ASSESSMENT OF COPPER AND ZINC STATUS OF SOME SOILS OF IRINGA DISTRICT

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ABSTRACT

The objectives of this study were to select suitable extractants for determining available copper and zinc in soils of Iringa district and to assess the fertility status of the two nutrients in the district. Two sets, each of ten soils for one element, were selected for glasshouse studies using maize as a test crop. The soils were treated with 0 and 5 kg ha^{-1} of either copper or zinc in their respective trials. Three extractants, viz: 0.1$\underline{M}$ EDTA-$(NH_4)_2CO_3$, 0.005$\underline{M}$ DTPA and 0.1$\underline{N}$ HCl were tested for their suitability to extract these elements. The concentrations of these elements in maize shoots were also determined. A total of 61 samples were collected from the district and analyzed for copper and zinc using the methods found to be suitable. Copper and zinc application slightly increased dry matter in four and eight soils, respectively, out of the ten soils tested. However, the increase was not statistically significant. The 0.1$\underline{N}$ HCl extractant was superior to the other two in extracting zinc but none of the methods was suitable for copper.

The tentative critical concentration for zinc was found to be 0.28ppm. Application of either of these elements in the soils, significantly increased their concentration in the plants. The tentative critical copper concentration in maize shoots was 6.30ppm.

For zinc, the critical concentration in shoots was not determined because all the values obtained were above critical concentration range reported elsewhere. Using the 0.1N HCl extractant, zinc concentration in the soil ranged from 0.14 to 27.30 ppm. For zinc, two fertility classes: medium and high were obtained. The proportions of soils which fell in the medium and high zinc fertility classes were 8.20 and 91.80%, respectively.

DECLARATION

I, Chaboba Zaid Mkangwa, do hereby declare to the Senate of the Sokoine University of Agriculture that this dissertation is my original work and that it has never been submitted for a degree in any other University.

Signature..............

Chaboba Zaid Mkangwa

Date...16.11.1992....

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DEDICATION

Dedicated to the late Mzee Zaid, my father, whose life-long work always insisted the importance of acquiring higher academic qualification; and to my first born Zaid who was born during the preparation of this dissertation.

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1. INTRODUCTION

Iringa district has for a long time been a very productive area in both maize and tobacco. But since about a decade ago, the production of these two crops has been found to decrease gradually. Their quantities and quality (in case of tobacco) have been generally low despite repeated annual applications of high doses of NPK and small dose of boron. Efforts to rectify the problem by either increasing the fertilizer rate per hectare (ha), or changing the fertilizer grade or both have not been very successful (Farmers, personal communication, 1986).

Many problems were suspected to contribute to this low production. Some of these were: low price offered to the farmers, limited acreage cultivated and poor agronomic practices due to a small number of extension staff in the area (DADO, Iringa, personal communication, 1986). The suspected problems were addressed by increasing the number of extension staff, the price offered to farmers and the number of hectares cultivated. Still, production remained low. Following the unsuccessful response to these efforts, an alternative solution to the problem was thought to be the use of fertilizers, and in this case, micronutrients other than boron. A preliminary study conducted in Iringa district by Semoka *et al* (1981) on this aspect revealed that some soils were deficient in copper or zinc or both. Such soils were found to contain less than 1.00 ppm of either nutrient element (equivalent to less than 2.0 kg/ha). These concentrations have been reported to be inadequate for nutrition of many crops including maize and tobacco (Chapman, 1973). Semoka *et al* (1981) also reported that application of these nutrients to soils in which they were found to be deficient increased the yield and quality of tobacco significantly. However, their study was limited to only a few sites of the District, and therefore their findings can not be applied to the whole district with certainty. According to Akehurst (1965), the District is covered mainly by medium-coarse granitic sands in the north, east and west and sandy loams and loams in the south. Investigations conducted elsewhere indicated that soils with coarse texture are low in both copper and zinc (Brady, 1984). The levels of these nutrients in such soils were found not adequate for the nutrition of citrus and pastures (Lindsay, 1972; Macias, 1973). Although Kamasho (1980) found 0.005M diethylene-triamine-pentaacetic-acid (DTPA) to be a suitable extractant for assessing availability of copper and zinc in soils from Mbeya district, it was still important to test this extractant and others for their suitability in the Iringa district.

In view of the above, this research was undertaken with following objectives:-

(a) To generate more information on copper and zinc status of soils of Iringa district.

(b) To select a suitable extractant(s) for assessing the available fraction of these nutrients and determine their critical concentrations.

(c) To delineate copper and zinc fertility classes in the District.

2. LITERATURE REVIEW

2.1 Historical perspective

The value of both copper and zinc as plant nutrients as well as their toxicity to plants when present in excessive amounts are well documented in the literature (Mengel and Kirby, 1982). The use of these two elements as plant nutrients on field crops dates back to about 1931 (Camp, 1945).

The useful effect of copper on plant growth was noted before 1917 when copper salts were used as fungicides. Floyd (1917), cited by Camp (1945) experimented with dieback of citrus for a number of years and obtained beneficial results by the application of copper sulphate to soil and bordeaux mixture as a foliar spray. He then recommended these treatments for control and cure of the disease. Some years later, Felix (1927) obtained improvement in the growth of plants on several peat soils by the application of copper sulphate either to the soil or in solution to the leaves. Allison, Bryan and Hunter (1927), were able to produce crops on unproductive peat soils of the Florida Everglades by the application of copper sulphate. Bryan (1929), also obtained greening effects in chlorotic leaves of plants grown in peat soils by treating them with solutions of copper sulphate or manganese sulphate.

Beneficial effects of zinc were reported on *Aspergillus spp.* about 1900 (Javillier, 1912). Later this researcher extended his work to green plants and recommended the use of zinc as a fertilizer for maize. Maze (1914), found that zinc was necessary for the growth of maize in solution culture. Sommer and Lipman (1926) and Sommer (1928), confirmed the essentiality of zinc in the nutrition of plants.

2.2 Copper and zinc in soils

2.2.1 Copper

2.2.1.1 Total copper

Soil copper is contained in minerals like chalcopyrite ($CuFeS_2$), bornite ($CuFeS_4$) enargite ($CuAsS_4$), charcociate (Cu_2S) and in oxides such as Cu_2O and CuO (Goldschmidt, 1945).

Total copper in soils ranges from 1 - 3 ppm (where its deficiency occurs) to values of up to 200ppm or more in soils where excessive copper has accumulated from residues of copper-bearing sprays, dusts or any other sources (Fiskel, 1965). Haff (1951) reported total copper of up to 500 ppm in soils that are near copper deposits.

2.2.1.2 Available Copper and soil parent material

Available copper in the soil is closely related to the type of the soil parent material and the extent of its weathering (Pinkerton, 1967; Lal and Biswas, 1973; Nyandat and Ochieng, 1976; Kamasho, 1980). Pinkerton (1967) investigated copper deficiency in Nakuru area, Kenya by examining soils derived from unconsolidated pumice, alluvial deposits, lake deposits, basalt, tranchyte and phonolite. He observed that soils derived from pumice and ash from Mount Mengai were associated with low available copper. Lal and Biswas (1973) found that old alluvial soils formed from alluvium-arenaceous materials had lower copper than less weathered desert soils formed from aeolian deposits of fine sand. They also observed that relatively more weathered gray brown-, red foot-hill-, yellowish brown-, and black-soils derived from various sedimentary alluviums contained high available copper. Nyandat and Ochieng (1976) analyzed 121 soil samples, using ethylene-diamine-tetraacetic-acid (EDTA). They observed that 34 samples had deficient levels of copper. Of these 14 were derived from volcanic ash and pumice, 8 from sand, sandstone or shale, 5 were developed from phonolite and the rest (7) were derived from various other rocks. Similar results on available copper in pumice were reported by Kamasho (1980). He studied the DTPA extractable copper and its distribution pattern in Mbeya district, Tanzania, and found that the pumice layer invariably contained less available copper than the overlaying or the underlaying horizons. Generally, soils derived from certain materials e.g. volcanic ash, pumice, quartz, shale and phonolite contain low levels of available copper.

2.2.1.3 Available copper distribution in the profile

On the distribution of available copper in the profile, some investigators have reported that it decreases with depth, while others have found that it increases with depth. Mehta *et al* (1964) in Gujarat, India, found that available copper in the profile of black cotton soils was high in the top and at 60 cm depth. In Louisiana, Karim, Sedberry and Miller (1976) observed that the majority of the 72 agriculturally important soils they analyzed, had highest available copper in the B horizon. Mayona (1977) analyzed soils from profiles in Tukuyu and Tanga, Tanzania, using 0.1N HCl and observed that available copper increased with depth in the profiles in Tukuyu while in Tanga it decreased with depth except in one site which had high available copper in the plough layer, low in the following horizon and highest in the lowest horizon.

Results from non-coffee growing areas of Kilimanjaro region, Tanzania, showed that there was high EDTA (1%)-extractable copper in the upper horizon, low in the middle and high again in the deeper horizon (Moshi *et al.* 1981). From Mbeya district, Kamasho (1980) reported that DTPA-extractable copper increased with depth in some of the profiles, and in other profiles it increased with depth except in the pumice layer where the amount was much lower than that in the overlain or underlain horizon. He then concluded that copper in the pumice layer had leached down to lower horizon. In contaminated soils, however, available copper is high in the A horizon and decreases sharply with increasing depth in the profile. Such results have been reported by Moshi *et al* (1981) in soils from coffee growing areas of Kilimanjaro region and Magalhaes, Sequeira and Lucas (1985) in soils from vineyards in Portugal. They argued that, its accumulation was associated with prolonged application of copper-containing fungicides as dusts and sprays.

From the above paragraph, it is evident that there is no consistent trend of available copper distribution in the profile. While in some profiles available copper is higher in upper part and lower in the lower part, other profiles have higher levels in both upper and lower parts and low in between.

2.2.1.4 Available copper in relation to organic matter

The availability of copper is also associated with organic matter (OM) content. The availability of copper decreases with increasing OM content. This is because large amounts of copper are retained as highly stable organo-copper complexes which are not immediately available to plants. Retention is highest in peats and mucks where deficiencies of copper are common (Hodgson, Geering and Norvell 1966; Singh, Prasad and Sinha 1986).

The relationship between OM and available copper using 0.1N HCl and chelate has been studied extensively. It appears that the correlation between OM and available copper using 0.1N HCl, EDTA or DTPA as extractants varies considerably from one study to another. Martens (1967), working with Virginia soils reported non significant, positive correlation (r=+0.483) between 0.1N HCl extractable copper and OM. Osiname, Schulte and Corey (1973), in soils of Western Nigeria, also observed that OM was not significantly correlated (r=-0.270) with available copper using 0.1N HCl extractant. In pasture soils of Salamanca, Spain, however, Macias (1973) reported a negative and significant correlation (r= -0.2969) between OM and 0.1N HCl extractable copper. Mayona (1977) reported negative, non significant correlation (r= -0.23) between extractable copper and OM with Tukuyu soils and no correlation (r= +0.01) with Tanga soils. He used 0.1N HCl extractant in both locations.

With chelates, (DTPA and EDTA), Singh, Prasad and Sinha (1986), reported significant correlations between EDTA extractable copper and OM (r= +0.5709), and between DTPA-extractable copper and OM (r= +0.579). They, however, reported a non-significant correlation between 0.1N HCl extractable copper and OM (r = - 0·146)

2.2.1.5 Relationship between copper availability and soil pH

Soil pH is another factor which affects copper availability in soils. According to Lindsay (1972), the solubility of copper in the soil decreases slightly from the acid toward the alkaline pH ranges. Mayona (1977) reported a non significant, negative correlation (r= -0.46) between extractable copper and soil pH for soils of Tukuyu. The soil pH for Tukuyu soils was generally acidic. Similar results were reported by Martens (1967) who obtained a negative correlations (r= -0.258) between extractable copper and soil pH, in acid soils.

Haynes and Swift (1985) studied the effects of liming on the extractability of iron, manganese, zinc and copper. They reported a general decline in 0.1N HCl and 0.005M DTPA-extractable copper with increasing pH. The decrease in extracted copper was from 3.4 to 1.5ppm for HCl and from 2.6 to 1.0ppm for DPTA.

2.2.1.6 Effect of phosphorus on copper availability

High doses of phosphorus fertilizers and/or prolonged use of phosphorus fertilizers have been found to interfere with the supply of soil available copper. Bingham, Martin and Chastain (1958) observed severe copper deficiency in citrus on soils in which 360kgP/ha or more were applied in California. Applications of copper corrected the symptoms and increased the growth of citrus. Bingham and Garber(1960) obtained significant decreases in the concentration of copper in sour orange seedlings as the rate of phosphorus increased from 100 to 900 kg P/ha. Macias (1973), in pasture soils of Spain, reported a negative and significant correlation (r= -0.5116) between soil phosphorus and 0.1N HCl-extractable copper.

2.2.2 Zinc

2.2.2.1 Total Zinc

Zinc is found in the following minerals: sauconite ($ZnSiO_3$), zincite (ZnO), smithsonite ($ZnCO_3$) and in reducing conditions exists as sphalerite (ZnS) (Lindsay, 1972). Total zinc in soils generally lies in the range of 10 - 300ppm (Swaine, 1955); Jensen and Lamm, 1961). The average total zinc of the lithosphere according to Goldschmidt (1945) is approximately 80ppm.

2.2.2.2 Available Zinc

Soil available zinc is usually very low. Available zinc levels ranging from 0.5 to 0.9 ppm are very common especially in cultivated soils (Wear and Sommer, 1948; Sillapaa, 1982). In exceptional cases, as in areas surrounding zinc smelting plants, extractable zinc levels can be as high as 21,660 ppm (Singh and Lag, 1976).

2.2.2.3 Available zinc distribution in the profile

The distribution pattern of available zinc in the profile differs widely. Swaine and Mitchell (1960) using acetic acid (2.5%) and 1N ammonium acetate buffered at pH 7.0 reported that zinc extracted by these extractants decreased sharply with depth in the profile. Similar observations were reported by Alston and McConaghy (1965), Kanehiro and Sherman (1976), John (1974), Udo and Fagbami (1979), Orabi, Meshk and Ismail (1981) and Fagbami, Ajayi and Ali (1985). Alston and McConaghy (1965), cited by Lindsay (1972), reported that EDTA - extractable zinc decreased sharply with depth in the profile. Kanehiro and Sherman (1967) observed that in most of the 19 series of Hawaiian soils, the highest concentration of available zinc was in the surface soils and decreased with the profile depth. John (1974) investigated zinc concentrations in seven alluvial horizons, and reported that available zinc decreased with increasing depth of sampling within a profile. Udo and Fagbbami (1979) analyzed some Nigerian soils using DTPA and 0.1N HCl extractants. They reported that available zinc was highest in surface soils and decreased with depth in the profile. In Egypt, five profiles of alluvial, sandy and calcareous soils were examined for zinc status to depths of one metre by Orabi, Meshk and Ismail (1981). The extractants used were 0.1N HCl and DTPA. They reported that available zinc decreased with depth in all the profiles. Fagbami, Ajayi and Ali (1985) studied the nutrient distribution in profiles of 20 basement complex soils of the tropical, dry rainforest part of southwestern Nigeria using HCl, EDTA and DTPA extractants. They reported that HCl available zinc was highest in the surface horizons and decreased with depth in most of the profiles.

In contrast, studies conducted in Tanga and Tukuyu (Ngaiza, 1977) and Mbeya (Kamasho, 1980) in Tanzania, revealed that there was no specific distribution pattern of available zinc in the profiles studied. Moshi *et al* (1981) analyzed soils from coffee - and non coffee - growing areas of Kilimanjaro region and reported that while available zinc decreased with soil depth in non - coffee growing areas, the pattern was different in soils of coffee growing areas where available zinc was high in the surface and lower horizons and low in the middle horizons.

2.2.2.4 Zinc adsorption in soils

Zinc as Zn^{2+} can be held by exchange sites and adsorbed by various minerals found in the soil. Elgabaly (1943) showed that in minerals with Al^{3+} in octahedral arrangement, Zn^{2+} is fixed, probably in the lattice not occupied by Al ions and in minerals with Mg^{2+} in octahedral positions, Zn^{2+} substitutes for Mg. He also showed that the type of fixation in minerals containing Al^{3+} is accompanied by a decrease in the cation adsorption capacity, and an increase in the anion - adsorption and that the type of fixation in minerals containing Mg^{2+} does not affect the adsorption properties of the mineral. The soil minerals which showed this fixation were Mg - clay, vermiculite and brucite. Elgabaly and Jenny (1943) concluded that some adsorbed Zn^{2+} becomes non - extractable by entering the octahedral layer of montmorillonite. Chatterjee (1974) studied the effect of zinc treatment on adsorption properties of colloidal clays. He reported that a considerable amount of Zn^{2+} remained fixed in soils having montmorillonite as the dominant clay whereas in kaolinite - and/or illite - dominant soils, fixation of Zn^{2+} was very low. Thus, mineralogical composition of soils may be one of the most important factors in determining availability of zinc in soils.

