COPPER LEVELS IN SOILS COLLECTED FROM COFFEE FARMS ALONG RUIRU RIVER IN KIAMBU DISTRICT AND RUTUI RIVER IN KIRINYAGA DISTRICT

BY

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This is my original work and has not been presented in any other University

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A B S T R A C T

The total copper content was determined in river water, sediments, soil, potato shoots and tubers, weeds, coach grass, coffee leaves and coffee berries using atomic absorption spectrophotometry (AAS). Plant available copper in the soil was also determined using AAS and the values obtained compared with the copper content in coach grass, coffee leaves and coffee berries. Also compared was the total copper and the EDTA extractable copper (plant available Cu) content in the soil.

The variation of total copper content in the soil with time, depth and rainfall was studied. This study was done in a garden where a known quantity of a copper based fungicide had been sprayed on the soil surface.

The values obtained in river water showed no significant pollution and the same was true of the potatoes analysed.

AAS was chosen for all analysis due to its convenience both timewise and economically. Analysis of certified samples proved the AAS technique to be accurate.

Soils from Kirinyaga District had a higher

copper content than those from Kiambu District. Soils from Kirinyaga had copper levels ranging between 25 ppm and 527 ppm, while those from Kiambu had levels ranging between 9 ppm and 140 ppm. Plant available copper content was found to be proportional to the total copper content in the soil. River water from the two regions had a low copper content ranging between 4 parts per billion and 20 parts per billion. For potatoes, the peels had a higher copper content than any other tissue. In the case of coffee leaves and beans, leaves had a higher copper level than the beans. Generally for plants, the copper content ranged between 2 parts per million and 200 parts per million.

DEDICATION

To my parents and my son Wanjohi

A C K N O W L E D G E M E N T S

I have to express my heartfelt thanks to Professor A.H.S., El-Busaidy whose assistance, as my supervisor and as the chairman of Chemistry Department, has made completion of this project possible. I also wish to thank the University of Nairobi, Board of Post-Graduate Studies (BPS) for the sponsorship. I am also grateful to the research officers at the Coffee Research Station (CRF) whose guidance made it possible for me to start this project. I feel deeply indebted to my father for his support and encouragement. Many thanks are also extended to my colleagues, especially Mr. Joseph Mbugua Ng'ang'a who assisted me in sample collection, and Mr. Frank Waiharo who helped in running of the analytical equipment.

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CHAPTER 1

INTRODUCTION

1:1 General Introduction

Kenya's economy is highly dependent on agriculture. Agricultural products are used for domestic purposes within the country and for fetching the country's income from the external markets. Pesticides and fertilizers are thus increasingly being introduced into the enviroment for improvement of agricultural production. Pesticides are used to inhibit the development of destructive pests[1].

The use of pesticides has a long historical background since even gardners of the earliest days had their troubles with pests. With little known of entomology or pathology,their methods of protecting crops were very crude. Naturally their methods were directed towards mechanical methods for control, through either direct removal of insects and the affected part, or the use of repellents, while charm and incantations were highly considered[2].

Even to the present day, the method of direct removal of insects and affected part is still practiced especially in coffee stems for removing the stem borer (an insect that feeds on the pith of the stem). Bacterial wilt in potatoes in the present day has no known control measure other than removing and throwing away the affected plant plus the soil around it.

The oldest reported chemical control measures

for pests were sulphur sprays, which were employed over two hundred years ago. Copper sprays have no historical background. However, copper sulphate was tried on roses in 1861 to control mildew but burned the foliage[3]. Real progress in copper sprays was stimulated by the introduction of downy-mildew of the grape from America to France. Sulphur was found to be of no value in controlling this disease, and only the discovery of bordeaux mixture saved the European Grape Industry. Bordeaux mixture was generally used in areas where plants of the potato family were grown for controlling alternarior and septoria blight[4].

Presently, the state of knowledge has led to alot of improvement on food production. New chemical compounds have been introduced for use as pesticides in crop protection. By defination, the use of pesticides is detrimental to certain forms of life, the pest and pathogens and the danger is that this toxicity may be exerted in unwanted directions, to the detriment of the user, the consumer and to the biological environment in which the materials are used. The hazards associated with the use of pesticides are usually scrutinized by appropriate authorities, and if necessary, safeguards are put into effect, either by statutory regulations or by advisory means. The adequacy of these safeguards is obviously dependent on a strict adherence by the user to the

rules and recommendations proposed.

Unfortunately however, from my own observation, these regulations are rarely adhered to especially in small scale farming. It is usually recommended that, during application of pesticides the workers should be in a proper attire e.g. use headmasks, hand groves, gumboots, etc, but none of these are adhered to in most observed cases. It is also common that workers are supplied with food inside the farm during application of pesticides and this food has 100% chance of getting contaminated. Also, in small farms pesticides are sprayed using small mannually operated sprayers where one person does the pumping from the container while the other does the spraying. In most cases, the two individuals (with no protective clothings) will be talking to each other and incidents occur where the person doing the pumping is sprayed right inside the mouth, thus ingesting the toxic chemical directly. Another area where regulations are directly broken is in mixing the pesticides where instead of using plant branches for stirring the mixture some people just use their bare hands. It is also common to find that after finishing the application, the equipments are washed in the same river from where people gather water for their domestic purposes.

Even though the chemist has been successful in

recent years in finding pesticides of selective toxicity, and yearly, the least of the hazardous pesticides being reduced by introduction of less noxious alternatives, the danger posed by use of pesticides is still on the increase. The continous accumulation of pesticides in the ecosystem may lead to levels toxic to living organisms.

One of the areas where pesticides use is on the increase is in coffee farms. Coffee is a major cashcrop in Kenya and is usually attacked by many pests. As such, use of pesticides in coffee farms is inevitable. There are many methods of applying pesticides of which spraying and dusting are most common.

One of the most destructive coffee pests is a fungi known as Colletotricum Coffeanum which causes a disease called Coffee Berry Disease (CBD). This disease attacks the coffee berries at any stage of development and it ends up reducing the yield drastically. Several fungicides are used against this disease amongst which are copper based fungicides, delan (dithianion), dyrene (anilazine), etc. The copper based fungicides are the more commonly used especially in areas of low rainfall, because they are cheaper and also control other diseases eg. coffee leaf rust (causes yellowing of leaves), and bacterial bright of coffee (BBC). Most of the copper fungicides

are formulated as wettable powders, and are sprayed on the whole plant mostly on leaves and berries.

Due to scarcity of land, small scale farmers do plant other food crops inside their coffee farms. Another factor leading to planting of food crops inside the coffee farms is the fall in coffee market over the last few years in Kenya to date. These crops include beans, potatoes, tomatoes and many others. These crops are thus direct recipients of the pesticides being used on the farm. The pesticides can be washed down by rain water and may also be spread to nearing gardens or grasslands by wind. Also there is a possibility that elements like copper are in excess in the soils where copper fungicides are commonly used. The levels may have exceeded lethal limits for some crops or the crops may even have taken too much of the elements to an extent of being unfit for human consumption.

For the protection of living organisms against toxic substances as a result of pesticide use, there is need to investigate the levels of the pesticides in the soil, plants, water, and if possible on living organisms where pesticides are in common use. If these levels are beyond tolerable limits, this would pose a problem and then and only then can solutions be sought.

The area of study are two coffee growing zones

drained by rivers Ruiru in Kiambu District and Rutui in Kirinyaga District (Fig 3.1 and 3.2).

Also studied is the variations of copper in the soil with time and possibility of uptake of copper by potatoes planted in a plot where a known quantity of a copper based fungicide has been applied. Also included is an overview of pesticides generally used. Water pollution has also been sighted.

1:2 WATER POLLUTION AS A RESULT OF PESTICIDE USE

Water is the most abundant compound on the earth's surface and is the principal constituent of all living organisms. Its quality is therefore of utmost importance. The act of man (anthropogenic) has had several effects, mostly adverse on the quality of natural water, thus inducing pollution. At the same time, water pollution can occur from natural origin eg. colour change during run off. Anything causing or inducing objectionable conditions in any water course and affecting adversely any use to which the water may thereof be put is considered as a pollutant[5]. Pollution markedly affects the flora and fauna of a stream and can alter the number of individuals as well as the number of species[6].

Toxic chemicals that are of polluting character to river water include sewage disposal, industrial effluents, fertilizers and pesticides in agriculture etc. These chemicals enter into water courses via

soil erosion, blowing of spray particles by wind, animals from cattle dips crossing rivers or going to drink water there, industrial effluents flowing into the river, sewage disposal into the river prior to treatment, and many other ways.

Self purification of the rivers may be considered to be playing an important role in rendering the water suitable for use, but with the increased deposition of substances of polluting character, limits may soon be or might already have been exceeded. The effects of these pollutants need be closely monitored before they result in serious enviromental deterioration and adverse health effect.

1:3 CLASSIFICATION OF PESTICIDE COMMONLY USED IN KENYAN COFFEE

1:3:1 Fungicides[7,8].

The fungicides used for control of coffee berry disease include:

1. Captafol (difolaton or orthodifolaton)
2. Chlorothalonil (daconil)
3. Dithianon (delan)
4. Anilazine (dyrene)
5. Cuprous oxide (red copper eg.copper nordox, copper sandoz MZ, copcel etc)
6. Cupric chrolide [copper oxychloride (green copper) eg. cobox, recop, microcop_50, fungulan, cuprocal etc.
7. Cupric hydroxide (blue copper eg. kocide-101,

parasal etc.)

8. copper sulphate plus lime proprietary premix eg. procidar bordeaux mixture.

These compounds are also used for the control of leaf rust in coffee, bacterial bright in coffee(BBC) especially in the Rift Valley areas, and bacterial bright in potatoes and tomatoes.

The fungicides are applied eight times in a year between February and August at four weeks interval especially in the upper zones where CBD is very common[9].

1:3:2 Insecticides.

In the earlier days, insecticides which were being used were so noxious to human beings that their effects on insects were unquestioned. A few of these included Derris, Arsenical compounds, Nicotine, etc. DDT was introduced in the year 1920 and became widespread in 1942 during world war II. Most of the recently developed insecticides are either chlorinated hydrocarbons or organophosphates. Chlorinated hydrocarbons are ussually contact poisons. Phosphorous compounds are inhibitors of enzymes which occur in insects, particularly in the tissues of the nervous system. They include parathion, marathion, etc. Organophosphates are not as persistent as chlorinated hydrocarbons. Most of the organophosphates are systemic, that is, they are

absorbed into the sap stream of the plant. Some are highly toxic to man but others like marathion, menazon and trichlorphan have a reduced toxicity to man. Fentrothione (sumithione), fenthion (laybouacid), and ambush (mainly on vegetables and potatoes) are also commonly used insecticides. The insecticides are normally applied during outbreaks of insect pests. Some are mixed with fungicides during application in order to reduce the labour cost.

1:3:3 Herbicides

There are many classes of herbicides used for killing weeds. They may either be systemic hormone type translocated or contact herbicides. Some are selective for certain types of weeds. Commonly used in coffee farms are:

1. Paraquat (gramoxone) a contact herbicide for killing broad leaved weeds. It's activity is neutralized on contact with the soil.
2. Roundup for killing grasses e.g couch grass etc. It is a systemic herbicide.

The above classes of pesticides are just a few of the many available ones. The mammalian toxicity of chemical compounds is normally given in terms of LD50 (lethal dose fifty -a calculated dose of a substance which is expected to cause the death of 50% of the entire defined experimental animal population, as determined from the exposure to the substance, by any

route other than inhilation of a significant number from that population. Other lethal dose percentages, such as LD1, LD10, LD30, LD39, may be used for specific purposes of the scientist)[10,11].

Pests may adapt to presence of pesticides by changes in species diversity or by adaptation of enzyme systems, so that a pesticide may be more rapidly metabolized by an already adapted microbial population in soil where the same or related pesticide has been used before[12,13].

The environmental hazards of pesticides residues have been reported in details in the literature[14,15].

Other than using these chemicals which are hazardous to the environment, other control measures especially for insects can be used. These include[16]:

a) Biological control where parasites and preditors are introduced to reduce the number of pests.

b) Legislative control where a government policy is laid to prevent introduction of the more important foreign pests and diseases, and to minimize the planting of diseased material.

c) Cultural control e.g crop rotation to prevent the buildup of eelworms which attack crops like potatoes, cereals and bulbs, cultivation of soil at certain times of the year thus exposing the insects to predation by birds, etc.

1:4 C O P P E R

1:4:1 Occurence:

The occurence of copper in the earth's crust, and its levels in several countries has been reported extensively in literature[17,18,19,20]. The copper minerals (simple & complex sulphides) are quite easily soluble in weathering processes and release copper ions, especially in acid environments. Copper is thus considered among the more mobile of the heavy metals in hypogenic processes. However, copper is a very versatile trace cation and in soils or depositional materials exhibits a great ability to chemically interact with minerals and organic components of soil.

The copper ions can also readily precipitate with various anions such as sulphide, carbonate, and hydroxide. Thus copper is a rather immobile element in soils and shows relatively little variation in total content in soil profiles[21]. Soluble, and therefore available and mobile, forms of copper in soils are of great importance in agronomic practice.

Copper occurs in the soil principally as Cu^{2+} adsorbed by clay minerals or tied up by organic matter[22]. Copper can readily combine with any free complexing agent that may be available. It has a large capacity to combine with organic matter. The quantity and quality of organic matter affects its ability to combine with copper. The fixation of copper by

organic matter has always been considered the cause of copper deficiency in organic soils [23,24,25]. However, low copper content also cause deficiency in organic soils other than fixation alone. The common characteristic of copper distribution in soil profile is accumulation in the top horizons.
This phenomenon is an effect of various factors, but above all, copper concentration in surface soils reflects the bioaccumulation of the metal and also recent anthropogenic sources of the element[26].

Several ionic species of copper may occur in the soil although the most common mobile copper is the divalent ion Cu^{2+}. Copper ions are held very tightly on both organic and inorganic exchange sites. The process controlling fixation by soil constituents are related to the following phenomena:

a) adsorption
b) occlusion and coprecipitation
c) organic chelation and complexing
d) microbial fixation.

