinc in plant tissues are characterized by concentrations in the range of 20 to 25 ppm. Ample, but not excessive levels fall in the range 25 to 150 ppm. All levels reported are well within this latter range, suggesting that these soils adequately supplied zinc under these experimental conditions. Furthermore, barley is said to belong to the group of "insensitive plants" to zinc deficiency (85).

Table 14 shows the yields of manganese in mg per pot. It can be observed that for Brazilian soils the greatest uptake of manganese occurred on soils treated with salt forms of micronutrients plus the addition of 5% peat to the soil. Most of this increased uptake or yield of manganese is a reflection of greater dry weight production from this treatment, but some is due to greater plant concentration. No other pertinent differences were apparent. Lower yield of manganese were much greater from the Blodgett soil than from the Brazilian soils.

The application of peat in Brazilian soils was generally beneficial to the yield of manganese. Considering the concentration of micronutrients in the peat, as determined by chemical analysis, and the quantity of peat added, the amounts of manganese added in this

Table 14. Manganese yields from barley plants grown on five different soils as influenced by fertility treatment and form of micronutrient.

Treatment	Ubu soils 0-20 cm	Ubu soils 20-40 cm	Sao Jose soil 0-20 cm	Sao Jose soil 20-40 cm	Blodgett 0-20 cm
	µg/pot		µg/pot		µg/pot
1. Check	34.21 c*	35.80 b	19.08 b	20.22 c	62.13
2. NPK	45.02 b	26.05 b	36.23 b	33.09 b	256.56 b
3. NPK + salts of Cu,Fe,Mn and Zn	56.84ab	35.59 b	50.34 b	50.26 b	341.00ab
4. NPK + resins of Cu,Fe,Mn and Zn	57.89ab	14.70 b	41.58 b	43.39 b	334.02ab
5. NPK + Chelates of Cu,Fe,Mn and Zn	40.28 b	22.37 b	38.93 b	44.33 bc	317.30ab
6. NPK + Chelates (- Cu)	44.75 b	27.24 b	41.39 b	54.00 b	370.41ab
7. NPK + Chelates (- Fe)	51.21 b	26.71 b	34.94 b	36.43 b	318.41ab
8. NPK + Chelates (- Mn)	30.76 c	26.03 b	29.46 b	39.10 b	255.43 b
9. NPK + Chelates (- Zn)	38.71 c	23.83 b	46.05 b	52.61 b	320.80ab
10. NPK + salts of Cu,Fe,Mn,Zn + 5% peat moss	69.97a	75.56a	94.03a	102.44a	467.58a

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

form was only 9.7 µg. The manganese yield was increased 30 to 50 mg. on the treatment where peat was added. It appears that this organic residue contributed more to improve the physical condition, rather than as a source of nutrient. Probably, by increasing the water holding capacity of those soils, manganese was ever ready to be adsorbed by the plants; it may also be that manganese was chelated by the organic compounds from the peat and then remained available for the plant use.

Table 15 presents the data related to the yields of zinc in µg per pot. For the plow layer of Ubu soil, treatments 10 (micronutrients as salts plus peat) did not differ significantly from micronutrients as chelate minus iron; this last one, on the other hand, was statistically similar to treatments 3, 5, 6, 8, and 9. In the 20-40 cm layer of the same soil, treatment 10 differed significantly from all the other treatment means. The opposite situation occurred on the Sao Jose soil. On the 0-20 cm layer of Sao Jose soil, the treatment 10 was significantly greater than all the other treatment means; however, in the subsurface layer treatment 10 was statistically equivalent to treatments 2 and 4 through 8.

In the Blodgett soil, all the treatments were statistically different from the check, with the exception of treatments including micronutrients as chelate (tmt 5) and micronutrients as chelate minus manganese (tmt 8), which were statistically equivalent.

Table 15. Zinc yield by barley plants grown in five different soils as influenced by fertility treatment and form of micronutrient.