2.2.2.5 Effects of phosphorus on zinc availability

High levels of available soil P have been reported as contributing to zinc deficiency in plants. Burnette *et al* (1936) found that application of superphosphate with zinc fertilizer reduced the effectiveness of zinc. In Utah, USA Thornes and Wann (1950) found that high levels of CO_2 soluble P were often associated with zinc deficiency on fruit trees. On sour orange seedlings, at Riverside, California Bingham and Garber (1960) reported that excess P resulted in acute zinc deficiency.

El-Kherbrawy and Sunders (1984) studied the effect of P status of a clay loam on zinc concentration in soil fraction and in clover. They reported that zinc concentration in the soil fraction was not affected by soil P status but zinc concentration in clover shoots was significantly lower when plants were grown on soils of high P status. Verma and Kachroo (1984) reported that increasing soil levels of P and zinc increased their concentration and uptake by plants, but more that 50ppm P had antagonistic effect on zinc nutrition. Meuser and Sidle (1985) reported that zinc levels were highest and P levels were lowers in the roots and stems of soyabeans grown in solution of highest P application and that P and zinc uptake was significantly inhibited in the leaves, stems and roots of plants grown at the highest zinc rate. Singh, Karamanos and Steward (1986) reported that applied P increased soil P levels and tissue P concentration, but resulted in a significant decrease in tissue - zinc. From the above observations, it can be noted that excess P interferes with metabolic functions (uptake, translocation or utilization) of zinc at certain sites within plant cells.

2.2.2.6 Zinc in relation to organic matter

It appears that OM can interact with zinc in two ways: First, soluble zinc can be mineralized and made available to plants. Second, zinc can be bound into organic constituents that are immobile in soils and constitute a fixation mechanism by which zinc is not readily released.

The presence of soluble zinc - organic complexes in soils was demonstrated by Hodsgson, Geering and Norvell (1965) and Hodgson, Lindsay and Trierweiller (1966). They concluded that on average about 60% of soluble zinc in soils is complexed. The degree of complexing of zinc was correlated with OM (r = 0.88). Stevenson and Ardakani (1972) reported that insoluble zinc complexes are most likely bound to the humic fraction, particularly humic acids, while soluble zinc complexes are mainly found in amino acids.

Follett and Lindsay (1970) showed a high correlation (r = 0.76) between OM content and DTPA extractable zinc. Osiname, Schulte and Corey (1973) reported a positive and significant correlation between OM and 0.1N HCl (0.382) and DTPA (0.4430) available zinc. Similar results were reported by Kanwar and Tripathi (1984) and Fagbami, Ajayi and Ali (1985). In Himachal Pradesh, India Kanwar and Tripathi (1984) analyzed zinc in soils using DTPA, and reported that DTPA available zinc was positively and significantly correlated with OM (r = + 0.457). Fagbami, Ajayi and Ali (1985) worked with the basement complex soils of the tropical, dry rainforest of southwest

Nigeria. They reported a positive and significant correlation between OM and available zinc using HCl (+ 0.767), EDTA (+ 0.783) and DTPA (+ 0.893) -extractants.

2.2.2.7 Relationship between zinc availability and soil pH

Soil pH is another factor which affects zinc availability, for its solubility in soils decreases with increase in soil pH. McBride and Blasiak (1979) worked on zinc solubility as a function of pH in soils, and reported that zinc solubility was reduced 30 fold for every unit pH increase, in the pH range of 5 - 7. Hayness and Swift (1985) evaluated the effects of liming on available zinc. They observed a general decline in 0.1N HCl-, 0.005M DTPA- and 0.04M EDTA-available zinc with increasing pH. Singh and Abrol (1985) reported that zinc solubility at pH higher than 7.9 was controlled by precipitation as $Zn(OH)_2$ and $Zn(CO_3)$.

El-Kherbrawy and Sunders (1984) examined the effect of pH of a clay loam on zinc concentration in soil fractions. They observed that soils with low pH had high available zinc. Haynes and Swift (1985) reported that concentration of zinc extracted by 0.1N HCl, 0.005M DTPA (pH7.3) and 0.04M EDTA (pH 6.0) were raised as the pH was lowered from 6.0 to 3.8. Joshi, Dhri and Gupta (1983) studied the influence of soil parameters of DTPA-extractable zinc in acid soils of Rajasthan, India. They reported that DTPA- available zinc was negatively correlated (r - 0.354) with pH in fine textured soils. Similarly, in Sub-Himalayan hill and forest soils, Sakal *et al* (1984) observed that available zinc extracted by four extractants tested were negatively correlated with soil pH. The correlation coefficients were -0.613, -0.124 and -0.412 for DTPA-$CaCl_2$ (pH 7.3)-, DTPA-NH_4HCO_3 (pH 7.6)-, EDTA-NH_4OAc (pH 7.0)- and EDTA $(NH_4)_2$ CO_3 (pH 8.6)- available zinc, respectively. These findings suggest that the sensitivity of zinc to soil pH is responsible for the observed zinc deficiency in crops upon liming acid soils.

2.3 Extractants used for assessing available copper and zinc in soils

Many extractants have been tested for their ability to extract available fractions of copper and zinc in soils. These include water and neutral salts (Stewart and Berger, 1965), acids, particularly 0.1N HCl (Hibbard, 1940; Jamison, 1942; Wear and Sommer, 1948; Cheng and Bray, 1953), and several chelating agents especially EDTA and DTPA (Viro, 1955; Jensen and Lamm, 1961). Of these, 0.1N HCl, EDTA and DTPA have been tested extensively, and the following review will concentrate on them.

2.3.1 Assessment of available copper

2.3.1.1 Dilute HCl extractant

In efforts to find suitable methods for extracting copper from the soil, dilute HCl was used to leach copper from Florida sandy soils by Jamison (1942). He evaluated the copper content leached by three chemicals, viz: 1N HCl, BaCl-HCl and NaCl-HCl. Cheng and Bray (1953) modified the method; instead of leaching they shook the soil with two extractants namely 0.1N HCl and versenate (1%). In addition they reported that the 0.1N HCl was simple and straight forward and seemed well adapted to the routine determination of available copper in the soil testing laboratory. Since then, 0.1N HCl has been widely tested for the extraction of copper from soils.

Several workers have compared the extracting ability of 0.1N HCl with other extractants, for the established extractant in one location can not be used with certainty elsewhere. Neelkantan and Mehta (1961) evaluated seven extractants for assessing the available copper in soils of Kaira district of India. The extractants tested included neutral NH_4OAc, 0.1NHCl, 0.5N NHO_3, 0.05M EDTA, 1N HCl, Morgans Universal solution and 1NHNO_3. A non - significant correlation (r = 0.217) between 0.1N HCl- available copper and copper uptake by sorghum plants was observed. NH_4OAc- extractable copper gave the highest and significant correlation coefficient (r = 0.8517).

Similar results on performance of 0.1N HCl-available copper have been reported by many workers. Martens (1967) working with 16 soil series from Virginia, reported that there was no correlation between 0.1N HCl- extractable copper and copper uptake (r = 0.55) by oat. Rai, Dighe and Pal (1972) determined the available copper in deep black cotton soils of Madhya Pradesh, using four extractants, namely neutral NH_4OAc, NH_4OAc (pH 4.8) 0.02M EDTA and 0.1N HCl. They reported that there was no correlation between wheat copper concentration or uptake with copper extracted by these reagents. The correlation coefficients for 0.1N HCl- available copper and plant copper concentration and uptake were 0.270 and 0.377, respectively.

In Mbeya district, Kamasho (1980) evaluated the extracting ability of 0.1N HCl, 0.05M EDTA and 0.005M DTPA using wheat as a test crop, and reported the least and non significant R^2 (0.28) value with respect to 0.1N HCl extractable copper and dry matter. In Bangladesh, Singh Prasad and Sinha (1986) evaluated five extractants, among which was 0.1NHCl. They reported that 0.1N HCl extractable copper had the least and non significant correlation coefficients in relation to copper concentration in wheat ($r = 0.109$), copper uptake ($r = 0.170$), relative yield ($r = 0.282$) and percentage copper in plants ($r = 0.072$).

From the available information, it can be concluded that extractable copper using 0.1N HCl is not significantly correlated with copper concentration in plants, copper uptake, relative yield or dry matter. These findings suggest that among many extractants tested on diverse soils, 0.1N HCl is not a suitable extractant for assessing the available fraction of copper in soils.

2.3.1.2 EDTA extractant

The need for a reliable measure of the available fraction of soil copper led to the development of the EDTA (pH 5.0) method by Cheng and Bray (1953). These workers showed that copper extracted by this method was closely related to that extracted by 0.1N HCl. Later, Viro (1955) compared 0.05M EDTA at pH 5.0 with 0.05M EDTA at pH 7.0 and 0.05M EDTA at pH 9.0. He reported that the copper extracted by 0.05M EDTA at pH 5.0 was much smaller than that extracted by 0.05M EDTA at pH 7.0 and that extracted by 0.05M EDTA at pH 9.0 was the highest.

Turkey and Kurtz (1955) extracted copper in 14 acid soils from Illinois and showed a highly significant correlation between various extractants including 0.007M EDTA buffered at pH 7.0 with NH_4OAc. Similar results with EDTA were reported by other researchers. Ranadive, Naik and Das (1964) showed a significant correlation between 0.02M EDTA- extractable copper with bioassay (r = 0.8584). Kamasho (1980) used 0.05M EDTA and found significant R^2_n value with respect to drymatter yield of wheat (o.41) and grain yield (0.68). He also found the critical concentration for 0.05M EDTA extractable copper to be 1.0 ppm below which copper deficiency in wheat was expected. In English soils, Tills and Alloway (1983) examined twenty topsoils from agricultural land of normal to low copper content covering a range of pH values, textural classes and organic matter contents. They used eight different extractants (including EDTA at pH 7.0) and reported a positive and significant correlation coefficient (0.8681) between EDTA-extractable copper and wheat copper uptake.

Using EDTA extractant, Nyandat and Ochieng (1976) in Kenya, reported that soils with extractable copper lower than 1.5 ppm were copper deficient. In Iringa district, Semoka *et al* (1981) reported that 0.05M EDTA extractable copper values of less than 1.0ppm were associated with low crop yields. Singh, Prasad and Sinha (1986) used EDTA-$(NH_4)CO_3$ at pH 8.6 to determine available copper in calcareous soils. They found EDTA-$(NH_4)_2CO_3$ extractable copper to be well correlated with plant uptake ($r = 0.859$), copper concentration in plants ($r = 0.859$) and relative yield ($r = 0.763$). The critical deficiency level using this extractant was 0.82 ppm.

In some cases, EDTA has been reported to be a poor extractant for copper giving non significant or negative correlations with plant parameters. Neelkantan and Mehta (1961) evaluated seven extractants including 0.05M EDTA for measuring available copper. They reported that there was no correlation between 0.05M EDTA-extractable copper and copper uptake by sorghum plants. Simmilar results were reported by Rai, Dighe and Pal (1972) for wheat. With the exeption of few cases cited, EDTA has prooved to be a good extractant, by providing more reproducible results in the determination of plant available copper in soils. Also, from the above literature, the critical concentration of EDTA- available copper deficiency is expected ranges between 0.8 - 1.0ppm.

2.3.1.3 DTPA extractant

DTPA as an extractant for micronutrients was developed in Colorado by Lindsay and Norvell (1969). They used it for the extraction of copper, zinc, iron and manganese and managed to separate 77 Colorado soils into zinc-deficient and non-deficient categories. Since then the method has been tested by many workers. Haq and Miller (1972) reported that DTPA was not a suitable extractant for copper for soils of Ontario, Canada using maize as a test crop. Contrary to the above findings, Proskovec (1976), cited by Lindsay and Norvell (1978) reported a significant correlation between 0.005*M* DTPA- extractable copper and plant copper uptake. He also reported a soil critical concentration of 0.20 ppm. However, this critical concentration was not certain because there was no response to copper fertilization on ten of the soils having less than 0.20 ppm DTPA available copper when maize and oats were tested in the green house. Kamasho (1980), after evaluating DTPA, EDTA and HCl, reported that 0.005*M* DTPA was the most suitable extractant for assessing copper availability in the soils of Mbeya district, because it yielded significant R^2_n values with respect to dry matter (0.91) and grain yield (0.71) of wheat. He reported a critical concentration of 0.70 ppm DTPA- available copper. Singh, Prasad and Sinha (1986) found that four out of six extractants tested were more promising for the predication of critical level and response of barley grown in pots to copper application on young alluvial soils of Bihar, India. The critical levels of available copper using 0.005*M* DTPA $CaCl_2$, EDTA-$(NH_4)_2CO_3$ (pH 8.6), NH_4-oxalate and $Mg(NO_3)_2$ (pH

5.9) were 0.65, 0.82, 0.73 and 0.53ppm, respectively. 0.005M DTPA was more promising than the other extractants tested since it gave the highest significant correlation coefficients with respect to copper concentration in plants (r = 0.981), copper uptake (r = 0.872), relative yield (r = 0.827) and percent copper uptake (r = 0.819).

From the surveyed literature, the DTPA extractant is likely to be a good extractant because it has given consistent results for the determination of plant available copper in a number of diverse soil types. The critical concentration for this extractant seems to be between 0.60 - 0.70ppm.

2.3.2 Assessment of available zinc

2.3.2.1 Dilute HCl extractant

Dilute HCl, particularly at the concentration of 0.1N has been widely tested in the extraction of micronutrients. Initially a concentration of 1N HCl was used (Hibbard, 1940), but this was modified to 0.1N HCl (Wear and Sommer, 1948). Later, Tucker and Kurtz (1955) reported that there was a good correlation (r values not given) between 0.1N HCl- extractable zinc and zinc deficiencies found in the field. Boawn, Viets and Crawford (1957) used 0.1N HCl and neutral NH_4OAc to extract added zinc fertilizers and reported that the former extracted twice as much zinc as the later extractant.

Contrary to the above findings, Steward and Berger (1965) reported that 1N HCl was not a very suitable extractant, especially when compared with other extractants, because they obtained a better correlation between 2N $MgCl_2$- extractable zinc and plant uptake (r = 0.93) than 0.1N HCl extractable zinc and plant uptake (r = 0.73). Similar results on performance of the 0.1N HCl extractant on available zinc have been reported by Wear and Evans (1968), Kamasho (1980), Sakal *et al* (1984), Nzabhayanga and Mnkeni (1989) and Singh *et al*.(1986). Wear and Evans (1968) planted maize in a growth chamber and assessed the extracting ability of three extractants of which 0.1N HCl was included. They reported lower but significant correlation coefficient (r = 0.82) between plant uptake and 0.1N HCl-extractable zinc. Kamasho (1980) observed that 0.1N HCl was not a very suitable extractant for soils of Mbeya district because although it was associated with a significant R^2_n value of 0.42 with dry matter yield of wheat, the relationship with grain yield was non significant (0.06). Sakal *et al* (1984), working with rice and 25 soils of Sub-Himalayan hill and Forest region in India, obtained a negative, non significant correlation coefficient (r = - 0.192) between 0.1N HCl-extractable zinc and plant uptake. In soils of Morogoro district, Nzabhayanga and Mnkeni (1989) obtained a lower correlation coefficient between double acid (0.1N HCl + 0.025N H_2SO_4) extractable zinc and maize dry matter yield (r = 0.98). They reported a critical concentration of 3.3ppm for 0.1N HCl as opposed to 1-2ppm reported by Kanehiro and Sherman (1967) using same extractant in Hawaiian soil profiles.

2.3.2.2 EDTA extractant

The EDTA extractant has been used for the extraction of zinc at various concentrations. In India, Ranadive, Naik and Das (1984) analyzed zinc in 24 surface soil samples by using seven extractants. They found that 0.02M EDTA extracted the highest quantity while others (eg. water and neutral NH_4OAc) extracted very small quantities of available zinc. Wear and Evans (1968) observed a significant but lower correlation coefficient (0.62) between 0.05M EDTA (pH 7.0)-extractable zinc and maize uptake as compared to an r value obtained by the double acid method (0.89). Similar observations were recorded by Kamasho (1980), and Nzabhayanga and Mnkeni (1989). Kamasho (1980) reported that 0.05M EDTA was not a very suitable extractant for the extraction of available zinc from soils of Mbeya district because it was associated with a non significant R^2_n value of 0.18 with respect to grain yield of wheat. Nzabhayanga and Mnkeni (1989) compared the extracting ability of four extractants including EDTA and reported that EDTA was relatively inferior because it yielded a non significant correction coefficient (0.74) with respect to dry matter yield of maize.