The following are the ionic species, compounds and bonds of copper occuring in soils CU-O-Fe; CU-O-Al; CU-O-Mn; Cu^{2+}; Cu^{+}; $CuOH^{+}$; $Cu(OH)_2^{2+}$; $Cu(OH)_2$; CuO; $Cu(OH)_2CO_3$; $CuCO_3$; $Cu(CO_3)_2^{2-}$; $Cu(OH)_4^{2-}$; $Cu(OH)_3^{-}$; CuO_2^{2-}; $HCuO_2^{-}$.

All soil minerals are capable of absorbing

copper ions from solution and these properties depend on surface charge carried by the adsorbent. The surface charge is strongly controlled by pH, therefore, the adsorption of copper ion species can be presented as a function of pH. This type of Cu adsorption is likely to be most important in soils with a large content of variable-charge minerals[27]. Copper can be adsorbed by minerals within the range from 0.001 to 1 micro-mole per decimeter cubed or from 30 to 1000 micro-moles per gram. There is a significant correlation between copper adsorption and the sum of bases for the surface soils[28]. Occlusion, coprecipitation, and substitution are involved in non-specific adsorption of copper. Some soil minerals, such as aluminium and iron hydroxides, carbonates and phosphates and to some extent also silicate clays, have a great affinity to bind a part of the soil Cu in a non diffusible form, which is the most stable portion of the metal in soil. Chelation and complexing are the key reactions governing Cu behaviour in most soils. Many kinds of organic substances form both soluble and insoluble complexes with Cu, thus Cu-binding capacities of soils and Cu solubility are highly dependent on the kind and amount of organic matter in soils. The maximum amount of copper that can be bound to humic and fulvuric acids is approximately equal to the content of acidic

funtional group. This in general corresponds to the sorption of from 48 to 160 mg of copper per gramme of humic acid. The maximum sorption capacities of different kinds of soil differ greatly according to the physical and chemical properties of organic substances. Humic and fulvuric acid are likely to form stable complexes when copper is present in small amounts and organic matter can modify several copper reactions with inorganic soil components.

In certain surface soil, microbiol fixation plays a prominent role in bidding of copper. The amount of copper fixed by microbiomass is widely variable and is affected by various factors such as metal concentration, soil properties and growing seasons. Microbiol fixation of copper is an important step in ecological cycling of this metal.

Copper metal is abundant in soil solutions of all types of soils. concentration of copper in soil solutions obtained by various techniques from different soils vary from 3 to 135 microgrammes per litre. Overall solubility of both cationic and anionic forms of copper decreases at about pH 7 to 8. It has been estimated that the hydrolysis of copper ($CuOH^+$ and $Cu_2(OH)_2^{2+}$) are the most significant species below pH 7, while above pH 8 anionic hydroxy complexes of copper become important. The solubility of $CUCO_3$ is not pH dependent and this compound seems

to be a major inorganic soluble form of copper in neutral and alkaline soil solutions while nitrates, chlorides, and sulphates do not complex a significant portion of copper in soil solution. However, the most common forms of copper in soil solutions are soluble organic chelates of these metals. About 80% of the soluble copper forms have been estimated to be organic chelates[29]. Organic complexing of copper has a prominent practical implication in governing the bioavailability and the migration of copper in soil. The bioavailability of soluble forms of copper depend most probably on both the molecular weight of copper complexes and the amount present. Compounds of low molecular weights liberated during decay of plant and animal residue as well as those applied with sewage sludges may greatly increase the availability of copper to plants.

1:4:2 Soil contamination with copper[27].

The contamination of soil by copper compounds results from utilization of copper containing materials such as fertilizer, sprays, and agricultural or industrial emissions. Some local and incidental copper inputs into the soil may arise from copper alloy construction material (e.g., electric wires, pipes, etc). Surface soils have a great Cu affinity resulting in accumulation of this metal, and as a consequence, copper contents of some soils has already

built up to about 3,500 ppm Cu from industrial sources of pollution and about 1500 ppm Cu from agricultural origins of the metal. The threshold value of a 100 ppm copper has been exceeded in several contaminated surface soils[27]. Copper stored in surface soils influences their biological activity and may become available to plants in various conditions.

1:4:3 Copper in plants

Copper in plant roots tissues occurs almost entirely in complexed forms; however it is most likely that the metal enters root cells in dissociated forms. According to studies carried out by Graham[30] on the absorpion of copper by higher plant roots, the rates of absorption of copper are amongst the lowest of the essential elements, varying from picco to micromole per hour per gramme of roots in the physiological concentration range (0.01 to 20 micromoles of copper).

It has been observed that there is a strong capability of root tissues to hold copper against the transport to shoots under conditions of both copper deficiency and copper excesses. The concentration of copper in xylem and phloem saps range from traces to 140 micromoles per litre and seems to correlate with the concentrations of aminoacids. The copper mobility within plant tissues strongly depends on the level of copper supplied, being highest with luxury supply[31]. However copper has low mobility relative to other

elements in plants and most of these metals appear to remain in roots and leaf tissues until they senesce; only small amounts may move to young organs. Therefore, the young organs are usually the first to develop symptoms of copper deficiency.

The distribuion of copper within plants is highly variable. The highest concentrations have been found in the embryo of cereal grains and in the seed coat (2 to 18 ppm in embryo, and 2 to 23 ppm in seed coats), while in whole seed, highest value 4 ppm[32]. However, a more uniform distribution of copper in barley grown has been reported[33].

The appropriate content of copper in plant is essential both for health of the plant and for the nutrient supply to man and animal. Some plants have a great tolerance to increased concentrations of copper and accumulate extremely high amounts of this metal in their tissues.

The concentration of copper in plants tissues seems to be a function of its level in the nutrients solution or in soils. The pattern of these relationship, however, differs among plants species and plant parts. Opinions appear to vary considerably as to which factor, soil or plant affects concentrations of copper in plant tissues into a higher degree. copper in ash of a variety of plant species is reported to range from 5 to 1500 ppm[34].

In several species growing under widely ranging natural conditions, copper content of whole plant shoots do not often exceed 20 ppm, and thus this value is most often considered to indicate the threshold content. However, under both natural and man induced conditions, the majority of plants can accumulate much more copper, especially in root storage tissues. The significance of elevated copper contents in feed and food plants that reflect man made pollution needs evaluation from the environmental health point of view.

1:4:4 Copper in water

Normally, rivers spring from rocky areas. Since all rocks in the earth's crust contain copper as mentioned earlier, then some copper should naturally be expected in river water. This is in accordance with the fact that natural waters at some stage make contact with and react with the minerals of the earth's crust, altering them and accompanying this interaction by changes in their own composition. The chemical composition of rocks determines the elemental composition of natural water, since water is the primary agent in rock weathering.

The chemical mechanisms of trace elements transport in natural waters include: [35].

_ Dissolving of ionic species and inorganic compounds;

_ Formation of complexes with organic molecules in solution, adsorption in solids;

_ Precipitation and coprecipitation on solids (metallic coating);

_ Incorporation in solid biological materials;

_ Incorporation in crystalline structures.

Copper has been found to be transported mainly in crystalline solids. It has been suggested that, the dissolved inorganic species of copper in sea water include Cu^{2+}, $CuCO_3$, $CuSO_4$, OH^- and Cl^- species. However, some considerable work needs to be done in this field. As with other trace elements, copper in natural waters occurs in very low concentrations.
In North America,concentrations of copper in large rivers ranges between 0.83 and 105 micrograms per cubic decimeter[36].

1:4:5 Biochemical functions of copper in plants

Copper is involved in the mechanisms of disease resistance. This resistace of plants to fungal diseases is likely to be related to an adequate copper supply.Plants with enriched copper concentrations are likely to be susceptible to some diseases.

Copper controls the production of DNA and RNA, and its deficiency greatly inhibits the reproduction of plants (reduced food production, pollen sterility).

copper influences water permeability of xylem vessels and thus controls water relationships.

copper plays a significant role in several physiological processes-photosynthesis,respiration, carbohydrate metabolism, and cell wall metabolism.

Copper occurs in compounds with no known functions as well as in enzymes having vital functions in plant metabolism.

Copper is mainly complexed with organic compounds of low molecular weight and with proteins.

According to these phenomena, the role of copper in disease resistance is an indirect one. The most important implications are related to deficiency and toxicity of copper. Plant production is affected by its deficiency since deficiency affects physiological processes.

The deficiency levels of copper in plants show large genetic differences, and differ according to plant species. Copper levels in soils below 2 ppm are likely to be inadequate for most plants[37]. Soils containing 3 to 12 ppm plant exchangeable copper are

not defficient but addition of fertilizers containing copper can improve crop yield[38]. Removal of copper by crops is negligible when compared to its content in the soil. Comparation of excesses of copper applied and the ammount removed in farm produce and leached with percolating water showed that depletion of soil reserves is an unlikely explanation for the appearance of copper deficency over a short period[39].

Copper seems to be involved in the synthesis of cytochrome oxidase and possibly increases chlorophyl and carotenoids in plants[40]. Yates and Hallsworth (1963)[41] investigated the role of copper in the metabolism of nodulated clover and found its effect to vary with the supply of combined nitrogen. When copper was defficient plants receiving nitrate-nitrogen accumulated amino acids, whereas plants relying upon symbiotic fixation of nitrogen showed that a continuous increase in soluble amino acids correlated with the level of copper. They obtained evidence suggesting that copper is directly concerned in the formation of gamma-amino-n-butylic acid in the plant nodules and as this acid is a particular constituent of nodule protein, the effect of copper appears to be a unique requirement.

Other than being essential to plants, copper has numerous biological effects as a toxicant. General symptoms related to copper toxicity in plants show

that copper induced chlorisis (due to copper preventing uptake and translocation of iron) and root malformation are the most characteristic symptoms of its toxicity. Studies of copper toxicity in relation to soil pH, with equal available copper contents, have shown that this toxicity increases with decreasing soil pH[42,43].

The processes induced by an excess of Cu^{2+} and Cu^{+} ions may be summarized as follows:[39]

I) Immobilization of copper in cell walls, in cell vacuoles, and in non-diffusible copper protein complexes.

ii) Tissue damage and elongation of root cell.

iii) Peroxidation of chloroplast membrane lipids and inhibition of photo synthetic electron transport.

iv) Alteration of membrane permeability, causing root leakage of ions (eg K^{+}, PO_4^{3-}) and solutes.

Not only should there be appropriate amount of active copper in the cells, for optimal development, plants must also have a balance of chemical elements. There are many complex interactions of copper with other elements within plant tissues and also in the external root media, particularly in the uptake-transport processes.

It has been shown that as little as 0.1 ppm alluminium seriously reduces copper uptake by wheat

roots[44]. This effect was overcome by increasing the available copper and thus it appears that copper and alluminium were competing for common binding sites in the root surfaces. Coffee plants found to contain high ammounts of copper (300 ppm) in their leaves exhibit magnesium deficiency symptoms in spite of adequate magnesuim in the soil[45]. Several other interactions between copper and other elemets have been reported e.g Cu-F, Cu-P, Cu_Ni, Cu-mn, Cu-Se, Cu-Mo etc[46,47]. Liming is the most frequent practice in the amelioration of copper contaminated soils. The relatively common occurences of reduced copper contents in plants that have an increased supply of some nutrients are often related to secondary effects of copper dilution resulting from enhanced growth rates of the plant. Copper is also important in its enzymatic activities. It is long established as a constituent of several plant enzymes, eg tyrossinases, including the mono and polyphenol oxidases; laccases and the ascorbic acid oxidases[48].

1:4:6 Effect of copper on animals

Copper is not only important to plants and lower forms of life but also to mammals. Its effects are highly influenced by factors such as form and level of copper exposure, species of organism, diet, disease state, and individuality.

Due to its importance in life, copper deficiency

in mammals and other animals may result to serious drawbacks. At the same time, copper excesses have their drawbacks too. Disorders that have been associated with a relative copper deficiency in various animal species include anaemia, depressed growth bone disorders, depigmentation of hair and wool, abnormal wool growth, neonatal ataxia, impaired reproductive performance, heart failure, cardiovascular defects, and gastrointestinal disturbances[49]. Many factors influence the severity of these dysfuntions, especially species, age, dietary interelationships, environment, sex and even breed or strain characteristics.

Copper interacts with other elments like Mo, Zn, and Fe in animal tissues. Imbalance of these may result to dysfunctions. Drastic scouring disease of cattle known as teart, is a manifestation of chronic molybdenum poisoning that can be controlled by treating the cattle with large amounts of copper[50,51].

Copper deficiency in non-ruminant results in anaemia, bone deformities and reduced calcification cerebral edema and cortical necrosis, achromotrichia, fetal absorption and aortic rupture. The level of ceruloplasmin and copper in serum and the levels of cytochrome oxidase and copper in tissues decreases in animals fed on copper deficient diet[52].

Ingestion of copper can result in poisoning to

animals and human beings. Cattle are poisoned by 20-100 mg per Kg single dose. In acute poisoning by large oral doses of copper formulation, vomition, excessive salivation, abdominal pain, and diarrhoea (greenish tinged fluid feaces) are usual signs. Normal levels of copper in the blood range between 75 to 135 micrograms per 100mls (0.75-1.35 ppm); but at the onset of hemolytic crisis, concentrations may be much higher[53].

Systemic toxic effects of copper poisoning include hemolysis, hapatic necrosis, gastrointestinal bleeding, oliguria, azotemis, hemoglobinuria, hematuria, proteinuria, hypertension, tachycardis, convulsions, coma and death[54,55].

Human copper toxicity may occur in several situations. An example is Wilson's Disease (Hepatolenticular or hepatocerebral degeneration). Patients with this disease exhibit a deficiency of the plasma copper protein ceruloplasmin and an excess of hepatic copper[56].