Treatment	Ubu soil 0-20 cm	Ubu soil 20-40 cm	Sao Jose soil 0-20 cm	Sao Jose soil 20-40 cm	Blodgett 0-20 cm
	µg/pot		µg/pot		µg/pot
1. Check	17.59 d*	22.89 c	15.76 d	26.21 b	42.10 b
2. NPK	25.98 cd	41.13 bc	25.08 cd	76.39ab	80.91a
3. NPK + salts of Cu,Fe,Mn, and Zn	35.67 bcd	43.04 bc	39.93 b	37.05 b	95.96a
4. NPK + resins of Cu,Fe,Mn and Zn	28.72 cd	41.12 bc	24.31 cd	39.57ab	92.53a
5. NPK + Chelates of Cu,Fe,Mn and Zn	40.35 bc	59.64 b	39.87 b	48.63ab	63.35ab
6. NPK + Chelates (– Cu)	34.14 bcd	44.90 bc	33.64 bc	105.44a	90.10a
7. NPK + Chelates (– Fe)	48.62ab	60.37 b	32.67 bc	40.16ab	82.57a
8. NPK + Chelates (– Mn)	40.93 bc	64.37 b	32.61 bc	42.44ab	79.24ab
9. NPK + Chelates (–Zn)	37.49 bc	51.84 b	42.14 b	34.07 b	98.19a
10. NPK + salts of Cu,Fe,Mn,Zn + 5% peat moss	63.05a	125.16a	70.57a	61.20ab	93.57a

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

At least for Ubu soil and the A-horizon of Sao Jose soil, it appears that the application of zinc as salt combined with peat was more available than the other forms in which it was supplied. Concerning, the Blodgett soil and the second layer of Sao Jose soil, the form of zinc applied has no profound influence on the yield of zinc.

Table 16 shows the means of the percent phosphorus in barley plants grown on two Brazilian soils and one Montana soil. The phosphorus contents of plants grown on Brazilian soils were relatively uniform. Most treatments were interrelated statistically with none of them being highly different from another. However, in the Blodgett soil, the treatment micronutrient as salts plus peat (tmt 10) was significantly greater than all other treatment means.

The correlation between ppm of Zn and percent P in plants was highly significant only for the surface layer of the Ubu soil. The surface layer of Sao Jose soil showed a significant correlation at the 6% level of probability. This seems to indicate that the greatest amounts of the available forms of the plant nutrients are found in the surface layers of these soils. This finding agrees with the literature (4,47,113). However, the positive correlation obtained does not support the action of antagonism between phosphorus and zinc in these soils, as has been the case in many situations.

Table 17 presents the data for the yield of phosphorus in mg per pot. At the 0-20 cm layer of Ubu soil, the check treatment

Table 16. Phosphorus concentration of barley plants grown on five different soils as influenced by fertility treatment and form of micronutrient.

Treatment	Ubu soil 0-20 cm	Ubu soil 20-40 cm	Sao Jose soil 0-20 cm	Sao Jose soil 20-40 cm	Blodgett 0-20 cm
	%	%	%	%	%
1. Check	0.94 b*	0.80 c	0.70	0.87 b	0.22 bcd
2. NPK	1.20ab	1.28ab	1.21a	1.40a	0.25 b
3. NPK + salts of Cu,Fe,Mn and Zn	1.55ab	1.00 bc	1.14a	1.10ab	0.24 bc
4. NPK + resins of Cu,Fe,Mn and Zn	1.32a	1.10abc	1.34a	1.18ab	0.18 d
5. NPK + Chelates of Cu,Fe,Mn and Zn	1.48a	0.90 c	1.20a	1.07ab	0.21 bcd
6. NPK + Chelates (− Cu)	1.38a	1.10abc	1.38a	1.46a	0.21 bcd
7. NPK + Chelates (− Fe)	1.26ab	1.10abc	1.37a	1.15ab	0.20 cd
8. NPK + Chelates (− Mn)	1.49a	1.00 bc	1.26a	1.08ab	0.22 bcd
9. NPK + Chelates (− Zn)	1.35a	1.10abc	1.31a	1.41a	0.22 bcd
10. NPK + salts of Cu,Fe,Mn,Zn + 5% peat moss	1.26ab	1.30a	1.30a	1.25ab	0.28a
Correlation between ppm An and ppm P in plants	1.48*	0.04 n.s.	0.34 n.s.	0.02 n.s.	0.009n.s.

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

Table 17. Yield of phosphorus by barley plants grown on five different soils as influenced by fertility treatment and form of micronutrient.