Contrary to the above finding, Sakal *et al* (1984) reported that EDTA-$(NH_4)_2CO_3$ was the most efficient extractant by having a highly significant R^2_n value of 0.824 with respect to dry matter yield of rice. A similar observation was reported by Mehrotra (1986). He compared three extractants namely: EDTA-$(NH_4)_2CO_3$ (pH.8.6), 0.1N HCl and DTPA (pH 7.3) and observed a positive and highly significant correlation coefficients between EDTA-$(NH_4)_2CO_3$(pH 8.6)-extractable zinc and dry matter yield (r=0.919) and zinc tissue concentration (0.685) of maize.

In the development of EDTA-$(NH_4)_2CO_3$ method for the determination of zinc, Trierweiler and Lindsay (1969) compared it with dithizone and 0.1N HCl using maize as the test crop. The correlation coefficients (all significant) between zinc uptake and the soil test values obtained were 0.87, 0.89 and 0.80 for EDTA-$(NH_4)_2CO_3$, dithizone and 0.1N HCl extractants, respectively. However, based on response to zinc fertilization, Trierweiler and Lindsay (1969) felt that EDTA-$NH_4)_2CO_3$ was a more suitable extractant.They also obtained a soil critical level of 1.40ppm zinc using EDTA - $(NH_4)_2CO_3$ -extractant. Alley *et al* (1972) in Virginia using maize as the test corp, reported a soil critical concentration of 0.80ppm for EDTA-$(NH_4)_2CO_3$-extractable zinc.

In Tanzania, EDTA has been used by several researchers (Adam 1977; Semoka *et al* 1981; Moshi *et al* 1981) for the extraction of zinc. Adam (1977) used 0.05M EDTA in six soil samples from Mbeya region and reported that they contained 4.4 to 14.1ppm extractable zinc. Semoka *et al* 1981 found that most of the soils they tested from Iringa district had less than 1ppm EDTA-extractable zinc. In coffee and non coffee growing areas of Kilimanjaro region, Moshi *et al* (1981) reported that there was high amount of EDTA (1%)-extractable zinc in upper horizons on both areas.

From the aforegoing observations, it can be inferred that the EDTA extractant seems to be among the best extractants for the estimation of the available zinc fraction from soils because there were only a few cases which reported it as inferior or a completely unsuitable extractant. The soil critical level for EDTA-extractable zinc below which zinc deficiency is expected using maize as a test crop ranges between 0.80 - 1.40ppm.

2.3.2.3 DTPA extractant

The use of DTPA as an extractant for assessing the availability of zinc, iron, manganese and copper in soils was reported by Lindsay and Norvell (1969). The extractant consisted of 0.005M DTPA, 0.01M $CaCl_2$ and 0.1M triethanolamine (TEA) buffere at pH 7.3. Using this extractant they managed to separate 77 Colorado soils into zinc deficient and non deficient categories. In California, Brown, James and Eddings (1971) examined 92 soils for extractable zinc and tested each soil in the greenhouse of plant response to zinc fertilization. They found the critical level of DTPA-extractable zinc to be 0.5ppm and that the DTPA extractant was 83% effective in identifying soils on which response to zinc fertilization was obtained. The DTPA extractant was more successful than dithizone, EDTA or dilute HCl. Lauer (1971), cited by Lindsay (1972), labelled 30 soils with ^{65}Zn and subjected them to alternate wetting, drying and mixing cycles for approximately one month. Maize was grown on these soils, and zinc was extracted using various extractants. The mean labile zinc as determined by zinc removed by the maize plants, the DTPA and 0.1N HCl extractants was 4.6, 4.3 and 7.7ppm, respectively. The labile zinc values reflected by the maize plants and DTPA were almost identical and highly correlated ($r=0.98$).

The larger labile value for 0.1N HCl (mean value of 7.7ppm) suggested that 0.1N HCl was extracting zinc that was not available to plants and not extracted by DTPA. A significant correlation between DTPA-extractable zinc and plant zinc uptake was also reported by Haq and Miller (1972). They used four extractants on 85 soils to predict available zinc, copper and manganese. For zinc, the correlation coefficient relating maize plant zinc to DTPA-extractable zinc was 0.602, and when pH was included in the regression equation the correlation coefficient increased to 0.759. Their finding suggests that when DTPA is used to measure available zinc in soil below pH 7.0, inclusion of pH in the regression equation may improve its suitability. This is because zinc solubility in soil is strongly pH-dependent (Lindsay and Neorvell, 1969). In Isri, India, Singh and Takker (1981) evaluated the efficiency of soil test methods for zinc and their critical values in salt affected areas for rice. They reported that the DTPA method correlated highly with zinc uptake (0.72) and the soil critical level was 0.80ppm. In Mbeya district, using wheat as the test crop, Kamasho (1980) obtained significant R^2 values between DTPA extractable zinc with dry matter yield (0.63) and with grain yield (0.31).

In some cases DTPA was not a suitable extractant for estimating soil available zinc fraction. Sedberry, Miller and Said (1979) reported that there was no significant correlation between DTPA - $(NH_4)_2CO_3$ - extractable zinc and zinc concentration in maize (r = 0.332), zinc uptake (r = 0.388) and dry matter yield (r= 0.326). Similarly, for Morogoro soils, DTPA has been reported to be a relatively inferior extractant when compared with the double acid (HCl + H_2SO_4) method (Nzabhayanga and Mnkeni, 1989). These workers reported that DTPA extractable zinc gave significant but slightly lower correlation coefficient (r = 0.78) than double acid (r=0.93) with dry matter yield. They obtained a soil critical concentration of 0.85ppm DTPA-extractable zinc . The DTPA extractant may not provide a reliable measure of zinc availability in soils with pH values higher than 7.0 (Sedberry, Miller and Said 1970; Sakal *et al* 1985).

In view of the above observations, it can be pointed out that, DTPA is a promising extractant for most soils tested, except in a few cases where it has been reported to be relatively inferior to other extractants.

2.4 Response to copper and zinc fertilization

2.4.1 Crop response to copper

Crop response to copper application, has been tested for many crops; some of which responded while others did not. Lucas (1948) studied the growth of various crops on muck soils and their response to copper application. He reported that the yield of 13 crops out of 16 increased due to copper application at a rate of 112kg copper sulphate/ha. Bridger, Salutsky and Starostka. (1962) reported on $Cu(NH_4)PO_4H_2O$ as a source of copper for foliar and soil applications for sorghum, turnips, radishes and snap beans. According to their results this compound appeared to be an effective source of copper with both methods of application. Berger (1965) cited by Murphy and Walsh (1972), investigated the copper requirements and responses of crops in Wisconsin and reported yield increase of oats, red beets, carrots, cabbage, potatoes, field and sweet corn, and onions from applications of 28kg copper oxide/ha.

Copper deficiencies in crops in Scotland have been investigated by Reith (1968). He noted corrections of copper deficiencies in spring - seeded oats by soil applications of 11 to 12kg copper sulphate/ha. Barnes and Cox (1973) in North Carolina, reported that a rate of 2.8kg copper/ha from either complexed or sulphate sources increased significantly the yield of wheat and soyabeans. Makarim and Cox (1983) working with maize, wheat and soyabeans, reported that there were yield increase due to copper application at three out of seven sites with wheat and two out of five sites with soyabeans. Maize did not respond in all the sites tested.

Kruger, Karamanos and Singh (1985) conducted a number of field trials on several soils belonging to classes 2 (<0.2ppm) and 3 (0.2 - 0.4ppm) using the DTPA extractant and wheat as the test crop. They reported that in six of the eight experiments carried out in soils of class 2 there was an increase in grain yield of up to 50% and in soils of class 3, there was no increase in yield as a result of copper fertilization.

In Mbeya district, copper deficiency in wheat and barley has been observed as far back as 1973. At Mbimba Experimental Station, root malformation was observed in wheat especially where copper was not applied and on soils with 1.50 - 2.00ppm DTPA extractable copper. Application of copper together with N and P enabled wheat and barley to head and to produce yield (Nilsson 1973). Round potatoes also responded to copper application at Uyole Agricultural Centre (UAC) and at Mbimba Experimental Station (Jakobsen 1976; Kamasho and Ley 1976). Also, Kamasho (1980), reported that application of copper at 5kg/ha increased both dry matter and grain yield of wheat substantially in Mbeya district. In Iringa district, Akehurst and Sreedharn (1966), fertilized flue-cured tobacco with copper and obtained a slight response in two out of the three seasons tested. They concluded that copper was not a limiting nutrient in soils of Iringa.

Semoka *et al.* (1981), working with soils of Iringa district, observed that there was a significant response on flue-cured tobacco when copper was applied to soils testing less than 1.00ppm-EDTA-extractable copper. A summary showing crops that are high, medium and low in copper response was given by Murphy and Walsh (1972).

They reported that the high copper responsive crops include wheat, spinach, onions, oats, lettuce and carrots while the medium copper responsive ones are barley, cabbage, maize and sweet corn, and the low copper responsive crops are beans, peas, potatoes and soyabeans.

2.4.2 Crop response to zinc

Long term trials in Iringa district by Akehurst and Sreedharn (1986), indicated a slight response to zinc fertilization on tobacco in one out of the three seasons tested. They concluded that zinc was not deficient in the soils of Iringa district. Semoka *et al.* (1981), reported that there was a significant increase in yield of flue-cured tobacco when zinc was applied to soils of Iringa district containing less than 1.00ppm EDTA-extractable zinc.

At the Uyole Agricultural Centre (UAC) there was no response of wheat, lucerne and maize to zinc applied at the rate of 10kg/ha (UAC Annual report, 1974). However, at Mbimba Experimental Station, Kamasho and Ley (1976), obtained a response to zinc fertilization on round potatoes when large amounts of copper were applied.

Nzabhayanga and Mnkeni (1989) observed that only two out of eight soils from Morogoro district responded to zinc fertilization with maize as the test crop. The soils which responded to zinc application contained less than 2.8ppm double acid extractable zinc.

Reports from elsewhere indicate that field crops may or may not respond to zinc fertilization. In India, Kanwar (1962), reported that there was 15% yield increase on potatoes due to zinc application. Dry matter yield of maize was significantly increased by application of zinc (Singh and Steenberg, 1974). Singh (1986) fertilized 17 zinc-deficient soils (containing <0.54 DTPA extractable zinc) with zinc fertilizer and obtained marked response of cluster beans in all the soils. The percent mean response at 10kg zinc/ha was 70%. Raju, Reddy and Reddy (1985), evaluated rice response to zinc, phosphate and potash application alone and in combination. The grain yield data revealed that all elements tested, positively increased yield both alone and in combination.

Contrary to the above results, Safaya and Malakondaiah (1981), reported that none of the tested plants (wheat and barley) showed any serious disorder even when the DTPA-extractable zinc in the soil was as low as 0.28ppm.

In Virginia and Dakota, Hilton and Zubriski (1985) reported that there was no response to zinc fertilization by maize and sunflower even when the extractable zinc was below 0.50ppm DTPA-$(NH_4)_2CO_3$-extractable zinc.

In soils of Saskatchewan, Canada, Singh, Karamanos and Stewart, (1987), obtained a significant response to zinc in only one trial out of 23 trials using wheat, barley, peas, alfalfa and maize as test crops.

The above observations indicate that the susceptibility of crop plants to zinc deficiency varies considerably depending on species and even variety. According to Viets, Boawn and Crawford (1954), cereals such as oats, barley, wheat and rye are rather insensitive to zinc. Other crops such as potatoes, tomatoes, and lucerne are only moderately sensitive whilst maize and field beans are highly susceptible to zinc deficiency.

2.5 Copper and zinc in plants

2.5.1 Copper in plants

Optimum copper contents in plants differ with plant species, plant parts, stage of maturity and soil conditions, but generally they are in the range of 5-25ppm. In citrus leaves, the adequate copper range has been reported as 5 to 16ppm (Jones and Smith 1964; Reuther and Smith 1953). The optimum copper content in flue-cured tobacco ranges between 14.9 -21.1ppm (Tso, 1972) whereas for wheat plants it ranges between 2.8 - 9.8ppm (Makarim and Cox, 1983) as compared to ranges of 3.7 - 8.6ppm reported by Kamasho (1980), and for maize in the earleaf at silking stage it is in the range of 3-15ppm (Jones, 1970).

Rodgers (1975) analyzed the copper content of some range grass from Selous Game Reserve-South East Tanzania. He reported that *Londetia spp* had 2.6 - 6.2ppm when the leaves were dry and 8.1 - 11.6ppm when the leaves were green, and *Andropogon spp* had 2.8 - 8.2ppm when the leaves were green. The copper levels observed were adequate for the nutrition of range animals.

Differences in the concentration of copper varies from one plant part to another. Jones (1972) reported that the copper content of mature soyabean plants were 7 and 13ppm for stems and leaves, respectively. For oats Mathur, Hamilton and Preston (1979), reported the mean copper concentration in roots, straw and grain to be 80.95, 6.84 and 5.46ppm, respectively. A similar trend was observed in roots and tops of silver bean by Merry, Tiller and Alston (1985). The copper concentration in the tops was 91ppm while in the roots it was 205ppm.

The stage of maturity or age has some implications on copper content of a plant grown on the same soil conditions. Jones (1972) noted that at ten days after emergence of soyabean the copper concentration in leaves was 12ppm, this increased to 15ppm at pod formation and then decreased to 13ppm at maturity. Sekhon, Arora and Soni (1975), reported copper concentration of wheat plants at initial tillering to be 6-62ppm and while at heading it was 1-60ppm. In rice, Haque *et al.* (1979) reported copper concentration values of 5.50ppm and 3.30ppm at 30 and 60 days after transplanting, respectively.

Since copper requirements differ from plant to plant, critical levels also differ considerably. Karim and Vlamis (1962) reported the critical level for copper in mature rice plants to be 6ppm. Jones and Eck (1973) reported the critical levels of copper in maize as 5ppm. Other critical levels reported are 10ppm for soyabeans (Small and Ohlrogge, 1973), 4ppm for wheat (Makarim and Cox, 1983) and 6.75ppm for barley (Singh, Prasad and Sinha 1986).

2.5.2 Zinc in plants

The usual levels of zinc in plants range from 10-100ppm for most field crops and pastures (Chapman, 1973). Zinc content is generally highest in very young seedlings and decreases with age (Carrol and Loneragan, 1968). The concentration of zinc varies from one plant or one plant part to another. According to Karlson (1952), optimum zinc content for most pasture plants range between 14-18ppm zinc. Optimum growth for tobacco was recorded when leaf zinc content was 51-84ppm (Tso, 1972). Maize grew optimally when the earleaf zinc content was in the range of 20-70ppm (Barber and Olsen, 1968), and for maize at 32 days the range was between 54.5 - 73.2ppm (Ragab, 1980).

Differences in Zinc concentration between crops are exhibited even under excessive zinc fertilization. Boawan and Rasmussen (1971) reported zinc concentrations of various field crops after the application of 100ppm zinc in a growth chamber as follows: field maize 205ppm, sweet corn 255ppm, barley 220ppm, wheat 185ppm, field beans 66ppm, snap beans 46ppm, alfalfa 71ppm, clover 81ppm, pea 132ppm, alaska pea 104ppm, lettuce 96ppm, spinach 338ppm, potato 67ppm, sugar beat 162ppm and tomato 150ppm.

Age of the plant has some impact on zinc concentration even from the same soil conditions. Sekhon, Arora and Soni (1975) reported that, the concentration in wheat plants was 7-210ppm at initial tillering while at heading it was between 2-27ppm. Jones (1972) working with soyabeans reported that zinc concentration of the stem decreased from 38ppm at 10 days after emergence to 19ppm at maturity.

Some plants seem to have greater ability than others to accumulate zinc from the same soil nutrient solution. Mascianica and Baker (1979) reported that when the soil was supplied with 50ppm ZnEDTA, the zinc content of radish shoots ranges from 178 to 249ppm while the root content ranged from 123 to 184ppm. Using rice as the test crop and soils treated with 75kg zinc sulphate/ha, Singh and Singh (1976) reported that zinc concentrations in the roots, leaf sheaths and leaf blades were 90.0, 63.6, 68.2ppm, respectively.

Due to differences in zinc requirements between plant species, the critical levels also differ considerably. Using maize as the test crop Coffman and Miller (1973) reported that at 30 days after emergence the critical level of zinc in maize above which no further significant increase in dry matter yield occurred was 12ppm.

The critical zinc concentrations in leaves of 12 to 18ppm (Sauchelli, 1969, 20ppm (Jones, 1972) and 15ppm (Delas and Dartiques, 1970) have been quoted for maize. Andrew, Johnson and Haydoch (1981), worked with 8 tropical and subtropical pastures and legumes which were grown in pots. The tentative critical zinc levels observed were 20, 34, 22, 22, 24, 19, 17 and 16ppm for *Centrosema pubescens, Stylosanthes humilias, Lotononis bainessi, Neonotania wightii, Macroptilium atropurpureum, Desmodium nitortum, Vigna senensia* and *Medicago sativa,* respectively.

