EFFECTS OF SPRAYING COFFEE WITH COPPER FUNGICIDES ON THE COPPER STATUS OF SOILS OF MOSHI DISTRICT, TANZANIA

GERARD ISAAC MKINDI

A DISSERTATION SUBMITTED IN PARTIAL FULFILMENT FOR THE DEGREE OF MASTER OF SCIENCE IN AGRICULTURE OF SOKOINE UNIVERSITY OF AGRICULTURE

1990

1/4/93

ABSTRACT

A series of investigations were conducted to assess the effects of spraying coffee with copper (Cu) fungicides on the Cu status of some soils of Moshi district, Tanzania. The studies involved analysis of soil samples taken from coffee fields sprayed with Cu fungicides for durations of 10 years, 10-30 years, >30 years and from fields which have not been sprayed. Copper from the soils was extracted using 0.005M DTPA. Then three glasshouse experiments were set up to assess the effects of different Cu levels in soils and soil pH on the growth of beans and Cu concentration in the shoots. In addition coffee leaves were collected from selected coffee fields and analysed for Cu content.

The results indicated that DTPA extractable Cu in the topsoil (0-5cm) increased from an average of 5.6 ppm in farms that had never been sprayed with copper fungicides to 186.2 ppm in farms sprayed for more than 30 years. Shorter durations of spraying gave intermediate values of extractable Cu. The extractable Cu decreased sharply with depth.

Beans grown in soils ranging in DTPA Cu contents from 3.7 to 368 ppm had an average Cu content in the shoots of 23.2 ppm and no toxicity symptoms were observed in any of the treatments. Application of 200µg Cu/kg

soil increased the average Cu content of shoots to 25.6 ppm but again the plants were free from any Cu toxicity. Coffee leaves from sprayed fields contained higher levels of copper (up to 60 ppm) but were also free from Cu toxicity symptoms. However, when pH was lowered to 5.1 or less, copper concentration in bean shoots increased to 35 ppm or greater and caused copper toxicity to bean plants.

It was concluded that spraying coffee with copper fungicides increased the amount of copper in the soil and that the largest increase occured in the 0-5 cm layer of soil. The copper accumulated in the soil was not toxic to either coffee or bean plants but could become toxic if the pH of the soils decreased below 5.2.

DECLARATION

I, Gerard Isaac Mkindi, do hereby declare to the Senate of 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.

Date:13/6/90 Signature:.....

Gerard I. Mkindi

COPYRIGHT

ACKNOWLEDGEMENTS

A study of this magnitude is not the product of one man. There were several institutions and individuals who contributed to the completion of this dissertation.

First, I wish to thank Dr. J.M.R. Semoka for his guidance and encouragement during the period of study. I would also like to thank Dr. B.R. Singh of the Agricultural University of Norway for his constructive suggestions in the initial planning of this work.

Secondly, I am thankful to Tanzania Coffee Marketing Board for allowing me to pursue this course and to the Norwegian Agency for International Development (NORAD) for financing it. I am also grateful to the Sokoine University of Agriculture for providing the facilities for conducting the study.

I also take this opportunity to express my appreciation to all the technical staff in the Soil Science Laboratory for their assistance and co-operation. Messrs Shamte, Salum, Ezekiel and Miss Kafui deserves special thanks.

I should also mention the goodwill and encouragement I received from the entire staff of the Coffee Marketing Board, Morogoro Branch.

This work would not have been possible without the patience of Mama Fatuma, my wife and the children Fatuma, Pia, Issa, Henry and Anjela. Their constant encouragement and understanding throughout the period of study is appreciated.

Lastly, I wish to thank all the coffee farmers in Moshi district who tirelessly answered my questions and allowed me to collect samples from their farms, without forgetting Mr. Eric Sungusia and Frank Ngowi the driver, who were always with me in the field.

In the end I am thankful to E.R. Mkulasyai for typing the initial draft of this work and Judy Mbena for typing the final dissertation.

DEDICATION

This work is dedicated to all peasant coffee farmers in Moshi district,

and

my family Leonarda, Fatuma, Pia, Issa, Anjela and those to come.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

ALIST OF PLATES

1. INTRODUCTION

The importance of coffee in Tanzania's economy has been increasing over the years. Coffee has been ranked the number one crop in terms of monetary value, occassionally changing position with cotton. Apart from its importance to the national economy, many people derive their livelihood from coffee. Between 10 and 15 percent of the population of Tanzania is dependent on coffee as an industry (Mbilinyi, 1976). They include those individuals directly involved in its cultivation and people who participate in marketing, processing and transportation of the crop. The continued cultivation of coffee in Tanzania is therefore vital.

Coffee plants are, however, attacked by two important fungal diseases namely coffee leaf rust (Hemileia vastatrix) and coffee berry disease (C.B.D.) (Colletotrichum coffeanum). Coffee berry disease is capable of causing up to 60 percent crop losses if not controlled (Okioga, 1978) and an estimation by Bujulu (1978) shows that about 50 percent of coffee crop can be lost due to uncontrolled coffee leaf rust. The diseases which started in the 1930s (Coffee leaf rust) and mid 1960s (coffee berry disease), have constantly threatened the continued cultivation of coffee in the main coffee growing areas of the country, especially Moshi district.

A number of investigations on the control of these diseases were undertaken between 1956 and 1960 (Bock 1963; Nutman and Roberts, 1960a; 1960b). Studies on the use of various fungicides to control the diseases have been going on since then (Bujulu, 1978; Okioga, 1978).

During this period, the most effective fungicides were found to be formulations containing 50 percent copper and phenyl mercuric acetate, sprayed up to 8 times a season. The phenyl mercuric acetate proved phytotoxic and was abandoned (Okioga, 1978). Studies by Bujulu (1978) and on-going research at Lyamungu Coffee Research Centre still recommend copper compounds for the control of the coffee diseases. Other products, bavistin, derosal, benomyl and orthodifolatan were also tested and proved better but were withdrawn for fear of creating resistance or for being carcinogenic or due to high cost.

Copper fungicides such as cuprous oxide (perenox), copper oxychloride (cupric chloride 50 percent wettable poweder), and cupric hydroxide (50 percent W.P.), therefore, are likely to continue playing an important role in the control of fungal diseases of coffee until economic and more effective fungicides have been found to replace them.

As a result, farmers in the coffee growing areas and particularly in Moshi district, have found themselves committed to near monthly sprays of copper fungicides in their farms. Coffee is usually intercropped with maize and beans. These crops may be sensitive to high copper concentrations in the soil.

The fungicides are applied at rates ranging from 5-11 kg per hectare depending on the type of fungicide and the disease being controlled, and as pointed above the applications are made for a minimum of 8 times per season (per year) (TARO, Lyamungu, 1986). The potential for copper accumulation in the soils of these areas is therefore rather high.

Moshi et al. (1982) has estimated that the higher rate of application (11 kg/ha) when applied 8 times per season would increase the copper content of soils by 8 ppm Cu per season. Over many years, large amounts of copper are likely to accumulate in the soils since losses from the soil via crop uptake or leaching to the subsoil are relatively small (Lucas, 1948; Gilbert, 1952; Lexmond, 1980).

Indeed large accumulation of copper in soils have been reported in other areas. Dickinson et al. (1984) found up to 236 ppm Cu in a 68 year old coffee plantation.

Aduayi (1976) reported an increase in available copper in soils under coffee in Kenya. Moshi et al. (1982) analysed a few soils from selected locations in Moshi district and observed that copper fungicide sprays increased the available copper level from 2.0 ppm in the control to 61.5 ppm on fields receiving copper sprays. Reuther and Smith (1953) reported large accumulations of copper in soils as a result of Cu fungicide applications which were toxic to citrus seedlings.

Although at present there is no evidence of copper toxicity on coffee or on the intercrops in Moshi district, the possibility of reaching harmful levels of copper in future exists especially for sensitive crops. This research work was therefore undertaken to provide information on the effects of spraying coffee with copper fungicides on the copper status of soils of Moshi district and its effect on other crops such as beans. The research work was also designed to assess the suitability of some copper extraction methods in estimating the availability of copper to plants.

2. LITERATURE REVIEW

2.1. Coper in Soils

2.1.1. Sourccs of copper in soils

Soils inherit their copper from rocks which have undergone various processess of geochemical and pedochemical weathering during soil formation. Other sources of soil copper are the products of decay of plants and animals, natural waters, materials from the atmosphere, fertilizers, insecticides and fungicides (Graham, 1953; Swainc and Mitchell, 1960). The forms of copper in soils have been summarized by Krauskopf (1972). Copper mainly occurs as sulphides, both simple and complex, oxides, carbonates, silicates and sulphates. Simple sulphides include chalcocite (Cu_2S) and covellite (CuS). Complex sulphides include chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4) and enargite ($Cu_3A_5S_4$) just to mention a few. Examples of oxides are cuprite (Cu_2O) and tenorite (CuO). Copper also occurs in forms of carbonates such as malachite $Cu_2(OH)_2CO_3$ and azurite ($Cu_3(OH)_2(CO_3)_2$), silicates such as chrysocolla ($CuSiO_3.2H_2O$) and sulphates such as brochantite ($Cu_4(CH)_6SO_4$).

2.1.2. Normal copper content of soils

The average copper concentration in the earths crust has been estimated to be 70 ppm and its total content in soils as 2 - 100 ppm (Hodgson 1963; Guony and Cornillo, 1970). Copper in uncontaminated soils is quoted as being 20 ppm (Swaine, 1955). According to Sillanpää (1982), the amount of EDTA - extractable copper usually

ranges from 1 - 18 ppm. The amount reported by him for Tanzania is 4.8 ppm EDTA - extractable copper. These figures are similar to those of Berrow and Reeves (1985) who found that EDTA - extractable copper for a number of soils in Scotland was between 0.08 - 9.6 ppm with a mean of 8.6 ppm. Tiwari and Kumar (1982) reported a mean value of 5.11 ppm 0.05 M EDTA - extractable copper. Gough et al. (1980) reported values of 0.3 - 15 ppm in uncultivated soils while Haq et al. (1980) reported 2.8 ppm in a control while studying contaminated soils which had up to 188 ppm DTPA extractable copper. Holmes (1943) extracted copper with concentrated nitric acid from a large group of profile samples. He found that extractable copper varied from 6 to 67 ppm.

Reuther et al. (1952), found virgin sandy soils in Florida to contain 3 ppm Cu when extracted with concentrated nitric acid, while Cheng and Bray (1953) extracted copper from a number of soils using 0.1 N HCl and found that the concentration of copper varied from 2 - 11.4 ppm. Fiskell (1965) reported that the amount of copper in agricultural soils lies between 1 - 3 ppm in soils that are likely to be deficient.

2.1.3. Copper accumulation in agricultural soils resulting from the use of copper fungicides and other Cu containing substances

Interest on copper accumulation in agricultural soils started when studies by Reuther and Smith (1953) showed that the application of copper fungicides for extended periods could increase copper to toxic levels in orchard soils.

Many formulations of copper containing fungicides have been used for vines almost a century ago and for horticultural crops (Bowen, 1966). These sprays were found quite effective and got widespread use. The copper in these sprays becomes incorporated into the leaf litter and eventually into the soil as a result of biological cycling and cultivation to become a source of copper contamination of agricultural soils.

Soils affected by copper containing sprays have been reported by various researchers in Florida (Reuther and Smith 1953), in orchard soils of Ontario (Frank et al., 1976) in Australian orchard soils (Merry, 1980). In these orchards, copper has accumulated at an average rate of 1 - 4 ppm per year. Reider and Schwertmann (1972) reported an increase of 12 ppm copper per year in a German hop field.

Other examples of excessive copper in soils are reported by McBride and Bouldin (1984) who found total copper of 3150 ppm, over half of which was extractable by DTPA, in extracts from a soil contaminated at least a century ago, and by Sposito *et al*. (1983) who reported that the EDTA extractable fraction of copper was found to increase with time in soils amended with sewage sludge.

In coffee soils associated with copper sprays, we have a report from Aduayi (1975) who found soils from copper sprayed coffee estates in Kenya to have twice as much EDTA extractable copper as those from unsprayed estates. Studies by Venkataramaiah and Singh (1974) showed that there is an increase in available copper in soils where coffee had been sprayed with copper fungicides. Arabica coffee which had received "bordeaux mixture" sprays for more than 40 years was found to contain an average of 100 ppm extractable copper (0.1 *N* HCl) in the surface 15 cm. The unsprayed farms had only 10 ppm extractable copper. Dickinson *et al*. (1984) found the surface litter of a 68 year old large scale coffee plantation receiving continued applications of copper fungicides to contain about 2000 ppm total Cu (extracted with 71 percent H NO_3) and the surface soil (10 cm) to have a total concentration of 236 ppm.

A preliminary investigation by Moshi et al. (1982) estimated an increase in soil copper to be 8 ppm per year in the top 15 cm of coffee soils in Moshi district, the district covered by this study. In these coffee growing areas, available copper ranged from 38 ppm to 68.5 ppm while in the control, the amount of copper was 2.0 ppm. Information about copper contamination of coffee soils is however, scarce in Tanzania.

2.1.4. Soil properties affecting copper availability

2.1.4.1. Coppor vs pH

The availability of plant nutrients is known to be highly related to soil pH (Lucas and Knezek, 1972). The effect of pH on copper concentration in plants, however, is variable according to various researchers, and can be negative, none and even positive. Peech (1941) found that the amount of exchangeable copper decreased as the soil pH was raised and postulated that this was due to a decrease in solubility of copper compounds at higher pH. Other examples provide evidence that supply of copper is reduced as pH is increased. Van Luit and Henkens (1967) found maximum concentrations in ryegrass when soil pH was between 4.5 and 5.0, and Younts and Patterson (1964) found that concentration in wheat was reduced when pH was raised above 5.1. It has also been shown (Lexmond, et al. 1981) that toxic effects of copper to soil grown plants is alleviated by raising the pH and

consequently liming is usually considered the corrective treatment to be applied to copper polluted soils. A suggestion was made (Cavallaro and McBride, 1980) that an increase in pH adds to soil power to bind copper, thus reducing the concentration of Cu^{2+} ions in solution, which is generally assumed to be the biologically active form of copper. McBride and Blasiak (1979) and Lexmond (1980) have confirmed the decrease in Cu^{2+} ion activity with increasing soil pH.

2.1.4.2. Soil copper and organic matter

Many aspects of the chemistry and mobility of copper in soils are known to be affected by the presence of organic matter (Stevenson and Ardakani, 1972). The role of organic matter in influencing copper in soils was revealed by McLaren and Crawford (1973) who in one of the most successful schemes for fractionating soil copper, developed a method for fractionating soil copper and applied it to 24 soils representing a range of British soil types. From one fifth to one half of the copper in the 24 contrasting soils was accounted for in organically bound forms. By using a sequential extraction procedure, Tessler et al. (1979) also found that approximately 25 percent of the copper in two sediments was accounted for in organically bound form.

The ability of soluble organic matter to complex copper was shown by McLaren et al. (1980), whose experiment demonstrated the strong Cu adsoptive capacity of soil organic matter and the soils oxide fraction the two materials likely to influence copper concentration in the soil solution. Complexation by organic matter has also been recognized as an effective mechanism of copper retention in soils (McBride, 1978). The Cu^{2+} ion is directly bonded to two or more specific organic functional groups (mainly carboxylic, carbonyl, and phenolic) so that the ion is immobilized in a rigid inner sphere complex. Earlier, Stevenson and Ardakani (1972) had suggested that compounds involved in binding Cu included simple aliphatic acids, amino acids, phenolic acids, peptides and proteins, polysaccharides and humic and fulvic acids. A similar view was given by Senesi et al. (1985) who reported that fulvic acids have a high potential binding capacity of copper II added at various ratios in acqueous solutions.

The copper binding organic substances are said to be essential for plant nutrition and soil formation (Hodgson, 1963). Some of the complexes so formed are insoluble, others do precipitate while they form and others are kept in solution. Organic substances so formed can then keep appreciable amounts of metal in solution. Stevenson and Fitch (1981) have reported that

the concentration of copper in the soil can be regulated through complexation. When excess copper is present, complexation may reduce the concentrations of Cu^{2+} ions to non toxic levels. Likewise in conditions under which copper tends to precipitate e.g. in calcareous soils, complexation will serve to maintain copper in soluble forms.