Treatment	Ubu soil 0-20 cm	Ubu soil 20-40 cm	Sao Jose soil 0-20 cm	Sao Jose soil 20-40 cm	Blodgett 0-20 cm
	mg/pot		mg/pot		mg/pot
1. Check	2.13 b*	1.20 c	1.56	1.69	2.25
2. NPK	7.82ab	6.87 b	6.57 b	12.00abc	4.52 bc
3. NPK + salts of Cu,Fe,Mn and Zn	11.35a	6.54 b	9.85ab	8.59 c	4.76 b
4. NPK + resins of Cu,Fe,Mn and Zn	10.35a	6.10 b	8.55ab	11.12abc	3.52 d
5. NPK + Chelates of Cu,Fe,Mn and Zn	13.43a	8.46 b	7.31 b	10.42 bc	3.84 bc
6. NPK + Chelates (- Cu)	8.51a	5.15 bc	9.16ab	16.47ab	4.33 bc
7. NPK + Chelates (- Fe)	10.01a	6.59 b	7.02 b	11.02abc	3.96 bc
8. NPK + Chelates (- Mn)	13.82a	8.59 b	8.97ab	12.65abc	4.37 bc
9. NPK + Chelates (- Zn)	12.70a	7.10 b	12.13a	15.20abc	4.38 bcd
10. NPK + salts of Cu,Fe,Mn,Zn + 5% peat moss	13.87a	12.76a	12.79a	18.07a	6.45a
Correlation between the yields of P and the yields of Zn	.66**	.81**	.74**	.63**	.61**

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

yielded significantly less phosphorus than all other treatment means, with the exception of NPK treatment. For the second layer of the same soil, the treatment micronutrient as salts plus peat was signicantly greater than all other treatment means. There were no significant difference between means of treatments 2 through 9, but the check yield of phosphorus was less.

Considering both Sao Jose and Blodgett soils, it was observed that the check treatments on these two soils gave significantly lower yields of phosphorus than all the other treatment means. A few other minor differences may be observed.

The correlation between the yields of zinc and the yields of phosphorus was highly significant for all the soils.

From the results presented in this table, it appears that these soils need a balanced fertilizer in order to express their full production potential. Probably an efficient management and fertilization system would result in a better utilization of the plant nutrients applied.

SUMMARY AND CONCLUSIONS

A study was conducted to determine the retention of zinc and copper by soil samples from 0-20 cm and 20-40 cm depths of two Brazilian "tabuleiro" soils and the surface soil of Blodgett soil from western Montana. In this study, soils were mixed with slight excesses of solutions of copper or zinc at various concentrations and allowed to equilibrate for four hours. The solutions were extracted and analyzed to determine the quantity of original copper or zinc removed by the soil.

Both copper and zinc were readily adsorbed by the 0-20 cm layers of the two Brazilian soils. Retention of copper and zinc was two to three times greater than that of the 20-40 cm layer of the same soils. Sao Jose soil retained more than Ubu soil at the same depth. The organic fractions of these soils retained five to ten times more than the corresponding mineral fraction of the same soil. A Montana soil used for comparison (Blodgett course sandy loam) retained 10 times more copper than the Brazilian soils at equivalent depth. There was no apparent difference between the Blodgett and the Brazilian surface soils in their retention of zinc.

Another study was conducted to determine leaching of copper and zinc from the soils when added from different sources. For the Brazilian soils the leaching also was done in soil with the organic matter removed. The soils were leached with distilled deionized water daily at the rate of 1 ml of water per gram of soil. Starting from time

zero, 10g of soil were taken weekly for copper and zinc analysis by the DTPA-TEA extraction procedure.

Copper leaching from the sandy Brazilian soils was found to be less when copper sulfate was used as compared to the resin or chelated forms of copper. These latter two forms of copper were leached sometimes up to essentially 100 percent of the original copper added.

The failure of the chelate form of copper to prevent copper leaching in the Brazilian soils is probably related to 1) the instability of the copper chelate in these soils and the displacement of copper by a more strongly complexed metal ion; or 2) the actual leaching of the entire chelate molecule, with its copper ion, from the soil. In soils with high surface area and more normal cation exchange capacities, this would probably not occur as readily, as expressed by results from the Blodgett soil, where the chelated copper was not easily leached out. The removal of O.M. from Brazlian soils or addition of peat to all three soils had little influence on copper leaching.

Zinc reacted similarly to copper, i.e. the salt form of this element was generally the best retained, but the advantage was not as distinct as in the case of copper. Zinc resin performed better than copper resins, and the addition of peat appeared to improve its retention in the soil, however, no influence of peat was noted on the other forms of added zinc. It appears that the chelated forms

of both zinc and copper would be rather ineffective in solving the deficiencies of these elements on the Brazilian soils studied.

A study also was conducted to determine which micronutrient(s) was lacking and at the same time identify which form of the element could be applied to achieve correction of the deficiency. Barley (Hordeum distichon L., variety Hypana) was used as the test plant. The treatments were mixed with 500 grams of air dried soil and placed in plastic pots. Barley seedlings were thinned to 5 per pot. The plants were grown in a growth chamber set for 10 hour dark and 14 hour light periods. The temperature varied from 13°C to 27°C. Distilled deionized water was added as required. A randomized complete block design was used, with 10 treatments and four replication.