1:5 PREVIOUS WORK IN THIS FIELD

Copper levels from soil and coffee plant materials have been determined for various locations in Kenya. This work has been done by the Coffee Research Station in Ruiru, chemistry section. For materials sampled from Bahati-Solai area, Nakuru District in Kenya, it was found that EDTA extractable

copper averaged 14.1 ppm for subsoils and 102.9 ppm for top soils. Total copper averaged 32.2 ppm for subsoils and 175.1 ppm for top soils. Copper levels in plant materials was variable, 311.7 ppm in branches and 21.0 ppm in coffee beans[57]. For Meru, Bungoma and Kisii in Kenya, it was found that available copper ranged from 1.0-146ppm and 1.0-170 ppm for top soils and subsoils respectively. Total copper ranged from 1.0-370 ppm for top soils and 1.0-240 ppm for subsoils. Copper concentrations in branches ranged from 12.0-158 ppm, while it ranged from 8.0-98.0 ppm for the leaves[58]. Reuther et.al. (1953)[59] studied the interaction between soil available copper and nutrient concentration and observed high levels of copper in the top soil. Accumulation of copper in the top soil means that any damage to roots would be confined largely to the top soil zone. On studying the effects of increasing rates of copper sprays on soil and leaf nutrient concentration and on the yield of mature coffee grown in the field, Adote(1973)[60] found that the foliage of trees recieving different rates of copper sprays for a period of about two years did not show any copper toxicity symptoms. Instead, the fungicidal role of copper was observed as seen in the varying degree of fungal attacks on the leaves and on the green berries and the differences in growth of the plants. He also found that soil pH increased in both

depth and with increase in copper spray concentrates.

1:6 OBJECTIVES OF THE PRESENT STUDY

The present study was aimed at:

a) Finding the total copper content in the soil from several coffee farms where copper had been previously used.

b) Finding if there is a correlation between exchangeable and total copper in the soil;

c) Finding if there is a correlation between exchangable copper and plant copper content;

d) Finding the copper levels in river water taken from rivers in two coffee areas;

e) Finding the concentration of copper in coffee berries and leaves;

f) Finding the concentration of copper in a food crop eg. potatoes harvested from a copper sprayed area and an area where no spraying has been done;

g) Finding the variation of copper levels in the soil with time and depth.

C H A P T E R 2

THEORY OF ANALYTICAL TECHNIQUES.

SPECTROSCOPY

2:1 Introduction

Atomic spectrometry can be done by Atomic emission, Atomic Absorption or atomic fluorescence. Analysis by emission spectroscopy is the determination of an element by means of its emission spectrum, obtained from a suitably excited source. Qualitative analysis is based on the wavelength of the lines characteristic, and quantitative analysis on the intensity of these lines. Optical absorption is used in two ways[61,62,63] Colorimetry and spectrophotometry. Colorimetric analysis is the determination of the concentration of coloured substances by the colour intensity, i.e. by the absorption from a white light flux in a specific spectral region. Atomic absorption spectrometry is an analytical technique for the determination of elements based upon the absorption of radiation by free atoms[65]. The basic reaction underlying atomic spectrometry may be simply stated:

$N(0) + hv = N(0)^*$

where N(0) is the ground-state atom

N(0)* is the excited state atom

h is the planct's constant

v is the frequency.

The ground state atom N(0) absorbs energy to yield the excited state N(0)* and emits radiation following de-excitation. Atomic fluorescence is a result of resonance radiation absorption followed by re-emission at the same or some lower frequency[64]. Details of the principples governing spectroscopic analysis are given in literature[66,67].

2.2 Comparation of atomic absorption with atomic emmision spectrometry

Atomic absortion spectrometry is dependent upon the ground state atom population N(o), whereas atomic emission results from de-excitation process. The potential superiority of AA depends upon the intensity (radiance) as compared with the theoretical black body radiator at the flame temperature and line wavelength[68]. AA is the superior technique where long wavelength resonance lines are used. Minor temperature fluctuations have a far greater effect upon the number of atoms populating the excited (j) level than the ground state atoms N(o), so that atomic emission is quite sensitive to this parameter, thus appropriate safeguard must be taken.

Absorption by atoms take place within a very narrow spectral regions, of the order of 100th of an Angstrom , and in the laboratory, only those involving the ground state are observed, yielding simple

spectra. Absortion involving the ground state are therefore known as resonance lines. This means there is little possibility of coincidence of resonance lines, and therefore very little spectral interferance, thus accounting for one of the major advantages of AAS.

In 1955 came two reports showing the advantages of absorption methods over emission methods one by Alkemade and Milatz and one by Walsh[69]

The main advantages of absorption as stated by Walsh are[70]:

1) There is virtually no interference between resonance lines of different lines.

2) The light source used in atomic absorption (hollow cathode and high-frequency tubes) give a fairly simple spectrum of the element being analysed with well-pronounced resonance lines and little background. This allows use of instruments of low resolving power.

3) In emission analysis, a difficulty is that the intensities of the lines depend strongly on the temperature of flame because small variations in temperature affect the relative concentration of atoms in the different excited states.

4) In atomic absorption measurements, the ratio of the transmitted signal to the absorbed signal is recorded, rather than the absolute value of a signal.

Combustion flames provide a remarkably simple means for converting inorganic analytes in solution into free atoms. It is only necessary to introduce an aerosol of the sample solution into an appropriate flame, and a fraction or all of the metallic ions in the aerosol droplets are eventually converted into free atoms.

2:3 Atomic absorption spectrophotometry

The use of flame absorption spectra instead of emission-spectra was first proposed and developed by Walsh[71]. The equipment for atomic absorption analysis comprises of a light source, a dispersive system and a detector, or essentially main parts are:-

1. A source of radiation (lamp).
2. A means of isolating the required wavelength.
3. Sampler burner compartment.
4. Detecting and measuring means for the intensity of radiation.

The instrument used in the present analysis uses a double beam arrangement. In this kind of arrangement, one beam (sample beam) passes through the flame and its intensity gets reduced due to sample absorption, while the second beam (reference beam) does not pass through the flame. This arrangement reduces flame interferences. The instrument was a Perkin Elma Model 2380[78] ,which is a microprocessor controlled atomic absorption spectrophotometer, and controls are

incorporated to facilitate automatic averaging and statististical treatment of the results.

In practice, a solution of the element is sprayed into a relatively cool flame in which the atoms tend to remain in the ground state. Radiation from a hollow cathode discharge lamp is passed through the flame and the decrease in intensity is measured using a monochromator and detector system. This decrease is related to the concentration of the element in solution.

The flame gases are treated as a medium containing free, unexcited atoms capable of absorbing radiation from an external source when the radiation corresponds exactly to the energy required for a transition of the test element from a ground electronic state to an upper excited electronic state. Unabsorbed radiation passes through a monochromator that isolates the exciting spectral lines and into a photodetector. ie, the monochromator separates AA analysis lines from adjacent non-absorbing lines of the test element. It is better than using filters for the complex spectra of heavy metals.

Absorption is measured by the difference in transmitted signal in the presence and absence of test element.

An expression for the absorbed energy per unit time and flame cross-section is given by:-

$I(A) = S\ I^{\wedge}[1-\exp(-k^{\wedge}b)]d^{\wedge}$

Where: ^ = lambda (wavelength)

S represents integral

I (A) = Absorbed radiation intensity (integrated; energy per unit time per unit energy);

I^ = Intensity of source emission at wavelength ^;

k^ = Atomic absorption coefficient at wavelength ^;

b = cell path length or length of the flame horizontally.

For a line source which is considerably narrower than the absorption line width, the above expression boils down to the basic Beer-Lambert's expression A=const. N(o)b.

where N(o) represents atomic concentrations

A= Absorbance =log[I(o)/I]

I(o)=Absorbed part of the radiant energy of the incident light beam.

I=Intensity after passage through the absorption media or in otherwords transmitted intensity.

I=exp(-K(v)cd)...general form of Beer-Lambert's Law

where K(v)=absorption coefficient and d is the average thickness of absorbing medium, ie, the path length of the flame horizontally. From the basic Beer-Lambert's Law A=const.N(O).b, it can be seen that a plot of absorbance(A) versus N(0) or, more practically the atomic concentration (C) should be linear. Various processes act to cause bending of the curve at higher

concentrations and at low concentrations.

Around the central frequency, there will exist a finite bandwidth due to absorption line broadening within the flame gases and a broadening of the emission source. The principal courses of broadening are Doppler and Lorentz, or pressure broadening. Lorentz broadening is due to collissions of the absorbing atoms with other molecules or atoms present in the flame gases.

One of the most important components of the AAS is the Lamp (light souce). As external light sources, both hollow cathode lamps and electrodeless discharge tubes are used. A hollow cathode lamp has a pyrex body and an end window of quartz. The lamp is filled with an ultrapure monoatomic gas (to avoid molecular continuum spectra), usually neon, occasionally argon at a low pressure.

For easily worked metals, the whole cathode is made of the metal. But for expensive metals, a thin liner is inserted into a copper cathode.

Neon gas is prefered because it gives a better intensity and also tends to supress the ionic spectrum of some elements. Argon is substituted only when a neon spectral line occurs in close proximity to a resonance line of the metal liner.

Increasing the lamp current increases its intensity but lowers the sensitivity due to line broadening

and/or self-reversal for some elements. For a given atomic line, the Doppler broadening is proportional to the square root of temperature. For narrow spectral lines from the source, the temperature of the radiating plasma should be kept as low as possible. This is done by keeping the lamp current low. Self-absorption is due to absorption of radiation by non-emitting atoms in the source and depends on the length of the non-emitting cloud through which the radiation must pass. It can be reduced by shortening the path length and the concentration of vapour through which the emitted light must pass. The single element lamps with their narrow band emissions provide virtually complex specifity for each element.

A stable source can be obtained by chosing a stable filler gas pressure, outgassing, and suitable electrode design. It may be that the development of conventional hollow-cathode lamps has reached its limit but the problem of instability still remains and leads to fluctuations of the order 0.1%.

Other important components of the AAS include the nebulizer and the burner, and their details can be found in literature.[72,73,74,75]. Nebulization produces an aerosol of the the solution under analysis.

2:4 Flames and flame temperatures.

As soon as the aerosol produced by the

nebulization is transported into the flame, the following sequence of events occurs in rapid succession:-

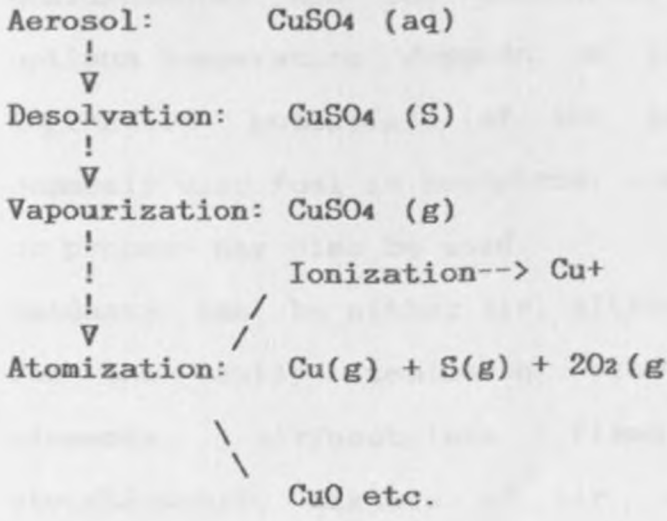
1) The solvent is evaporated, leaving minute particles of dry salt (salts).

2) The dry solids are converted into gaseous states.

3) A part of all the gaseous molecules are progressively dissociated to give neutral atoms or radicals; the atomization step. These neutral atoms are the species that absorb in AAS and AFS, and are potentially the emitting species in FES. The efficiency with which the flame produces neutral atoms of the analyte is of equal importance in each of the flame techniques.

4) A portion of the neutral atoms may be thermally excited by collisions with partially burnt components in the flame gases, or even ionized. The fraction excited is important in FES, but a nuisance in AAS.

5) Some of the neutral atoms may combine with radicals in the flame gases to form new gaseous compounds such as metal monoxides. This gives rise to chemical interferences in all the three flame techniques. As an example, an aerosol containing copper sulphate the sequence would be:



The entities emit their characteristic radiations at different wavelengths.
The main requirements of a satisfactory flame are that it has the proper temperature and fuel/oxidant ratio to carry out the enumerated functions of the flame, and that the spectrum of the flame itself does not interfere with observation of the emission or absorption features being measured. Components of the flame gases limit the usable range to wavelengths longer than 210nm.

The flame temperature value depends on the fuel/oxidant ratio and is usually highest for a stoichiometric mixture.

To be taken into account when selecting the flame is: the signal-to-noise ratio (which is due to emission of interfering elements); the stability of

the source (which determines the precision of measurements) and the economy of the analysis. The optimum temperature depends on the excitation and ionization potentials of the analyte. The most commonly used fuel is acetylene, even though hydrogen or propane may also be used.

Oxidants can be either air, nitrous oxide or oxygen. For the easily atomizable elements eg. alkali elements, air/acetylene flame is used. A stoichiometric mixture of air acetylene has a temperature of 2400°C and a burning velocity of 160-266 cm per second. Acetylene/nitrous oxide stoichiometric mixture flame has a temperature of 2800°C and a burning velocity of 260cm per second. The hotter flame allows the sensitive analysis of additional elements whose refractory oxides are not reduced to the atomic state in the air/acetylene flame.

A fuel-rich acetylene flame provides a reducing atmosphere necessary for the production of a large free-atom population of those elements that have a tendency of forming refractory oxides. The region of optimum emission is the interconal zone because of the presence of many carbon-containing radical species.

2:5 <u>The sensitivity of AAS</u>

Sensitivity as applied to atomic absorption is a measure of the amount of absorption produced by a

given concentration and is generally given as p.p.m/1% absorption. Absolute sensitivity is the minimum amount of element needed to produce the signal which confirms its presence (given in grams,micrograms or moles). Relative sensitivity is the minimum concentration of the element in a sample which can give the signal, confirming its presence. Sensitivity depends on the whole instrumental system employed.

A very important feature is the quality of the hollow-cathode lamps. The limit of detection for any single element varies from lamp to lamp. Secondly, the sensitivity and stability obtainable with a particular lamp deteriorates with age. The precision of analysis can be within a standard deviation of 3% to 5% if care is taken to check the calibration frequency[77].