2.1.5. Interaction of copper with other elements

Interactions of plant nutrients, both macro and micro modify the nutrition of plants (Olsen, 1972). Studying micronutrients interaction is important as a change in quantity of one may affect the performance of the other.

Copper interacts with other elements, so that its change in concentration in the soil affect the other elements. Phosphorus interaction with Cu may result from heavy or prolonged use of phosphatic fertilizers (Bingham, 1963). A decrease in concentration of Cu was noted as P levels increased, but the plants were not Cu deficient. Spencer (1966) observed that P applications reduced Cu concentrations in leaves and roots of 'Cleopatra Mandarin' seedlings at four levels of applied Cu from 0 - 250 ppm. In cases where applied Cu had become toxic for the growth of citrus, applied P reduced the Cu toxicity.

Wallace et al. (1981) observed that when P deficiency and Cu toxicity were both imposed upon bush bean plants in nutrient solution, the interaction was synergistic when the pH was about 4. When the solution pH was above 8, the interaction was protective antagnostic against copper excess.

Copper deficiency in sensitive crops can be induced by prolonged or excessive use of nitrogen (Chaudry & Loneragan, 1970; Bingham, 1963). In a study of the effect of copper on zinc absorption, Brar and Sekhon (1976) found that copper concentration in the nutrient solution inhibited zinc absorption, and Hawf and Schimid (1967) reported that copper competitively inhibited zinc absorption by plants.

Aduayi (1975) studied increases in soil copper, resulting from continuous copper fungicide sprays. At high copper content, there was an increase in the amount of N. Available P in the soil decreased with an increase in copper content. Topsoil K was unaffected but Ca showed an inconsistent trend. In the same experiment, there was a consistent trend towards increased leaf N, P and K with increased rates of copper spray. He concluded that increasing copper spray, increased the concentrations of N, P, K, Ca and Mg, and decreased Fe concentrations in leaves.

2.1.6. Distribution of copper in the soil profile

Copper is one of the least mobile of the trace elements, with the result that many soil profiles show little variation of total copper concentration with depth (Hodgson, 1963). Available copper however, varies with depth in the profile (Swaine and Mitchell, 1960) and is commonly higher in the organic rich surface layer than in the lower horizons. The tendency of applied copper, especially through sprays to be retained in the surface horizons of profiles was known many years ago (Reuther, 1953; Delas, 1963; Reider and Schwertman, 1972). Merry and Tiller (1980) found no evidence of accumulations of copper at depth below 25 cm in soil profiles in Australian orchard soils. Similar observations were reported by Venkataramaiah and Singh (1974) who noted that in soils from farms which never received copper sprays, the concentration of extractable copper was low and did not vary very much with depth; high amounts of extractable copper were observed in the surface (0 - 15 cm) which decreased with depth. Aduayi (1976) working in sprayed and non sprayed farms also found most of the copper in the surface horizons (0 - 15 cm) which decreased with depth. The topsoil (0 - 15 cm) of unsprayed farms had 3.3 ppm while the subsoil (5 - 30 cm) had 1.8 ppm. In the sprayed farms the topsoil (0 - 15 cm) had a concentration of 7 ppm while the subsoil (15 - 30 cm) had 3.3 ppm.

Studies by Moshi et al. (1982) show that most of the extractable copper from farms receiving regular sprays was within the 0 - 15 cm depth, while in the nonsprayed farms the amount of copper was low and showed no variations within the profile.

The movement of applied copper within the soil profile is restricted because of its strong affinity for soil colloids (Delas,1963). It has been also noted by Gilbert (1952) that leaching of copper in soils is negligible. Korte et al. (1976) classified copper as having low mobility in soils.

2.2. Comparison of Methods of Extracting Copper

Soil scientists have been striving to improve the existing soil tests to predict the loading capacities of soils for the elements in order to prevent toxic levels in plants. Soil test extractants for copper include various concentrations and combinations of dilute acids, chelates and complexing agents, and ideally they should extract Cu from the same labile pool as the plants and the amount extracted must be meaningfully related to the amount taken up by plants (Lindsay and Cox, 1985).

A large proportion of soil copper is often associated with organic matter (McLaren and Crawford, 1973) and a portion of this fraction appear to be accessible to plant roots (Viets and Lindsay, 1973). Extractants

capable of extracting copper from these fractions are required. Extractants which have commonly been used to assess the availability of copper in soils are dilute acids (e.g. 0.1 N HCl) and chelating agents such as ethylenediaminetetraacetic acid (EDTA) and diethylene triamine pentaacetic acid (DTPA) (Viets and Lindsay, 1973).

Nelson et al. (1956) used 0.1 N HCl to extract copper from soils. He reported a non - significant correlation between 0.1 N HCl - extractable copper and response of oats to copper fertilization. The cooper extracted by 0.1 N HCl (Tiwari and Kumar, 1982) showed significant relationship with plant uptake in peaty, red and alluvial soils. Cheng and Bray (1953) extracted copper with 0.1 N HCl and found out that the copper extracted varied from 2.0 to 11.4 ppm.

Hydrochloric acid (0.1 N) has been used to extract soils for copper also in Kenya, Jamaica and Hawaii (Lindsay and Cox, 1985) where critical levels were reported as being between 2 - 3 ppm.

Martens (1968) however expressed fear that acidic solvents such as HCl appeared to extract copper from pools which are not available to plants and therefore tended to overestimate the available copper status of soils.

Since much of the copper in soils is complexed or organically bound, organic chelating agents such as EDTA and DTPA in various concentrations have of late been tested extensively as extractants for Cu.

The citrate EDTA method was developed by Cheng and Bray (1953). They showed that the amount of Cu extracted with this reagent was closely related with that extracted with 0.1 N HCl. Viro (1955) used 0.05 M EDTA and reported a good recovery of added copper and zinc and concluded that EDTA was a good extractant for acid soils. The same extractant was used by Adam (1977) for six soil samples from Mbeya region where it was found to extract between 0.7 - 2.9 ppm Cu. In his study of copper in soils of Mbeya district, Kamasho (1980) also found 0.05 M EDTA suitable for copper extraction. EDTA 0.05 N was also used in a wide micronutrient survey by Sillanpää (1982) and proved reliable in extracting soil copper.

Another chelating agent, DTPA, was developed by Lindsay and Norvell, (1969) for simultaneous extraction of zinc, manganese, iron and copper. This extractant consists of 0.005 M DTPA, 0.01 M $CaCl_2$ and 0.1 M trieth - nolamine. Using this reagent, Lindsay and Norvell (1978) reported critical values of 0.2 ppm Cu. The extractant then achieved wide use and Haq et al. (1980) used it for soils contaminated with Cu and reported amounts of extractable copper ranging from 2.8 - 188 ppm. DTPA was also

used to extract copper from uncultivated soils (Gough *et al*. 1980) where it extracted between 0.1 - 1.2 ppm copper.

The three extractants discussed above namely 0.1 N HCl, 0.05 M EDTA and 0.005 M DTPA were compared by Norvell (1984) and he concluded that the suitability of the extractants was in the order, 0.1 N HCl > 0.05 M EDTA > 0.005 M DTPA. Robson and Reuther (1981) gave a summary of the copper extractants to be used in different soil conditions. For acid and near neutral soil they proposed the use of EDTA in (NH_4OAc) pH 7 as reviewed and recommended by Borggaard (1976). For near neutral and calcareous soils, they recommended the DTPA method of Lindsay and Norvell (1978).

2.3. Copper in Plants

2.3.1. Normal levels of copper in plants

The evidence of the essentialityof copper for green plants was reported as far back as 1931 (Sommer, 1931). Reuther and Labanauskas (1966) reviewed literature concerning copper levels in plants covering 26 crops. They found the copper concentration to range from 2 - 22 ppm. Bowen (1979) has reported that in most plants, the range of copper concentration is from 5 - 15 ppm and in crop plants, the usual range is 5 - 20 ppm (Jarvis, 1981). The common copper content found in plant tissue of various vegetable crops is 1 - 40 ppm and for beans (*Phaseolus vulgaris*) the concentration is between

15 - 30 ppm (Geraldson et al. 1973). Low copper content in plant materials were reported by Gough et al. (1980) for Western wheatgrass (0.34 - 9.8 ppm).

Literature on copper content of coffee is rather scant. Aduayi (1975) however, found mature coffee leaves from a nonsprayed coffee farm to contain 15 ppm

2.3.2. Excessive contents of Cu in plants

It has been observed by Jarvis (1978) that in most plant species, Cu concentrations seldom exceeds 30 ppm even when very large additions of Cu have been made either to soils or solution culture. The possibility of some plant species to accumulate much higher amounts of copper in their shoots have, however, been given by Reilly (1969). Wallace et al. (1981) grew bush beans in a solution culture with excess levels of Cu and after analysis, he found the trifoliate leaves of bush beans to contain up to 89.3 ppm. Aduayi (1976) in his study of the composition of soil and coffee leaves under varying copper fungicide spray regimes reported that leaves sampled from sprayed farms contained between 46 - 100 ppm Cu in comparison with the leaves from unsprayed farms which contained between 10 - 34 ppm Cu. In an earlier study, Aduayi (1975) found coffee leaves from farms receiving routine sprays of copper fungicides to contain between 35 - 95.5 ppm as compared to 15 ppm in the control experiment.

Abnormal concentrations of copper in coffee leaves have also been reported by Dickinson et al.(1984) and Lepp et al. (1984)

2.4 Effect of Copper Accumulation to Coffee and other Plants

Most early reports of Cu toxicity were associated with copper accumulations in the surface horizons of acid soil (Delas, 1963). Reuther and Smith (1953) reported Cu toxicity to citrus seedlings growing in sandy soils with pH less than 5 and total copper concentrations greater than 150 ppm. Drouineau and Mazoyer (1956) reported copper toxicity in spinach on soils of similar acidity and copper concentrations higher than 100 ppm (extracted by neutral ammonium acetate). These results may however need qualification by other pH related factors such as aluminium toxicity, which affects root development, iron and manganese concentrations, which can affect the appearance of symptoms of chlorosis.

Studies of Walsh et al. (1972) using a copper sensitive crop (snapbeans), gave some indication of lower limits of soil Cu levels likely to depress plant growth when high concentrations are applied under field conditions. Yields decreased by about one - third when Cu extracted by 0.1 N HCl or DTPA (Lindsay and Norvell, 1978) was greater than 40 ppm or by 0.01 M EDTA was greater than 30 ppm. The results of Purves (1977)

obtained in a pot experiment indicate that toxicity of Cu to oats may be expected at Cu concentrations between 100 -200 ppm (0.04 M EDTA). Patterson (1971), reports only slight toxic symptoms in maize when soils contained 245 ppm Cu extracted by 0.05 M, EDTA.

Wallace et al. (1981) grew beans in a culture solution applied with high levels of Cu (5×10^{-5}M) enough to cause stress on the plants. At a concentration of 89 ppm in trifoliate leaves, the yield reduction of bush beans, Phaseolus vulgaris was 42 percent.

At present, there is no concrete evidence that excessive amounts of copper in soils cause toxicity to coffee plants. Dickinson et al. (1984) reported that the coffee crops in Kenya showed no symptoms of copper toxicity and that yields of good quality coffee remained high although copper in the soil was found in great concentrations in the surface 10 cm (236 ppm total copper). This however could be explained by the observation by Delas (1963) who reported that in soils where high levels of Cu have been concentrated in the surface horizon (e.g. following prolonged use of copper containing fungicides), deep rooted perennial species are rarely affected, but shallow rooted annuals often fail to establish.

Studies conducted by Okioga (1978), hinted that spraying coffee with copper fungicides can cause phytotoxicity to plants characterized by the shortening and hardening of internodes of new bearing shoots coupled with significant reduction in the size of developing leaves which appear hardened, brittle and slightly chlorotic. Whether or not the toxicity results in reduction in yield, is not presently known. Aduayi, (1972) found characteristic toxicity symptoms such as corrugation, yellowing and necrosis of leaves followed by dieback in coffee seedlings when grown in solution containing 750 ppm copper.

Applied copper may take several years before becoming effective. Gartrell (1980) observed that availability of applied copper in mineral soils persited for a long time before being effective. He found that Cu applied four years earlier was two to three times more effective in increasing the copper content of wheat plants than current applications. His continuing experiment showed that copper applied 12 years earlier was still two to three times more effective in increasing copper uptake by cereal than current applications.

3. MATERIALS AND METHODS

3.1. Description of the Area Under Study

Moshi district is located on the southern slopes of mount Kilimanjaro. It lies between the latitudes of $3^{o}15'S$ and $3^{o}20'S$ and between the longitudes of $37^{o}15'E$ and $37^{o}30'E$ (Fig.1). The altitude ranges from 860 to 3,300 meters.

The geology of the district is composed of volcanic rocks consisting of agglomerate basalt, phenolytes and trachytes (Sheehy and Green, 1969). The dominant soils are deep, dark reddish or dark yellowish brown clay loams on lower slopes and dark brown silt loams over reddish brown silty clay loams on the upper slopes. Areas of very rocky brown loams with outcrops of bedrock occur throughout the area. There is variation in rainfall within the district depending on elevation. Rainfall varies from 900 mm in the lower areas to 1,650 mm in the higher areas.

Approximately two thirds of the area is under cultivation. The lower areas are used for maize, beans, finger millet and bananas. Coffee is the main crop in the middle and higher areas and is produced both in large estates and in small peasant farms where it has been grown for more than 40 years usually intercropped with bananas, maize, beans and vegetables. Local farmers in the district

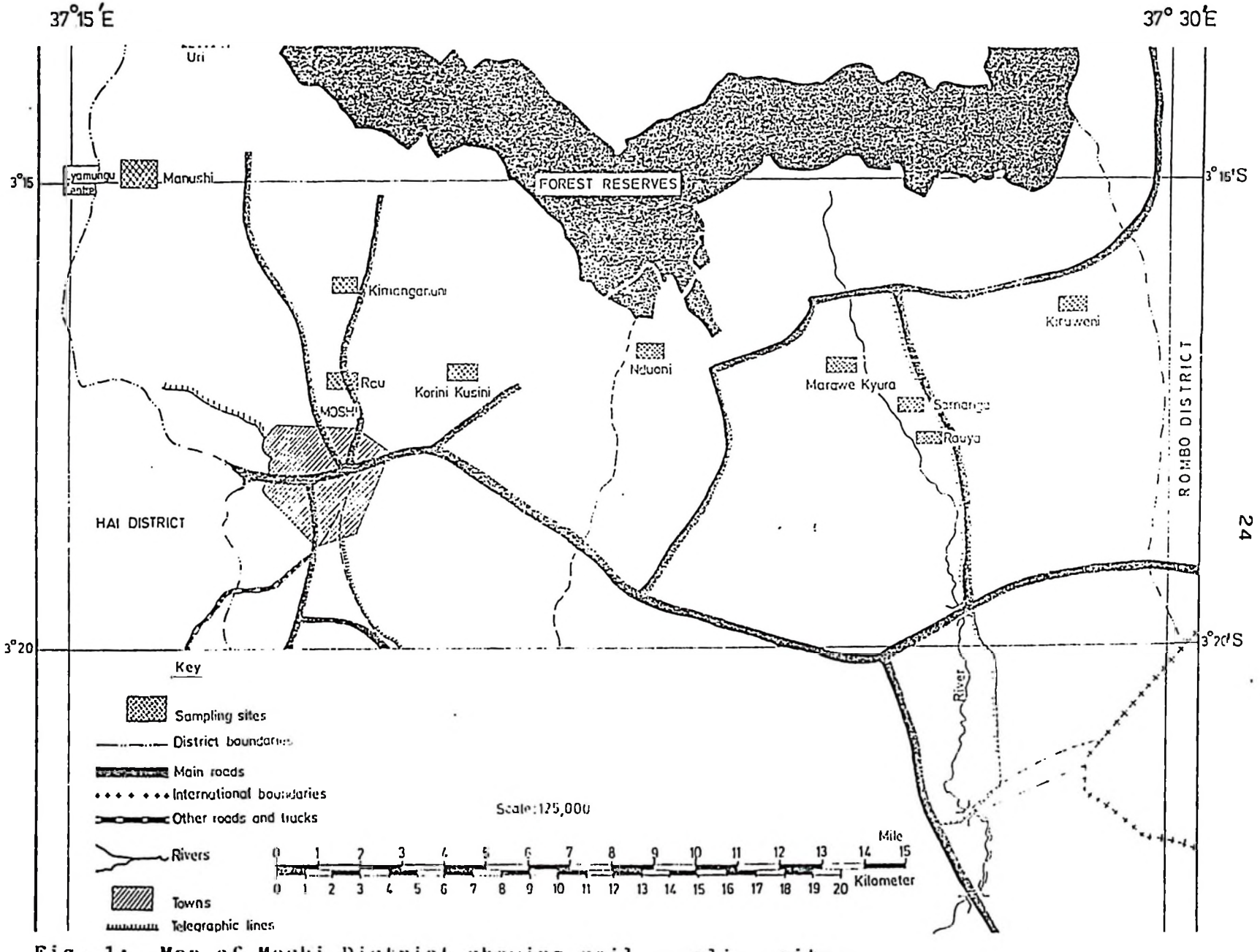

Fig. 1: Map of Moshi District showing soil sampling sites

grow approximately 40,000 hectares of coffee in 114 villages. The district has a good potential for agriculture especially where the slopes are gentle. Above the coffee growing areas are forest reserves (Fig.1).