From the literature surveyed, it can be pointed out that crops differ in their sensitivity to zinc supply or in zinc requirements. Some crops including maize and wheat require more zinc while others like tobacco require less.

3. MATERIALS AND METHODS

3.1 General description of the study area

3.1.1 Location

Iringa District is in the southern highlands of Tanzania and lies between 7^0 -$8^0$6'S and $34^0$2'-37^0E, with an area of approximately 38,870 km^2 (Akehurst,1965). The neighbouring regions are Dodoma in the north, Morogoro in the east, Singida in the north-west and Mbeya in the west. To the south it is bordered by Mufindi District.

3.1.2 Altitude and topography

The district is approximately 160 m above sea level (m.a.s.l.), however considerable variations in altitude and climate exist. To the south west, the altitude rises fairly rapidly to 1800 m.a.s.l. continuing to over 2100 m.a.s.l. in the south. In the northern part the altitude starts at 700 m and rises to 1250 m.a.s.l. in the west (Akehurst,1965). General, the district is characterized by either undulating or rolling hills with slopes ranging between 2 and 16 % with a few flat or almost flat areas where much of the agriculture is concentrated.

3.1.3 Soils

Geologically, the rocks in the district belong to the Dodoma system and the basement complex (FAO-UNESCO,1974). The Dodoma system consists of coarsely metamorphosed rocks and associated magmatites and granites. The basement complex is composed of quartzite crystalline limestone, amphibolite and hornblende as well as intrusive. The soils have been classified by FAO - UNESCO (1974), with the equivalent soil classes in the soil Taxonomy System given in the brackets as Chromic Cambisols (Inceptisols) around the district headquarters, Eustic Nitosols (Alfisols) in the south, Planosols (Aridisols) in the north west and Humic Gleysols (Ultisols) in the north.

The soils studied were from the plough layer and therefore no profile description was made. The soils are deep and well drained especially those which are suitable for tobacco production (Akehurst,1981).

3.1.4 Vegetation and Land use

The natural vegetation in most parts of the district is miombo bush forest changing to rainforest in the south part. The dominant tree species are *Brachystegia spiciformis, Pterocarpus angolensis, Dalbergia melanoxylon, Jubenalia spp and Terminalia spp* of varying density (Akehurst,1965). With the exception of large parts of the western part of the district where Ruaha National Park is located, little virgin land exists and the cultivated land tends to be overcropped. The main crops gown are tobacco (*Nicotiana tabacum L.*), maize (*Zea mays L.*), rice (*Oryza sativa L.*) and *Citrus spp.* The most common natural grass species in the district are *Themeda spp* and *Andropogon spp.*

3.1.5 Climate

The ten years (1976-1985) mean annual rainfall at the Iringa Airport Meteorological Station, 25 km north of the Iringa township is 675 mm with a variation of between 450 mm and 700 mm. The rainfall distribution is unimodal and with negligible exceptions, all the rain falls between November and May. But over the period quoted the respective means for November and May were only 29 mm and 14 mm, respectively. There are thus 5 month of fairly reliable rainfall and 7 month of drought. Temperatures are relatively low. The mean maximum temperature shows a consistent annual pattern falling from 32^0C in November to 24.5^0C in april. The mean annual minimum temperature is 14.5^0C with the absolute minimum of slightly lower than 10^0C occurring in July.

3.2 Soil sampling

3.2.1 Sampling for preliminary information and glasshouse study

Prior to sampling, the historical background of the sites were collected on how long the land has been in use,the performance of tobacco/maize on such land following fertilizer application and types and rates of fertilizers used. The information enabled division of the area (wherever applicable) into areas cultivated: For over ten years, those cultivated for less than five years and those that have not been cultivated.

Twenty one sites were selected and representative soil samples were collected from all the sites. A representative sample was composed of 15 subsamples taken in a zigzag pattern to a depth of 15 cm from an area of about a hectare. These subsamples were thoroughly mixed. Enough sample was collected from each site for laboratory analyses and glasshouse studies. The sites selected are shown in Figure 1.

3.2.2 Sampling for survey of copper and zinc status

After screening for the best extractant (section 4.2), 40 soil samples were collected from most parts of the district, excluding the locations sampled for preliminary information, National parks and locations considered not suitable for agriculture (Figure 1).

3.3 Analysis of the soils

The soil samples collected (Section 3.2.1 and 3.2.2.) were air-dried and ground to pass through a 2.00mm mesh steel screen prior to analysis.

3.3.1 Routine analyses

3.3.1.1 Soil pH

The soil pH was obtained using 1:2.5 soil-water and soil-0.1 M calcium chloride mixture. Ten gramme soil sample was taken and to it 25 ml of water were added. The mixture was shaken for 30 minutes on a reciprocating shaker and the pH read using a pH meter. The same was done when 0.1 M calcium chloride was used.

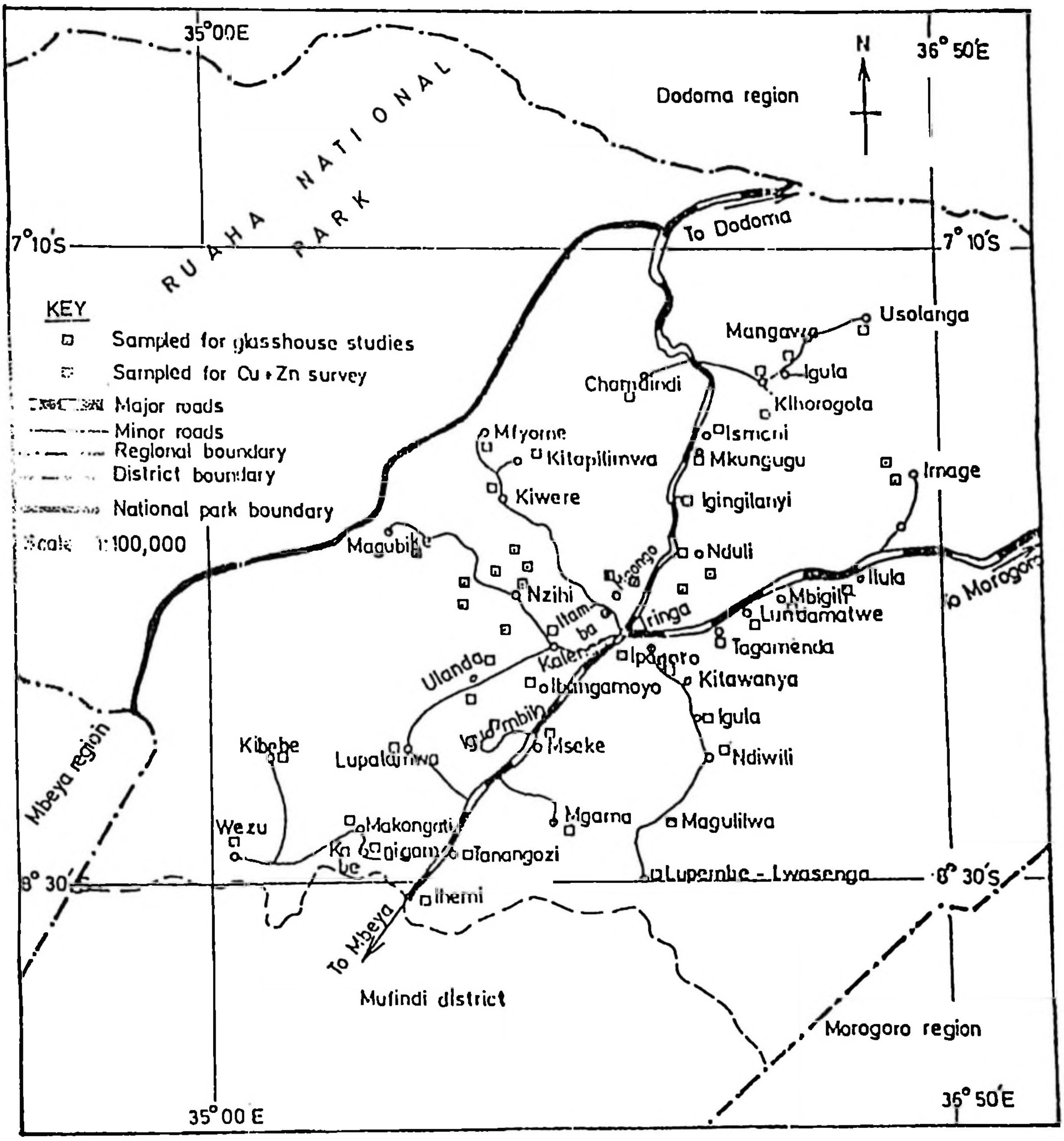

Figure 1. Sampled sites, Iringa district (Tanzania)

3.3.1.2 Available phosphorus

Available phosphorus was extracted with NH_4F + 0.025N HCl as described by Bray and Kurtz (1945). Phosphorus in the extract was determined colourimetrically at 882 mµ wavelength after developing blue colour with ascorbic acid as described by Murphy and Rikey (1962). A standard curve was made in order to get the amount of phosphorus in the aliquot.

3.3.1.3 Organic carbon

Organic carbon was determined by the wet digestion method of Walkley-Black (Allison, 1965). Norman $K_2Cr_2O_7$ and concentrated H_2SO_4 were used to oxidise the organic carbon. The amount of the dichromate reduced was a measure of organic carbon content in the soil after multiplying it with 1.33 as a recovery factor.

3.3.1.4 Total nitrogen

Total nitrogen was determined by the macro-Kjeldahl digestion-distillation method (Bremner, 1965). One gramme of soil sample was digested with concentrated H_2SO_4 in the presence of a catalyst (K_2SO_4) $CuSO_4$ and selenium powder in the ratio of 10:10:1 by weight). The digest was distilled after the addition of NaOH (40%) solution. The liberated ammonia was received in a 4% boric acid-mixed indicator solution which was subsequently titrated with standard HCl. The titre was used to calculate total nitrogen in the sample.

3.3.1.5 Cation exchange capacity (CEC) and exchangeable bases

The CEC was determined by the ammonium saturation method (Chapman, 1965). The soil was saturated with neutral normal NH_4 OAc and filtered; the filtrate was saved for the estimation of exchangeable bases (K, Na, Ca and Mg). The free NH_4OAc entrapped in the soil was washed out with methyl alcohol. The NH_4-saturated soil was equilibrated with KCI (4%) solution and filtered. The amount of NH_4-N in the filtrate was determined and used to compute the CEC. The amounts of K, Na, Ca and Mg in the NH_4OAc- filtrate were determined using atomic absorption spectrophotometry (A.A.S).

3.3.1.6 Particle size analysis

The particle size analysis of the soil was performed by the hydrometer method as described by Allison (1965).

3.3.2 Determination of available copper and zinc in soils

Three extractant were tested in the analysis of copper and zinc of the soil. These were 0.005<u>M</u> DTPA (pH 7.3), 0.01 <u>M</u> EDTA-$(NH_4)_2CO_3$ (pH 8.6) and 0.1<u>N</u> HCl. In order to reduce contamination, all glassware used for copper and zinc analysis were thoroughly rinsed in 6<u>N</u> HCl and distilled water prior to analysis. In each case duplicate samples and a blank were employed in order to increase accuracy.

3.3.2.1 0.005M DTPA (pH 7.3) available copper and zinc

The method used is as described by Lindsay and Norvell (1969). The method consists of shaking 10g soil with 20ml extract for two hours on a reciprocating shaker at 120 revolutions per minute (r.p.m.), filtering the suspension through Whatman no.42 filter paper and determining copper and zinc by A.A.S. at wavelengths of 324.8 and 213.9 mm for copper and zinc, respectively.

3.3.2.2 0.01 M EDTA -$(NH_4)_2CO_3$ (pH 8.6) available copper and zinc

The method used was developed by Trierweiller and Lindsay (1969). In this 20 ml of the extractant were added to 10 g soil, shaken for 30 minutes at 125 r.p.m. and filtered using Whatman no.42 filter paper. Copper and zinc were determined in the filtrate by A.A.S. The results from this analysis (Appendix 2) were used to select 10 soils from the 21 soils for glasshouse studies.

3.3.2.3 0.1N HCl - available copper and zinc

The method used was first employed by Fiskel (1965). The procedure required shaking 10 g of soil with 50 ml 0.1N HCl for one hour at 120 r.p.m. The mixture was then filtered through Whatman no.42 filter paper and analysed for copper and zinc by A.A.S.

3.4 Glasshouse experiment

Two pot experiment, one for each element were conduct in the glasshouse. A randomized block design with four replication was used for each element and two levels of 0 and 5 kg/ha for either copper or zinc were tested. To avoid the deficiency of nutrients other than copper and zinc, applications of nitrogen, phosphorus,potassium, manganese, and boron, also zinc to the copper experiment and copper to the zinc experiment were made. Reagent grade chemicals were used in all cases. Nitrogen, phosphorus, potassium, boron, copper and zinc were applied as ammonium nitrate, calcium phosphate, potassium sulphate, borax, copper sulphate and zinc sulphate in amounts equivalent to 80, 40, 50, 2.5, 2, 5 and 5 kg/ha, respectively. The rates were calculated on a weight basis by assuming the weight of a plough layer of 1 ha to be 2 million kg. The nutrients were added prior to planting to 5 kg air-dried soil sieved through 2 mm mesh screen, mixed thoroughly by hand and placed in plastic pots with a capacity of five litre. Soils were brought to approximately field capacity with distilled water, and therefore five maize (*Zea mays L.* var.Ilonga composite) seeds were planted in each pot. Watering was done using distilled water whenever required to ensure that the plants did not experience any serious moisture stress throughout the growth period. Seven days after germination, the seedlings were thinned to two plants per pot. Additional nitrogen was applied two weeks after germination at a rate equivalent to 40 kg/ha.

3.5 Plant sampling, sample preparation and analysis

The plants were harvested five weeks after germination by cutting the shoots close to the soil surface. The shoots were cleaned (using water which contained soap, followed by distilled water) of any adhering soil particles,placed in clean envelopes, dried at 70^{0}C and weighed to get weight of dry matter.

The samples were then chopped by a pair of scissors into small pieces (about 1 cm), ground to pass through 40 mesh sieve and stored in polythene bags ready for analysis of copper and zinc.

Copper and zinc in plant material was analysed using dry - ashing method as described by Chapman and Pratt (1961). One gramme of the ground plant material in the crucible was ashed in the muffle furnace at 450 - 500^{0}C for five hours. To the ash 1$\underline{N}$ HNO_3 was added and boiled to dryness on a hot plates.

The residue was then dissolved in 10 ml of 1$\underline{N}$ HCl, filtered using Whatman no.42 filter paper, washed by three portions of 10 ml 0.1$\underline{N}$ HCl and made to the volume of 50 ml using 0.1$\underline{N}$ HCl. Copper and zinc were measured from this solution by A.A.S.

3.6 Data analysis and interpretation

The dry matter yield from the glasshouse experiment and the soil-test values were used to evaluate the suitability of the extractant for assessing available fraction of copper and zinc in the soils. Evaluation was based on the degree of correlation between soil - test values due to an extractant and percentage yields as calculated according to the discontinuous linear regression model of Cate and Nelson (1971) and Nelson and Anderson

(1973). The percentage yields was calculated as:

$$\text{Percentage Yield} = \frac{\text{Yield at 0-level of nutrient being studied; other factors at adequate but not excessive level}}{\text{Yield where all factors are at adequate but not excessive levels.}} \times 100$$

Using the soil-test value due to the extractant and corresponding yield data, a series of coefficient of determination (R^2) were calculated as shown in Appendix 4. The soil - test value corresponding to the maximum R^2 (R^2_m) for each extractant was taken as the critical value. The extractant leading to the highest and significant R^2_m value was considered the most suitable method for the soils of Iringa District.

Limits for soil fertility classes, were identified using the soil critical concentration and the percentage yield data. The soil-test values corresponding to percentage yields of 75 to 90 % were rated as indicating medium fertility class while those giving percentage yields above 90 % were considered to indicate high fertility class (Cope and Rouse, 1973).

4. RESULTS AND DISCUSSION

4.1 Some propeties of the soils used in the glasshouse

4.1.1 Soil pH

Soil pH data as determined in water and in calcium chloride are presented in Table 1. The pH values ranged from 5.1 to 6.6 and 4.2 to 5.8 for water and calcium chloride, respectively. Using water, there were six soils with pH values below 6.0 and eight soils with pH values of 6.0 or more. The pH range obtained is almost similar to that obtained by Akehurst and Sreedharn (1966) and Semoka *et al.* (1981) in some soils of Iringa district. Akehurst and Sreendharn (1966) obtained the pH range of 5.1 to 6.6, where as Semoka *et al.* (1981) reported the pH range of 5.5. to 6.6. This soil pH range is optimum for crop production.