2:5:1 Adjustments for maximum sensitivity

i) The lamp current is set according to specifications by suppliers for each element e.g. 15 mA for copper.

ii) The lamp is aligned to give maximum intensity by moving it forwards, backwards, upwards, sideways and rotating until the highest reading of intensity is attained.

iii) The wavelength is then fine adjusted until maximum reading is attained.

iv) Using a specified standard solution of element to be analysed, the flame (fuel/air ratio), the burner

height and the path length (by tilting the burner head) are adjusted for maximum absorbance reading.
eg. 5 ppm of Cu standard should read 0.25 absorbance units.

For the present analysis of copper, the wavelength reading was always 324.8nm; sensitivity 0.23 units for 5 ppm standard solution; slit width 0.7; lamp current 15; Flame acetylene/air; Residence time=0.5 seconds, number of readings per recording = 5; Rate of flow of sample =7ml/s

2:6 Disadvantages of flame atomization

1. The premixed or laminar flow burner is limited to the use of solution or very fine suspensions. Rarely can solid samples be atomized directly.

2. Sensitivity is limited because the nebulizer mixing chamber is wasteful of sample. Only about 10% of the sample effectively reaches the flame as a fine aerosol that ultimately becomes atomized.

3. The residence time of an atom within the optical beam is extremely short(approximately 0.001 second), thus giving little time for attaining a steady state (achieving an equilibrium content of element in the optical beam).

2:7 Interferences

1. Background absorption:

This occurs in AAS as molecular absorption and light scattering by particles in the flame. It occurs

when matrix species are vapourized along with the analyte atomic species and absorb a portion of the analyte atomic resonance light emitted from the light source.

2. Spectral line interferences:

This occurs when a line of interest cannot be readily resolved from a line of another element or from a molecular band. Interference of this kind is usually associated with the resolving power of the monochromator.

3. Vapourization interference:

This occurs when some sample component influences the rate of vapourization of the salt particles containing the desired analyte. It can arise from a chemical reaction that alters the vapourization behaviour of the solid, or it can be a physical process in which the vapourization of the matrix controls the release of analyte atoms trapped within: Hotter flames provide less vapourization interference. Elements such as Na, Cu, Tl, Ag and Zn are practically completely atomized in the flame; they do not form molecular compounds with flame partners in noticeable proportions. Metals such as La, Al and Ti form refractory oxides which are extremely stable.

4. Ionization effects:

At the temperature of Acetylene/nitrous oxide flame, many elements and especially the alkali metals, are

appreciably ionized. Ionization depopulates the neutral atom levels, both ground and excited, thus lowering sensitivity. This problem is readily overcome by adding a readily ionized element, such as potassium, cesium or strontium, as an ionization suppresant, to sample and standard solutions. The ionization suppresant is usually added in the range 100-1000 micrograms per millilitre in using the hotter flames to determine elements that have ionization potentials below 7.5 ev. As the ionization constant, K(i) of the suppressant decreases a smaller quantity is effective in repressing the analyte ionization. To ensure that ionization interference is suppresed, the product K(i)C(i) of the suppresant should be 100 times the product for the analyte.

5. Flame interferences

The flame may emit some light of the wavelength in use but in practice, this can be eliminated by using a modulated source and an amplifier in the detector circuit tuned to the frequency of modulation.

C H A P T E R 3

MATERIALS AND METHODS

A) FIELD SAMPLES

3.1 Description of study areas

3.1.1. Description of Rutui river zone.

Rutui river is a small river in Kirinyaga District starting from the slopes of Mt Kenya. The river springs from a tea growing zone called Kangaita (fig 3.1). The area is hilly, altitude around 6300 ft above sea level[79]. Temperatures there average around 19 degrees centigrade and there is rain most of the time in the year. About one kilometer downstream starts the coffee zone. Around two kilometers downstream is the first coffee factory called Githioro coffee factory along the river. From the same area (Githioro) is a water supply plant for Kerugoya town (Kirinyaga District Headquaters). There are three more coffee factories downstream namely Gathera factory (around Kerugoya town), Rutui factory (about 8km downstream) and Karia factory (around 11km downstream).

Near Kerugoya town, Rutui river joins another river called Kandakame, further downstream joins Mukengeria, Kiringa and several other small rivers before finally joining a big river called Thiba at Kutus town (Fig 3.1).

Kirinyaga District is one of the smallest

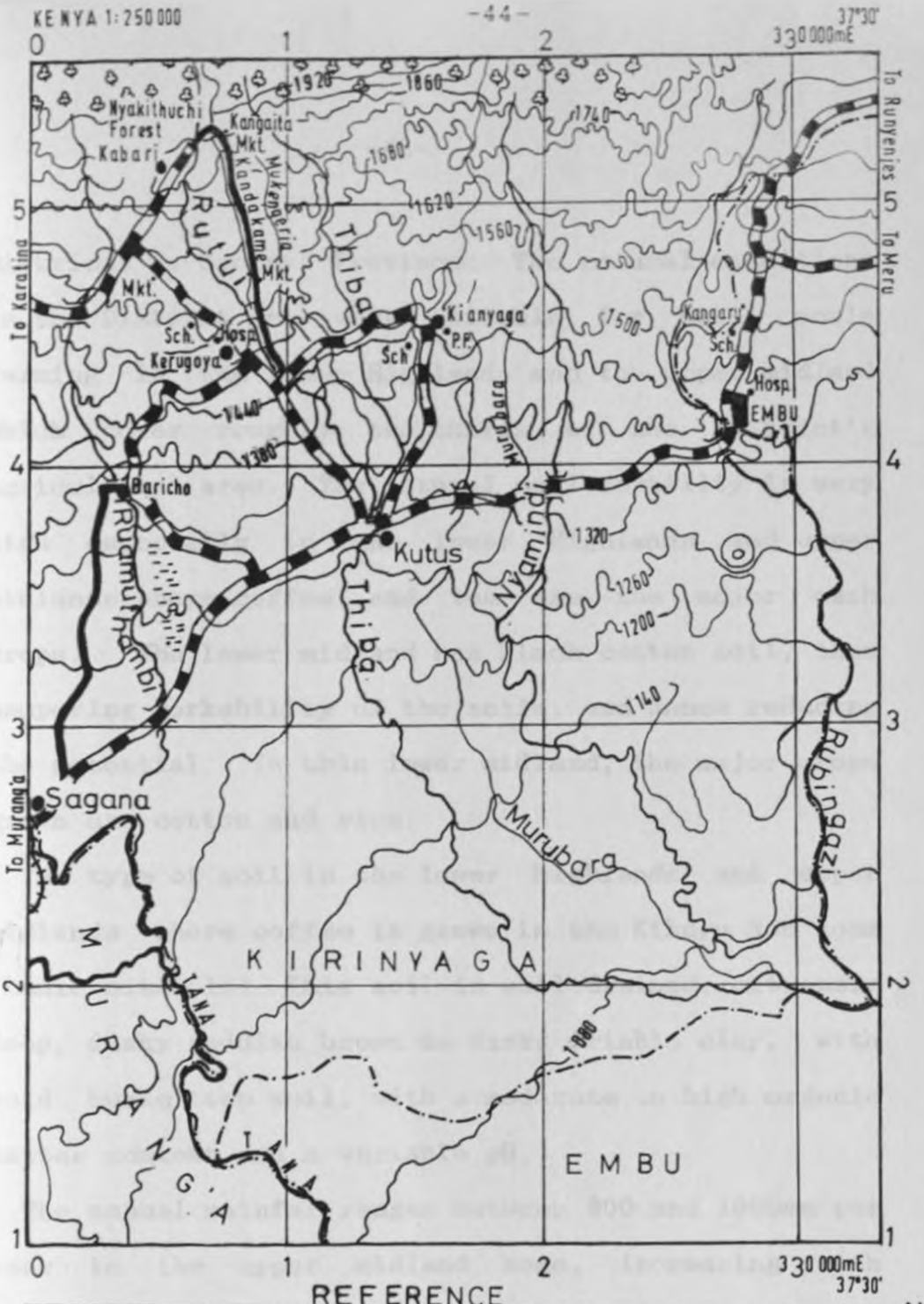


Fig. 3.1: Map of Kirinyaga District showing the sampling areas

Districts in Central Province. The natural conditions in the District are very suitable for small scale farming in the lower Highlands and the upper midland which cover roughly two_thirds of the District's agricultural area. The natural soil fertility is very high especially in the lower Highlands and upper midlands where coffee and tea are the major cash crops. The lower midland has black cotton soil, thus hampering workability of the soils, and hence reducing the potential. In this lower midland, the major crops grown are cotton and rice.

The type of soil in the lower highlands and upper midlands where coffee is grown is the Kikuyu Red loam (humic nitosols). This soil is well drained, extremely deep, dusky reddish_brown to dark, friable clay, with acid humic top soil, with a moderate to high organic matter content and a variable pH.

The annual rainfal ranges between 900 and 1800mm per year in the upper midland zone, increasing with latitudes.

Soil, sediment and water samples were taken in coffee farms along Rutui river starting from the river source in Kangaita down to around Rutui factory. Samples from some coffee farms along Kandakame river (Major tributary of Rutui river) were also taken. It is within the region from Githioro (described above) to Karia (around 11km downstream) where most coffee

farms are situated. The farms are located on both sides of the river, at a distance of about 100 metres away from the river banks upslope.
The farms are mostly on the area of highest slope.

A detailed description of the District has been given by Erhart, et al.[80].

3.1.2. Description of Ruiru river Zone.

Ruiru river is one of the rivers in Kiambu District which runs all the way from around Githunguri Division via Ruiru town and beyond (Fig 3.2). The sampling along the river was done starting from Ruiru Dam in Githunguri down to Ruiru town bridge. In Ruiru Dam is one of the main water supply plant for Nairobi town.
Along the river are generally large scale coffee farms (estates) and a few small scale coffee farms especially around Githunguri area. The river has several tributaries one of which joins the river at Jacaranda (Next to the Coffee Research Station (C.R.F). There are several coffee factories along the river. There are also other process factories along the river, especially a towels factory near Ruiru town.

The upper midland zone of Kiambu District (Githunguri area) has the Kikuyu red soils (humic nitosols). The lower zone (Ruiru town area) has variable soil types. Some parts have well drained,

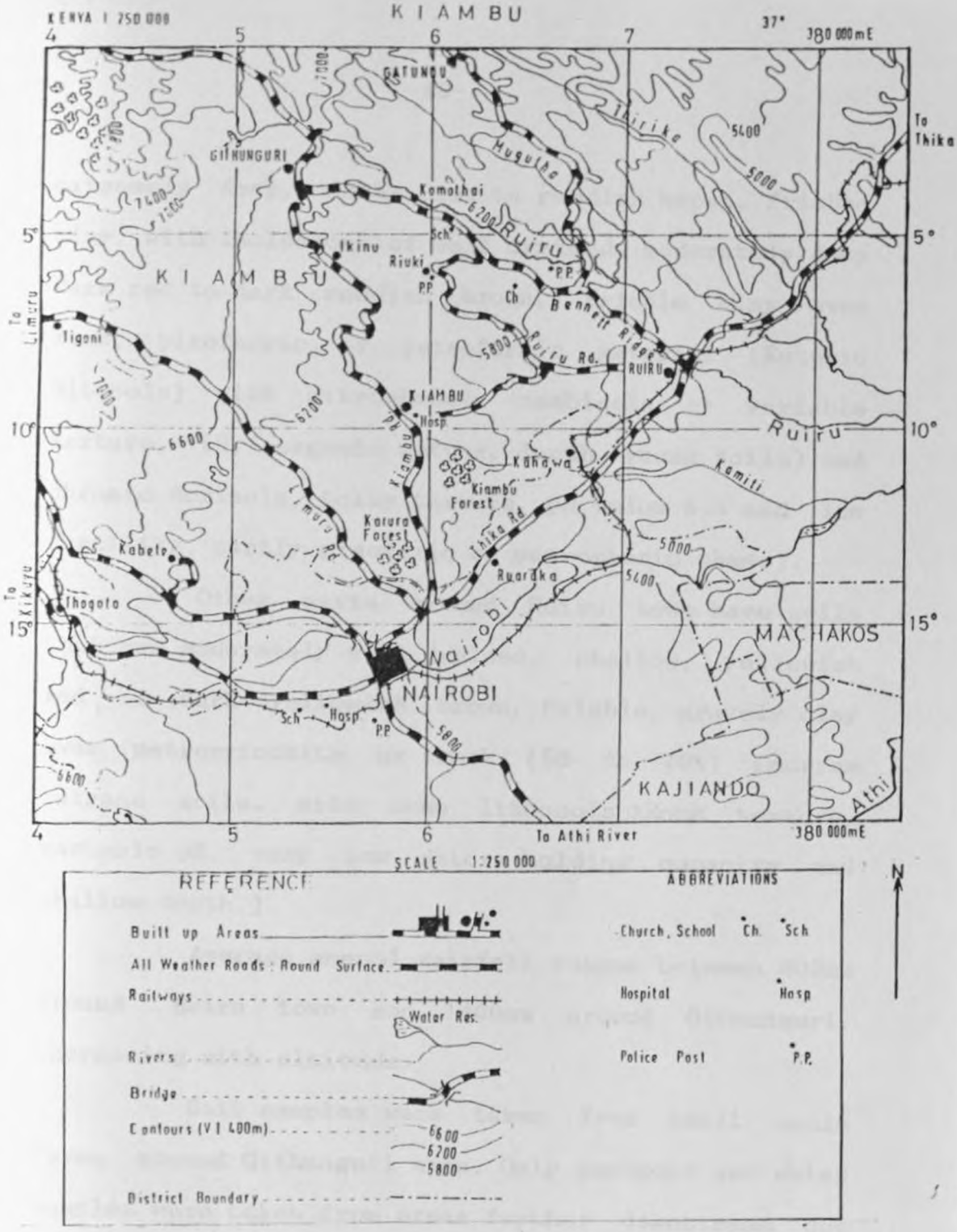


Fig. 3.1: Map of Kiambu District showing the sampling areas.

extremely deep, dusky red to reddish brown, friable clay, with inclusions of well drained, moderately deep dark red to dark reddish brown, friable clay over rock, pisoferric or petroferric material (Euteric Nitosols) with nitrochromic cambisols -> variable texture, pH, organic matter, depth, young soils) and chromic Acrisols, (clay texture, pH below 5.5 and low fertility, partly pisoferic or petropheric phase).