3.2. Selection of Farms for the Study

The study was conducted on peasant farms across the coffee growing areas of the district (Fig.1). To obtain farms for the study, all the coffee growing subdivisions were listed and from these the farms to be studied were randomly picked. The history of the farms including fungicide spraying regimes for the past 30 years was obtained from the farmers and through this past experience, the farms were divided into four categories. The first category included farms which have been under copper fungicide sprays for less than ten years. Farms that have been sprayed for 10 to 30 years were placed in a separate category and a group of farms that have been sprayed for more than 30 years were put in another category.

Finally another group of farms was chosen to contain farms in which no spraying activities have been done. These were to act as control for the study.

Ten farms were therefore picked from each category so that 40 farms were included in the study. From these farms, soil samples were taken for study as shown in the following sections.

3.3. Soil Sampling

3.3.1. Soils for survey work

Samples were taken from each site using an auger at depths of 0-5, 5-10, and 10-20 cm. For each of the three depths, a composite sample was obtained from at least 8 spots, these were mixed together for each depth. From each farm three samples, were collected for analysis. The samples were air dried and then ground and sieved to pass through a 2 mm sieve and stored for chemical analysis. A total of 120 samples were obtained.

3.3.2. Soils for glasshouse experiments

3.3.2.1. Soils with different DTPA copper content

After preliminary analysis of the survey soils, twelve soils of different DTPA copper content were collected from the study area for further study in the glasshouse, as shown in Table 1.

The soils were selected in order to cover a wide range of DTPA extractable Cu. Twenty kg of soil were collected from each site, taking care that the soils are approximately collected from the same area where the soils for the original survey were taken. The soils were taken from a depth of 0-15 cm to represent the plough layer. At least 8 spots composed a composite sample. The soils were throroughly mixed, divided into three portions of 4 kg each and transferred to the glasshouse. There were 36 pots i.e. 3 pots of each of the 12 soils. Before planting

Table 1: Soils selected for glasshouse experiment one

Village	Duration of spraying coffee with Cu fungicides (years)			
	0	<10	10-30	>30
	Cu content (pmm)			
Marawe Kyura	3.7	54.0	200.0	292.0
Boro	4.4	27.0	35.5	368.0
Kuruweni	7.4	30.0	100.0	100.0

the soils were mixed with triple super phosphate fertilizer at the rate of 80 kg P/ha. Five bean seeds (Phaseolus vulgaris) were planted per pot and these were thinned to 2 plants per pot after germination. Optimum moisture in the pots was maintained by addition of distilled water when needed. Fourteen days later, nitrogen fertilizer was applied in each pot at the rate of 100 kg N/ha. Sulphate of ammonia fertilizer was used. Bean plants were grown for 28 days after which they were harvested. This period coincided with the period just before flowering.

3.3.2.2. Effect of a high rate of copper oxychloride on bean growth

Five soils were also collected from the study area in the manner described in section 3.3.2.1. These soils however were taken from farms sprayed with copper fungicides for more than thirty years and those found to contain the highest amount of DTPA extractable copper. An amount of copper oxychloride, 200 mg copper oxychloride/ kg of soil, equivalent to 200 ppm Cu, was mixed with each soil and potted. Each pot contained 4kg of the treated soil and three replicates of each soil were prepared giving a total of 15 pots. The rate of copper oxychloride used was based on the amount of Cu which will be

applied through spraying coffee for 20 years as calculated in appendix 5.

Prior to planting, the soil was also mixed with TSP fertilizer at a rate of 80 kg/ha and planted with beans. Five beans were planted and thinned to two after germination. Fourteen days later the pots were dressed with sulphate of ammonia fertilizer at the rate of 100 kg N/ha.

The bean plants in this experiment were also left to grow for 28 days when they were harvested for processing.

3.3.2.3. Effect of soil pH on Cu availability and bean growth

Copper toxicity is actually known to be intensified by acidifying the soil (Wastgate, 1952; Reuther et al., 1953; Lexmond and Van der Vorm, 1981). Similarly, Cu availability in soil is known to increase with a decrease in pH (Peech, 1941; Piper, 1942). Thus the effect of soil pH on Cu availability and growth of beans was also studied. Five soils of known pH values were collected as explained in section 3.3.2.1. above from farms sprayed with Cu fungicides for over 30 years and then pH values were adjusted as follows:

For each soil, a suspension of 20 g soil and 20 ml distilled water (1:1 soil water) was made, and the pH measured as explained by Peech (1965). The suspension was then titrated with dilute HCl and the volume used to obtain a predetermined pH value was noted. These titrations were done until a constant pH was obtained. The volume of HCl used per 20 g soil was then used to calculate the amount of acid to be used to lower pH to predetermined values. The range of pH obtained is shown in Table 2.

The soils were mixed with 80 kg P/ha of phosphate fertilizer (TSP) and planted with 5 bean seeds, as explained earlier. After germination seedlings were thinned to two per pot and after 14 days 100 kg N/ha fertilizer were added. The growth of beans was then observed for 28 days after which the plants were harvested and analysed for Cu content as explained below.

Table 2: Soils selected for glasshouse experiment three

Village	Original pH of soil	Adjusted pH
Uri	5.3	4.8
Boro	6.2	5.1
Marawe Kyura	6.3	5.4
Kirua Vunjo	5.7	5.7
Korini Kusimi	6.2	6.0

3.4. Plant Samples

3.4.1. Coffee leaves

Coffee leaf samples were collected from the same farms where soil samples were taken. The fourth pair of leaves counting from the fully open leaves at the tip of a primary branch was chosen. Fifty leaf pairs from different trees constituted a sample. The leaves were washed with 0.1 N HCl, soap solution and then rinsed with distilled water as outlined by Ashby (1969). The samples were dried for 48 hours in an oven at 65°C, and ground to pass through a 1 mm sieve and stored for chemical analysis.

3.4.2. Bean leaves

Bean leaf samples were collected 28 days after germination, just before flowering. Recently matured leaves, the third trifoliate from the top, were picked.

The remaining plants were cut just above the soil. The samples (leaves and plants) were washed with 0.1 N HCl, soap solution and rinsed with distilled water, using the procedure of Ashby (1969). These samples were dried for 48 hours in an oven at 65°C, and ground to pass through a 1 mm sieve and stored for chemical analysis.

3.4.3. Bean roots

The roots in each pot were carefully shaken out of the soil, washed and dried in an oven at 65°C for 48 hours. The roots from each pot were then weighed, and the weight recorded.

3.5. Analytical Procedures

3.5.1. Soil analysis

3.5.1.1. Soils for survey work

The soil pH was measured in water (1:1 soil: water) using a pH meter (Peech, 1965). The particle size distribution was determined by the Bouyoucos hydrometer method as outlined by Day (1965). The hydrometer reading was corrected for temperature and for the density of calgon used to disperse the soil. Organic carbon was determined by the wet digestion method of Walkley and Black (Allison, 1965). A recovery factor of 1.33 was employed.

Exchangeable Ca, Mg, Na and K were extracted by leaching with 1 N NH_4OAC at pH 7 and determined by atomic absorption spectrophotometry (Chapman, 1965). Cation exchange capacity (C.E.C.) was determined by the ammonium saturation method (Chapman, 1965). Total N in the soil was determined by the macro Kjeldahl method (Bremner 1965). Available P was extracted with 0.03 N NH_4F + 0.025 N HCl as described by Bray and Kurtz (1945). Ascorbic acid was used for colour development.

Copper, Zn, Fe and Mn were extracted by the DTPA method of Lindsay and Norvell (1978). The extracting solution was composed of 0.005 M DTPA, 0.01 M $CaCl_2$ and 0.1 M triethanolamine adjusted to pH 7.3. The elements were determined directly in the soil extract by means of atomic absorption spectrophotometry.

3.5.1.2. Soils for glasshouse experiments

After the glasshouse experiments, Cu in the soils was extracted using 0.1 N HCl (Fiskell, 1965), 0.05 M EDTA (Viro, 1955) and 0.005 N DTPA (Lindsay and Norvell, 1978). A ratio of 1:10 (soil: extractant) was used for 0.1 N HCl Cu extraction. Five grams of soil were shaken with 50 ml 0.1 N HCl for two hours and then filtered through a whatman no.42 filter paper. Copper from the extract was determined directly by atomic absorption spectrophotometry. The extraction of EDTA Cu, was done using a 1:5 (soil:extractant) ratio. Ten grams of soil were shaken with 50 ml EDTA solution for two hours in an automatic shaker, filtered through a whatman no.42 filter paper, and copper from the extract was determined by atomic absorption spectrophotometry.

Copper was also extracted by the DTPA method of Lindsay and Norvell (1978) using a 1:2 (soil: extractant) ratio and shaking the suspension for two hours. After filtering through whatman no. 42 filter paper the filtrate was used to determine Cu as well as Zn, Fe and Mn. The determination was made by the atomic absorption spectrophotometer.

3.5.2. Leaf sample analysis

3.5.2.1. Coffee leaf samples

Prior to the determination of different elements in the coffee leaves, the samples were ashed in a muffle furnace at 450°C for five hours. The residue was allowed to cool and then dissolved in 10 ml. 1 N HNO_3 and evaporated to dryness on a hot plate. The samples were then dissolved in 10 ml. 1 N HCl and finally filtered into a 50 ml volumetric flask through whatman no.42 filter paper and made to volume using 10 ml. 0.1 N HCl portions, as outlined by the Association of Official Analytical Chemists (1970). Copper was determined in the extract by atomic absorption spectrophotometry. Calcium, magnesium, zinc, iron and manganese were also determined in the same way.

Phosphorus was determined from the same extract colourimetrically. Ascorbic acid was used for colour development and the absorbance was read in a spectrophotometer at a wavelength of 880 nm and the concentration was obtained from a standard curve.

3.5.2.2. Bean samples

The bean plant samples were processed and analysed in the same way as described in section 3.5.2.1. above.

4. RESULTS AND DISCUSSION

4.1. Properties of Soils Used in the Study

4.1.1. Soil pH, organic carbon and total nitrogen

The pH of the soils ranges from 5.2 - 7.1 (Table 3) with most soils being between 6.1 -6.5 (Appendix 2) which is a favourable range for the availability of nutrients (Brady, 1974). Organic carbon ranges from 1.69 - 6.58% with most soils being between 2.29 - 3.5 percent. Total nitrogen ranges between 0.10 - 0.47% with most soils being between 0.2 - 0.4%. These two propertie total nitrogen and organic carbon, are used to assess the nitrogen fertility status of soils and generally organic carbon values of 2.25 percent and total nitrogen values $\geq$ 0.23 percent are ranked as high, implying high N fertility (ILACO, 1981).

4.1.2. Phosphorus and potassium

Available P in the soils under study ranges from 2.8 - 119.3 ppm with most soils being between 23.7 and 49.1 (Appendix 3). Phosphorus deficiency symptoms often occur when soils contain less than 15 ppm available P (Sperow, 1975). Singh and Uriyo (1980) found the P critical level to be 25 ppm for maize in Morogoro, Tanzania.

Exchangeable K in soils range from 0.32 - 5.9 me/100 g with most soils being between 1.3 - 2.9 me/100 g. The soils had clay content of between 40.6

TABLE 3: Properties of soils used in the study

Soil category (treatment)		pH	OC %	Clay %	Total N %	Available P (ppm)
Control, no application of Cu	Range	5.2-7.1	1.61-4.58	46.4-58	0.12-0.38	8.42-110.5
fungicide	Mean	6.1	3.11	53.8	0.23	23.7
Cu fungicide used for 10 years	Range	5.2-6.7	1.86-6.58	44-8-57	0.19-0.47	9.12-119.3
	Mean	6.4	3.67	48.9	0.37	41.93
Cu fungicide used for 10-30 years	Range	5.2-7.0	1.65-6.28	39.9-66	0.1-0.50	2.8-78.6
	Mean	6.5	3.70	51.8	0.32	41.25
Cu fungicide used for 30 years	Range	5.3-7.1	1.83-6.28	40.6-66	0.27-0.67	13.3-9.40
	Mean	6.4	4.34	52.6	0.46	49.12

Table 3 Cont.

Soil category (treatment)		Exchangeable cations				CEC
		K	Ca	Mg	Na	(me/100g)
		(me/100g soil)				
Control no application of Cu	Range	0.51-3.97	0.63-8.75	0.73-6.67	0.36-1.33	42 - 52
fungicide	Mean	1.33	5.13	3.38	0.65	47.2
Cu fungicide used for 10 years	Range	0.51-5.9	3.75-5.9	1.93-11.04	0.38-1.26	46 - 50
	Mean	2.85	8.82	5.88	0.66	48.7
Cu fungicide used for 10-30	Range	0.41-1.03	2.19-14.38	1.2-12.4	0.39-1.03	41 - 53
years	Mean	2.18	9.66	6.62	0.68	46.3
Cu fungicide used for 30 years	Range	0.32-3.33	1.56-17.81	1.56-11.35	0.27-1.9	41 - 61
	Mean	1.99	11.68	7.07	0.60	55.6

and 52.6 percent. Soils with heavy textures are higher in potassium bearing minerals and therefore contain higher reserves of available K.

4.1.3. Calcium and magnesium

Calcium in the soils ranges between 0.63 - 17.8 me/100 g with most of the soils being between 5.13 to 11.68 me/100 g. According to Doll and Lucas (1973) the average content of exchangeable Ca is about 4.0 me/100 g. Their figure for exchangeable magnesium is 1.6 me/100 g. The soils in the study had a content of Mg of between 0.73 me/100 g and 12.4 me/100g with most soils being being between 3.38 and 7.07 me/100g.

From the above soil properties, the soils in Moshi district can be cansidered to be of high agricultural potential. This observation is shared also by Sheehy and Green (1969) who made this conclusion in their survey of land resources of Northern Tanzania which included the area under this study.

4.1.4. Properties of soils in relation to time under cultivation

The percent organic carbon an indication of soils organic matter was found to increase with increasing number of years under cultivation ($r= 0.93$, $P \geq 0.01$). Similarly total N, P and K increased with the time under cultivation. This trend indicates good soil management

practices in coffee farms. This is attributed to the use of farm yard manure and crop residues as mulch, which is common among coffee farmers in Moshi (Kasembe et al., 1983).

4.1.5. Other trace elements

Other trace elements namely iron and manganese were present in adequate amounts (Appendix 2). Extractable iron content ranged between 7.4 - 48.8 ppm while manganese was found to range between 7 - 146 ppm. Data for zinc content show variable quantities between 1 - 18 ppm with many soils falling below 10 ppm, DTPA extractable zinc. Kamasho (1980) found volcanic soils in Mbeya district to contain between 1.1 - 6.9. ppm DTPA zinc. The zinc content of soils in Moshi district can also be considered to be normal.