4.1.2 Organic carbon

The organic carbon of the soils tested ranged from 0.49 to 2.29%, with an average of 0.82%. The amounts of OM in these soils were rather low especially when compared with the data reported by Birch and Friend (1956) for some soils of East Africa which averaged 1.77%. Prolonged cultivation on the same piece of land and repeated burning of crop residues may account for the low organic carbon observed in the soils of Iringa district.

4.1.3 Total nitrogen

The data for total nitrogen of the 14 soils used in the glasshouse study are presented in Table 1. The total nitrogen content ranged from 0.015% for soils of Nzihi E to 0.070% for soils of Nzihi D. The average total nitrogen which is not adequate for plant growth was 0.04%. The average total nitrogen was slightly higher than that 0.03% reported by Semoka *et al.* (1981) for some soils of Iringa district.

4.1.4 Available phosphorus

The available soil phosphorus in the 14 soils used in the glasshouse study ranged from 8.2 to 150.7ppm with an average of 63.67ppm. Most soils contained more than 50.00ppm phosphorus (Table 1). If compared to the critical level fo 10-15ppm for susceptible crops like maize (Mengel and Kirkby, 1982), the soils tested contain adequate levels of available phosphorus. The available phosphorus in some soils of Iringa district has increased considerably, especially when compared to the ranges of 6 - 54ppm and 8.8 - 77.2ppm reported by Akehurst and Sreedharn (1966) and Semoka *et al.* (1981), respectively. Repeated annual application of high doses of NPK may account for high available phosphorus in these soils.

Table 1: Some properties of the soils used in glasshoused studies

Soil	pH(1:2.5)		O. C. (%)	Total N (%)	Available P (ppm)	Exchangeable bases(me/100g)				C.E.C. (me/100g)	Particle size analysis (%)		
	H_2O	$CaCl_2$				Ca	Mg	K	Na		Clay	Silt	Sand
Nzihi A	5.60	4.90	0.51	0.056	91.2	0.68	0.25	0.64	0.51	2.5	8.5	1.5	90.0
Nzihi B	5.50	4.70	0.72	0.032	150.7	0.53	0.24	0.92	0.42	3.0	11.0	4.0	85.0
Nzihi C	6.40	5.60	0.70	0.056	8.4	2.31	1.94	0.59	0.47	6.0	13.5	5.5	81.0
Nzihi D	6.30	5.40	1.33	0.070	57.7	8.16	1.25	1.68	2.31	13.5	28.5	6.5	65.0
Nzihi E	5.60	4.70	0.49	0.015	123.3	0.51	0.24	0.44	0.33	2.5	9.0	3.5	87.5
Nzihi F	5.50	4.60	0.57	0.035	76.6	0.32	0.59	0.44	0.33	2.5	9.0	1.0	90.0
Nduli A	6.60	5.80	1.10	0.058	77.2	4.23	0.59	1.19	2.51	9.5	13.5	16.5	70.0
Nduli B	5.80	4.50	0.67	0.032	30.4	0.53	0.59	0.54	1.87	4.5	11.0	4.0	85.0
Nculi E	5.10	4.20	0.62	0.027	41.2	0.56	0.59	1.04	1.27	4.8	16.5	3.5	80.0
Itamba A	6.30	5.60	2.29	0.060	21.1	0.70	1.50	0.94	2.69	9.0	14.5	16.0	70.5
Image A	6.30	5.30	0.66	0.032	8.4	1.29	0.53	0.59	1.65	4.5	13.5	1.5	85.0
Image B	6.40	5.50	0.57	0.031	46.6	1.72	0.79	0.95	1.29	5.0	11.0	4.0	85.0
Mgongo	6.40	5.20	0.69	0.032	84.2	0.62	1.01	0.74	0.75	3.5	8.5	1.5	90.0
Magubike	6.00	5.10	0.54	0.036	74.0	0.32	0.77	0.94	1.56	5.2	11.5	6.0	82.5

4.1.5 Exchangeable calcium

The exchangeable calcium (Table 1) varied from 0.51 to 8.16me/100g with an average of 1.90me/100g. Abruna, Chandler and Pearson (1970) in Puerto Rico, reported that 0.4 me exchangeable calcium/100g were inadequate for tobbaco nutrition. Chapman (1973) reported that soils with pH 5.0 or lower are likely to be deficient in calcium. Since the soils studied had exchangeable calcium value greater than 0.4me/100g and pH values above 5.0, it can be speculated that the soils contain adequate levels of exchangeable calcium.

4.1.6 Exchangeable magnesium

The data on exchangeable magnesium are presented in Table 1. The exchangeable magnesium ranges from 0.24 to 3.94 me/100g, with an average of 0.78me/100g. Embleton (1973) reported that soils having 0.5 - 1.0me/100g are magnesium - deficient. Some soils studied especially those from Nzihi contain less than 0.5me/100g and are therefore deficient in magnesium.

4.1.7 Exchangeable potassium

The exchangeable potassium data is given in Table 1. It ranged from 0.44 - 1.68me/100g, with an average of 0.83me/100g. Doll and Lucas (1973) reported a critical concentration of potassium of 0.217 me/100g for sands and loamy sands for most field crops. Thus, the soils studied contain adequate potassium levels. In some soils of Iringa district, Akehurst and Sreedharn (1966) and Semoka *et al.* (1981) reported potassium ranges of 0.04 - 0.50 and 0.09 -

0.28me/100g, respectively.

4.1.8 Exchangeable sodium

Table 1 gives the data for exchangeable sodium, which ranged from 0.33 to 2.69 with an average value of 1.28me/100g. These levesl are not expected to interfere with the nutrition of most crops.

4.1.9 CEC

The CEC of the soils tested ranged from 2.50 to 13.50me/100g with an average of 5.43e/100g. This range is a typical CEC range of sands and loamy sands.

4.1.10 Particle size analysis

The soils used slightly varied in clay, silt and sand fractions. The clay, silt and sand fractions ranged from 8.5 to 28.5, 1.5 to 16.5 and 70.5 to 90.0%, respectively (Table 1). The texture of the soils varied from sandy clay loam to loamy sand.

4.2 Selection of suitable extractant(s) for available copper and zinc

4.2.1 Relative effeciency of extractants for available copper and zinc

4.2.1.1 Available copper

Ten soils used in the glasshouse study were extracted for available copper by three extractants, namely, 0.1N HCl, 0.01M EDTA

$(NH_4)_2CO_3$ (pH 8.6) and 0.005M DTPA (pH 7.3). The results are given in Table 2. The amounts of copper extracted ranged from 0.57 to 1.92ppm for 0.1N HCl, 0.12 to 2.33ppm for 0.01M EDTA -$(NH_4)_2CO_3$ and 0.005M DTPA, respectively. Thus on average, 0.005M DTPA extracted more copper followed by 0.01M EDTA -$(NH_4)_2CO_3$ while 0.1N HCl extracted the least. Similar trends on the amount of copper extracted by these extractants have been reported by other workers. Neelkantan and Mehta (1961) working with some soils of Kaira district, India, reported that the average values of 0.05M EDTA-and 0.1N HCl-extractable copper were 8.25 and 4.96ppm, respectively. Rai, Dighe and Pal (1972) worked with black cotton soils of Madhya Pradesh, India, using wheat as the test crop. They obtained average values of 1.50 and 8.03ppm for 0.1N HCl- and 0.02M EDTA-extractable copper.

Using alluvial soils, Singh, Prasad and Sinha (1986) reported that the average extractable copper values for 0.1N HCl, 0.005M DTPA and 0.01M EDTA extractants were 0.61, 1.10 and 1.57ppm, respectively. The probable reason for the higher amounts of available copper extracted by chelates was due to their ability to react with metal ions in solution. These metal ions form soluble complexes which decreased the activity of the free metal ions in solution. This reaction cause labile solid phases to release more metal ions into the solution (Lindsay, 1972).

Table 2: Available copper as determined by 0.1N HCl, 0.01M EDTA-(NH4)$_2$CO$_3$ and 0.005M DTPA in soils used in glasshouse studies.

Location	Soil available copper (ppm)		
	0.1N HCl	0.01M EDTA-$(NH_4)_2CO_3$	0.005M DTPA
Nzihi A	0.57	0.12	0.21
Nduli A	0.67	0.96	1.28
Nzihi F	0.67	0.69	0.40
Nzihi D	0.75	2.33	3.50
Nduli B	0.75	0.69	0.59
Nzihi E	1.11	0.89	0.89
Image A	1.11	1.02	0.98
Magubike	1.11	1.02	0.39
Itamba A	1.29	1.40	2.15
Nzihi C	1.92	1.84	2.05
Range:	0.57-1.92	0.12-2.3	0.21-3.50
Mean copper extracted:	0.99	1.10	1.29

Contrary to the above observations, Kamasho (1980) reported that 0.1N HCl extracted more copper than 0.05M EDTA and DTPA. He reported average copper values of 9.43, 1.25 and 0.74ppm for 0.1N HCl, 0.05M EDTA and DTPA extractants, respectively. According to Martens (1967), this was probably due to the ability of HCl to extract some organic-bound copper which is usually not available to plants. The average organic carbon in soils of Iringa is 0.82% (Table 1) and lower than the 3.44% for soils of Mbeya district reported by Kamasho (1980). From such observations it appears that available copper from the soils of Iringa district is extracted chiefly from adsorbed Cu^{2+} and various copper complexes and smaller quantities from OM which is very low.

Soils of Iringa district contained relatively lower available copper when compared to soils of other areas. In Virginia, Martens (1967) reported that the average 0.1N HCl-extractable copper was 1.29 ppm. Macias (1972) in Spain, reported that the mean copper concentration was 3.20ppm for the 0.1N HCl extractant. Thus, soils of Iringa district appear to be inherently low in copper content. In addition, continuous cultivation and the coarse texture of the soil may have agravated the problem.

4.2.1.2 Available zinc

The amounts of zinc extracted from the ten soils used in the glasshouse study by the three extractants are given in Table 3. The results indicate that the ranges of extractable zinc were 0.14-1.19, 0.33-2.32 and 0.24-2.15ppm, for 0.1N HCl, 0.01M EDTA-$(NH_4)CO_3$ and 0.005M DTPA, respectively. The average values obtained by these estractants were 0.58ppm for 0.1N HCl, 0.88ppm for 0.01M EDTA-$(NH_4)_2CO_3$ and 0.67ppm for 0.005M DTPA. On average the relative efficiencies of the three extractants were in the order: 0.01M EDTA-$(NH_4)_2CO_3$ > 0.005M DTPA > 0.1N HCl. Similar observations were reported by Osiname, Schulte and Corey. (1973). They reported that the mean extractable zinc using 0.01M EDTA and 0.1N HCl extractants were 4.5 and 4.0ppm, respectively. The possible explaination is provided by Lindsay (1972), that chelating agents combine with free Zn^{2+} according to the reaction: $Zn^{2+} + L^{n} \rightleftharpoons ZnL^{(n-2)-}$ where L represents the chelating ligands and n the negative charge of free ligand. During the reaction, chelating zinc accumulates in solution as the chalting agent combines with Zn^{2+} , causing more Zn^{2+} to be released from the labile solid pool.

However, the observations made in this study are contrary to studies reported by Kamasho (1980) and Nzabhayanga and Mnkeni (1989). Kamasho (1980) reported that 0.1N HCl extracted more zinc followed by 0.05M EDTA while DTPA was the least. The mean available zinc values were 61.1, 12.53 and 3.81ppm for 0.1N HCl, 0.05M EDTA and DTPA extractants, respectively. The mean organic carbon in these soils was 3.44%. In Morogoro, Nzabhayanga and Mnkeni (1989) reported that the mean zinc contents in soils studied were 1.25, 3.98 and 4.26ppm for DTPA, EDTA and 0.1N HCl extractants, respectively. The average OM content of these soils was 1.19%. The

Table 3: Available zinc as determined by 0.1N HCl, 0.01M EDTA-$(NH_4)_2CO_3$ and 0.005M DTPA in soils used in the glasshouse studies.

Location	Soil available zinc (ppm)		
	0.1N HCl	0.01M EDTA-$(NH_4)_2CO_3$	0.005M DTPA
Mgongo	0.14	0.33	2.15
Image A	0.28	1.73	0.32
Nzihi E	0.28	0.43	0.64
Nzihi A	0.28	0.40	0.32
Nzihi B	0.35	0.49	0.48
Nzihi C	0.49	1.29	0.24
Itamba A	0.56	2.32	0.48
Magubike	0.56	0.63	0.56
Image B	0.91	0.60	0.80
Nduli A	1.91	0.62	0.72
Range:	0.14-1.91	0.33-2.32	0.32-2.15
Mean:	0.58	0.88	0.67

relatively higher values obtained with acidic extractants compared to the chelating agents were due to the ability of acids to acidify the soil and in this way may cause the soil to release organically bound zinc during extraction (Lindsay and Norvell, 1978), whereas chelates keep the pH close to that of the soil. Since soils of Iringa are low in OM it is likely that available zinc is mainly from Zn^{2+} ions adsorbed on minerals and various zinc complexes which can easily combine with the chelates, and small quantities from soil organic matter. This might account for relatively higher zinc values extracted by the chelates than 0.1N HCl in the soils of Iringa district.

The mean available zinc of soils of Iringa district is relatively low compared to the values from other areas. Kanehiro and Sherman (1967) obtained an average of 4.5ppm available zinc using 0.1N HCl as extractant.

Macias (1973) using 0.1N HCl in some soils of Salamanca, Spain, obtained and average of 5.70ppm extractable zinc. In Morogoro, Nzabhayanga and Mnkeni (1989) observed that the mean available zinc extracted by 0.1N HCl, DTPA and EDTA were 4.26, 1.25 and 3.98ppm, respectively.

4.2.2 Maize response to copper and zinc fertilization

4.2.2.1 Glasshouse observations

Visual observations made at the end of second and third weeks after emergence revealled that in all control treatments, there were no deficiency symptoms of either copper or zinc.

In mild copper deficiency, the edges of the upper maize leaf turn brown, dried and become highly coloured. In the advanced stage it causes yellowing between leaf veins. The youngest leaves turn yellow, particularly at the base, curl and twist at the tip. (IITA,1982).

Zinc deficiency shows up very clearly in maize, and it is used as an index plant for zinc deficiency (Viets, Boawn and Crawford, 1954). Under mild zinc deficiency, the base of the upper leaves become whitish yellow white stripes on their blades. Frequently, the lower leaves turn purple and die (IITA, 1982).

However, mild tip burns on the older leaves were observed on some controls. In some plants the older leaves and the lower parts of the stems were dark red or purple probably resulting from an accummulation of xanthocyanin in these parts. The soils which produced mild tip burns on the older leaves were from Mgongo, Nduli A, Nduli B, Nzihi A, Nzihi B, Nzihi C and Nzihi D for the zinc trial, and Nzihi B for the copper trial. The dark red or purple colourations which disappeared during the fourth week were observed on soils from Mgongo, Nzihi B, Nzihi C, Nzihi D, Nzihi E, Image A and Image B. Mild tip burns on older leaves were probably due to senescence.

4.2.2.2 Dry matter and percentage yields of maize in the copper trial

Table 4 gives the effect of copper application on dry matter and percentage yields of maize. The dry matter yield ranged from 8.26 to 12.48g in controls and drom 9.53 to 12.48g in copper-treated soils. The dry matter yield increased by 3.6 to 17% in only four soils. In the remaining six soils dry matter yield was depressed by 2.5 to 21.0% by application of copper. The percentage yield ranged from 85.5 to 125.3% suggesting that there was little response to copper fertilization and therefore no copper problem in the soils of Iringa district. As indicated in section 4.2.3.1., the amount of copper extracted by chemical methods does not correpond to the dry matter yield of maize.

Low or no response to copper application has been reported by Akehurst and Sreedharn (1966) and Semoka *et al.* (1981) in Iringa and elsewhere by Makarim and Cox (1983) and Kruger, Karamanos and Singh (1985). Using tobacco as a test crop Akehurst and Sreedharn (1966) reported that it was not necessary to apply copper on soils of Iringa district. Semoka *et al.* (1981) reported significant response on some locations, when tobacco was fertilized with copper on soils with less than 1.00ppm EDTA extractable copper and little

Table 4: Effect of copper fertilization on dry matter and percentage yields of maize for some soils of Iringa district.

Soil	Copper rate (kg/ha) 0	5	Crop Response (%)	Percentage yield (%)
	Dry matter yield (g/pot)			
Nzihi A	11.21	12.30	9.72	91.01
Nduli A	12.45	9.83	-21.04	126.7
Nzihi F	8.26	9.66	16.95	85.50
Nzihi D	12.48	9.96	-20.19	125.3
Nduli B	11.15	9.53	-14.52	117.0
Nzihi E	9.96	9.40	-5.62	106.0
Image A	11.38	11.00	-3.34	103.5
Magubike	10.26	10.00	-2.53	102.6
Itamba A	12.05	12.48	3.57	93.85
Nzihi C	11.00	11.8	7.36	93.14

response on soils with more than 1.00ppm. Makarim and Cox (1983) noted that maize did not respond to copper application in soils with DTPA-extractable copper which ranged from 0.21 to 0.95ppm. In soils of Saskatchewan, Canada, Kruger, Karamanos and Singh (1985) reported that there was no increase in yield of wheat as a result of copper fertilization in soils with copper concentration which ranged from 0.2-0.4ppm DTPA-extractable copper.