Other parts around Ruiru town have soils that are moderately well drained, shallow, yellowish red to dark yellowish brown, friable, gravely clay over petroprinthite or rock (50 to 70%) [murram cuirass soils, with some lithosols_>Rock texture, variable pH, very low water holding capacity and shallow depth.]

Average annual rainfall ranges between 600mm around Ruiru town and 1400mm around Githunguri, increasing with altitude.

Soil samples were taken from small scale farms around Githunguri area. Only sediment and water samples were taken from areas further downstream due to restriction of penetration into the coffee estates within those areas.

Further details of Kiambu District have been given by Erhart, et al.(1983)[80].

3.1.3 Sampling time

Sampling in the areas described above was done between

September 1989 and October 1990.

3.2 Cleaning of equipments[81]

All equipments involved in sample collection, sample storage, sample preparation etc. were thoroughly cleaned to avoid any possible contamination. For digging the soil samples from the earth a soil auger (of bit 2.5cm diameter) was used. For each subsequent sampling, the auger bit was cleaned with river water, followed by de-ionized water and dried with a clean piece of cloth.

All other apparatus which included plastic bottles for water samples, glasswares, pipettes, measuring cylinders, volumetric flasks conical flasks, boiling tubes, watch glasses, etc, pestle and mortar, 50ml plastic sample containers etc, were first thoroughly cleaned with soap and tap water, dipped in 2.5MHNO_3 overnight and rinsed thrice with de-ionized water. The apparatus were then dried in the oven at 40 degrees centigrade prior to usage.

3:3 SOILS

3.3.1 Sample collection[82]

a) Implement

The samples were collected using a soil auger with a bit diameter of one inch (2.5cm). Before the auger was used, the bit was first cleaned in water followed by de-ionized water and wiped to dryness using a clean piece of cloth for each sample. Each sample was put

inside a clean polythene bag after collection from the ground.

b) Sample combinations

Three samples from within seven metres to each other and from the same depth were combined together and mixed thouroughly to make one sample. The three samples were randomly picked.

The combined sample was then given a field number depending on the place and depth.

3.3.2 Sample transportation and storage

The polythene bags containing samples were all sealed and put inside a carton . The samples were transported to the laboratory, each sample spread on a clean paper (computer sheet) for air drying.

After three days, the air dried sample was ground in a mortar and pestle to approximately two millimeter to ensure more thorough mixing. The grinding was over after the whole sample could pass through a 1 mm plastic sieve[83]. The sample was then stored in a plastic container for the next step.

3.3.3 Measurement of pH[84]

5 grams of the fine soil sample (2 mm fine earth) was mixed with 25 mls of one molar potassium chloride (1M KCl) solution. The mixture was allowed to stand for approximately one hour prior to measuring. For measuring the pH, a grass calomel elecctrode full of potassium chloride solution in

combination with a mercury (Hg/Hg_2Cl_2) electrode were used, the values being read on a pH meter. The electrodes were dipped into the soil paste, and the pH recorded after a constant reading had been obtained.

3.3.4 Sample treatment (digestion)[85]

0.25 grams of the oven dried fine sample was weighed into a boiling tube, 2mls of a mixture of Analar Nitric acid, Analar perchloric acid and Analar Sulphuric acid (10:4:1) was added. The contents were shaken slightly to ensure soaking of whole sample. The contents were then heated to dryness in an electric plate. A further 2mls of the acid mixture was added to the boiling tube and heating continued again until the contents were dry. 10mls of 0.5N Hydrochloric acid (A.R Grade) and 2 ml of 0.5% freshly prepared sodium Nitrite (buffer) (A.R Grade) were added into the contents of the boiling tube and heating at a very low temperature (approximately 40°C) continued for a further 10 minutes. The low temperature was for preventing spatting from taking place. Also the low temperature was to ensure uniform dissolution of the ions into the hydrochloric acid. The contents were then put into a 20ml or 25ml volumetric flask and diluted to the mark with deionized water. The boiling tube was washed three times with deionized water and the washings put into the volumetric flask containing the sample prior to

adjusting to the mark. The volumetric flask plus contents was shaken thoroughly to ensure mixing and then left to stand overnight for the silt to settle. The sample was then filtered using a whatmann No. 40 filter paper into a plastic sample container prior to analysis by AAS. The silt settled on the volumetric flask and the filtrate were thrown away. Analysis of this silt using dry ashing would be recommended.

3.4 SEDIMENT SAMPLES

Sediment samples were collected from the river banks and put into plastic bags. The samples were transported to the laboratory and air dried for three days. The samples were further treated in the same manner as the air dried soil samples prior to analysis by AAS.

3.5 WATER SAMPLES

3.5.1 Sample collection and storage

A clean 500ml plastic container was rinsed twice with river water from the sampling site and then filled with water from the site. The sample was properly sealed and put inside an ice box containing ice cubes. The samples were then transported to the laboratory, the pH of the sample adjusted to approximately 2 with Nitric acid (A.R Grade); using a pH universal indicator and stored in cold room at 4°C.

3.5.2 Preconcentration of sample[86]

100 mls of each sample was put into a clean

250ml conical flask and boiled at 70 degrees centigrade until only about 4 mls of the sample remained. 5mls of concentrated Nitric acid (AR Grade) was added and heating at 50 degrees centigrade continued for approximately 30 minutes. 10cm cubed of concentrated Hydrochloric acid (A.R Grade) was added and heating continued until the solution turned light brown or colouress. The solution was then put into a clean ion free 25ml volumetric flask and made to the mark with deionized water. The solution was then filtered into a plastic bottle using Whattman No. 40 filter paper and stored prior to analysis by Atomic absorption spectrophotometry

3.6 PLANT AVAILABLE COPPER (EXCHANGEABLE COPPER)

Defination :-Plant available copper is the copper in the soil that is not in bound form and can thus be absorbed by plants[87].

Plant available copper was extracted from the soil using three techniques[88].

3.6.1 Method a:-using ammonium acetate solution

1M Ammonium acetate (AR) was prepared and the pH adjusted to 7 using ammonia solution. 25ml of the solution was put into a plastic container having 1 gram of powdered sample.The bottle was covered and shaken thoroughly for one hour using a mechanised shaker. The sample was then filtered using whattman filter paper number 40, and volume adjusted to 30 ml

with de-ionized water prior to analysis by AAS.

3.6.2 Method b:- using dilute acids

Dilute Hydrochloric acid (0.1M) was mixed with 0.0125M sulphuric acid in equal ratios. 25 ml of the resulting solution was used in place of NH_4AC above.

3.6.3 Method c:- using Sodium ethylenediaminetetraacetate (Na-EDTA)

25 ml of 0.05M Na-EDTA at pH 7 (adjusted with ammonia solution) was used in place of NH_4AC above.

3.7 SAMPLE ANALYSIS

3.7.1 Stock solution

For the preparation of a stock solution, copper sulphate $CuSO_4.5H_2O$ (A.R Grade) crystals was used.

Calculation of concentration

Molecular weight of $CUSO_4.5H_2O$ = 249.68g.

Purity of the Analar $CUSO_4.5H_2O$ was given as 99.5%.

1 gram of copper was thus contained in

(249.68/63.54)x(100/99.5)=3.949234 grams of $CUSO_4.5H_2O$ (99.5% pure)

Weight of $CUSO_4.5H_2O$ required in 250ml to make 1000 ppm Cu^{2+} = (3.949234/4) grams = 0.9873098 grams.

Procedure for the preparation of stock solution

0.9817 grams of $CUSO_4.5H_2O$ was weighed into a clean

ion free 250ml volumetric flask and 100ml of deionized water added. The contents were thoroughly shaken, 5ml of concentrated Nitric acid (AR Grade) added to enhance disolution and solution shaken further. Deionized water was added to the mark, the solution then transfered into a clean ion free plastic bottle for further use.

Error introduced during weighing can be calculated as:_ (0.9873-0.3817/0.9873)x100=0.568%

3.7.2 Standard Solutions

All apparatus were first soaked in soap, rinsed in de-ionized water and dilute nitric acid. The cleaning procedure was repeated every time before the apparatus could be re-used.

10ml of 1000ppm stock solution was pipetted into a 100ml volumetric flask and solution made to the mark using de-ionized water resulting in a 100ppm Cu^{2+} solution. The 100ppm solution was used to make solutions of 10ppm, 5ppm, 4ppm, 3ppm, 2ppm, and 1ppm. The 10ppm solution was used for making 0.7ppm, 0.5ppm, 0.3ppm and 0.1ppm Cu^{2+}solutions.

The 5, 4, 3, 2, 1, 0.7, 0.5, 0.3, and 0.1ppm Cu^{2+} solutions were used as standards for the analysis of copper by Atomic Absorption Spectrophotometry(AAS).

3.7.3 Determination of Absorption

Using a Perkin-Elmer 2860 Atomic Absorption Spectrophotometer, the absorption of the standard

copper solutions and of the digested samples was determined.

a)Copper lamp

A hollow cathode copper lamp was fixed in its position at the AAS machine and aligned using the laid down procedure for maximum precision.

b)Sensitivity setting

After lighting the burner, the sensitivity of the instrument (AAS) was adjusted using the 5ppm Cu^{2+} standard solution. This was done by centering the burner, adjusting the burner height, adjusting the path length, adjusting the fuel flow and adjusting the air flow until the 5ppm Cu^{2+} solution gave the maximum absorbance reading (approximately 0.25 absorbance units).

The instrument was zeroed (zero absorbance reading) using de-ionised water; absorbances of the standard solutions, samples and blank read and recorded.

3.7.4 Preparation of 0.5N HCl and 0.5% $NaNO_2$

For each acid digestion of samples, fresh buffer 0.5% Sodium Nitrite ($NaNO^2$) was prepared.

a) Sodium Nitrite (0.5%)

0.5g of Analar $NaNO_2$ was weighed into a 100ml volumetric flask and with thorough shaking de-ionized water added to the mark.

b) 0.5N Hydrochloric acid

Concentrated hydrochloric acid (Aristar grade) of specific gravity 1.18 and percentage W/W 36.4 was used to prepare the 0.5NHCl solution.

Since one mole of HCl weighs 36.36g, then 0.5 moles should weigh 36.46/2=18.23 grams.

For 100% HCL, volume equivalent to 0.5 moles solution is 18.23/1.18=15.45mls.

Therefore for 36.4% HCl, volume equivalent to 0.5 moles is (15.45/36.4)X100=42.45mls.

Thus, 42.45mls of 36.4%HCl in 1000mls of solution is equivalent to 0.5moles.

Since HCl has only one equivalent, then its molarity =normality.

Thus 42.45 ml of 36.4 w/w hydrochloric acid (AR grade) was put into a 1000 ml volumetric flask and solution adjusted to the mark with de-ioized water to make 0.5N HCl.

3.7.5 Special equipment

Heating Block[89] and Paraffin Oil

Since the soil samples were many, and each sample was to be analysed in triplicate, heating devices which could accomondate many samples at one go were used. A rectangular alluminium block with eighteen evenly distributed holes and of uniform depth and diameter was used. Each hole could fit one boiling tube. The block was thus accomondating five samples in triplicate and three blanks. Other than

allowingmany samples to be heated per turn, the block also ensured uniform distribution of heat for all the samples.

Paraffin oil in an oil bath was also used for the same purpose as the heating block. Several boiling tubes containing samples plus the digestion mixture were inserted in the oil bath and heated together.

B) CHIROMO GARDEN SAMPLES

3.8 Introduction

The field samples were collected from small scale farms. Most small scale farmers do not follow the laid down procedure for pesticides application. At the same time the farmers do not keep any records of how and when they use pesticides.

To try and follow up the result of the samples obtained from the field, a small garden was cultivated within the college compound and sprayed according to the directions given by the coffee research station to farmers.

In most small scale farms, food crops are planted inside the coffee plantation where pesticides are generally used. The most common are vegetable crops for example potatoes, tomatoes etc, and sometimes these crops grow wildly in the coffee farms but people still harvest them for food.

To check whether copper fungicides have rendered the foodcrops unsuitable for human

consumption by exceeding toxic levels, potatoes were planted in the garden prior to spraying with a copper based fungicide.

3.8.1 Preparation of the garden

a) A small portion of land 6 metres square was cultivated at Chiromo University of Nairobi botanical garden starting from January 12th 1990. The portion had not been previously cultivated and was overgrown with wild grass and weeds of many types. The grass and weeds were slashed to surface level using a slasher and a panga. The weeds were then raked out to make digging easy. The plot was then fenced.

Tilling of the soil was done using a jembe and the large lamps of soil smashed to reduce them to the smallest possible size.

Since there was no rain at the time of preparing the land, water was sprinkled on the plot to soften the soil and ease tillage of the land. The plot was then harrowed using a rake, and the plant remains removed. The harrowing was done until the ground surface was reasonably flat and uniform and with no large lumps of soil. The plot was then divided as per the sketch (fig 3.3) below , using trenches of about 30cm deep.

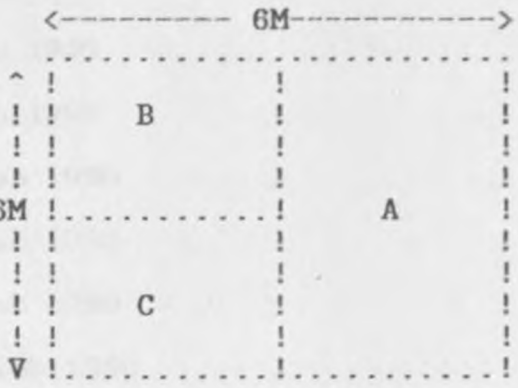


Figure 3.3: Experimental garden in Chiromo Campus

3.8.2 Potato planting.

Potatoes were planted on areas B and C (shown in the above sketch) on 2nd February 1990. The spacing was 60cm between plants and 60cm between lines. Area B was planted with four lines, each line having four plants. Area C was planted with three lines, each line having three plants. No manure or fertilizer was used on the plot.