4.2. DTPA Extractable Copper of Soils in Relation to the Use of Copper Based Fungicides

The DTPA extractable Cu in soils that had received no copper sprays ranges from 1 - 16.5 ppm in the surface (0 - 5 cm) soil with most of the soils being between 1 - 5 ppm (Table 4). The Cu content decreased with depth in the profile. On comparison with DTPA - extractable Cu values of Kamasho (1980) in some volcanic soils of Mbeya Tanzania, the values reported here from soils free from Cu contamination are high. This is probably due to difference in parent material. While the soils of Mbeya are formed from volcanic ash and

pumice those of Moshi district are formed from volvanic lava. Pinkerton (1967) examined copper deficiency in soils derived from various parent materials and observed that deficiency was associated with soils derived from recent volcanic ash and pumice. Nyandat and Ochieng (1976) also confirmed that most of the Cu deficiencies occured in wheat plants grown in soils derived from ash and pumice. Gough et al. (1980) extracted native plant available copper in the Great Plains USA with DTPA. He observed values between 0.1 - 1.2 ppm.

In surface soils of farms sprayed for less than ten years, the Cu content was between 6.9 - 125 ppm, with most of the soils being between 16.5 - 59 ppm. Where farms received annual fungicide sprays for 10 - 30 years, the Cu content of the surface soils was between 28 - 316 ppm with most soils being in the region of 100 - 200 ppm. When farms were sprayed for more than 30 years the copper content was between 54 -368 ppm with most soils lying between 120 - 290 ppm. The data show that the Cu content of the surface soils increased by about 10 times during the first ten years of spraying with copper fungicides, doubled in the next 10 to 20 years and increased by a further 1.4 times for farms sprayed for over 30 years. The increase in Cu content was expected since the Cu fungicides applied to the leaves soon become a component of the soil as the leaves drop and decompose and become

Table 4: DTPA extractable Cu content of soils in relation to the duration of use of copper fungicide sprays

Treatment (Duration of sprays)	Depth (cm)	Range of Cu content (ppm)	Mean (ppm)
Control (no fungicide sprays)	0-5	1.0 - 16.5	5.6
	5-10	1.1 - 7.4	3.4
	10-20	1.0 - 5.9	2.2
Fungicide sprayed for 10 years	0-5	6.9 - 125	35.9
	5-10	1.6 - 44	18.0
	10-20	1.3 - 30	8.4
Cu fungicide sprayed for 10 - 30 years	0-5	28.0 - 316	122.9
	5-10	18.0 - 77.0	70.2
	10-20	13.0 - 66.0	20.3
Cu fungicide sprayed for 30 years	0-5	54 - 368	186.2
	5-10	10.0 - 121	89.5
	10-20	15.0 - 37.5	32.8

Table 4: DTPA extractable Cu content of soils in relation to the duration of use of copper fungicide sprays

Treatment (Duration of sprays)	Depth (cm)	Range of Cu content (ppm)	Mean (ppm
Control (no fungicide sprays)	0-5	1.1 - 18.5	[illegible]
	5-10	1.1 - 7.4	[illegible]
	10-20	1.1 - 5.3	[illegible]
Fungicide sprayed for 10 years	0-5	5.3 - 125	[illegible]
	5-10	1.5 - 44	[illegible]
	10-20	1.3 - 30	[illegible]
Cu fungicide sprayed for 10 - 30 years	0-5	23.0 - 316	[illegible]
	5-10	18.0 - 77.0	[illegible]
	10-20	13.0 - 66.0	[illegible]
Cu fungicide sprayed for 30 years	0-5	54 - 368	[illegible]
	5-10	10.0 - 121	[illegible]
	10-20	15.0 - 37.5	[illegible]

N HCl) in the top 15 cm of arabica coffee farms which has received "bordeaux mixture" spray for more than 40 years. In the unsprayed blocks the Cu content was only 10 ppm in the surface horizon.

Spraying coffee with copper fungicides therefore, increased copper concentration in the soil. Lepp et al. (1984) also produced evidence that spraying coffee with copper fungicides increased copper content of the soil and the increase was a function of age of the farm and soil depth. Highest levels were concentrated in the 0-20 cm zone of the 24 year old stand. In vineyards associated with copper fungicide sprays in central Portugal, Megalhae's et al. (1985) found that the accumulation of Cu was in good agreement with the estimated amount of Cu applied in fungicides and that levels of total and extractable Cu were highest in the surface layers and decreased with depth. Many other observations are in agreement with findings of this research, that Cu increased in the surface horizons and decreased with depth. Merry (1980) reported that high copper concentrations which had accumulated in contaminated soils tend to be largely retained in the surface horizons. The same observation was again made by Malewar et al. (1978) and Kornegay et al. (1976).

4.3. Relationship between DTPA - Extractable Copper and Selected Soil Properties

4.3.1. Copper and organic carbon

The organic carbon in the soils under study was found to increase with the years under routine spraying of coffee with copper fungicides and so was the extractable copper content of the soils. However, the increases in these two soil properties did not show any trend between each other. When correlation coefficients between soil organic carbon (as measure of organic matter) and extractable copper in the four categories of farms studied were calculated inconsistent correlations of r = 0.06, - 0.4, - 0.16 and 0.28 were obtained (Tables 5, 6).

Some studies involving soil copper and organic matter however, have given impressions that there exists a relationship between these two properties of soils. Stevenson and Ardakani (1972) for example have reported the ability of soil organic matter to form combinations with soil copper. Studies by McLaren and Crawford (1973) on the role of organic matter and exchangeable fractions of copper in soils imply that organic matter and soil copper should have a relationship. Detailed studies by Mclaren *et al*. (1980); Stevenson and Fitch (1981) recognize the effect organic matter has in the chemistry of copper in the soil, thus indirectly suggesting that the availability of copper in soils depends in the organic matter content. According to these observations it

Table 5: DTPA copper content in relation to organic carbon

	0 sprays		0 - 10 years		10 - 30 year		Over 30 years	
	Cu ppm	OC%	Cu ppm	OC%	Cu ppm	OC%	Cu ppm	OC%
	3.7	2.0	54.0	3.6	200.0	3.5	292	2.9
	4.0	3.7	25.0	5.1	316.0	4.8	152	4.6
	1.4	4.0	6.9	3.7	80.0	3.9	196	5.7
	2.1	1.7	20.0	2.3	252.0	1.9	136	3.9
	11.3	3.2	21.5	4.0	44.5	3.4	292	5.1
	4.0	2.5	33.0	2.3	28.0	3.6	368	2.9
	4.4	3.2	27.0	4.0	35.5	3.4	100	3.4
	7.4	2.6	30.0	2.9	100.0	4.5	148	6.3
	1.0	4.6	16.5	6.6	11.5	4.6	124	4.4
	16.5	3.7	12.5	2.4	154.0	3.7	54	4.2
Agerage	5.58	3.12	35.89	3.69	122.15	3.71	186.2	4.34
r	0.06 NS		- 0.40 NS		0.16 NS		- 0.28 NS	

Table 6: Correlation cofficients of DTPA extractable Cu with soil pH and soil organic carbon

Soil property	Duration of copper fungicide sprays			
	No spray	10 years	10 - 20 years	over 30 years
	r			
pH	0.31 NS	0.43 NS	- 0.3 NS	- .12 NS
OC	0.96 NS	- 0.40 NS	- 0.16 NS	- 0.28 NS

would be expected that soils high in organic matter would also have the highest available copper, something not observed in this study.

Data obtained in this study suggest that the observations of the above researchers are not always the case. It has also been observed by other workers that in some cases the views on the relationship between copper and organic matter could differ. William and McLaren (1982) for example, reported that the amount of copper immobilized by individual soils did not appear to be related to soil organic matter content. Similarly, Brenan et al. (1980) in his study on the extent of decline in copper availability and how it differed among soils, found out that the differences did not appear to be specifically related to organic carbon. The same observations were made by Dragun and Baker (1982) who conducted an experiment to determine the soil properties which controlled copper availability and found that organic matter content was not significantly correlated with available copper.

The above arguments suggest the possibility of the existence of other factors that modify the relationship between organic matter and soil copper content, especially in situations where there has been additions of soil copper from other sources such as copper fungicide sprays.

4.3.2. Copper and soil pH

Data for the soil pH and DTPA extractable copper is presented in Table 7. The data does not show that there is any relationship between the two soil properties. The correlation coefficient of r - 0.31, 0.43, - 0.3 and - 0.12 (Tables6 and 7) for the four categories of farms imply that there could be negative correlation, a positive correlation and in some cases no correlation at all. Such results are different from observation usually encountered in studies of these soil properties. For example, Peech (1941) found a negative correlation between the availability of soil copper and pH which agrees with those of Tiwari and Kumar (1982) and Dragun and Baker (1982).

Results obtained in this experiment, however, do agree with some workers who argue that the relationship between copper and soil pH can be variable. Piper and Beckwith (1949) found that the concentration of copper in a number of species was almost entirely unaffected by a range of soil pH from 4.5 to 7.5. In a similar manner, Lunabald et al. (1949) concluded that lime content and pH of soils did not affect the availability of copper as measured by plant uptake. These observations are also in agreement with those of Archer (1971) and Brenan et al. (1980).

Table 7: DTPA copper content in relation to pH

	0 spray		0 – 10 years		10 – 30 years		Over 30 years	
	Cu ppm	pH	Cu ppm	pH	Cu ppm	pH	Cu ppm	pH
	3.7	6.5	54.0	6.9	200.0	6.5	292.0	6.3
	4.0	5.6	25.0	5.9	316.0	6.1	152.0	6.3
	1.4	5.6	6.9	5.8	80.0	6.5	196.0	6.0
	2.1	6.5	20.0	6.8	252.0	6.6	136.0	6.6
	11.3	6.3	21.5	6.0	44.5	6.7	292.0	6.4
	4.0	6.3	33.0	6.6	28.0	7.0	368.0	6.7
	4.4	6.0	27.0	6.5	35.5	6.6	100.0	6.6
	7.4	6.2	30.0	6.4	100.0	6.3	148.0	5.4
	1.0	6.0	16.5	6.3	11.5	6.0	124.0	6.6
	16.5	6.3	125.0	6.6	154.0	6.3	54.0	7.1
Average	5.58	5.13	35.89	6.38	122.15	6.46	182.2	6.4
r	– 0.31 NS		0.43 NS		– 0.30 NS		– 0.12 NS	

The observations imply that the relationship between the availability of soil copper and pH is variable probably depending on prevailing soil conditions.

4.4. Effect of Soil Copper Status on Copper Content of Coffee Leaves

Tables 8 shows the soil DTPA copper content (ppm) and the concentration of copper in coffee leaves from plants which have been sprayed with copper fungicides for different durations ranging form less than 10 years to more than thirty years. Coffee leaves from farms that have never been sprayed with copper had a leaf Cu concentration of 10 ppm. The data shows that coffee leaves from farms sprayed for less than 10 years had a copper concentration of an average of 58.7 ppm, while leaves from farms under continuous spray for 10 - 30 years had an average leaf copper concentration of 60.8 ppm. Coffee leaves from the farms that have been sprayed for more than 30 years had an average Cu content of 56.3 ppm. The results indicate that spraying coffee with copper fungicide increased the leaf Cu content from 10 ppm to above 50 ppm Cu in ten years. The copper content of the leaves tend to be constant after this as can be implied from the average of 60.8 ppm and 55.3 ppm leaf Cu for the period of spraying for 10 to more than 30 years. The normal copper concentration of coffee leaves is quoted as being between 15 and 34 ppm Cu (Aduayi, 1975; 1976). For many crop plants this value is between 5 - 20 ppm leaf copper content (Bowen,

Table 8: DTPA extractable Cu and copper content of coffee leaves in relation to the duration of spraying coffee with copper fungicides

	Duration of spraying Cu fungicides (years)					
	10		10 - 30		30	
	Soil	Leaves	Soil	Leaves	Soil	Leaves
	ppm					
	54.0	43.4	200.0	43.5	292.0	69.4
	25.0	32.8	316.0	58.0	152.0	36.4
	6.9	36.0	80.0	94.5	196.0	50.9
	20.0	110.0	252.0	32.3	136.0	88.0
	21.5	102.0	44.5	62.0	292.0	50.9
	33.0	39.7	28.0	50.9	368.0	39.7
	27.0	50.9	35.5	121.4	100.0	54.6
	30.0	65.7	100.0	43.4	148.0	50.9
	16.5	69.4	11.5	50.9	124.0	43.9
	125.0	47.1	154.0	50.9	54.0	60.0
Average	35.89	59.7	122.2	60.78	186.2	56.33

Copper content of coffee plant which have not been sprayed with Cu fungicides was 10 ppm.

1979). According to Jarvis (1981) in many plant species, copper seldom exceeds 30 ppm in the leaves even when large additions have been made to soils or solution culture. The high leaf copper concentration values reported here are however supported by Reilly (1969) who found that some plants species could actually accumulate very much higher concentrations of copper in their shoots when there are high concentrations in the soil, and it can be implied from the present data that coffee plants could be one of such plant species. Indeed, Aduayi (1976) reported an average of 77 ppm copper concentration in mature leaves of coffee plants taken from farms that had regularly been sprayed with copper fungicides and which did not show any physiological disorders because of high leaf copper content. Copper toxicity was also not observed by Dickinson et al. (1984) from coffee leaves of a 68 year - old large scale coffee plantations with continuous application of copper fungicides, although the foliage contained up to 400 ppm Cu. There are two possible explanations of the tolerance of coffee to high copper concentrations. The first is the possibility of immobilization of copper at the root surface which reduces its translocation to other tissues as suggested by Mengel and Krikby (1982). This is supported by Hardiman et al. (1984) for bean plants. Hardiman et al. (1984) concluded that for heavy metals including copper, most of the total metal absorbed by plants was retained in the roots and the proportion retained increased in response to concentrations in the soil.

The second explanation is that suggested by Reilly (1969) for the Rhodesian copper flower plant which was observed to tolerate high levels of copper in its tissues. This explanation seems to explain the presence of up to 400 ppm copper in coffee leaves as reported by Dickinson et al. (1984)

It is worthwhile to mention that the use of leaf analysis in predicting crop response to native or added copper has caused reservation by some researchers. Lepp et al. (1984) produced data which made him conclude that coffee leaf analysis was not a good indicator of the behaviour of copper added into the soil through copper fungicide sprays. Results of Sims (1986) produced inconsistent correlations and low r values of all models involving copper and illustrated the difficulty in predicting crop response to native or added copper.

4.5. Glasshouse Experiments

4.5.1. Beans grown in soils with different extractable Cu contents

4.5.1.1. Glasshouse observations

The beans germinated four days after sowing. The growth was normal. Healthy and vigorous plants were obtained (plate 1) and there were no symptoms of any nutritional disorders until the plants were harvested after 28 days for processing and analysis as explained in chapter 3.