4.2.2.3 Dry matter and percentage yields of maize in the zinc trial

Table 5 presents the data on dry matter and percentage yields of maize as a result of zinc fertilization. The dry matter yields for control and zinc-treated soils ranged from 8.61g to 14.43g and from 9.01 to 14.84g, respectively. The percentage response to zinc fertilization ranged from -6.00 to 21.20%. With the exception of Nduli A and Nzihi B, the other eight sites responded positively to zinc fertilization. The percentage yield ranged from 82.5 to 106.4%.

These results are similar to those reported by Semoka *et al* . (1981) who found that application of zinc fertilizer to soils of Iringa significantly increased tobacco yield. These responsive soils contained less than 1.00ppm EDTA-extractable zinc. In Norway, dry matter yield of maize was significantly increased by application of zinc on a soil with 0.90ppm 0.2N HCl-extractable zinc (Singh and Steenberg, 1974). Singh (1986) fertilized 17 soils which had less

Table 5: Effect of zinc fertilization on dry matter and percentage yields of maize for some soils of Iringa district.

Soil	Zinc rata (kg/ha) 0	Zinc rata (kg/ha) 5	Crop Response (%)	Percentage Yield (%)
	Dry matter yield (g/pot)			
Mgongo	12.10	13.80	14.05	87.7
Image A	12.24	14.84	21.24	82.5
Nzihi E	8.80	9.35	6.25	94.1
Nzihi A	8.61	9.01	4.65	95.6
Nzihi B	10.11	10.02	-0.89	100.9
Nzihi C	9.94	10.25	3.12	97.0
Itamba A	10.58	11.38	7.56	93.5
Magubike	10.80	11.55	6.94	93.5
Image B	8.96	10.29	14.84	87.1
Nduli A	14.43	13.56	-6.03	106.4

than 0.54ppm DTPA-exchangeable zinc with zinc fertilizer. He reported that in all 17 soils, cluster bean responded to zinc application and the mean response was 70% at 10kg Zn/ha.

Lack of response to zinc fertilization as found in some sites in this study has been reported by many workers as well, in Iringa and elsewhere. Akehurst and Sreedharn (1966) did not get response to zinc fertilization with tobacco in Iringa district. Safaya and Malakondaiah (1981) reported that barley and wheat did not show deficiency symptoms even when the zinc level was lower than 0.28ppm DTPA-extractable zinc. In Virginia and Dakota, Hilton and Zubriski (1985) reported that there was no response to zinc fertilization by maize and sunflower even when the extractable zinc was lower than the soil critical level of 0.50ppm, 0.005M DTPA-extractable zinc adopted from Saskatchewan soil testing laboratory.

Unlike copper, some soils of Iringa district contain marginal levels of zinc, and as such addition of zinc to such soils significantly increased dry matter yield of maize.

4.2.3 Critical levels of copper and zinc in soils and suitability of extractants tested

4.2.3.1 Copper

The graphical method and the discontinuous linear regression model of Cate and Nelson (1965; 1971) and Nelson and Anderson (1973) were used to estimate the critical levels of copper in soils and to find the most suitable extractant(s). For the discontinuous linear regression model, a series of R^2 values were computed for each extractant using soil test values (Table 2) and percentage yield data (Table 4) and presented in Appendices 4.1, 4.2 and 4.3.

Figures 2 and 3 give scatter diagrams of R^2 plots for extractants that gave slightly high R^2_n values, ie. 0.01M EDTA-$(NH_4)_2CO_3$ and 0.005M DTPA. Table 6 gives the R^2_n values for the three extractants tested as 0.16, 0.35 and 0.35 for 0.1N HCl, 0.01M EDTA-$(NH_4)_2CO_3$ and 0.005M DTPA, respectively. None of the R^2_n values were significant, suggesting that none of the extractants tested extracted copper which was related to plant growth. This observation was also reflected by the lack of response to copper fertilization by maize plants in these soils (Section 4.2.2.2.), none significant R^2_R (0.095) between dry matter and copper concentration in plant tissue (Section 4.3.1). and lack of correlation between tissue copper concentration and 0.1N HCl-, 0.01M EDTA-$(NH_4)_2CO_3$ and 0.005M DTPA-extractable copper (Section 4.3.1.).

The unsuitability of the three extractants tested to estimate the available fraction of copper from the soil has been reported by other workers as well. In Mbeya district Tanzania, Kamasho (1980) reported a non significant maximum coefficient of determination (R^2_n = 0.28) value with respect to 0.1N HCl-extractable copper and dry matter yield of wheat. In India, Singh Prasad and Sinha (1986) reported non significant correlation coefficients with respect to 0.01M EDTA-$(NH_4)_2CO_3$, 0.005M DTPA and 0.1N HCl-extractable copper and

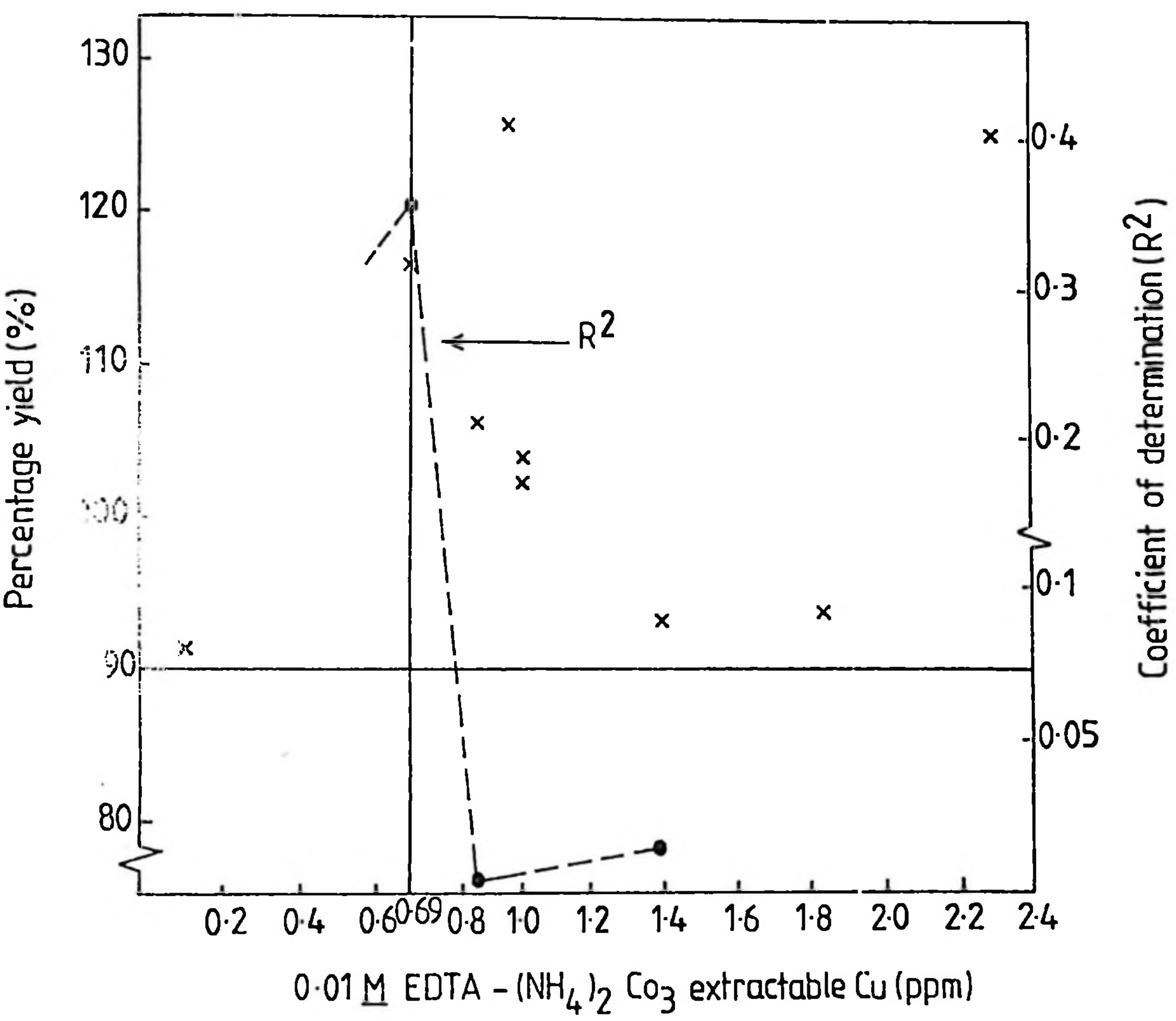

Figure 2 . Scatter diagram and R^2- plot showing relationship between 0·01 M EDTA - $(NH_4)_2CO_3$ extractable Cu and percentage yield

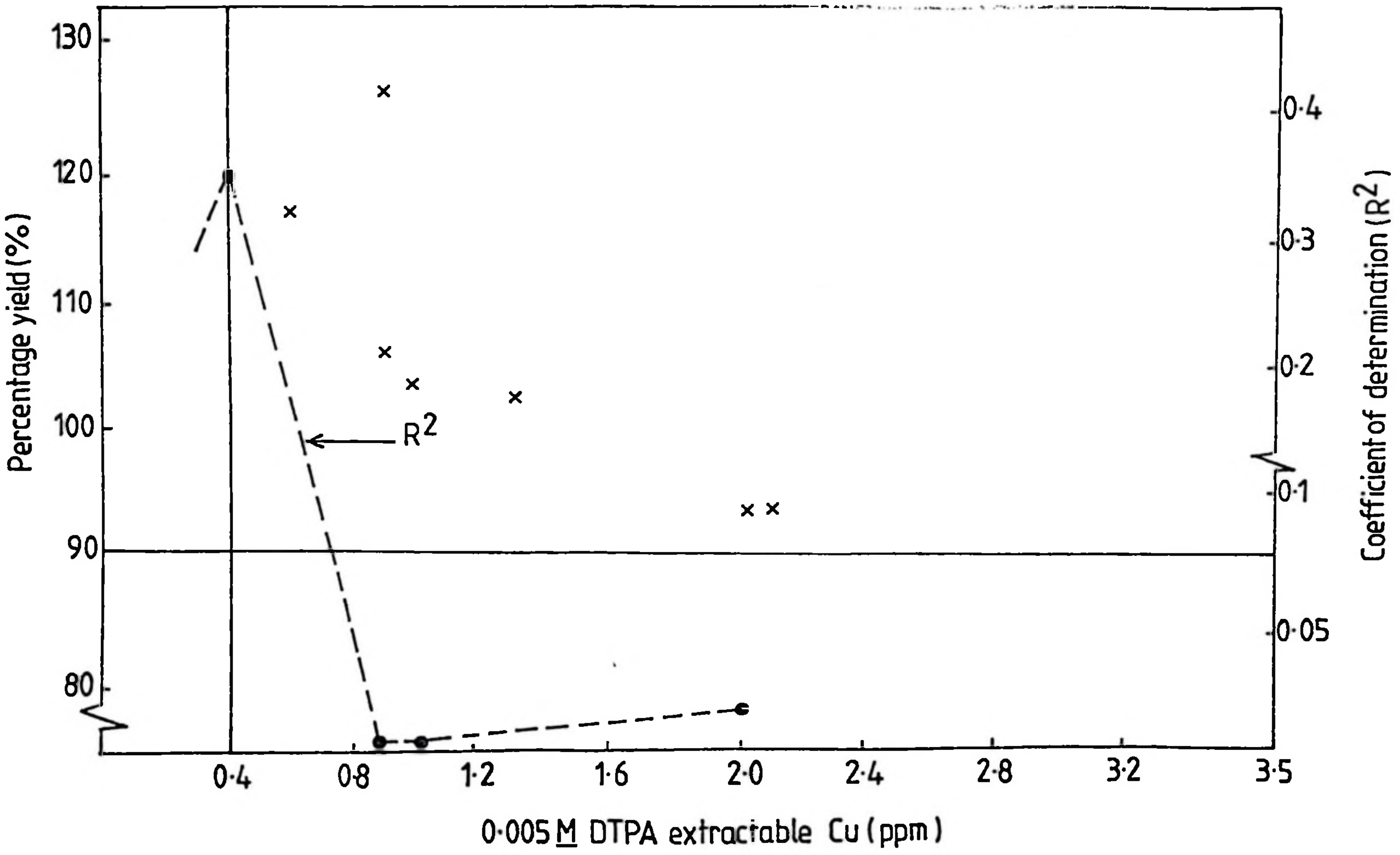

Figure 3 . Scatter diagram and R^2– plot showing relationship between 0·005 M DTPA extractable Cu and percentage yield

Table 6: Range of soil-test, R^2 and critical soil-test values for extractants used for assessing copper availability in some soils of Iringa district.

Extractant	Range of soil-test value covered(ppm)	Maximum R^2 values (d.f.8)	Critical soiltest value(ppm)
0.1N HCl	0.57-1.92	0.16 n.s	1.11
0.01M EDTA-$(NH_4)_2CO_3$	0.12-2.33	0.35 n.s	0.69
0.005M DTPA	0.21-3.50	0.35 n.s	0.40

n.s. = not significant

dry matter yield of barley. The correlation coefficients (r) were 0.257, 0.221 and 0.104 for EDTA-$(NH_4)_2CO_3$, DTPA and HCl extractants respectively.

4.2.3.2 Zinc

Both the graphical method and the discontinous linear regression model of Cate and Nelson (1965; 1971) were used to estimate the tentative critical soil test values for 0.1N HCl-extractable zinc. For the discontinuous linear regression model, a series of R^2 values were computed for each extractant using the soil test values (Table 3) and the percentage yield data (Table 5) and presented in Appendices 4.4, 4.5 and 4.6.

Figure 4 gives the scatter diagram and R^2 plot for the 0.1N HCl extractant. The 0.1N HCl extractant was found to be more suitable (Table 7) than 0.01M EDTA - NH_4CO_3 and 0.005M DTPA extractants. The figure shows that the tentative critical soil test value below which maize would likely respond to zinc fertilization was 0.28ppm 0.1N HCl-extractable zinc.

Table 7 shows the R^2_n values of the extractants tested. The R^2_n values for the three extractants were 0.43, 0.21, and 0.23 for 0.1N HCl, 0.01M EDTA-$(NH_4)_2CO_3$ and 0.005M DTPA, respectively. The 0.1N HCl extractant yielded a significant R^2_n value ($p<0.05$) while 0.01M EDTA-$(NH_4)_2CO_3$ and 0.005M DTPA yielded non significant R^2_n values with respect to dry matter yield of maize. Therefore, among the

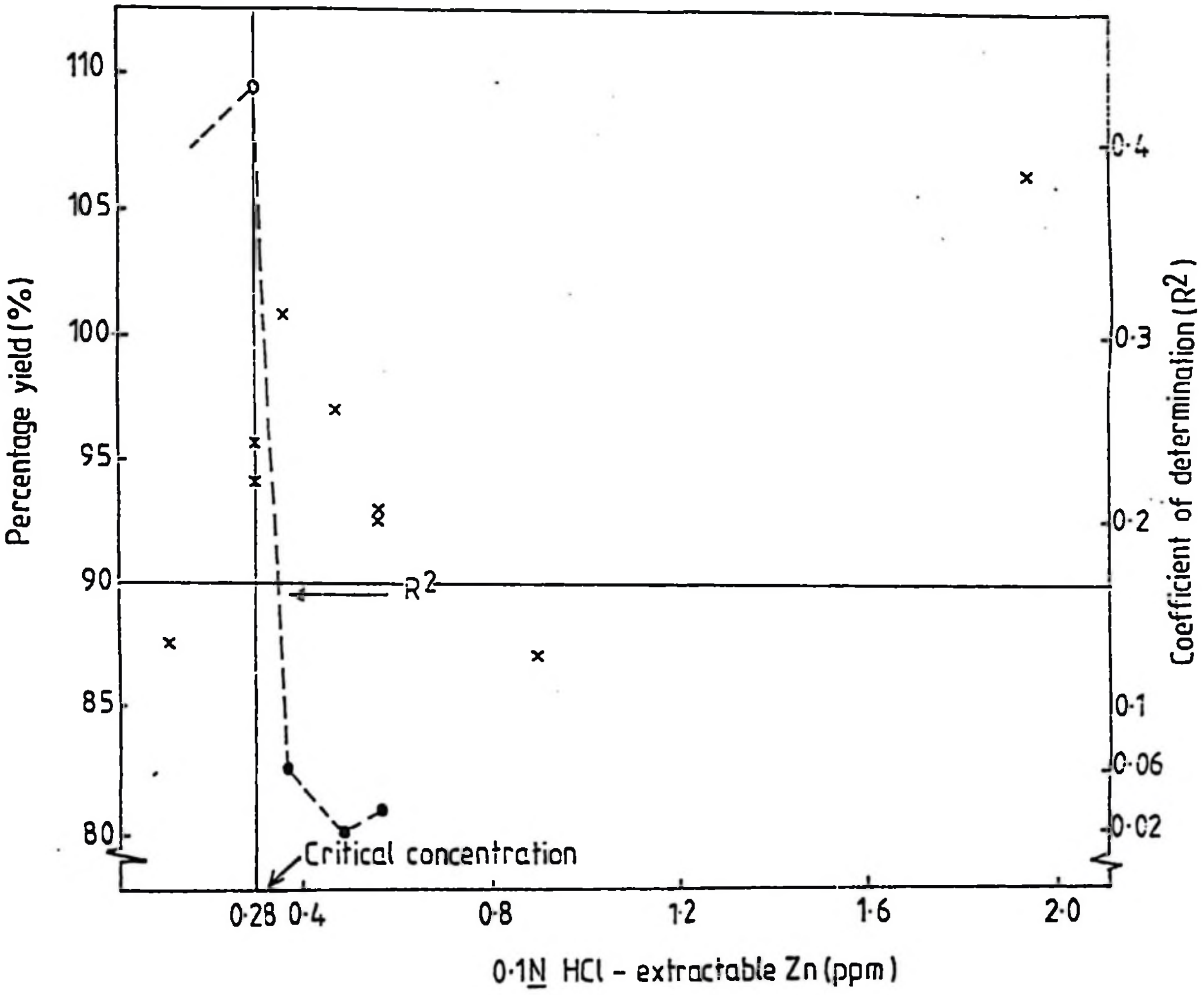

Figure 4 . Scatter diagram and R^2 - plot showing relationship between 0·1N HCl - extractable Zn and percentage yield

Table 7: Range of soil-test, R^2 and critical soil-test values for extractants used for assesting zinc availability in some soils of Iringa district.