3.8.3 Spraying

Area A and B, were sprayed with copper oxychloride (cobox) 42 grams in 6 litres of de-ionized water. The spraying was done immediately after planting, and as evenly as possible using a small hand sprayer.

3.8.4 Watering the garden

The areas in the plot planted with potatoes B and C were watered to provide moisture for the growth of potatoes according to the following

schedule.

i) 6th Feb 1990

ii)7th Feb 1990

iii)8th Feb 1990

iv)12th Feb 1990

v) 13th Feb 1990

vi) 15th Feb 1990

vii)16th Feb 1990

viii)19th Feb 1990

The wetering was stopped immediately the rains started. The watering was done at 4.00p.m. in all cases.

3.8.5 Collection of samples from the garden.

a) The samples were collected using a spattula, marked for different depths 5cm 10cm and 15cm. Samples were taken from each area A, B, and C. Three samples from the same area eg A and same depth eg 0-5 cm were thouroughly mixed to represent the sample from the area ie Area A, 0-5cm etc.The samples were carried to the laboratory on clean polythene bags, air dried, oven dried and acid digested using the same procedure as for soil samples described previously. The samples were then analysed for copper by Atomic Absorption Spectrophotometry.

b) Time of collection

The first sample was collected from the surface of the garden just before spraying with copper oxychloride.

The second batch of samples were collected immediately after spraying constituting zero time samples. The samples were then collected on weekly intervals, two weeks interval and finally one month intervals. The samples were collected upto the twenty fourth week . The whole process took place between 2nd Feb,1990 to 17th July 1990. Each batch of soil samples was analysed for copper immediately after collection.

3.8.6 Growth of potatoes and spraying against disease

The first potato plant emerged from the soil on 19th Feb 1990. By 12th March 1990, all the plants had emerged. At this time, the plant leaves were sprayed with Bayleton (non copper based) fungicide to prevent leave bright. The formulation was 2 grams in 1 litre of de-ionized water for 25 potato plants.

3.8.7 Potato leave samples

Fresh potato leaves (green) were plucked just before bloom for analysis of copper on 29th March 1990.

Two plants were sampled from area B (sprayed with copper) and two from area C. For each plant, the leaves taken were the first three from the bottom.

The leave samples were immediately transported to the laboratory and washed in detergent and 0.1m HCl to remove dust, tap water and thoroughly rinsed with deionized water. They were then dried in the oven at 40°C for 48 hours, ground into powder and stored in

polythene bags.

3.8.8 Acid digestion of plant samples[90]

1 gram of the grounded plant sample was weighed into a boiling tube and the weight recorded. A mixture of AR Nitric acid (HNO_3) and AR Perchloric acid ($HClO_4$) in the ratio of 3:1 was added to the sample. This was then slowly heated under close check (to avoid spillage). When the colour changed to black for the whole sample, the sample was immediately removed from the heat to avoid ignition. 10ml of 0.5 Hydrochloric acid followed by freshly prepared 0.5% sodium nitrite (1ml) buffer was added. Heating was continued for a short while and sample transfered into a volumetric flask (25ml). Deionized water was added to the mark and contents mixed by shaking thoroughly. After standing for overnight, the sample was filtered into a plastic sample container and stored prior to analysis by atomic absorption spectrophotometry.

3.8.9 Harvesting and treatment of potatoes.

Before the plants matured ie, just before the leaves started drying out, two potatoes were harvested from Area B and two from area C. At the same time, weed samples were taken from areas A, B, and C for analysis of copper. Only one type of weed was taken. The potato branch was analysed as a whole, using the same procedure as for leaves but volume of acid mixture used depended upon the weight of the whole

branch plus roots. The weeds were also analysed in whole using the same procedure but volume of the acid mixture used dependent on weight. Large samples were digested using conical flasks instead of boiling tubes.

After harvesting, the potatoes were first washed with tap water to remove soil, and then dipped in deionized water. The top peel was then separated using a sharp stainless steel implement to a depth of approximately 0.5mm. The peels and inner bit were then dried in the oven at 80°C for 24 hours. This was followed by grinding the two parts separately using a pestle and mortar. The powdered samples were stored in polythene bags. Digestion of the peel and inner part was done using the same procedure as for the leave samples.

C H A P T E R 4

RESULTS AND DISCUSSION

4.1 RUTUI RIVER RESULTS

The concentration of copper obtained in soils taken from along Rutui river are given in table 1.

TABLE 1

CONCENTRATION OF COPPER IN PARTS PER MILLION (ppm) FOR SOIL SAMPLES OBTAINED FROM FARMS ALONG RUTUI RIVER.

SITE	1	2i	2ii	2iii	3i	3ii
DEPTH						
0-15	33.66 ±0.01	35.47 ±0.03	111.50 ± 0.24	31.16 ±0.11	33.57 ± 0.24	43.75 ±0.04
15-45	39.46 ± 0.28	31.03 ±0.06	39.77 ±0.02	26.86 ±0.06	25.07 ±0.01	43.79 ±0.03
45-75	36.32 ±0.03	25.39 ±0.01	37.59 ±0.02	28.41 ±0.02	18.21 ±0.02	36.96 ±0.01

SITE	3iii	3iv	4i	4ii	4iii	4iv
DEPTH						
0-15	238.90 ±9.95	48.94 ±0.31	26.68 ±11.61	456.10 ±288.70	526.80 ±12.12	24.76 ±3.40
15-45	59.23 ±0.05	33.61 ±0.01	16.12 ±0.01	160.70 ±0.04	272.90 ±1.70	18.49 ±0.00
45-75	55.11 ±0.01	26.78 ±0.01	16.14 ±0.03	85.65 ±0.10	100.30 ±0.10	15.25 ±0.00

Each value given is the mean of three replicates(i.e n=3) ±standard deviation . The soil Depth is given in centimetres. The numbers (1, 2, etc.) represent the site and the Roman numbers the subsites.

4.1.1 Comparission within sites

Site 1 was a small garden in a homestead. The landscape was uniform and the area being under

cultivation for planting of potatoes. It was previously a glassland for grazing livestock. The whole of that area is covered with tea farms and no coffee is grown near there.

The top soil (0 to 15 cm deep) in this place had a lower copper concentration (33.66 ppm) than the subsoil (39.46 ppm for 15 to 45 cm and 36.32 ppm for 45 to 75cm deep) . However, the difference in concentration with depth was quite small (34 ppm and 39 ppm). Since no coffee is grown in this area it was expected that the copper concentration would be quite small as fungicides are not generally used. Also the difference in concentration with depth was expected to be small which actually was the case. The increase in concentration with depth was rather unusual as the opposite was expected.

It is probable that the garden had been previously cultivated to the depth of 45 cm or more such that the top soil had been submerged that far. Normally when a grassland is being cultivated for other crops, large lumps of soil are overturned to burry the grass. This ends the top layer of the soil deep down. Another likely reason could be that the grass had absorbed some of the copper available on the top soil thus lowering the concentration.

The second site comprising of subsites 2i, 2ii and 2iii was the first coffee farm downstream. For this

site, the concentration of copper was decreasing with depth. The top soil had the maximum concentration decreasing at depth 15 to 45 cm, but concentration at depth 45 to 75 cm was comparable to that at depth 15 to 75 cm. Subsite 2i was a steep gradation within the coffee farm whereas 2ii was a flat section of the coffee farm. The difference in concentration between samples from the two subsites was quite big. The best explanation for this difference would be that during rains, erosion takes place more in the slopy ground and thus sweeping the top soil. The coffee plants in the two sections looked quite different, with those on the sloping section weaker. According to the owner of the farm, the whole farm is looked after uniformly on the basis of pesticide application, digging etc. In that case the weakening of the plants in the slopy section could be attributed to erosion. The third sampling subsite 2iii was a garden within the farm near the banks of Rutui river. The section was about 50 metres away from the coffee farm and about 10 metres away from the river banks. The was a gentle gradation sloping towards the river. Tomatoes were planted here. The concentration of copper here was not very different from that in 2i.

Runoff during rains was expected to affect the concentration at this point. The soil eroded from the slopy section of the coffee farm could also be

deposited around this region. But being so close to the river, the soil around the region was subject to being swept away during overflow of the river. Thus any pesticides deposited here might have been swept away during river overflow.

The third site comprising of subsites 3i, 3ii, 3iii and 3iv in the table was another coffee farm around Rutui factory (8 km downstream). Subsite 3i was a section of the farm which had nappier grass for animals. This part was about 10 metres away from the river banks and a gentle gradation sloping towards the river. The coffee plantation was quite far upslope (about 200 metres away) from here. The concentration of copper for the top soil (34 ppm) in this region was low as compared to the values obtained in other parts of the same farm. The concentration decreased with depth in the part. Accoding to the land terrain in this region, there is a very low possibility of soils from the coffee farm upslope being deposited here. This could account for the copper levels being lower in this region than other parts of the farm. The nappier grass in the section might also be a contributory factor to the low levels, though this might call for further investigation.

The subsite 3ii was on a flat (uniform landscape) section of the farm, furthest away from the river banks. The section had been cleared with maize and

beans being planted. The section was about 10 metres away from the coffee farm. The concentration of copper (44 ppm) found here was relatively not very different from that obtained in one of the sections inside the coffee plantation. When coffee is being sprayed, the spray particles can be easily carried by the wind and deposited in the sorrounding areas. This section (subsite 3ii), was most probably a victim of such deposition. The section chosen for sampling within the coffee farm (subsite 3iv) had a concentration of 49 ppm copper for the top soil. Concentration decreased with depth here. This part was on a relatively uniform landscape and with strong looking coffee plants as most other areas in the plantation. But on the same plantation, a sample was taken around a coffee stem that had dried out due to unknown reasons (subsite 3iii) and the concentration of copper (239 ppm for the top soil) was extremely high as compared to all other sections in the farm. The possible reasons to this high value are discussed later in the text.

Site 4 was another coffee farm along Rutui river and samples were taken from subsites 4i, 4ii, 4iii, and 4iv. Subsite 4i was 8 metres away from coffee plantation, a banana plantation just next to the coffee farm. The concentration of copper obtained here (27 ppm for top soil) could be a reflection of

the naturally occuring copper plus some copper due to deposition during spraying. But the value was not very different from that obtained in subsite 4iv (25ppm) which is about 40 metres away from the area where spraying is usually done. However, in both subsites, blowing of spray particles by wind could have resulted in copper being deposited, but the percentage resulting from such deposition shoud be quite low. In either case, there was a decrease in concentration with depth. Two subsites 4ii and 4iii showed an excessively high concentration of copper (556 ppm and 526 ppm for top soil). Samples here were taken around coffee stems which had dried out. The copper concentration in either case decreased with depth. Possible causes of the drying are discussed later in the text.

4.1.2 Comparison over the whole sampling region

In general the levels of copper ranged between 25 ppm and 48 ppm for the top soil, disregarding the extreme values. For the depth 15 to 45 cm, the concentration ranged between 16 ppm and 44 ppm whereas at depth 45 to 75 cm, the level of copper ranged between 15 and 37 ppm. The highest concentrations of copper were found around coffee stems that had previously died out of an unknown cause subsites 3iii, 4ii and 4iii in table 1). This could mean that the death of these stems may have been caused by the high

levels of copper. But there is also a possibility that the high levels around the dried stems resulted from spilling of the pesticides during mixing etc.

The areas around the dry stems had been cleared of the dead plants. The area was thus the most spacious in the plantation, making it the best part for placing equipments during spraying. These equipments include the spray pump, container for pesticide/water mixture, etc. Spillage of the pesticide during pumping or stirring can cause high levels within the area.

Leaving the copper level around the dry stems aside, the highest concentration of copper in other sections was 111.5 ppm Cu. The sample having this value had been got from a flat section of a well managed coffee farm. The uniformity of the landscape in that section could mean that materials deposited in the soil there would not be carried away by erosion during runoff. As such, high copper levels in the section may be as a result of accumulation.

In most instances, small scale farmers have the tendency of concentrating their effort on those coffee plants that appear most productive i.e those plants with a promising high coffee yield. They thus apply more nutrients or pesticides in such plants than on others. Areas that were well managed had higher copper levels than those which were poorly managed. In non-coffee areas, low copper levels were obtained.

The difference in copper levels in well managed coffee farms and non coffee areas was quite significant. In poorly managed coffee farms copper levels were relatively similar to those in non-coffee areas. The high levels found in some coffee farms could thus have resulted from application of copper based pesticides.

Taking all values in Table 1 into consideration, the levels of copper in the top soil ranged between 25 ppm and 527 ppm. This range was somehow similar to the range found in Bahati-Solai by Maroko J.B.,(Aug. 1987)[91], where the levels ranged between 35 ppm and 597 ppm for well managed coffee farms. Nyandat and Ochieng (1979)[92] have reported levels of copper ranging from 5 ppm to 157 ppm in uncultivated soils. In the present study, soils from within depth 15 cm to 45 cm had copper concentrations ranging between 18 ppm and 273 ppm. The range for the soils at depths greater than 45 cm was between 15 ppm and 100 ppm. The level of copper is thus decreasing with depth, being higher in the top soil than in the sub soil.

A 'correlation analysis carried out for different depths yielded the following results:-

i) Depth 0 to 15 cm versus Depth 15 to 45 cm

Fig. 4.1 (extreme values discarded) $R^2=0.5550$

Fig. 4.2 -straight line (with extreme values included) $R^2=0.8949$; Fig. 4.2 -curve (with extreme values included) $R^2=0.9570$

ii) Depth 0 to 15 cm versus Depth 45 to 75 cm.