The dry matter production of barley plants grown of Ubu soil was relatively higher on those treatments which received micronutrients as salts, and the results were far better when 5 percent peat was added to the soil. This treatment produced 3 to 5 times more than check treatments. Copper appears to be the most limiting micronutrient of those studied. On the 0-20 cm layer of Sao Jose soil, the treatment supplying micronutrients as salts produced the highest yield. Peat apparently had no effect. These results may have been influenced by steam sterilization of the soils from Brazil. The efficiency of chelates was not confirmed under the condition of these experiments. For the Blodgett soil, the only requirement for

barley under these conditions seems to be for supplemental nitrogen, phosphorus and potassium.

After the plants were harvested, soil analyses were made to determine the residual of DTPA extractable copper, iron, manganese and zinc. Results of copper analysis on the soils after plants were harvested showed that that the copper sulfate form was still present in Brazilian soils. Results from other forms varied from very low to nil. All treatments of the Blodgett soil had detectable copper, however, the salt form had the highest amount.

The addition of peat had tremendous influence on the presence of extractable iron after the growth of the plants in both Brazilian soils. The amount of residual iron was five to eight times as great as from the same treatment but without peat added. However, peat had no effect on the residual iron in the Blodgett soil.

The addition of peat had a marked influence on extractable manganese on Brazilian soils. The amounts varied from 4 to 20 times that of the treatments where micronutrients were added as salts without peat. Blodgett soil showed no effect from treatments or addition of peat.

The residual extractable zinc of Blodgett soil was not influenced by its addition to the soil regardless of form added. On the Brazilian soils, peat addition had a positive effect on the zinc in the plow layer of Ubu soil only. Zinc additions had no detectable

influence.

To determine the concentrations of elements in the plants a perchloric acid digestion of plant tissue was made. The only micronutrient cations detected in the plant extract were manganese and zinc. Iron and copper were below the level of detection by the procedures used. Phosphorus was the only macronutrient determined.

The concentration of manganese of barley plants was not influenced by the form in which the element was applied, however, if this element is not included its concentration decreased. The manganese concentration of plants grown on the Blodgett soil was two to four times greater than that from Brazilian soils. Results of zinc analysis provided similar data to those for manganese. However, both elements were higher in concentration on plants from the check treatments, suggesting that the lack of plant growth on these treatments was caused by insufficient macronutrients, resulting in excessive micronutrient concentrations.

The application of peat in Brazilian soils was generally beneficial to the yield of manganese, nevertheless, this influence is interpreted as due to improvement of physical rather than chemical conditions. Chemical analysis of the peat supports this interpretation.

From the yield of zinc obtained it was concluded that, at least for Ubu soil and the 0-20 cm layer of Sao Jose soil, the application

os zinc as salt plus peat was better than the other forms in which zinc was supplied. On the Blodgett soil and the 20-40 cm layer of Sao Jose soil, the form of zinc seemed to have no influence on the yield of zinc in plants.

The phosphorus content of barley plants grown on two Brazilian soils was relatively uniform. However, on the Blodgett soil, the treatment micronutrient as salt plus peat (tmt 10) gave significantly greater phosphorus contents than any other treatment.

The positive correlation between ppm of Zn and percent P in plants was highly significant only for the surface layer of the Ubu soil. For the same layer of Sao Jose soil, the positive correlation found was at the 6 percent level. These positive correlations obtained do not support the action of antagonism between zinc and phosphorus in soils, as has been the case in many situations.

The yields of phosphorus in plants from both Sao Jose and Blodgett soils wer least from the check treatments. The correlation between yields of zinc and yields of phosphorus was highly significant for all soils.

Results of these studies suggest that these soils need a well balanced fertilization in order to express their full potential to produce. Highly efficient management practices and adequate fertilization systems would result in a better utilization of the plant nutrients applied.

Only future on-site research can provide definite answers to the micronutrient requirement of these soils. The availability of micronutrient cations is very sensitive to changes in the soil environment. Undoubtedly, steam sterilization of these soils altered their chemistry considerably from that found under natural conditions. The availability of zinc, copper and sometimes manganese was found to be very low in previous work conducted on similar tabuleiro soils, but under natural soils conditions.

In spite of these differences, results of the current study can be applied qualitatively to tabuleiro soils. Micronutrient cation retention or leaching and effectiveness of various materials should be similar under natural conditions. Field trials or experiments with Brazilian crops under controlled conditions, but with non-sterilized soils, must be conducted to determine the quantitative aspects of micronutrient cation fertility problems of the tabuleiro soils. Results from studies reported here should provide considerable insight into the types of experiments now required.

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