Extractant	Range of soil-test value covered(ppm)	Maximum R^2 value (d.f.8)	Critical soil-test value(ppm)
0.1N HCl	0.14-1.19*	0.43	0.28
0.01M EDTA-$(NH_4)_2CO_3$	0.33-2.32	0.2 n.s	1.29
0.005M DTPA	0.24-2.15	0.23	0.72

n.s.: not significant

* : significant at $P \geq 0.05$.

extractants tested 0.1N HCl appears to be better than the other two for soils of Iringa district. It accounted for 43.0% of the variation in relative yields due to dry matter. The 0.1N HCl extractant has been reported to be suitable by Nzabhayanga and Mnkeni (1989). The DTPA extractant has also been reported to be an unsuitable extractant for zinc by Sedberry, Miller and Said (1979) who obtained a non significant correlation coefficient (0.326) between DTPA-extractable zinc and dry matter yield.

The critical value of 0.28ppm 0.1N HCl-extractable zinc was very low ocmpared to the critical concentration reported by Baker and Amacher (1982) and Nzabhayanga and Mnkeni (1989). Baker and Amacher (1982) reported a critical value of 1.40ppm while Nzabhayanga and Mnkeni (1989) obtained a critical value of 3.30ppm-0.1N HCl extractable zinc with maize as a test crop. The difference observed in critical concentrations can not be adequately explained with the available information.

Contrary to the observations made in this study, EDTA and DTPA have been reported as very suitable extractants for assessing available zinc in soils. Mehrotra, Khan and Agarwala (1986) observed a significant correlation coeficient between EDTA-extractable zinc and dry matter yield (0.919) of maize. Sakal *et al.* (1984) observed significant R^2_n values between dry matter yield of rice and EDTA-and DTPA-extractable zinc. The R^2_n values obtained were 0.824 and 0.77 for EDTA and DTPA extractants, respectively.

4.3 Copper and zinc concentration in maize shoots

4.3.1 Copper concentration in maize shoots

Copper concentration in maize shoots which were harvested 35 days after germination as influenced by copper application are presented in Table 8. Copper content of maize shoots in the controls ranged from 3.30 to 12.50ppm while those in copper-treated soils ranged from 5.00 to 25.00ppm. Thus, some maize shoots had copper concentration lower than 7.00ppm, which is the lower value of the sufficiency range for maize at 30-45 days after germination (Jones and Eck, 1973), and can therefore be considered to contain inadequate levels of copper. Haq and Miller (1972) found the copper content of maize shoots harvested 15 days after germination to range between 2.00 and 11.00ppm.

Application of copper at 5kg/ha increased the copper concentration in maize shoots significantly (paired t-test, $p<0.05$). The average copper concentration in maize shoots increased from 7.66ppm in the control to 13.56ppm in copper-treated soils. The tissue copper concentration was not significantly correlated with any of the methods used for extraction of copper from the soil. The simple correlation coefficients(r) between tissue-copper concentration and 0.1<u>N</u> HCl-, 0.01<u>M</u> EDTA-and 0.005<u>M</u> DTPA-extractable copper were 0.410, 0.140 and-0.030, respectively. This indicates that the three extractants tested did not adequately reflect the ability of the soil to supply copper under the conditions of plant growth. Similar observations on the relationship of these extractants and tissue copper contents were reported by Martens (1967); and Haq and Miller, (1972). In Virginia, Martens (1967) working with 16 soil series reported that there was no correlation between 0.1N HCl-extractable copper and copper uptake ($r=0.55$) by oats. Haq and Miller (1972) reported non significant multiple regression correlations (R^2) between tissue copper concentration and EDTA-(0.468) and DTPA-(0.318) extractable copper. These results suggests that additional work for screening a suitable extractant for copper is required.

Contrary to the observations made in this study, Tills and Alloway (1983) reported that the EDTA soil test was positively and highly correlated ($r=0.8681$) with copper uptake. Singh *et al.* (1986) using wheat as a test crop, reported correlation coefficients of 0.859 and 0.827 which were highly significant between copper uptake and 0.005M EDTA and DTPA extractable copper, respectively.

Both the graphical method and the discontinuous linear regression model of Cate and Nelson (1965; 1971) were used to estimate the tentative critical value for copper in maize tissue. For the discontinuous linear regression model, a series of R^2 values were computed using the tissue copper concentration (Table 3) and the percentage yield (Table 4) indicated in Appendix 4.7.

Table 8: Effect of copper fertilization on tissue copper concentration

Soil	Copper rate (kg/ha)	
	0	5
	Copper concentration (ppm)	
Nzihi A	3.30	10.00
Nduli A	3.30	5.00
Nzihi F	6.30	20.00
Nzihi D	7.50	8.00
Nduli B	12.50	18.75
Nzihi E	11.30	25.00
Image A	9.00	9.80
Magubike	8.80	11.50
Itamba A	30.30	15.00
Nzihi C	11.30	12.50
Range	3.30-12.50	5.00-25.00
Mean	7.66	13.56*

* Significantly higher than control ($P < 0.05$)

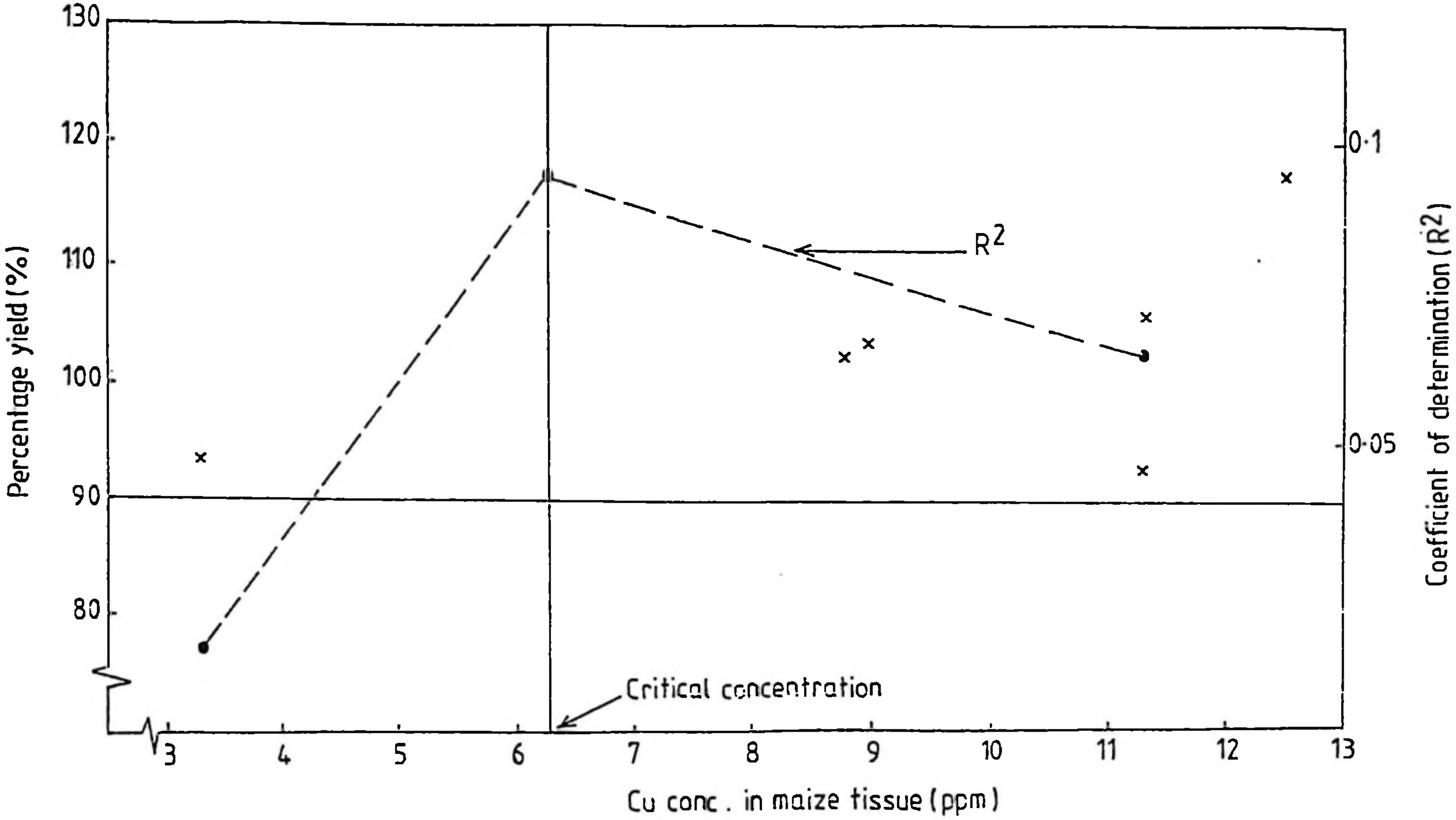

Figure 5. Scatter diagram and R^2-plots showing relationship between copper tissue concentration and percentage yield.

The scatter diagram and R^2 plots are given in Figure 5. The tentative critical value of copper in plant shoots below which maize would likely respond to copper fertilization was 6.30ppm. This means, that plants with less than 6.30ppm copper may be deficient in copper and may benefit from copper fertilization. The tentative critical concentration reported in this study is close to that of 7.00ppm which is the lower value of the sufficiency range for maize at 30-45 days after germination (Jones and Eck, 1973) and can be considered as the critical value. The R^2 value (0.095) between dry matter and copper concentration in the tissue was not significant, showing that the dry matter yield was not very much influenced by copper concentration in the plants.

4.3.2 Zinc concentration in maize shoots

Zinc concentration in maize shoots which were harvested 35 days after germination as influenced by zinc application are presented in Table 9. Zinc content of maize shoots in the controls ranged from 38.50 to 66.50ppm while those for maize grown in zinc-treated soils ranged from 45.00 to 156.50ppm, which falls in the adequate range of 10-100ppm of most field crops and pastures (Chapman, 1973). Similar zinc ranges in maize shoots were observed by Ragab (1980). He harvested maize at 32 days after germination and reported the range of 54.5 to 73.2ppm zinc after application of 10kg zinc/ha. Relatively lower values which ranged from 9.00 to 50.00 ppm zinc in 15 days-maize plant were reported by Haq and Miller (1972). On the other hand, the soils used in the greenhouse study contained

Table 9: Effect of zinc fertilization on tissue zinc content

Location	Zinc rate (kg/ha)	
	0	5
	Zinc concentration (ppm)	
Mgongo	40.0	63.5
Image A	56.5	60.0
Nzihi E	58.5	156.5
Nzihi A	57.5	144.0
Nzihi B	59.5	158.5
Nzihi C	55.0	89.0
Itamba A	63.5	88.5
Magubike	66.5	94.5
Image B	53.5	54.5
Nduli A	38.5	45.0
Range	38.5-66.5	45.0-158.5
Mean	54.9	95.4*

* Significantly higher than control ($P < 0.05$)

very high available phosphorus (Table 1). The very high phosphorus might have affected tissue zinc concentration and subsequently affecting correlation between this parameter and soil test value.

Application of zinc at 5kg/ha significantly increased the zinc content in maize tissue (paired t-test, $P<0.05$). The tissue zinc concentration was not significantly correlated with any of the methods tested for extraction of available zinc. The simple correlation coefficients between tissue zinc concentration and 0.1N HCl-, 0.01M EDTA-and 0.005M DTPA-available zinc were 0.29, 0.37 and -0.05, respectively.

While by using the simple regression analysis indicated that the three extractants tested did not adequately reflect the ability of the soil to supply zinc under the conditions of plant growth the Cate and Nelson method (Cate and Nelson 1965; 1971) indicated 0.1N HCl extractant to be better than the other two. Similar poor correlation coefficients for EDTA-, DTPA- and HCl-available zinc and zinc uptake by plants have been reported by Sakal *et al*. (1984) and Sedberry, Miller and Said (1979). Sakal *et al*. (1934), working with rice and 25 soils of Sub-Himalayan hill and Forest region in India, obtained a negative and non significant correlation coefficient (0.192) between 0.1N HCl-extractable zinc and plant zinc uptake. Sedberry, Miller and Said (1979) reported that there was no significant correlation between DTPA-extractable zinc and zinc concentration in corn (0.332).

Contray to the findings observed in this study on poor correlations between plant zinc content and soil available zinc, Wear and Evans (1968) reported that 0.1N HCl-extractable zinc was significantly correlated with zinc uptake (0.82) of maize. Mehrotra, Khan and Agarwala (1986) observed significant correlation between EDTA-extractable zinc and zinc concentration (0.685) of maize. Haq and Miller (1972) found significant correlation between DTPA-extractable zinc and zinc concentration (0.602) of maize.

Since zinc content in maize tissue observed in this study was much higher than the critical values reported in literature which ranges between 12-20ppm zinc (Sauchelli, 1969; Delas and Dartiques, 1970 and Jones, 1970), it was not thought worth computing the critical level for zinc in maize tissue.

4.4 Copper and zinc status in soils of Iringa district

4.4.1 Copper

Data for 0.01M EDTA-$(NH_4)_2CO_3$ and 0.005M DTPA extractable copper are given in Appendix 3. The 0.01M EDTA-$(NH_4)_2CO_3$-extractable copper ranged from 0.12 to 37.70ppm with an average of 2.25ppm, while the range for 0.005M DTPA was 0.25 to 30.41ppm with an average of 1.85ppm. Since none of the extractants tested was found to be suitable for the assessment of copper status, a reliable critical level for copper for these soils could not be determined. Consequently, the delineation of copper fertility classes was not possible.

4.4.2 Zinc

The available zinc of 61 surface soil samples of the district as extracted by 0.1N HCl are presented in Appendix 3. Zinc content varied from 0.14 to 27.30 ppm, with a mean value of 1.76 pmm. On the basis of the critical concentration of 0.28 ppm zinc established in this study, the soils were divided into two classes. Class 1 with 5 soils i.e. 8.2% of all the soils tested contained <0.28ppm 0.1N HCl-extractable zinc and thus were expected to respond to zinc fertilization. However, the glasshouse study revealed that all the soils tested gave percentage yields greater than 75%. This means that even those soils which responded to zinc fertilization should be ranked as having medium zinc fertility, because of the relatively high percentage yield as recommended by Cope and Rouse (1973). Class II is for the remaining 56 soils i.e. 91.8% which had 0.1N HCl-extractable zinc >0.28ppm, suggesting little or no likelihood of response to zinc fertilization. These soils were thus classified as having high zinc fertility.

The 0.1N HCl-extractable zinc values were plotted on a map of Iringa district and approximate boundaries for the two fertility classes were delineated as shown in Figure 6. Medium zinc fertility rating was found in parts of Nzihi, Nduli, Image and Wezu. These areas were either under continuous cultivation for a long time or had coarse textured soils. These soils need zinc applications and from the glasshouse study 5kg zinc/ha appears to optimize yield. The remaining areas are high in zinc. Areas of high zinc fertility rating do not appear to require zinc application at present.