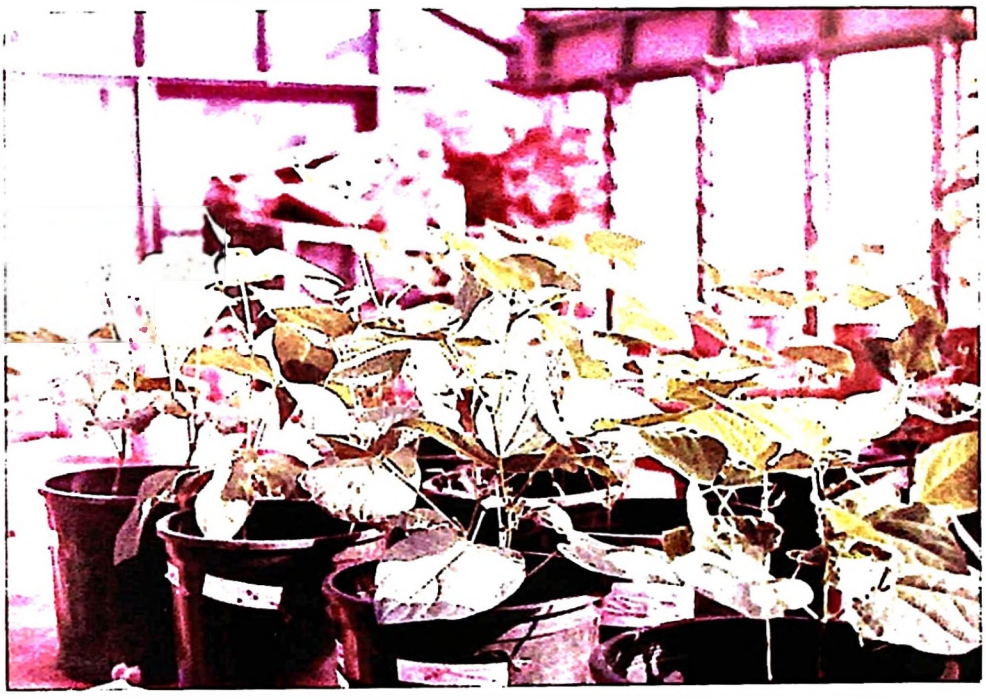

Plate 1: Bean plants (Phaseolus vulgaris) grown in soil with varying amounts of DTPA extractable copper

4.5.1.2. Copper extracted by different extractants from the soils used in the glasshouse experiment

Table 9 shows the different amounts of Cu extracted by three different extractants namely 0.1 N HCl (Cheng and Bray, 1953; Fiskell, 1965), 0.005 M DTPA (Lindsay and Norvell, 1978) and 0.05 M EDTA (Cheng and Bray, 1953; Viro, 1955). EDTA extracted the highest amount of Cu and gave an average of 290.1 ppm with a range of 55.2 - 848.3 ppm. This was followed by the amount extracted by 0.1 N HCl which gave an average of 158.8 ppm with a range of 24.0 - 430.4 ppm. DTPA extracted the least amount giving an average of 88.9 ppm with a range of 13.5 - 245.8 ppm. Fiskell and Westgate (1955) found values of up to 1000 ppm of 0.1 N HCl - extractable Cu in soils on which bordeaux mixture had been applied for many years and values of up to 300 ppm were reported in soils from citrus grooves that had received copper-bearing sprays for several years (Reuther et al., 1953; Spencer, 1954). The amounts obtained in this study for 0.1 N HCl extractable Cu are therefore not unusual in soils in which copper based fungicides have been used for many years. Haq et al. (1980) used, 0.01 M EDTA, and 0.005 M DTPA to extract Cu from soils contaminated with heavy metals and containing a maximum of 325 ppm Cu. EDTA (0.01 M) extracted a range of 2.7 - 135 ppm from 46 soils, while 0.005 M DTPA extracted a range of 2.8 - 188 ppm Cu, also supporting the observation that amounts obtained in this study are normal. Under normal uncontaminated situations, the amount of EDTA

Table 9: Plant Cu concentraton, root weight, dry matter yield and Cu uptake beans (Phaseolus vulgaris) in relation to Cu extracted by different extractants

Soil	DPTA	HCl	EDTA	Dry matter weight (g)	Weight roots (g)	Plant Cu concentrations (ppm)	Cu Uptake (µg)
1	13.5	24.0	55.0	5.9	0.78	25.6	151.0
2	22.9	28.6	95.8	5.2	1.12	22.9	119.0
3	23.7	62.8	114.6	5.6	1.13	16.6	92.0
4	24.6	32.6	80.6	7.8	1.15	16.6	127.0
5	44.4	64.2	177.2	5.3	1.17	25.6	136.0
6	52.7	80.0	161.5	5.1	1.17	25.6	131.0
7	57.6	91.5	195.9	6.7	1.19	23.2	155.0
8	99.8	196.5	371.2	5.7	1.29	25.6	146.0
9	119.6	384.3	305.4	9.7	1.30	22.6	219.0
10	125.2	114.7	352.2	6.5	1.34	25.6	166.0
11	237.0	430.4	723.3	8.0	1.47	25.9	207.0
12	245.8	395.9	848.4	7.6	1.50	22.9	174.0
average	88.9	158.8	290.1	6.4	1.22	23.2	152.0

extractable copper usually ranges from 1 - 18 ppm according to Sillanpää (1982). Berrow and Reeves (1985) produced EDTA extractable Cu amounts that had a range of 0.08 - 9.6 ppm with a mean of 8.6 ppm which are within the range reported by Sillanpää (1982). In another study Gough et al. (1980) extracted a range of 0.3 - 15 ppm EDTA Cu from normal soils associated with growing of wheatgrass. Critical values of DTPA extractable Cu from uncontaminated soils have been reported to range from 0.1 - 1.2 ppm (Gough et al. (1980) and to be 0.2 ppm by Lindsay and Norvell (1978).

4.5.1.3. Growth of beans, Cu concentration in bean shoots, dry matter yield, root weight and Cu uptake in relation to extractable copper content

Data for dry matter yield, root weight, plant Cu concentration and plant Cu uptake are shown in Table 9. The dry matter yield of plants increased from 5.1 - 9.79 g per pot with an average of 6.4 g per pot. The root weight also increased from 0.78 g per pot to 1.50 g with an average of 1.22 g per pot. The increase in shoot weight and root weight appears to be related to the increase in extractable copper (see details below). This trend was not expected because a response to copper at such high levels of extractable Cu appears unlikely.

The copper concentration of plants ranges from 16.6 - 24.9 ppm without any appa ationship

with extractable Cu. The average was 23.2 ppm. These concentrations are all in the normal range. Geraldson et al.(1973) reported the normal range of Cu in mature trifoliate leaves of beans to be 15 - 30 ppm. Jarvis (1981) reported that 30 ppm Cu in plant tissue was probably the limit for most plants, above which toxicity symptoms may be observed. Copper toxicity did not occur in this experiment as is evident from the appearance of the plants (plate 1), and the trend of shoot weight despite high levels of soil Cu. Lack of Cu toxicity under such conditions may be explained in two ways. Firstly, there is a possibility of immobilization of copper at the root surface thus reducing translocation of Cu to other tissues as suggested by Mengel and Kirkby (1982). Secondly, plants may be tolerant to high Cu levels in the tissues as has been observed by Reilly (1969) for the Rhodesian copper flower plant. The first situation fits the situation observed in this experiment. Indeed Cu tolerance in bush beans has been attributed to the ability of the plant roots to retain Cu (Hardiman et al., 1984). Hardiman et al. (1984) also found that the concentration of Cu in bush beans was relatively constant at all levels of copper contamination. A similar situation was observed in this experiment. With the exception of two pots whose plants contained 16.6 ppm, the rest ranged from 22.9 - 25.9 ppm which is a very small range forsuch a large change in soil Cu.

Table 10: Correlation coefficients between dry matter yield, weight of roots, plant Cu concentration and Cu uptake with Cu extracted by different extractants

Cu extractant	DM yield	Root weight	Plant Cu concentration	Cu uptake
0.005 M DTPA	0.68*	0.86**	0.32 NS	0.73**
0.1 N HCl	0.86***	0.78**	0.22 NS	0.83***
0.05 M EDTA	0.60*	0.84**	0.30 NS	0.63*

* = Significant at 0.05 level

** = Significant at 0.01 level

*** = Significant at 0.001 level

Data for copper uptake by bean plants is also shown in Table 9. There appears to be a relationship between Cu uptake and extractable Cu. The Cu uptake range from 92.0 µg per pot to 219 µg per pot and when correlation coefficients were worked out, 0.1 N HC1 - extractable Cu correlated best with Cu uptake ($r = 0.83, P \geq 0.001$) followed by DTPA - extractable Cu ($r = 0.73, P \geq 0.01$) and EDTA extractable Cu ($r = 0.63, P \geq 0.1$). The trend of increasing Cu uptake with increasing extractable Cu is an indication of a favourable response of beans to Cu, which as discussed above was evident from the good performance of the bean plants in the glasshouse.

The availability of Cu in soils is greatly influenced by many factors and the best way of assessing it is to correlate the amounts extracted from the soil by chemical extractants with plant uptake (Tiwari and Kumar, 1982). Such correlations are shown in Table 10. HC1 (0.1 N) extractable Cu gave the best correlation with Cu uptake ($r = 0.83, p \geq 0.001$) followed by 0.005 M DTPA extractable Cu ($r = 0.73, P \geq 0.01$) and lastly 0.05 M EDTA extractable Cu ($r = 0.63, P \geq 0.1$). Judging from these correlations, 0.1 N HC1 appears to be the best extractant under the conditions prevailing in this experiment. This observation is supported by Fiskell and Westgate (1955) on soils contaminated with

Cu containing sprays. Reuther et al. (1953) and Spencer (1954) produced evidence that support this conclusion. More recent researchers (Tiwari and Kumar, 1982 ; Fagbani et al. 1985) also found 0.1 N HCl a good extractant for soil Cu in comparison to 0.005 M DTPA and 0.05 M EDTA.

4.5.2. The effect of adding 200 mg Cu in a kg of soil to contaminated coffee soils on the growth of beans

4.5.2.1. Physical appearance of beans in the glasshouse

Bean plants grown in five soils treated with 200 mg Cu in a kg soil as Cu oxychloride as shown on plate 2 grew normally and were healthy and vigorous, throughout the period of the experiment, except for one pot in which the plants showed some chlorosis on the young leaves. The chlorosis appeared after seventeen days of growth but later disappeared and by the time of harvesting the plants were as good as those in other pots.

4.5.2.2. Extractable Cu, recovery of applied Cu, dry matter yield, Cu concentration and uptake as a function of Cu treatment

The extractable Cu determined after harvesting bean plants using 0.005 M DTPA and 0.1 N HCl as well as the fraction of applied Cu recovered by the DTPA

extractant are shown in Table 11. The dry matter yields, Cu concentration and uptake are also shown. It can be noted from the table that the plant copper concentration is uniform for all samples. This was unexpected but efforts to improve the data by adjusting the sensitivity of the atomic absorption spectrophotometer were unsuccessful and hence the data was reported as such. The average DTPA extractable copper before the experiment was 139 ppm while the corresponding value after the experiment was 237.6 ppm. The recovery was variable ranging from 24.4 to 88.1% probably as a function of soil factors, controlling Cu availability. The incomplete recovery in all cases is probably due to the incomplete dissolution of copper oxychloride which is insoluble in water. A fraction of soluble Cu may also be retained by soil components in forms not extractable by DTPA.

Application of 200 mg Cu as copper oxychloride in a kg of soil increased DTPA extractable Cu by 70.9 percent. The amount of Cu extracted by 0.1 N HCl was higher than that extracted by DTPA. Despite the increase in extractable Cu, bean plants were healthy and plant Cu concentrations were similar to those observed in the previous experiment. The same arguments are thus thought to account for these results. However, the results have an additional significance in that they indicate that for the soils under study an amount of Cu

Plate 2: Bean plants (Phaseolus vulgaris) grown in soil with a high dose of copper oxychloride

equal to that to be added in 20 years of spraying with Cu fungicides does not appear to have any detrimental effect on beans. This is probably due to favourable pH range of soils used in the study as well as high Ca and organic matter. Copper toxicity is strongly pH dependent, most of the reported cases occuring in strongly acid soils (pH 5) (Reuther and Smith, 1953). Influence of liming on the toxic action of excessive amounts of copper on plants were studied by Jurkowska and Rogoz (1977). Liming enabled the plants to grow normally even with very high strongly toxic doses of copper which agrees with the results of this experiment that in pH ranges between 5.3 - 6.0 the beans grew normally despite the high copper concentration in the soil. Calcium has also been implicated in moderating Cu toxicity probably by limiting Cu absorption through its effect on membrane permeability (Mengel and Kirkby, 1982).

4.5.3. Influence of soil pH on extractable Cu, growth and Cu uptake of beans

4.5.3.1. Physical appearance of the bean plants

The bean plants showed normal growth during the initial days of the experiment until after two weeks when some changes were observed. The plants in the pots with pH 4.8 developed chlorosis starting with young leaves and becoming more chlorotic with time, followed by stunting of the plants (Plates 3 & 4).

Table 11: Soils added with 200 ppm Cu into a kg of soil from copper oxychloride. Effect on Cu recovery, dry matter yield and Cu uptake by bean plants.

	Soil pH	Initial DTPA Cu	DTPA Cu after expt.	0.1 N HCl Cu after expt.	Cu recovery (%)	Dry matter (g)	Plant concentration (ppm)	Uptake (µg)
		ppm						
	6.5	148.0	200.9	232.5	26.5	7.3	25.6	186.9
	6.6	144.2	193.0	337.6	24.4	9.5	25.6	243.2
	5.4	122.5	211.8	403.3	44.7	8.3	25.6	212.5
	6.4	163.2	339.4	485.6	88.1	10.2	25.6	261.1
	6.2	117.2	243.1	232.2	63.0	10.1	25.6	232.5
Average	6.2	139.0	237.6	338.2	49.3	9.1	25.6	232.5

Later, plants in the soil of pH 5.1 also developed chlorosis but to a lesser extent than those at pH 4.8. Beans grown in soils of pH 5.4 were normal, healthy and vigorous to the end of the experiment.

4.5.3.2. Extractable Cu, dry matter yield, copper concentration and Cu uptake as influenced by changes in soil pH

Data of soil extractable copper determined after the experiment using 0.005 M DTPA and 0.1 N HCl is shown in Table 12. The pH of the soil before and during the experiment is also shown. The table also includes data on dry matter yield, plant Cu concentration and Cu uptake.

The amount of DTPA extractable Cu was found to be 393 ppm in the soil of pH 4.8 and 61.4 ppm in the soil of pH 6.0. Likewise, the amount of 0.1 N HCl extractable Cu was 1066 ppm in the soil of pH 4.8 while at pH 6.0 the extractable copper was 245.6 ppm. This situation shows that the amount of extractable copper increased as pH decreased. Soil pH was found to be negatively correlated with extractable Cu ($r = -0.81$ for DTPA extractable Cu and -0.69 for HCl extractable Cu). The values, however, were not found to be significant. The greatest increase in extractable copper occured as the soil pH dropped below 5.0.

Plate 3: Bean plants (Phaseolus vulgaris) grown in soil with different pH levels

Plate 4: Bean plants (Phaseolus vulgaris) grown in soil with pH 4.8 showing chlorosis and stunting due to copper toxicity.

Table 12: Dry matter yield, Cu uptake and Cu concentration of beans grown in soils adjusted to different pH values

Original pH	Adjusted pH	DTPA Cu	HCl Cu	Plant concentration	Dry matter yield g	Cu uptake µg
		ppm				
5.3	4.8	393.0	1066.0	61.3	6.0	367.8
6.2	5.1	127.3	209.0	35.2	6.0	211.2
6.3	5.4	86.4	150.2	26.5	6.7	117.6
5.7	5.7	73.9	81.4	26.5	5.9	156.4
6.2	6.0	61.4	245.6	26.5	6.0	159.0

The DTPA extractable copper increased six times as the the pH was lowered from 6.0 to 4.8, while the HCl extractable Cu increased by about four times with the same changes in pH. The increase in extractable copper is thought to be due to increased activity of cupric ions at low pH. Lexmond (1980) reported that the solution activity of cupric ions in soil increases with decreasing pH and concluded that the activity of cupric ions was governed by pH. Peech (1942) also reported that the amount of available Cu decreased in the soil as pH was raised and postulated that this was due to decrease in the solubility of copper compounds at higher pH. Piper (1942) found that at pH 4 and 4.7 the available copper in soil was greater than pH at 6.4 - 8. Soil pH was found to be negatively correlated with extractable Cu (Table 13). The values, however, were not found to be significant. The same observation was made by Neelakatan and Mehta (1961) who related pH and available copper in 64 Indian soils and obtained a correlation coefficient of 0.378 $P \geq 0.01$. The results of Dragun and Baker (1982) that Cu activity in soils was negatively correlated with pH ($r = -0.84$, $P \geq 0.01$) also agree with the above observations.

The copper concentrations in plants was higher in the lowest pH 4.8 than in the high pH 6.0. At pH 4.8 copper concentration in plants was 61.3 ppm while the concentration at pH 6.0 was 26.5 ppm and the trend

was that of increasing plant Cu concentration with decreasing pH, such that at pH 5.1 the plant concentration was still high, 35.2 ppm Cu (Table 12). The plant at these low pH values had chlorotic young leaves and were stunted. These results indicate that these symptoms were due to copper toxicity. The copper concentrations mentioned above, namely 61.3 ppm and 35.2 ppm exceeds that of 15 - 30 ppm reported by Geraldson et al. (1973) as the normal Cu concentration of mature trifoliate leaves of beans. These plant Cu concentrations are also above the value 30 ppm plant tissue reported by Jarvis (1981) as probably being the limit for most plants above which toxicity symptoms could be observed. Copper toxicity is actually known to be intensified by acidifying the soil (Reuther et al., 1953) and this has been attributed to an increase in the concentration of cupric ions in the soil solution. Thus more of the accumulated copper in the coffee soils is brought to solution at low pH and made available to plants to the extent of causing copper toxicity. In experiment 4.5.2. where a high dose of copper from copper oxychloride was deliberately added to the soil, copper toxicity on beans did not occur even when DTPA extractable copper was as high as 339.4 ppm (Table 11) as the pH of this soil was 6.4. This indicates that at pH $\geq$ 5.4 soils with high additions of copper through copper fungicide sprays are likely to be free of toxic quantities of Cu.