Fig. 4.3 $R^2=0.9461$

iii) Depth 15 to 45 cm vs 45 to 75 cm

Fig. 4.4 (extreme values eliminated) $R^2=0.8881$

Fig. 4.5 - Plotted using same data as for Fig. 4.4 but with all values included

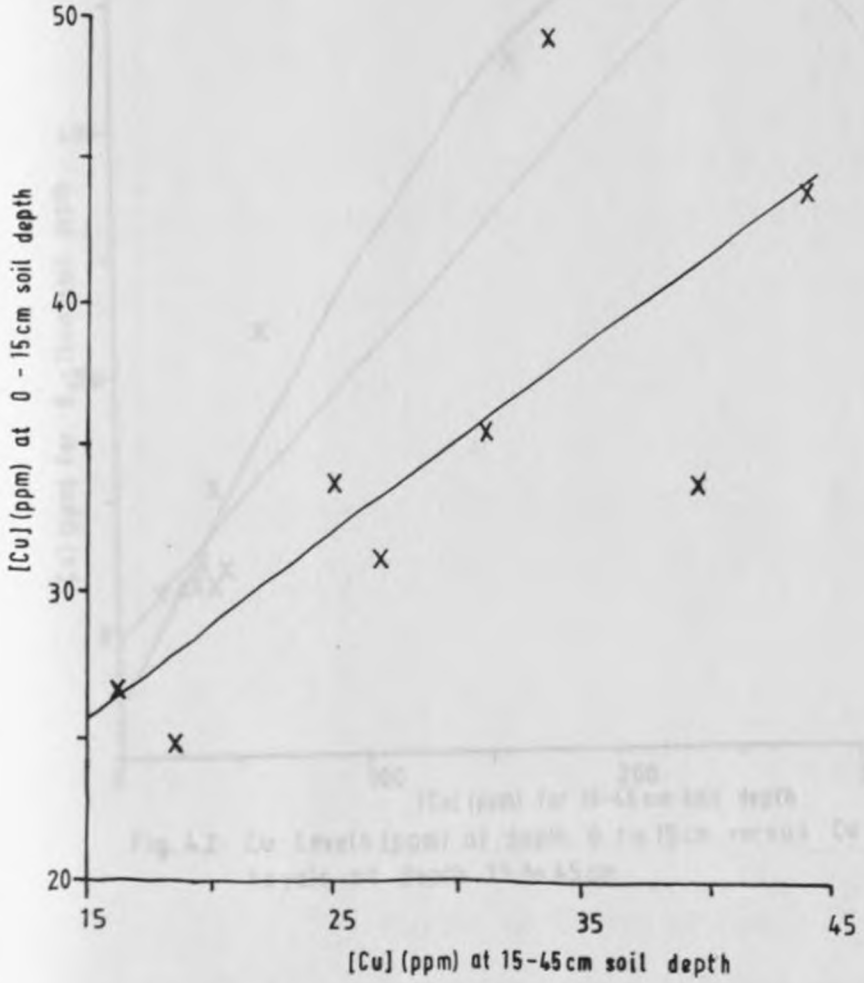


Fig. 4.1: Cu levels (ppm) at depth 0 to 15 cm versus Cu levels (ppm) at depth 15 to 45 cm.

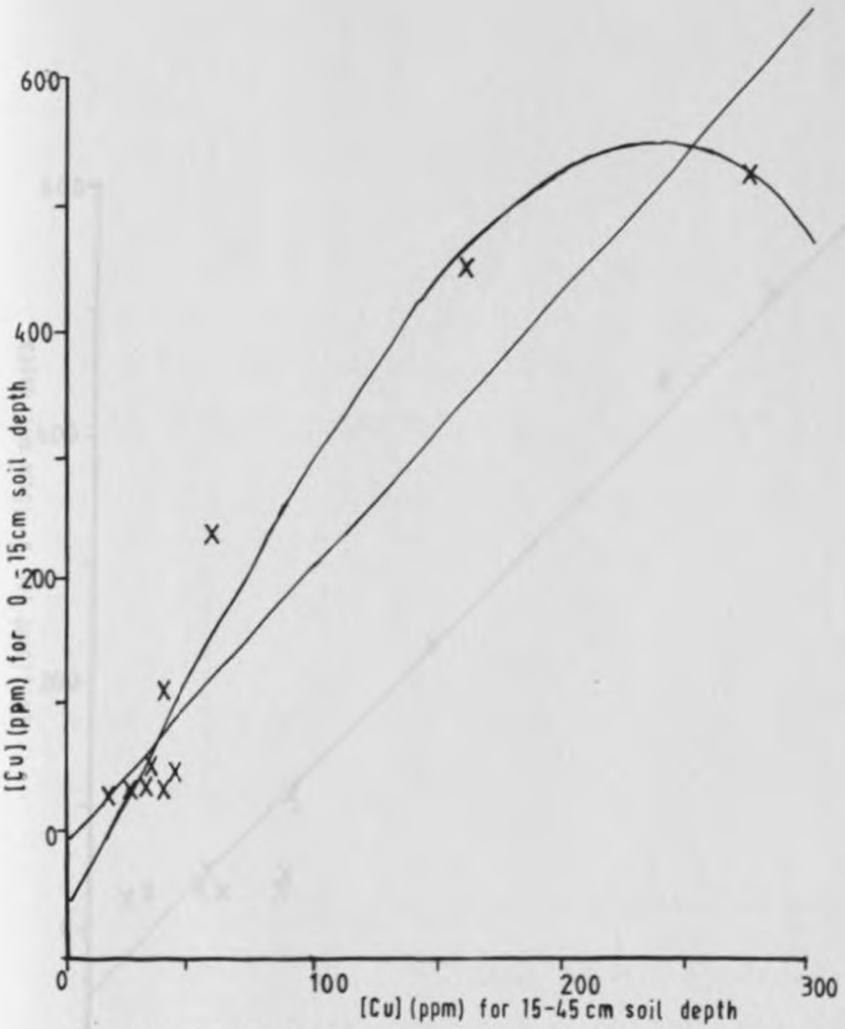


Fig. 4.2: Cu levels (ppm) at depth 0 to 15 cm versus Cu levels at depth 15 to 45 cm.

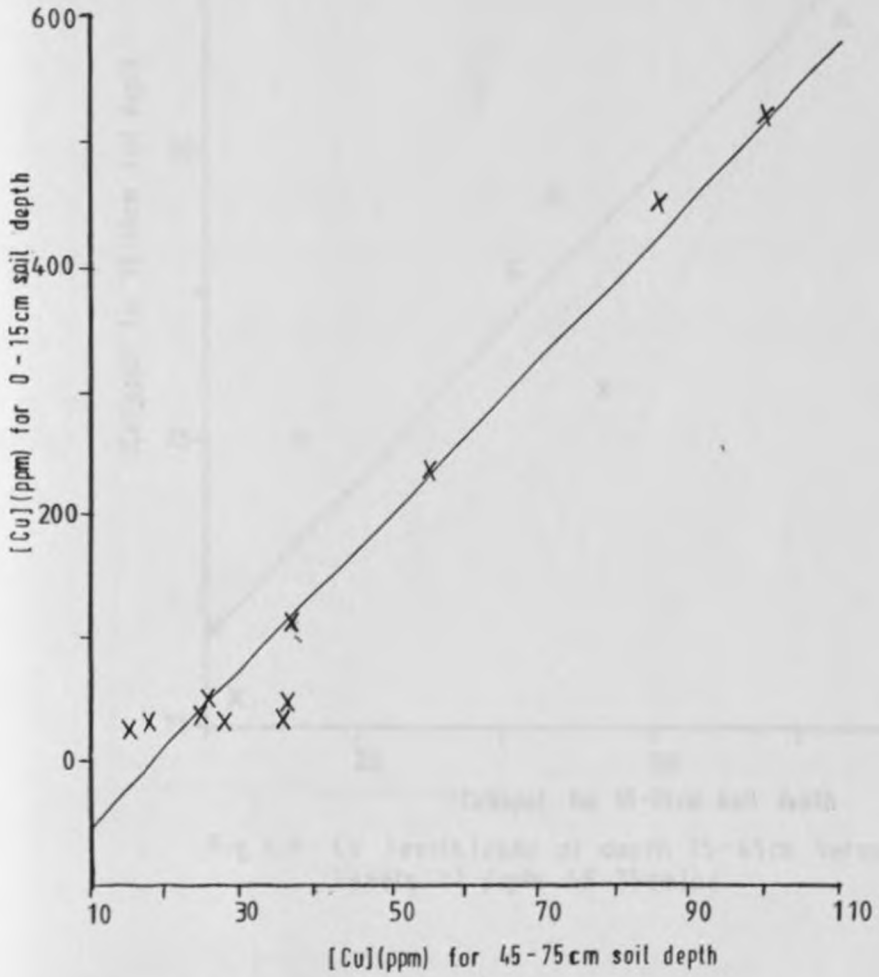


Fig. 43: Cu levels (ppm) at depth 0 to 0-15 cm versus Cu levels (ppm) at depth 45 to 75 cm.

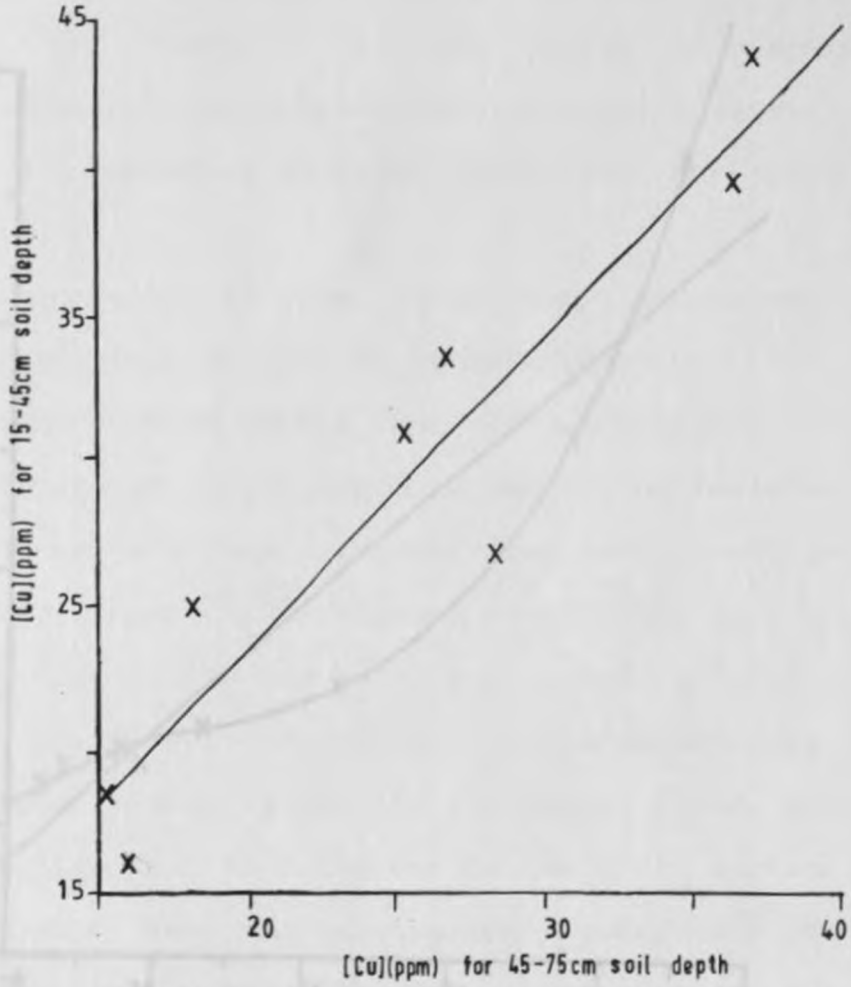


Fig. 4.4: Cu levels (ppm) at depth 15-45cm versus Cu levels at depth 45-75cm(a).

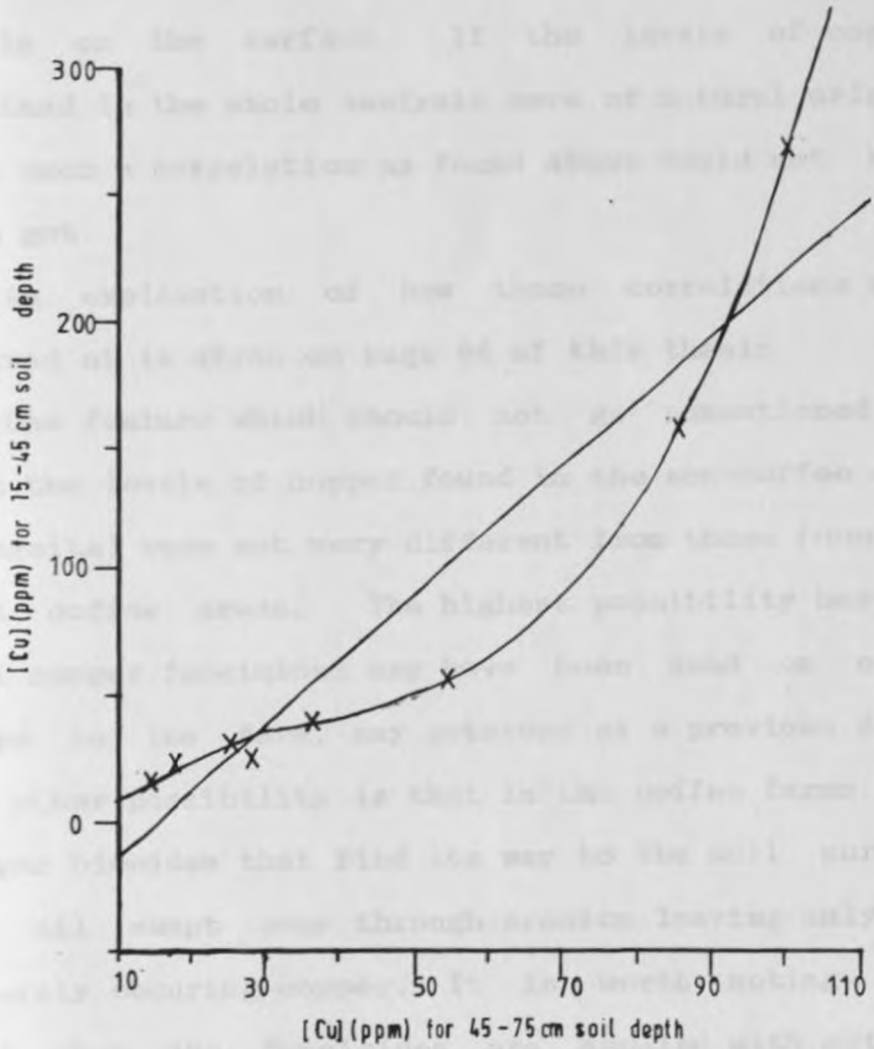


Fig. 45: Cu levels (ppm) at depth 15 to 45cm versus
Cu levels (ppm) at depth 45 to 75cm (b)

From this analysis, the levels of copper had the most linear relation between depths 0 to 15 cm versus 45 to 75 cm. This implies that the levels of copper at the deeper horizons are strongly affected by the levels on the surface. If the levels of copper obtained in the whole analysis were of natural origin, then such a correlation as found above could not have been got.