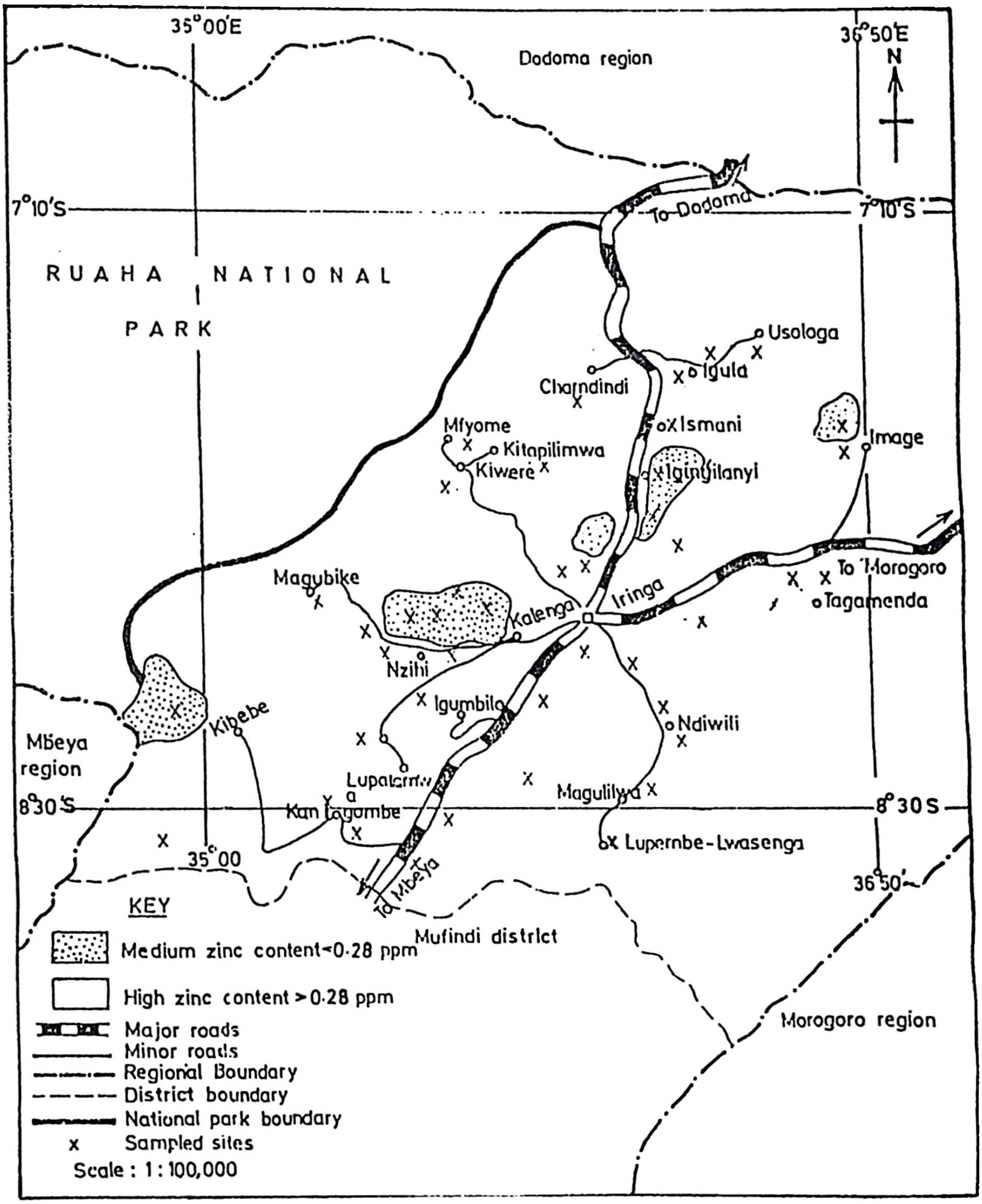

Figure 6. Zinc fertility status of soils of Iringa district, Tanzania.

5. SUMMARY AND CONCLUSIONS

In order to generate more information on copper and zinc in soils of Iringa district, 10 soils for each element were selected for detailed investigation. These soils were screened from 21 soils. Glasshouse studies were conducted for each element using the selected soils and maize as the test crop. The treatments tested were with and without copper for the copper trial and with and without zinc for the zinc trial. The rates were equivalent to 5kg/ha for both copper and zinc. Available copper and zinc from two sets of soils were extracted using 0.01$\underline{M}$ EDTA-$(NH_4)_2CO_3$, 0.005$\underline{M}$ DTPA and 0.1$\underline{N}$ HCl extractants, and the results were correlated with percentage yields of maize using the discontinous linear regression model of Cate and Nelson (1971) and Nelson and Anderson (1973). The extractant leading to the highest and significant R^2_r value was taken as the most suitable method and the soil-test value corresponding to the highest R^2_r for the best extractant was taken as the critical value. Plant shoots were also analysed for copper and zinc content. For survey of the fertility status of these elements, 61 soil samples were collected from locations considered suitable for agriculture in the district and copper and zinc were determined using the method found to be most suitable.

The results indicated that copper application at 5kg/ha increased maize dry matter yield in only four soils and the increase ranged from 3.6 - 16.9%. Application of 5kg zinc/ha increased maize dry matter yield in eight soils by 3.10 to 21.2%. However, compared to dry matter yields in controls, these increases were not significant. None of the methods tested was suitable for the assessment of available copper in soils. For zinc, the 0.1N HCl extractant was found to be better than the other two and gave a tentative critical value of 0.28ppm.

The copper concentration in shoots was significantly increased by copper application and ranged from 3.3. to 12.5ppm in the controls and from 5.0 to 25.0ppm in the copper treated soils. The tentative critical value for copper in the plant tissue was 6.3ppm. Similarly, the zinc concentration in shoots was significantly increased by zinc application and ranged from 38.5 to 66.5ppm in the controls and from 45.0 to 156.0ppm in the zinc treated soils. The tissue zinc concentrations were rather high and above the critical concentration range of 12-20ppm reported in the literature.

The HCl-extractable zinc in soils from different parts of the district ranged from 0.14 - 27.30ppm with an average of 1.76ppm. The data was grouped into two fertility classes namely medium and high. The proportions being 8.2% in the medium fertility class and 91.8% in the high fertility class. The range of extractable copper by the EDTA-$(NH_4)CO_3$ which gave slightly higher R^2_n value was 0.12 -32.70ppm with an average of 2.25ppm. However, it was not possible to delineate soil fertility categories since no suitable copper extraction method was found.

In view of the data obtained in this study, it was concluded that:

(a) The 0.1N HCl extractant could tentatively be adopted for zinc in the soils of Iringa district.

(b) Some few soils are likely to benefit from zinc fertilization, but this needs to be confirmed with field experimentation therefore concrete recommendations can be made.

(c) Further screening of extractants for copper need to be done, since no suitable method was found in this study.

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7. APPENDICES

Appendix 1 Key to the locations abbreviated

Location	Owner and land use
Nzihi A	Cambropolous Farm, Under tobacco/maize for > 10 years.
Nzihi B	Cambropolous Farm, Under tobacco/maize for < 5 years.
Nzihi C	Emmanuel's Farm, Reserved for future cultivation.
Nzihi D	Emmanuel's Farm, Under tobacco/maize for < 5 years.
Nzihi E	Emmanuel's Farm, Under tobacco/maize for > 10 years.
Nzihi F	Rousos Farm, Under tobacco/maize for > 10 years.
Nzihi G	Fliakos Farm, Under tobacco/maize for < 5 years.
Nzihi H	Rousos Farm, Under tobacco/maize for < 5 years.
Nduli A	Elias Farm, Under tobacco/maize for < 5 years.
Nduli B	Elias Farm, Reserved for future cultivation.
Nduli C	Elias Farm, Under tobacco/maize for > 10 years.
Nduli D	Elias Farm, Under tobacco/maize for < 5 years.
Nduli E	Elias Farm, Under tobacco/maize for > 10 years.
Ihemi A	Ujamaa village, under tobacco/maize for < 5 years.
Ihemi B	Ujamaa village, Reserved for future cultivation.
Image A	Ujamaa village, Under tobacco/maize for < 5 years.
Image B	Ujamaa village, Under tobacco/maize for > 10 years.
Itamba A	Mawere's Farm, Reserved for future cultivation.
Itamba B	Mawere's Farm, Reserved for future cultivation.
Itamba	Mawere's Farm, Under tobacco/maize for < 5 years.
Itamba D	Mawere's Farm, Under tobacco/maize for < 5 years.
Kitapilimwa A	Ujamaa village, Under tobbaco/maize for < 5 years.
Kitapilimwa B	Ujamaa village, Reserved for future cultivation.
Kiwere A	Ujamaa village, Reserved for future cultivation.
Kiwere B	Ujamaa village, Under tobacco/maize for < 5years.
Kitawanya A	Ujamaa village, Under tobacco/maize for < 5 years.
Kitawanya B	Ujamaa village, Reserved for future cultivation.
Mgeza A	Ujamaa village, Reserved for future cultivation.
Mgeza B	Ujamaa village, Under tobacco/maize for < 5 years.

Appendix 2 0.01M EDTA-$(NH_4)_2CO_3$ extractable copper and zinc in 21 soil samples

Location	Concentration (ppm)	
	Copper	Zinc
Nzihi A	0.12	0.72
Nzihi B	0.30	0.44
Nzihi C	1.00	1.29
Nzihi D	2.40	0.58
Nzihi E	0.47	0.29
Nzihi F	0.82	0.51
Nzihi G	0.30	0.51
Nduli A	0.66	0.01
Nduli B	0.82	1.29
Nduli C	1.00	1.08
Nduli D	1.00	0.51
Nzihi H	1.18	0.58
Nduli E	0.82	0.65
Image A	1.53	1.73
Image B	0.82	0.51
Itamba A	1.88	5.82
Itamba B	2.40	9.28
Itamba C	4.34	3.38
Itamba D	0.12	0.58
Mgongo	0.30	0.29
Magubike	0.30	0.29

Appendix 3 0.01M EDTA-$(NH_4)_2CO_3$ AND 0.005M DTPA-extractable copper and 0.1N HCL-extractable zinc from 62 surface soils of iringa district

Location	Copper concentration (ppm)		zinc concentration (ppm)
	0.01M EDTA-$(NH_4)_2CO_3$	0.005M DTPA	0.1N HCl
Nzihi A	0.12	0.21	0.28
Nzihi B	0.30	0.45	0.35
Nzihi C	1.00	2.05	0.49
Nzihi D	2.40	3.50	0.50
Nzihi E	0.47	0.89	0.18
Nzihi F	0.82	0.40	0.20
Nzihi G	0.12	0.25	0.23
Nzihi H	1.18	1.25	0.44
Nduli A	0.66	1.28	1.91
Nduli B	0.82	0.59	1.41
Nduli C	1.00	1.15	1.87
Nduli D	1.00	1.02	0.57
Nduli E	0.82	0.80	0.28
Ihemi A	4.70	3.58	2.75
Ihemi B	5.08	4.00	4.60
Image A	1.53	0.98	0.28
Image B	0.82	0.95	0.91
Itamba A	1.88	2.15	0.56
Itamba B	2.40	2.70	8.75
Itamba C	4.34	4.70	4.42
Itamba D	0.12	0.30	0.47
Kitapilimwa A	0.64	0.56	0.45
Kitabilimwa B	0.82	0.95	0.60
Kiwere A	1.60	1.40	0.32
Kiwere B	1.78	0.90	0.30
Kitawanya A	1.24	1.37	0.42
Kitawanya B	1.60	1.45	0.49

Appendix 3 cont.

Mgeza A	0.64	1.26	0.40
Mgeza B	1.42	0.74	0.55
Tangamenda	0.86	0.56	0.40
Igula	0.86	0.56	0.38
Ndiwili	1.24	0.56	0.48
Magulilwa	32.70	30.40	2.34
Lupembe-lwasenga	1.42	0.82	1.51
Mgama	1.42	0.90	0.42
Tanangozi	2.70	1.08	6.40
Mseke	2.70	1.26	2.40
Ipogoro	1.08	1.44	7.50
Ibangamoyo	1.42	0.90	2.40
Kalenga	1.06	0.38	0.56
Ulanda	2.34	1.08	1.00
Kibebe	1.06	0.56	0.38
Wezu	0.86	0.90	0.25
Makogati	1.21	0.74	1.42
Kaning'ome	3.42	1.08	1.25
Lupalamwa	4.16	1.26	0.52
Igumbilo	9.18	2.86	0.68
Lundamatwe	0.86	0.56	0.38
Mbigili	0.64	0.56	0.49
Ilula	2.14	1.62	1.62
Igingilanyi	1.50	1.00	1.35
Mkungugu	0.50	0.38	3.00
Ismani	3.60	2.70	1.42
Kihorogota	1.20	1.30	2.40
Igula	9.00	7.50	0.52
Mngawe	0.50	0.41	0.47
Chamdindi	2.40	2.70	2.09
Usolanga	2.50	3.50	27.30
Mgongo	0.30	0.25	0.14
Magubike	0.30	0.89	0.56

Appendix 4 Computed coefficients of determination (R^2)

Appendix 4.1 Percentage yield vs $0.01\underline{M}$ EDTA-$(NH_4)_2CO_3$ extractable copper.

Cu conc. (ppm)	P.Y. (%)	CSS	R^2
0.12	91.10		
0.69	85.50	653.59	0.3492
0.69	117.00	168.81	0.0919
0.89	106.00	139.17	0.00743
0.96	126.70	6.26	0.0033
1.02	103.50	3.72	0.0020
1.40	93.85	56.43	0.0301
1.84	93.14		
2.33	125.30		

Appendix 4.2 Percentage yield VS 0.005M DTPA-extractable copper

Cu Conc. (ppm)	P.Y (%)	CSS	R^2
0.21	91.10		
0.40	85.10	653.59	0.3492
0.59	117.00	168.81	0.0919
0.89	106.00	139.17	0.0743
0.89	126.70	6.26	0.0033
0.98	103.50	3.72	0.0020
1.28	102.60	0.59	0.00003
2.05	93.14	56.43	0.0301
2.15	93.85		
3.50	125.30		

Appendix 4.3. Percentage yield vs 0.1N HCl-extractable copper

Cu Conc	P.Y. (%)	CSS	R^2
0.57	91.10	49.08	0.062
0.67	126.70	48.64	0.0259
0.67	85.50	48.64	0.0251
0.75	125.30	46.92	0.0251
0.75	117.00	215.32	0.1150
1.11	106.00	254.98	0.1362
1.11	103.50	269.11	0.1439
1.11	102.60	300.07	0.1603
1.29	93.85		
1.92	93.14		

Appendix 4.4 Percentage yield VS 0.01M EDTA-$(NH_4)_2CO_3$

Extractable zinc

Zinc Conc (ppm)	P.Y. (%)	CSS	R^2
0.33	87.7		
0.40	95.6	11.35	0.02619
0.43	94.1	7.39	0.01706
0.49	100.9	4.22	0.00974
0.60	87.1	4.90	0.01131
0.62	106.4	34.66	0.07999
0.63	93.5	37.21	0.08588
1.29	97.0	90.91	0.20932
1.73	82.5		
2.32	93.0		

Appendix 4.5 Percentage yield vs 0.005M-DTPA extractable zinc

Zinc Conc (ppm)	P.Y. (%)	CSS	P
0.24	100.9		
0.32	82.5	10.82	0.02497
0.32	95.6	2.61	0.00601
0.48	97.0	0.33	0.00075
0.48	93.0	0.006	0.000014
0.56	93.5	0.016	0.000037
0.64	94.1	-112.95	-0.26071
0.72	106.4	101.766	0.23489
0.80	87.1		
2.15	87.7		

Appendix 4.6 Percentage yield vs 0.1N HCl-extractable zinc

Zinc Conc (ppm)	P.Y. (%)	CSS	R^2
0.14	87.7		
0.28	82.5	188.36	0.43
0.28	94.1	138.27	0.32
0.28	95.6	96.52	0.22
0.35	100.9	26.25	0.06
0.49	97.0	9.93	0.022
0.56	93.0	15.26	0.035
0.56	93.5	22.06	0.051
0.91	87.1		
1.91	106.4		

Appendix 4.7. Percentage yield vs copper concentration in maize tissue

Cu conc (ppm)	P.Y. (%)	CSS	R^2
3.3	91.1		
3.3	126.7	48.08	0.0257
3.3	93.35	0.46	0.0002
6.3	85.50	177.98	0.095
7.5	125.3	-1.0	-0.005
8.8	102.6	0.29	0.0002
9.0	109.5	2.55	0.001
11.30	93.14	122.58	0.055
11.30	106.0		
12.50	117.0		