Copper uptake by bean plants was 367.8 µg per pot at pH 4.8 (Table 12) and 159.0 µg per pot at pH 6.0. Copper uptake was also negatively correlated with soil pH ($r = -0.84$ $P \geq 0.1$). The increase in copper uptake at low pH may have resulted from more available copper in the soil solution. According to Piper (1942) copper absorption was appreciably greater at pH 4.0 and particularly at 4.7, than at pH 6.4 and 8, and this was shown by the proportion of Cu in the crops of oats. The availability of Cu in soils was also assessed by Tiwari and Kumar (1982) and they found copper uptake to be negatively correlated with pH ($r = 0.83$; $P \geq 0.01$).

There is, however, no clear explanation as to why there is increased Cu uptake by plants at low pH. It is nevertheless reported by Mengel and Kirkby (1982) that Cu is able to displace most other ions from the root exchange sites and when the cupric ions dominate the exchange sites, more copper is likely to be taken by the plants. The observation by Mengel and Kirkby (1982) also shows that copper uptake by plants is related to the levels of available copper in the soil.

The dry matter yield as seen in Table 12 shows little change in different pH values. It was expected that the dry matter yield of plants growing in pH 4.8 and 5.1 would be appreciably lower. Wallace *et al*.

(1984) found the dry matter of bush beans, (Phaseolus vulgaris) to be reduced by 42 percent when the plant copper concentration was 89.0 ppm. From this it can be implied that the plant copper concentration should be greater than 61.3 ppm to produce a notable decrease in dry matter yield.

Table 13: Correlation coefficients between different soil and plant parameters

Independent variable	Plant Cu	DM yield	Cu uptake	pH
0.005 M DTPA	0.99**	- 0.20 NS	0.99**	- 0.82 NS
01 N HC1	0.97**	- 0.21 NS	0.97**	- 0.69 NS
Soil pH	- 0.84*	- 0.05 NS	-0.84*	-

NS = non significant

* = Significant at 0.05 level

** = Significant at 0.01 level

SUMMARY AND CONCLUSIONS

The aim of the study was to examine the extent of copper accumulation in soils of Moshi district, resulting from continuous use of copper based fungicides for the control of coffee diseases. The study also examined the possibility of Cu reaching toxic levels to coffee plants and other crops such as beans which are often intercropped with coffee. This involved applying a rate of Cu as copper oxychloride equivalent to the amount which will be added by spraying this fungicide for twenty years and assessing its effect on bean growth in selected soils. In addition the effects of pH on soil available copper and their effects on growth of beans were also studied. Finally a preliminary evaluation of three chemical extractants for their suitability in assessing problems of Cu pollution in soils of Moshi district was made.

The study indicated that spraying coffee with copper fungicides increases the amount of copper in the soil and that the added copper is mainly accumulated in the top soil layer. The DTPA extractable Cu in the top soil layer (0 - 5 cm) increased from 5.6 ppm to 35.9 ppm during the first 10 years of spraying while spraying for 20 years increased the DTPA extractable Cu to 122.9 ppm and spraying for more than thirty years increased the extractable Cu to 186.2 ppm.

Based on twenty and thirty years average, the increase in DTPA extractable Cu was found to be 6 ppm Cu per annum.

The copper content of coffee leaves free from copper spraying was found to be 10 ppm. Coffee leaves from farms that had been sprayed with copper fungicides for less than ten years, twenty to thirty years and over thirty years had an average copper content of 60 ppm. The results indicated that the leaf copper content was increased by spraying copper fungicides but was not related to the duration of spraying. This observation further indicated that the high copper concentration in the coffee leaves may not have originated from the soil. Indeed copper through fungicides applied to coffee leaves could have been absorbed through the leaves. The high concentration of copper in the leaves, however, did not cause copper toxicity to coffee plants. These data suggest that coffee is tolerant to high levels of copper in the leaves.

Beans grew in soils with high DTPA copper content (up to 368 ppm) without problems. Absence of physiological problems on beans was noted even when an application of 200 mg Cu/kg soil was made to already contaminated soils. The growth of beans in those soils was normal, healthy and vigorous. When soil pH was adjusted to values of 5.1 and below, the copper concentra-

tion in bean shoots increased from 26.5 ppm to 61.3 ppm and toxicity symptoms were observed.

The three copper extractans evaluated viz. 0.005 M DTPA, 0.1 N HCl and 0.05 M EDTA, extracted different quantities of copper. The average amounts of copper extracted by 0.005 M DTPA was found to be 88.9 ppm while 0.1 N HCl extracted an average of 158.1 ppm and 0.05 M EDTA extracted 290.1 ppm. The amount extracted by 0.1 N HCl gave the highest correlation with plant Cu uptake ($r = 0.83$, $P \geq 0.001$) followed by 0.005 M DTPA ($r = 0.73$, $P \geq 0.01$) and lastly 0.05 M EDTA which gave a correlation coefficient of 0.63 ($P \geq 0.1$).

The following conclusions and recommendations may be made in view of the findings of this investigation:-

1. Application of copper fungicides was found to increase DTPA extractable copper in the soils of Moshi district. The increase in extractable Cu was found to be a function of the duration of spraying with copper fungicides. Much of the accumulated copper was found on the surface 0 - 5 cm depth of soil.

2. The copper accumulation in the soils does not presently cause copper toxicity to coffee plants or other crops such as beans because of favourable pH levels of the soils of Moshi district. However, decreasing soil pH to values below 5.2, resulted in Cu toxicity to beans. This suggests that the soils have to be managed such that the pH is maintained well above this pH.

3. Of the three extractants tested, 0.1 N HCl appeared to be more suitable for assessing the copper status of the soils as it correlated better with plant uptake. However, the critical concentration for toxicity could not be determined because this was not only a function of extractable Cu but was influenced by other soil properties as well, particularly soil pH.

REFERENCES

Adam, G.P. 1977. Analytical Report to Uyole Agricultural Centre, Phosyn. International Limited, London.

Aduayi, E.A. 1972. Observations on the water culture technique for studying the effects of copper concentrations on arabica coffee seedlings. E.A. Agric. For. J. 38: 62 - 68.

Aduayi, E.A. 1975. Effects of copper fungicide sprays on soils and leaf nutrient composition and yield of coffee trees. Turrialba 25 (2): 132- 138.

Aduayi, E.A. 1976. Composition of soil and coffee leaves on plantations under varying copper fungicide spraying regimes. Trop. Agric. (Trinidad) 53: 65 - 68.

Allison, L.E. 1965. Organic carbon. In. C.A. Black, D.D. Evans, J.L. White, L.E. Ensminger and F.E. Clark (eds.). Methods of soil Analysis pt. 2 pp. 1367 - 1378. Am. Soc. Agron., Madison, Wisconsin.

Archer, F.C. 1971. Trace Elements in Soils and Crops. p. 150 MAFF. Techn. Bull. 21 HMSO, London.

Ashby, D.L. 1969. Washing techniques for the removal of nutrient element deposits from the surface of Apple, Cherry and Peach leaves. J.Amer. Soc. Hort. Sci. 94: 266 - 268.

Association of Official Analytical Chemists (A.O.A.C.) 1970. Official methods of analysis 2nd ed. Washington, DC.

Beaton, J. J . 1972. Plant tissue analysis for micro-nutrients. In. J.J. Mortvedt, P.M. Giordano and W.L. Lindsay (eds). Micronutrients in Agriculture. Soil Sci. Soc. of Amer. Madison. Wisconsin.

Berrow, M.L. and G.A. Reeves. 1985. Extractable copper concentrations in Scottish soils. J.Soil Sci. 36 (1): 31 - 43.

Bingham, F.T. 1963. Relation between phosphorus and micronutrients in plants. Soil Sci. Soc. Am. Proc. 27: 389 - 391.

Brady, N.C. 1974. The Nature and Properties of Soils, 8th edition. McMillan Publishing Co., NY.

Brar, M.S. and G.S. Sekhon. 1976. Effect of copper and zinc ^{65} absorption by wheat seedlings and its translocation within the plant. Plant and

Soil 45: 137 - 143.

Bray, R.H. and Kurtz, L.T. 1945. Determination of total, organic and available forms of phosphorus in soils. Soil Sci. 39: 39 - 45.

Bremner, J.M. 1965. Total Nitrogen. In. C.A. Black, D. D. Evans. J.L. White, L.E. Ensminger and F.E. Clark (eds)., Methods of Soil Analysis pt. 2 pp. 1149 - 1178. Am. Soc. Agron. Madison. Wisconsin.

Brennan, F.F., J.W. Gartrell and A.D. Robson 1980. Reactions of copper with soil affecting its availability to plants I. Effects of soil type and time. Aust. J. Soil. Res. 18: 447 - 459.

Bock, K.R., 1963. The control of coffee berry disease in Kenya. Emp. J. Exp. Agric. 31: 97 - 107.

Borggaard, O.K., 1976. The use of EDTA in soil analysis. Acta Agric. Scand. 26, 144 - 150.

Bowen, H.J.M., 1966. Trace elements in biochemistry. Academic Press, New York.

Bowen, H.J.M. 1979. Environmental chemistry of metals. Academic Press, New York.

Bujulu, J.A., A.B. Gwandu, and H. Mero 1978. Chemical control of coffee berry disease in Northern Tanzania. E.Agric. For. J. 44 (2): 140 - 145.

Cavallaro, N. and B. McBride 1980. Activities of Cu^{2+} and Ca^{2+} in soil solutions as affected by pH. Soil Sci. Soc. Am. J. 44: 129 - 732.

Chapman, H.D. 1965. Cation - exchange capacity. In. C.A. Black, D.D. Evans, J.L. White, L.E. Ensminger and F. E. Clark (eds.). Methods of soil analysis pt. 2 pp. 891 - 901. Am. Soc. Agron. Madison, Wisconsin.

Chaudhry, F.M. and J.F. Loneragan 1970. Effects of nitrogen copper and zinc fertilizers on the copper and zinc nutrition of wheat plants. Aust. J. Agric. Res. 21, 865 - 879.

Cheng, K.L. and Bray, R.H. 1953. Two specific methods of determining copper in soil and plant materials. Anal. Chem. 25: 655 - 659.

Day, P.R. 1965. Particle fractionation and particle size analysis. In. C.A. Black, D.D. Evans, J. L. White, L.E. Ensminger and F.E. Clark (eds.). Methods of Soil Analysis pt. 2 pp. 545 - 567. Am. Soc. Agron. Madison, Wisconsin.

Delas, J.F. 1963. The toxicity of copper accumulated in soils. Agrochimica 7: 258 - 288.

Dickinson, N.M. and Nicholas, W. Lepp 1984. Copper contamination of a 68 year old coffee (Coffee arabica L) plantation. Environmental Pollution. (Series B.) 7: 223 - 231.

Doll, E.C. and R.E. Lucas 1973. Testing soils for potassium, calcium and magnesium. In. Walsh, L. and J.D. Beaton (eds.). Soil Testing and Plant Analysis. Soil Sci. Soc. Am. Inc. Madison, Wisconsin.

Dolar, S.G., D.R. Keeny and L.M. Walsh 1971. Availability of Cu, Zn and Mn in soils. III. Predictability of plant uptake. J.Sci. Fd. Agr. 22: 282-286.

Dragun, J. and D.E. Baker 1982. Characterization of copper availability and corn seedling growth by a DTPA soil test. Soil Sci. Am. J. 46: 921 - 925.

Drouineau, G. and R. Mazoyer 1956. Contribution to the study of copper toxicity in soils. Adv. Agron. 13: 31 - 53.

Fagbani, A., S.O. Ajayi and E.M. Ali 1985. Nutrient distribution in the basement complex soils of the tropical dry rainforests of South Western Nigeria. 2. Micronutrients Zinc and Copper. Soil Sci. 139 (6):531 - 537.

Fiskell, J.G.A. 1965. Copper. In, C.A. Black, D.D., Evans, J.L. White, L.E. Ensminger and F.E. Clark (eds.). Methods of soil analysis pt. 2 pp. 1078 - 1089. Am. Soc. Agron. Madison, Wisconsin.

Fiskell, J.G.A. and P.J. Wesgate 1955. Copper availability in high copper soils. Fla. State Hort. Soc. Proc. 68: 192 - 197.

Frank, B., H.E. Braun, K. Ishida and P. Suda 1976. Persistent organic and inorganic pesticide residues in orchard soils and vineyards of Southern Ontario. Can. J. Soil Sci. 56: 463 - 484.

Frank, B., C.M. Ishida and P. Suda 1976. Metals in agricultural soils of Ontario. Can. J. Soil Sci. 56: 181 - 196.

Gartrell, J.W. 1980. The residual effectiveness of copper fertilizers for wheat in Western Australia. Aust. J. Exp. Agric. Anim. Husb. 20: 270 - 276.

Geraldson, C.M., G.R. Klacan and A.O. Lorenz. 1973. Plant analysis as an aid in fertilizing vegetable crops. In. L.M. Walsh and J. Beaton (eds.) Soil Testing and Plant Analysis. Soil Sci. Soc. Am. Inc. Madison, Wisconsin, USA. pp. 365 - 379.

Gilbert, F.A. 1952. Copper in Nutrition. Adv. Agron. 4: 147 - 177.

Gough, L.P., J.M. McNeal and R.C. Sverson. 1980. Predicting native plant copper, iron, manganese and zinc levels using DTPA and EDTA soil extractants, Northern Great Plains. Soil Sci. Soc. Am. J. 44: 1030 - 1036.

Guony, P. and P. Cornillo. 1970. Trace element in France. Example of regional problem. The South East Annuals Agron. 21: 617 - 628.

Graham, E.R. 1953. Soil mineralogy as an index to trace element status of some Australian soils. Soil Sci. 75: 333 - 343.

Hardiman, R.T., B. Jacoby and A. Bariun. 1984. Factors affecting the distribution of cadmium, copper and lead and their effects upon yield and zinc content of bush beans (Phaseolus vulgaris) Plant and Soil 81 (1): 17 - 27.

Hawf, L.R. and N.E. Schimid. 1967. Uptake and translocation of zinc by intact plant. Plant and Soil 27: 249 - 260.

Haq, A.U., T.E. Bates and Y.K. Soon. 1980. Comparison of extractants for plant available zinc, cadmium, nickel and copper in contaminated soils. Soil Sci. Soc. Am. J. 44: 772 - 777.

Hodgson, T.F. 1963. Chemistry of the micronutrient elements in soil. Adv. Agron. 15: 119 - 159.

Holmes, R.S. 1943. Copper and zinc content of certain United States soils. Soil Sci. 50: 359 - 370.

ILACO, B.V. 1981. Agricultural Compendium for Rural Development in the Tropics. Elservier Scientific Publishing Company, Amsterdam,,Oxford, New York.

Jarvis, S.C. 1978. Copper uptake and accumulation by perrenial ryegrass grown in soil and solution culture. J.Sci. Fd. Agric. 29: 12 - 18.

Jarvis, S.C. 1981. Copper concentration in plants. In. Loneragan, J.F., A.D. Robinson and R.D. Graham (eds.). Copper in Soils and Plants pp. 265 - 285.

Jurkowska, H. and A. Rogoz. 1977. The influence of liming on copper concentration in plants in relation to the dose and kind of copper fertilizer. Polish Journal of Soil Science. 10 (2): 150 - 156.

Kamasho, J.A. 1980. Copper and zinc status of some volcanic ash soils in the Mbeya district. M.Sc. Thesis, University of Dar es Salaam.

Kasembe, J.N.R., J.M.R. Semoka and J.K. Samki. 1983. Organic farming in Tanzania. Proceeding of Workshop on resource efficient farming methods for Tanzania. University of Dar es Salaam, pp. 36 - 39.

Kornegay, E.T., J.D. Hedges, D.C. Martens and C.Y. Cramer. 1976. Effect on soil and plant mineral levels following application of manures of different copper contents. Plant and Soil. 45: 151 - 162.

Korte, N.E., J. Skopp, W.H. Fuller, E.E. Niebla and B.A. Alesh. 1976. Trace element movement in soils: Influence of soil physical and chemical properties. Soil Sci. 122: 350 - 359.

Krauskopf, K.B. 1972. Geochemistry of micronutrients. In. J.J. Mortvedt, P.M. Giordano and W.L. Lindsay (eds.). Micronutrients in Agriculture. Publisher City and State.

Kruger, G.A., R.E. Karamanos and J.P. Singh. 1985. The copper fertility of Saskatchewan soils. Can.J. Soil Sci. 65: (1) 89 - 99.

Krughlova, Y.K. 1962. Copper and its forms in the soils of the Bolodraga steppe and in cotton soils. Soviet Soil Sci. 516 - 521.

Lepp, N.W., N.M. Dickinson and K.L. Ormand. 1984. Distribution of fungicides derived from copper in soils, litter and vegetation of different aged stands of coffee. Plant and Soil 77: 263 - 270.

Lexmond, Th. M. 1980. The effect of soil pH on copper toxicity to forage maize grown under field conditions. Neth. J. Agric. Sci. 28 (3): 164 - 183.

Lexmond, Th. M. and P.D.J. Van der Vorm. 1981. The effect of pH on copper toxicity to hydroponically grown maize. Neth. J. Agric. Sci. 29: 209 - 230.

Lindsay, W.L. and W.A. Norvell. 1969. Equilibrium relationships of Zn^{2+}, Fe^{3+}, Ca^{2+} and H^{+} with EDTA and DTPA in soils. Soil Sci. Soc. Amer. Proc. 33: 62 - 68.

Lindsay, W.L. 1972. The role of chelates in micronutrient availability. In: E.W. Carson (ed.).

The Plant Root and its Environment. The University press of Virginia. Charlottesville.

Lindsay, W.L. and W.A. Norvell. 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. Soil Sci. Soc. Am. J. 42: 421 - 428.

Lindsay, W.L. and F.R. Cox. 1985. Micronutrient soil testing for the tropics. In. Paul, L.G. Vlek (ed.). Micronutrients in Tropical Food Crop Production. Development in Plant and Soil Sciences. Vol. 14.

Lucas, R.E. 1948. Chemical and physical behaviour of copper in organic soils. Soil Sci. 66: 119 - 129.

Lucas, R.E. and B.D. Knezek. 1972. Climatic and soil conditions promoting micronutrient deficiencies in plants. In. J.J. Mortvedt, P.M. Giordano and W.L. Lindsay (eds.). Micronutrients in Agriculture. Soil Sci. Soc. Am. Inc. Madison, Wisconsin. pp. 265 - 288.

Lundbald, K., O. Svanberg and P. Ekman. 1949. The availability and fixation of copper in Swedish soils. Plant and Soil 1. (4): 272 - 302.

Malewar, G.U., S.P. Varade and N.S. Jadhar. 1978. Distribution of manganese and copper in some soils of the citrus growing area of Marathwada. Indian J. of Agric. Res. 12 (4): 227 - 230.

Magalhaes, M.J., E.M. Squeira and M.P. Lucas. 1985. Copper and zinc in vineyards of Central Portugal. Water, Air and Soil Pollution. 26 (2) 1 - 17.

Martens, D.C. 1968. Plant availability of extractable boron, copper and zinc as related to selected soil properties. Soil Sci. 106: 23 - 28.

Mbilinyi, S.M. 1976. Economics of peasant coffee production in Tanzania. Kenya Literature Bureau.

McBride, M.B. and D.R. Bouldin. 1984. Long term reactions of copper II in contaminated calcareous soil. Soil Sci. Soc. Am. J. 48: 56 - 59.

McBride, M.B. 1978. Transition metal bonding in humic acid. An E.J.R. Study. Soil Sci. 126: 200.

McBride, M.B. and J.J. Blasiak. 1979. Zinc and copper solubility as a function of pH in an acid soil. Soil Sci. Soc. Am. J. 43: 866 - 870.

McLaren, R.G. and D.V. Crawford. 1973. The fractionation of copper in soils. J.Soil Sci. 24 (2).

McLaren, R.G., Williams, J.G. and R.S. Swift. 1980. Studies on factors affecting the availability of soil copper to plants. Annual Report. N.C.R.A. Project No. 269. International Copper Research Association 33 pp. New York. USA.

Mengel, K. and E.A. Kirkby. 1982. Principle of Plant Nutrition. International Potash Institute, Berne. Switzerland. p. 527.

Merry, R.H. 1980. The accumulation of copper, lead and arsenic in orchard soils and its effects on plants. M. Ag. Sc. Thesis. University of Adelaide.

Moshi, A.O., N.M. Lema, R.M.A. Meda and E.N. Shikony. 1982. Accumulation of copper in some coffee soils of Kilimanjaro, Tanzania. Soil Sci. Soc. of East Africa pp. 66 - 74.

Neelakatan, V. and B.V. Mehta, 1961. Cu status of soils of Western India. Soil Sci. 91: 251 - 256.

Nelson, L.G., K.C. Berger and H.J. Andries. 1956. Copper requirement and deficiency symptoms of a

number of field and vegetable crops. Soil Sci. Soc. Amer. Proc. 20: 69 - 72.

Norvell, W.A. 1984. Comparison of chelating agents as extractants for metals in diverse materials. Soil Sci. Soc. Am. J. 48: 1285 - 1292.

Nutman, F.J. and F.M. Roberts. 1960a. Investigations on a disease of Coffea arabica caused by a form of Colletotrichum coffeanum Noak. Some factors affecting infection by the pathogen. Trans. Br. Mycol. Soc. 42: 489 - 505.

Nutman, F.J. and F.M. Roberts. 1960b. Investigations on a disease of Coffea arabica caused by a form of Colletotrichum coffeanum Noak. Some factors affecting germination and infection and their relation to disease distribution. Trans. Br. Mycol, Soc. 43: 643 - 659.

Nyandat, N.N. and Ochieng, P.N. 1976. Copper content and availability in soils. A survey of arable and range areas of Kenya. E.Afr. Agr. For. J. 42: 1 - 7.

Okioga, D.M. 1978. The role of copper fungicides in the control of coffee disease in Kenya. Kenya coffee.

Olsen, S.R. 1972. Micronutrient interactions. In. J.J. Mortvedt, P.M. Giordano and W.L. Lindsay (eds). Micronutrients in Agriculture. Soil Sci. Soc. of Amer. Madison, Wisconsin.

Patterson, J.B.E. 1971. Metal toxicities arising from industry. In. Trace elements in soils and crops. Technical Bulletin 21: 193 - 207. The Great Britain Ministry of Agriculture, Fisheries and Food.

Peech, M. 1941. Availability of ions in light sandy soils as affected by soil reaction. Soil Sci. 51: 473 - 486.

Peech, M. 1965. Hydrogen ion activity. In. C.A. Black, D.D. Evans, J.L. White, L.E. Ensminger and F.E. Clark (eds.). Methods of Soil Analysis pt. 2 pp. 914 - 932. Am. Soc. Agron. Madison, Wisconsin.

Piper, C.S. 1942. Investigation of copper deficiency in plants. J.Agr. Sci. 32: 143 - 178.

Piper, C.S. and Beckwith, R.S. 1949. Brit. Commonw. Spec. Conf. Agric. Australia.

Pinkerton, A. 1967. Copper deficiency on wheat in the rift valley, Kenya, J.Soil Sci. 18: 18 - 26.

Purves, D. 1977. Trace elements contamination of the environment. Elsevier Scientific Publishing Company, Amsterdam, 26 pp.

Reider, W. and U. Scwertmann, 1972. Kupferanreichrungen in hopfengenutzten Boden der Hellertau. Landwirtsch Forsch. 25: 170 - 177.

Reilly, C. 1969. The uptake and accumulation of copper by Becium hombei (De Wild) Duvig and Plancke. New Phytol. 68: 1081 - 1087.

Reuther, W. and C.K. Labanauskas. 1966. Copper. In. H.D. Chapman (ed.). Diagnostic Criteria for plants and soils pp. 157 - 179. University of California. Division of Agricultural Sciences, Riverside, California, U.S.A.

Reuther, W. and P.F. Smith. 1952. Iron chlorosis in Florida citrus groves in relation to certain soil constituents. Proc. Florida State Hort. Soc. 65: 62 - 69.

Reuther, W., P.F. Smith and G.K. Scudder. 1953. Relation of pH and soil type to toxicity of

copper to citrus seedlings. Florida State Horticultural Society Proceedings. 66: 73 - 80.

Reuther, W. and P.F. Smith. 1953. Minor elements in relation to soil factors. Toxic effects of accumulated copper in Florida Soils. Soils Sci. Soc. Florida Proc. 14: 17 - 23.

Rourk, P.J. 1972. Coffee rust menaces Brazils' chief export sugar. Tropical Products Division, Foreign Agricultural Services.

Robson, A.D. and D.J. Reuter. 1981. Diagnosis of copper deficiency and toxicity. In. Loneragan J.F., A.D. Robson and R.D. Grahama. Copper in Soils and Plants. Academic Press.

Senesi, N., D.F. Bocian and G. Sposito. 1985. Electron spin resonance investigation of copper II. Complexation by soil fulvic acid. Soil Sci. Soc. Am. J. 49 (1): 114 - 119.

Sheehy, T.J. and H.B. Green. 1969. Land Resources of Northern Tanzania Report.

Sillanpää, M. 1982. Micronutrients and the nutrient status of soils. F.A.O. Bulletin No. 48.

Sims, J.T. 1986. Soil effects on the distribution and plant availability of Mn, Cu and Zn. Soil Sci. Soc. Am. J. 50 (2): 367 - 373.

Singh, J.P., R.E. Karamanos and R.G. Kachanoski. 1985. Spartial variation of extractable micronutrients in a cultivated and native prairie soils. Can J. Soil Sci. 65 (1): 149 - 156.

Sommer, A.L. 1931. Copper as an essential element for plant growth. Plant Physiol. 6. 339 - 345.

Spencer, W.F. 1954. A rapid test for possible excesses of copper in sandy soils. Fla. Agr. Exp. Sta. Bull. 544.

Spencer, W.F. 1966. Effect of copper on yield and uptake of phosphorus and iron by citrus seedlings grown at various phosphorus levels. Soil Sci. 102: 296 - 299.

Sperow, C.B. and R.P. Keeter. 1975. An introduction to soil science applied to East Africa. Morgantown, West Virginia University.

Sposito, G., G.C. Levesque, P.P. Laclaire and A.C. Chang. 1983. Trace metal chemistry in arid zone field soils amended with sewage sludge. III. Effect of

time on the extraction of trace metals. Soil Sci. Soc. Am. J. 47: 898 - 902.

Stevenson, F.J. and A. Fitch. 1981. Reactions with organic matter. In. Loneragan, J.F., A.D. Robson and R.D. Graham (eds.). Copper in soils and plants. National Library of Australia Cataloguing - in Publication.

Stevenson, F.J. and M.S. Ardakani. 1972. Organic matter reactions involving micronutrients in soils. In. J.J. Mortvedt, P.M. Giordano and W.L. Lindsay. Micronutrients in Agriculture. Soil Sci. Soc. Am. In. Madison, Wisconsin.

Swaine, J.D. 1955. The trace element content of soils. Commonw. Bur. Soil Sci. Techn. Commun. No. 48. Herald Printing Works, Coney St. York. England.

Swaine, D.J. and R.L. Mitchell. 1960. Trace element distribution in soil profiles. J.Soil Sci. 11: 347 - 368.

TARO, Lyamungu. 1986. Annual Report.

Tessler, A., P.G.C. Campbell and M. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry 51: 7.

Tiller, G.K. and R.H. Merry. 1981. Copper Pollution in Agricultural soils. In. J.F. Loneragan, A.D. Robson and R.D. Graham. (eds). Copper in soils and plant. 119 - 132 Academic Press.

Tiwari, R.C. and B.M. Kumar. 1982. A suitable extractant for assessing plant available copper in different soils (peaty, red and alluvial.). Plant and Soil 68: 131 - 134.

Uriyo, A.P., B.R. Singh, H.O. Mongi, M.S. Choudhury and J.M.R. Semoka. 1979. Introductory Soil Science. Tanzania Publishing House, Tanzania. 232 pp.

Van Luit, B. and C.H. Henkens. 1967. Effect of the copper status of the soil on the copper content of grass and clover. Versl. Landbouwk onderz. No. 695. 33 - 39.

Venkataramaiah, G.H. and M.B.D. Singh. 1974. Accumulation of copper in coffee soils. Journal of coffee Research. 4: 14 - 16.

Viets, F.G. Jr. and W.L. Lindsay. 1973. Testing soils for zinc, copper, manganese and iron. In. L.M. Walsh and J.D. Beaton (ed.). Soil testing and plant analysis. Soil Sci. Soc. Amer. Madison, Wisconsin.

Viro, P.J. 1955. Use of ethylenediaminetetraacetic acid in soil analysis. Soil Sci. 79: 459 - 465.

Wallace, A., E.M. Romney and G.V. Alexander. 1981. Multiple toxicities in plants. Journal of Plant Nutrition. 3 (1-4): 257 - 263. Westgate, 1952.

Walsh, L.M., W.H. Erhardt and H.D. Siebel. 1972. Copper toxicity in snapbeans (Phaseolus vulgaris). Journal of Environmental Quality. 1: 197 - 200.

Westgate, P.J. 1952. Preliminary report on Copper toxicity and iron chlorosis in old vegetable fields. Florida State Horticultural Society Proceedings. 65: 143 - 146 (Horticultural Abstracts 23 (1953) 3015.

William, J.G. and R.G. Mclaren. 1982. Effects of dry and moist incubation of soils on the extractability of native and applied copper. Plant and Soil 64: 219 - 224.

Younts, S.E. and R.P. Patterson, 1964. Copper lime interactions in field experiments with wheat: Yield and chemical composition data. Agronomy Journal 56: 229 - 232.

APPENDICES

Appendix 1: DTPA copper content of the soils in Moshi district

Village	Depth (cm)	No spray	0 - 10 years	10 - 30 years	Over 30 years
Marawe Kyura	0 - 5	3.7	54.0	200.0	292
	5 - 10	3.5	25.5	53.0	120
	10 - 20	3.1	8.9	18.0	20.5
Kirua Vunjo	0 - 5	4.0	25.0	152.0	316.0
	5 - 10	1.6	24.0	140.0	256.0
	10 - 20	1.0	19.0	121.0	66.0
Uchau Kask.	0 - 5	1.4	6.9	80.0	196.0
	5 - 10	1.1	1.6	83.0	118.0
	10 - 20	0.7	1.3	18.0	37.5
Samanga	0 - 5	2.1	20.0	252.0	136.0
	5 - 10	1.8	16.5	132.0	67.0
	10 - 20	1.4	7.1	29.0	15.0
Kimanganuni	0 - 5	11.3	21.5	44.5	292.0
	5 - 10	8.4	19.5	40.0	176.0
	10 - 20	3.5	4.9	21.5	21.5
Korini Kusini	0 - 5	4.0	33.0	28.0	54.0
	5 - 10	3.5	4.0	18.0	51.0
	10 - 20	1.4	5.9	10.5	20.0
Boro	0 - 5	4.4	27.0	35.5	368.0
	5 - 10	1.4	9.7	4.6	59.0
	10 - 20	1.0	2.4	1.5	17.0
Uri	0 - 5	1.0	16.5	11.5	148.0
	5 - 10	0.7	19.5	7.5	9.7
	10 - 20	0.4	11.2	1.3	-
Manushisinde	0 - 5	16.5	125.0	160.0	124.0
	5 - 10	7.4	44.0	77.0	35.5
	10 - 20	2.4	15.5	16.5	23.0
Kiruweni	0 - 5	7.4	15.5	100.0	100.0
	5 - 10	5.9	15.5	31.0	31.0
	10 - 20	4.9	8.3	8.7	20.0

Appendix 2: Some chemical properties of soils used in the study

Village		pH	OC %	Total N %	Availa-ble P ppm	Exch. Ca me/100g	Exch. Mg me/100g	Exch. K me/100g	Exch. Na ppm	Extract. Fe ppm	Extract. Zn ppm	Extra-ctable Mn ppm
Marewe Kyura	1	6.9	1.99	0.18	24.56	5.00	4.17	0.58	0.61	48.00	3.00	104.00
	2	6.9	3.55	0.38	94.74	9.38	11.04	2.24	1.43	12.00	3.40	19.00
	3	6.5	3.47	0.32	69.37	14.38	8.13	0.93	0.54	37.00	5.10	28.00
	4	6.3	2.85	0.27	42.81	10.31	7.08	1.51	0.38	29.00	11.00	32.00
Kirua Vunjo	1	5.6	3.67	0.29	8.42	1.88	1.41	0.80	0.39	34.00	0.80	10.00
	2	5.9	5.07	0.47	21.00	4.38	3.07	1.70	0.52	41.00	2.30	10.00
	3	6.5	3.47	0.32	69.37	14.38	8.13	0.93	0.54	37.00	5.10	28.00
	4	6.3	2.85	0.27	42.81	10.31	7.08	1.51	0.38	29.00	3.30	32.00
Uchau Kaskazini	1	5.6	3.99	0.37	8.42	2.50	1.04	1.41	0.82	35.00	1.00	7.00
	2	5.8	3.68	0.35	9.12	4.38	2.40	2.72	0.58	37.00	2.10	10.00
	3	6.5	3.85	0.38	15.44	7.50	5.00	3.97	0.61	39.00	9.00	10.00
	4	6.0	5.70	0.45	50.53	10.31	6.77	3.85	0.51	46.00	7.00	26.00
Samanga Rauya	1	6.5	1.69	0.12	33.30	4.38	4.27	0.80	0.51	39.00	1.20	59.00
	2	6.8	2.33	0.19	77.19	6.25	5.73	2.34	0.68	37.00	2.50	58.00
	3	6.6	1.65	0.21	78.60	9.69	8.44	1.09	0.61	41.00	13.00	23.00
	4	6.6	3.94	0.37	71.58	11.25	8.33	0.93	0.37	43.00	18.00	32.00

Appendix 2: Some chemical properties of soils used in the study

Village		pH	OC %	Total N %	Availa-ble P ppm	Exch. Ca me/100g	Exch. Mg me/100g	Exch. K me/100g	Exch. Na ppm	Extract. Fe ppm	Extract. Zn ppm	Extractable Mn ppm
	1	6.9	1.99	0.18	24.56	5.00	4.17	0.58	0.61	48.00	3.00	104.00
	2	6.9	3.55	0.38	94.74	9.38	11.04	2.24	1.43	12.00	3.40	19.00
Marewe Kyura	3	6.5	3.47	0.32	69.37	14.38	8.13	0.93	0.54	37.00	5.10	28.00
	4	6.3	2.85	0.27	42.81	10.31	7.08	1.51	0.38	29.00	11.00	32.00
	1	5.6	3.67	0.29	8.42	1.88	1.41	0.80	0.39	34.00	0.80	10.00
	2	5.9	5.07	0.47	21.00	4.38	3.07	1.70	0.52	41.00	2.30	10.00
Kirua Vunjo	3	6.5	3.47	0.32	69.37	14.38	8.13	0.93	0.54	37.00	5.10	28.00
	4	6.3	2.85	0.27	42.81	10.31	7.08	1.51	0.38	29.00	3.30	32.00
	1	5.6	3.99	0.37	8.42	2.50	1.04	1.41	0.82	35.00	1.00	7.00
	2	5.8	3.68	0.35	9.12	4.38	2.40	2.72	0.58	37.00	2.10	10.00
Uchau Kaskazini	3	6.5	3.85	0.38	15.44	7.50	5.00	3.97	0.61	39.00	9.00	10.00
	4	6.0	5.70	0.45	50.53	10.31	6.77	3.85	0.51	46.00	7.00	26.00
	1	6.5	1.69	0.12	33.30	4.38	4.27	0.80	0.51	39.00	1.20	59.00
	2	6.8	2.33	0.19	77.19	6.25	5.73	2.34	0.68	37.00	2.50	58.00
Samanga Rauya	3	6.6	1.65	0.21	78.60	9.69	8.44	1.09	0.61	41.00	13.00	23.00
	4	6.6	3.94	0.37	71.58	11.25	8.33	0.93	0.37	43.00	18.00	32.00

Appendix 2 Cont.

Village		pH	OC %	Total N %	Available P ppm	Exch. Ca me/100g	Exch. Mg me/100g	Exch. K me/100g	Exch. Na me/100g	Extract. Fe ppm	Extract. Zn ppm	Extractable Mn ppm
	1	6.3	3.21	0.28	8.42	6.88	3.65	1.06	0.61	37.00	3.25	146.00
	2	6.0	3.96	0.46	61.40	7.50	6.46	2.31	0.71	43.00	2.55	105.00
Kimanganuni	3	6.7	4.32	0.28	56.84	11.56	8.33	1.96	0.61	31.00	3.20	76.00
	4	6.4	5.11	0.21	36.50	10.94	8.33	2.66	0.60	27.00	13.00	69.00
	1	6.3	2.50	0.28	110.00	6.25	6.67	2.05	0.88	37.00	2.40	66.00
	2	6.6	2.29	0.21	11.23	7.50	5.83	2.47	0.60	32.00	3.50	46.00
Korini Kusini	3	7.0	3.59	0.26	57.54	12.81	12.40	2.95	0.85	34.00	4.15	32.00
	4	7.1	4.20	0.45	94.03	12.81	5.68	4.78	1.03	18.00	14.50	12.00
	1	6.0	3.19	0.26	12.63	8.13	4.10	2.12	0.77	29.00	2.70	95.00
	2	6.5	3.97	0.34	17.54	9.38	6.46	4.71	0.75	23.00	3.75	32.00
Boro	3	6.6	3.44	0.32	12.63	9.69	5.26	2.25	0.61	25.00	2.80	53.00
	4	6.7	2.98	0.62	44.91	17.81	9.27	2.72	0.63	21.00	2.20	33.00
	1	6.2	2.61	0.24	7.02	6.25	3.65	0.55	1.04	7.40	3.10	26.00
	2	6.4	2.86	0.32	53.63	5.94	4.90	0.71	0.85	46.00	12.75	70.00
Kiruweni	3	6.3	4.47	0.42	44.91	10.31	6.88	1.83	0.65	43.00	2.20	40.00
	4	6.6	3.44	0.34	64.56	12.19	9.27	0.45	0.48	41.00	5.65	28.00

Appendix 2 Cont.

Village		pH	OC %	Total N %	Available P ppm	Exch. Ca me/100g	Exch. Mg me/100g	Exch. K me/100g	Exch. Na me/100g	Extract. Fe ppm	Extract. Zn ppm	Extractable Mn ppm
	1	6.0	4.58	0.20	8.42	1.88	1.04	1.09	0.41	48.0	1.50	10.0
	2	6.3	6.58	0.61	11.23	16.88	7.50	5.90	3.06	41.0	7.30	16.0
Uri	3	6.0	4.60	0.43	2.81	3.50	1.72	1.41	0.54	25.0	2.50	1.9
	4	5.4	6.28	0.87	13.33	8.13	4.44	1.47	0.61	48.0	18.0	13.0
	1	6.3	3.70	0.27	15.44	18.13	3.75	2.85	0.61	23.0	2.05	61.5
	2	6.6	2.38	0.34	63.16	16.56	4.69	3.40	0.52	34.0	3.65	56.0
Munushisinde	3	6.3	3.70	0.10	55.44	11.56	5.52	2.76	0.53	35.0	3.65	23.0
	4	6.1	4.39	0.46	59.65	15.94	6.64	2.63	0.40	31.0	16.0	24.0

1 = No spray

2 = Cu spray 10 years

3 = Cu spray 10 - 30 years

4 = Cu spray 30 years

NB: Data given for 0 - 5 cm depth only

Appendix 3: Glasshouse experiment: DTPA extractable Cu, leaf Cu concentration, plant Cu concentration, dry matter yield, root weight of bean plants

	Sample No.	DTPA Cu ppm	Plant dm weight g	Trifoli_ ate leaf wt. g	Root weight g	Plant Cu ppm	Leaf Cu ppm
	1	24.9	4.69	1.39	0.95	16.6	35.2
	2	22.3	3.95	1.40	0.66	16.6	35.2
	3	24.0	3.72	1.72	0.73	16.6	35.2
	4	67.9	5.59	1.66	1.20	26.5	26.5
	5	47.1	5.10	1.39	0.93	16.6	26.5
Marawe Kyura	6	57.9	4.72	1.66	0.77	26.5	26.5
	7	294.3	6.95	1.61	1.14	35.2	26.5
	8	208.4	6.42	1.81	1.23	26.5	26.5
	9	208.8	5.53	1.70	1.20	16.6	26.5
	10	234.8	5.99	2.20	1.05	26.5	26.5
	11	274.5	5.22	2.03	1.15	25.6	26.5
	12	228.2	5.30	2.09	1.38	16.6	26.5
	13	24.0	4.13	1.48	0.63	26.5	26.5
	14	20.7	3.47	1.45	0.80	16.6	26.5
Boro	15	24.0	3.84	1.20	0.93	25.6	35.2
	16	30.6	3.45	1.12	0.63	16.6	35.2
	17	19.1	4.44	0.95	0.57	16.6	35.2
	18	24.0	3.20	1.38	0.77	16.6	35.2

Appendix 3 Cont.

	Sample No.	DTPA Cu ppm	Plant DM weight g	Trifoli- ate leaf wt. g	Root weight g	Plant Cu ppm	Leaf Cu ppm
	19	45.5	4.47	1.31	1.12	25.6	26.5
	20	43.8	3.30	1.17	1.15	25.6	26.5
	21	43.8	4.29	1.13	0.62	25.6	26.5
	22	109.3	4.68	1.51	1.06	25.6	35.2
	23	155.5	4.97	1.95	1.48	25.6	35.2
	24	110.8	4.64	1.62	1.23	25.6	26.5
	25	12.4	4.61	1.12	0.68	25.6	26.5
	26	15.7	4.45	1.31	0.57	25.6	26.5
Kiruweni	27	12.4	4.77	1.46	1.03	25.6	26.5
	28	44.7	4.17	0.92	1.02	25.6	26.5
	29	51.3	4.10	1.21	1.15	25.6	26.5
	30	62.0	3.94	1.09	1.21	25.6	26.5
	31	91.0	4.25	1.09	1.23	25.6	26.5
	32	124.0	5.08	1.20	1.48	25.6	26.5
	33	84.4	3.97	1.45	1.52	25.6	26.5
	34	124.0	7.57	2.23	1.49	25.6	35.2
	35	120.7	7.52	2.17	1.69	16.6	35.2
	36	114.1	7.78	1.85	2.81	26.5	35.2
	37	89.6	7.45	-	1.20	26.5	-

Appendix 3 Cont.

Sample No.	DTPA Cu ppm	Plant DM weight g	Trifoli-ate leaf wt. g	Root weight g	Plant Cu ppm	Leaf Cu ppm
38	80.0	5.21	-	0.93	26.5	-
39	89.6	7.44	-	1.12	26.5	-
40	70.8	6.49	-	1.02	26.5	-
41	70.8	5.10	-	0.96	26.5	-
42	80.0	6.11	-	1.01	26.5	-
43	136.7	5.67	-	0.95	35.2	-
44	108.4	6.17	-	1.14	35.2	-
45	136.7	6.16	-	0.77	35.2	-
46	428.0	5.75	-	1.03	61.3	-
47	380.0	6.30	-	1.20	61.3	-
48	371.6	5.95	-	1.49	61.3	-
49	61.4	7.21	-	1.69	26.5	-
50	61.4	5.02	-	0.62	26.5	-
51	61.4	5.77	-	1.06	26.5	-
52	200.9	5.72	1.58	1.13	25.6	26.5
53	201.0	5.88	1.67	1.81	25.6	26.5
54	200.8	5.64	1.77	1.21	25.6	35.2
55	183.6	7.63	1.81	1.31	25.6	35.2
56	202.4	7.52	1.49	1.47	25.6	43.9

Appendix 3 Cont.

Sample No.	DTPA Cu ppm	Plant dm weight g	Trifoli-ate leaf wt. g	Root weight g	Plant Cu ppm	Leaf Cu ppm
57	193.8	8.33	1.63	1.44	25.6	35.2
58	164.8	6.07	1.97	1.05	25.6	35.2
59	183.6	6.83	1.07	1.20	25.6	35.2
60	287.0	7.28	0.85	0.74	25.6	35.6
61	258.0	8.18	2.15	1.85	25.6	26.5
62	380.1	8.40	2.20	0.90	25.6	26.5
63	380.1	7.39	2.59	1.31	25.6	35.2
64	268.2	7.68	2.24	1.48	25.6	35.2
65	211.8	7.57	2.57	1.22	25.6	35.2
66	249.4	8.20	2.07	1.30	25.6	35.2

- = Measurements were not taken

Sample 1 - 36 = soils with different copper content

Sample 37 - 51 = soils with adjusted pH

Sample 52 - 66 = soils with an addition of copper oxychloride

Appendix 4: Copper extraction by different extractants

Sample No.	EDTA Cu ppm 1 : 5	DTPA Cu ppm 1 : 2	HCl Cu ppm 1 : 10
1	111.5	24.9	64.2
2	111.5	22.3	59.9
3	120.9	24.0	64.2
4	195.9	67.9	98.7
5	186.5	47.1	94.4
6	205.3	57.9	81.5
7	785.8	294.3	482.1
8	710.8	208.4	326.9
9	673.3	208.4	482.1
10	860.8	274.5	395.9
11	860.8	274.5	395.9
12	823.4	228.2	295.9
13	92.7	24.0	25.4
14	83.3	20.7	34.2
15	111.5	24.0	25.4
16	130.2	30.6	38.3
17	130.2	19.1	34.1
18	111.5	24.0	25.4
19	186.5	45.5	68.6
20	167.8	43.8	59.9
21	177.2	43.8	64.2
22	355.4	109.3	137.7
23	364.8	155.5	111.9
24	336.6	110.8	94.4
25	55.2	12.4	25.4
26	55.2	15.7	25.4
27	55.2	12.4	21.1
28	167.8	44.7	51.3
29	149.0	51.3	90.1
30	167.8	62.0	98.7
31	355.9	91.0	163.4
32	392.9	124.0	219.5
33	364.8	84.4	206.6

Appendix 4 Cont.

Sample No.	EDTA Cu ppm 1 : 5	DTPA Cu ppm 1 : 2	HCl Cu ppm 1 : 10
34	299.1	124.0	370.0
35	299.1	120.7	370.0
36	317.9	114.1	413.0
37	293.1	89.6	143.5
38	339.3	80.0	153.5
39	293.1	89.6	252.5
40	177.7	70.8	85.4
41	177.7	70.8	84.5
42	177.7	80.0	74.6
43	362.4	136.7	193.0
44	362.4	108.4	212.7
45	362.4	137.7	222.6
46	1447.4	427.0	1017.3
47	1678.4	380.0	1116.0
48	339.3	371.6	212.7
49	339.3	61.4	252.2
50	316.2	61.4	242.3
51	293.1	61.4	242.3
52	293.1	200.8	232.5
53	454.8	201.0	262.0
54	339.3	200.9	202.9
55	454.8	183.6	291.2
56	524.1	202-4	410.2
57	385.5	193.0	311.4
58	477.8	164.8	321.2
59	408.6	183.6	291.2
60	662.6	287.0	597.4
61	593.3	258.0	449.5
62	662.6	380.1	488.9
63	801.1	380.1	518.5
64	640.0	268.2	252.2
65	477.8	211.8	173.3
66	754.9	249.4	271.2

Appendix 5: Calculation of the amount of copper oxychloride used in section 3.3.2.2.

Rate of Cu oxychloride used per spray = 5.5 kg/ha or 5500g $CuCl_2$. $2CuO.4\ H_2O$/ha.

Since $CuCl_2.2CuO.\ 4H_2O$ contain 50 percent Cu, this amount is equivalent to $5000g \times \frac{50}{100} = 2750\ g$

Cu/ha. For 8 sprays per season, the amount of Cu sprayed

= 2750g Cu/ha x 8

= 2,200g Cu/ha.

Assuming that all the copper added falls to a hectare of soil which contain 2,200,000 kg soil, in a year, the amount of Cu added to the soil/kg = $\frac{22000}{2,200,00} = 0.01$ gCu/kg soil

= 10 mgCu/kg of soil.

If spraying is done for twenty consecutive years, the amount of copper added will be 20 x 10 mgCu/kg

= 200 mg Cu/kg of soil or

400 mg $CuCl_2.2CuO.4\ H_2O$/kg.