An explanation of how these correlations were arrived at is given on page 84 of this thesis.

One feature which should not go unmentioned is that the levels of copper found in the non-coffee area (Kangaita) were not very different from those found in most coffee areas. The highest possibility here is that copper fungicides may have been used on other crops in the farm, say potatoes at a previous date. The other possibility is that in the coffee farms, the copper biocides that find its way to the soil surface are all swept away through erosion leaving only the naturaly occuring copper. It is worth noting here that when the fungicides are applied with extreme care, very little find way to the ground. If it doesn't rain within the first few days of spraying, the fungicides stick on the plant surfaces (leaves, beans, branches) such that rain cannot wash down the fungicides to the ground. In such a case, low levels

of the fungicides would be expected on the soil and this may still be an explanation for similarlity of copper levels in coffee areas and non coffee areas.

4.2 RUIRU RIVER RESULTS

The concentration of copper obtained in soils taken from along Ruiru river are given in talbe 2

TABLE2

SOIL SAMPLES COLLECTED IN FARMS ALONG RUIRU RIVER

SITE DEPTH	A	B1	B2	B3
0-15	9.41 ±0.12	14.80 ±0.04	14.81 ±0.01	139.80 ±0.09
15-45	11.36 ±0.01	9.67 ±0.04	6.26 ±0.01	37.06 ±0.02
45-75	13.06 ±0.00	—	6.26 ±0.00	—
75-105	18.21 ±0.02	—	—	—

Depth (cm);n=3;concentration (ppm)± standard deviation.
The sites are represented by letters and the subsites by numbers.

Copper levels found in soils obtained along Ruiru river are given in Table 2 above. The first site A was a grassland and the sampling point was about 4 metres away from the banks of Ruiru Dam. The concentration of copper (9.41 ppm) at this point is

low as compared to Rutui river area. As per table 2, the soil copper content at this point increased with depth. According to information given by the people working in the Dam, the area from which the samples were taken used to be a road some years before. This might be the cause for an increase in copper concentrations with depth. However,comparing with the the first subsite in table 1 which was also a grassland, the trend was the same i.e increase of copper concentration with depth. Only the grasslands showed this trend in the whole study. Thus the increase of copper concentration with depth might be due to absorption of copper by the grass, thus reducing the concentration at the soil surface. The grass from these regions had not been sampled, otherwise analysis of the grass would have been a better indicator of the reasons behind the above findings.

The second subsite B1 in table 2 was a neglected coffee farm. The copper concentration here was 14.8 ppm in the top soil as per the table. The copper content of the soil here decreased significantly with depth. Bordering this farm was a cleared garden from which potatoes had been harvested two days prior to the sampling date. The level of copper here (showed under B1 in table 2) was similar to that in the neglected coffee farm, and decreased with depth within the first half foot depth. Next to the potato garden was a well managed coffee farm, B3, adjacent to the neglected coffee farm. In the well managed farm, the level of copper (140 ppm) was about ten times higher than in the neglected farm. According to information obtained from the owner of the well managed farm, copper based fungicides had been used severally before the sampling time. There was a large decrease of copper concentration with depth in this farm. The area, B1, B2, B3 was flat and the effect of soil erosion due to rain water should be minimal.

For the coffee areas under the present study, i.e Rutui and Ruiru, the trend in copper level distribution was rather similar. There is no much differece in the soil type for both areas. As mentioned earlier, both places have the kikuyu red loam soil, and the average annual rainfall is 1400 mm for Githunguri area and 1800 mm for Rutui area as

mentioned in the previous chapter. Samples from coffee farms along Ruiru river were taken only around Githunguri area as penetration into the large coffee estates downstream was difficult.

4.3 Comparison of copper in the soil with copper in plant tissues

TABLE 3

SAMPLE NUMBER	TOTAL COPPER	AVAILABE COPPER (a)	(b)	(c)	COFFEE LEAVES	COFFEE BEANS	COACH GRASS
1	30.48 ±0.00	0.01 ±0.00	4.28 ±0.00	9.23 ±0.00	--- ---	--- ---	29.56 ±0.00
2	367.00 ± 0.01	21.29 ±0.00	241.60 ±0.01	242.00 ±0.01	92.98 ±0.00	31.36 ±0.00	43.23 ±0.00
3	350.50 ±0.01	17.47 ±0.00	227.90 ±0.01	212.90 ±0.01	90.14 ±0.01	61.90 ±0.01	49.44 ±0.00
4	381.40 ±0.11	17.39 ±0.01	252.10 ±0.07	240.20 ±0.02	54.31 ±0.01	50.14 ±0.00	46.54 ±0.00
5	530.60 ±0.05	3.19 ±0.00	361.80 ±0.01	361.40 ±0.01	200.50 ±0.02	38.15 ±0.01	47.93 ±0.00
6	522.20 ±0.06	28.95 ±0.01	354.50 ±0.01	361.00 ±0.02	109.00 ±0.01	41.46 ±0.00	44.72 ±0.01
7	238.20 ±0.03	10.34 ±0.00	150.10 ±0.03	143.50 ±0.01	49.77 ±0.00	36.01 ±0.00	39.56 ±0.00
8	410.70 ± 0.07	17.25 ±0.01	277.00 ±0.01	306.10 ±0.05	89.34 ±0.01	57.90 ±0.01	45.41 ±0.00
9	360.20 ±0.02	8.09 ±0.00	237.20 ±0.03	241.60 ±0.03	60.94 ±0.00	63.84 ±0.00	44.25 ±0.00

KEY: All the values in the table are copper concentrations in parts per million ±Standard Deviation. Each value is an average of two replicate analyses.

Table 3 above shows the copper levels obtained in the soils as compared to copper levels in plant parts. These samples were taken from coffee farms

along a tributary of Rutui river (Kandakame; in Fig 1) in the month of September 1990. Each row in the table represents samples from same area e.g a soil sample analysed for total copper; plant available copper (using three methods of extraction, a, b, and c); coffee beans; coffee leaves; and coach grass from the same area as the soil sample. In the first method, a, the extractant was ammonium acetate; second method, b, extractant was a mixture of dilute sulphuric acid and dilute hydrochloric acid; third method, c, extractant was EDTA.

The first sample in table 3 was taken from a non-coffee farm in which napier grass for cattle feeding had been growing for several years. All the other samples were collected from coffee farms. Coach grass was chosen because it was the only common weed in the farms from which the samples were taken. The weed also takes a long period under the soil surface and can thus accumulate nutrients over a long period of time from the soil. The grass is considered a weed and thus its copper content has no effect to the human environment, but animals do feed on it and can possibly get affected if the copper levels are too high. It can also be a good indicator of how much copper food crops in the vicinity of a copper polluted environment can accumulate. In all cases, only the top soil was sampled.

In trying to find out the best among the three methods of extracting unbound copper in the soil, regression analysis was carried out between total copper and available copper obtained using each of the three methods. The analysis was also done for copper in plant tissues versus available copper obtained using each of the three methods. In each case, a linear regression (straight line graph) and a cubic regression (2nd order polynomial for curves) were done and plotted on the same graph, noting the value of squared regression coefficients (R-squared or 'coefficient of determination') in each case. The more the R-squared value is closer to unity, the better the correlation between the two variables under consideration[93]. The equipment used for all these analysis was a BBC microcomputer system.

The results of the analysis are as shown in tables 4 and 5 below:-

TABLE 4: Regression Analysis for total copper concentration versus available copper concentration (using methods a, b, and c described above)

Figure	R^2	Method	Line/Curve (L/C)	
4.6	0.2885	a	L	L = straight line
4.6	0.4546	a	C	C = curve
4.6	0.9997	b	L	
4.7	0.9829	c	L	

Out of the three methods a, b, and c, method (a)

had a poor correlation for both line and curve. This method was thus considered not reliable. The results

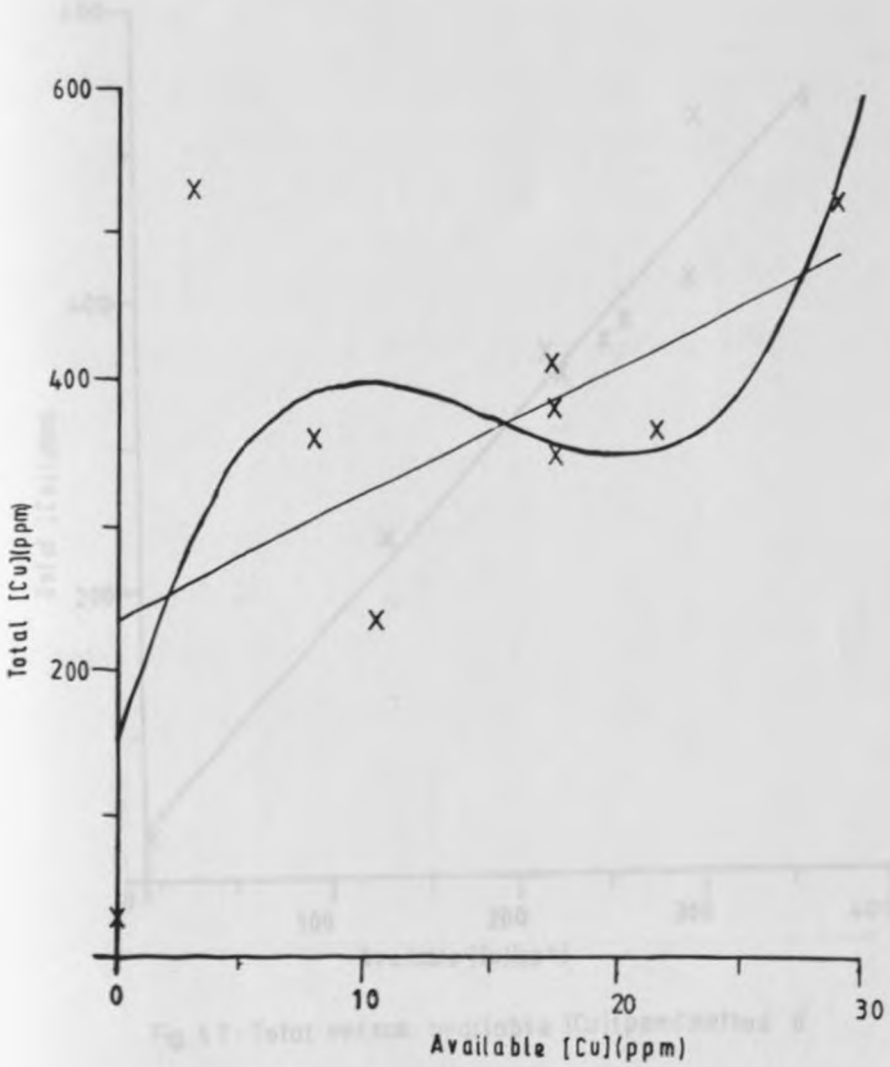


Fig.4.6: Total versus available [Cu](ppm)'method c'

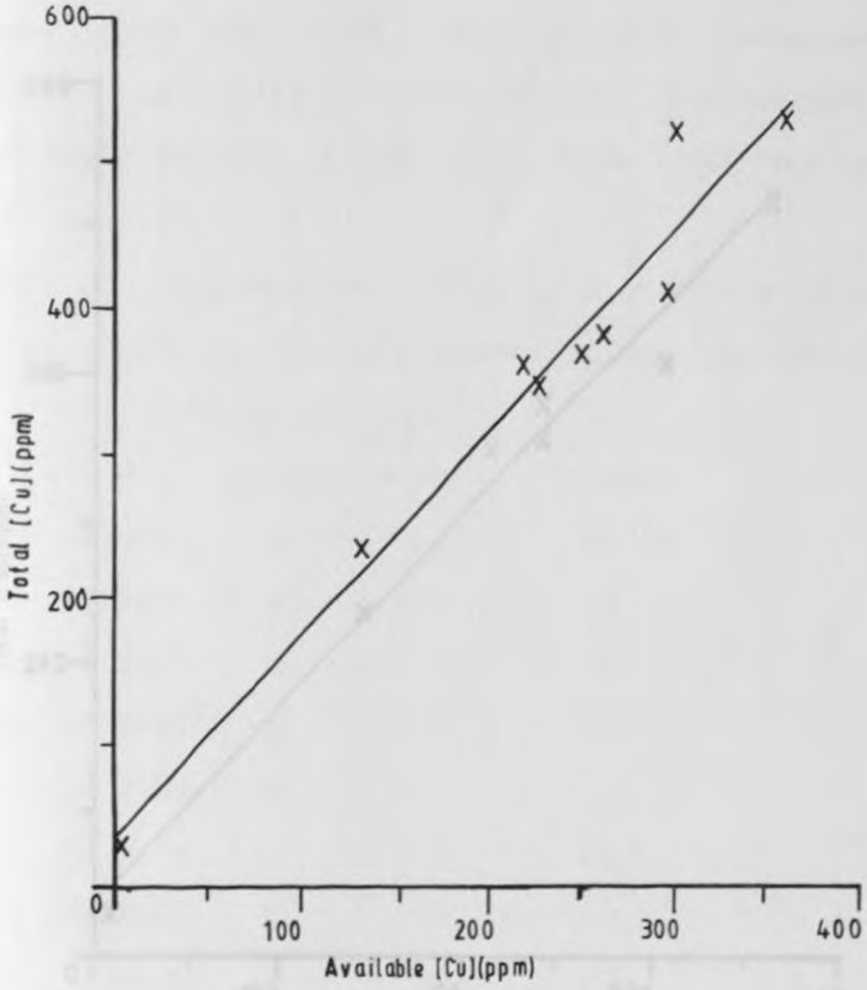


Fig. 47: Total versus available [Cu](ppm) method b

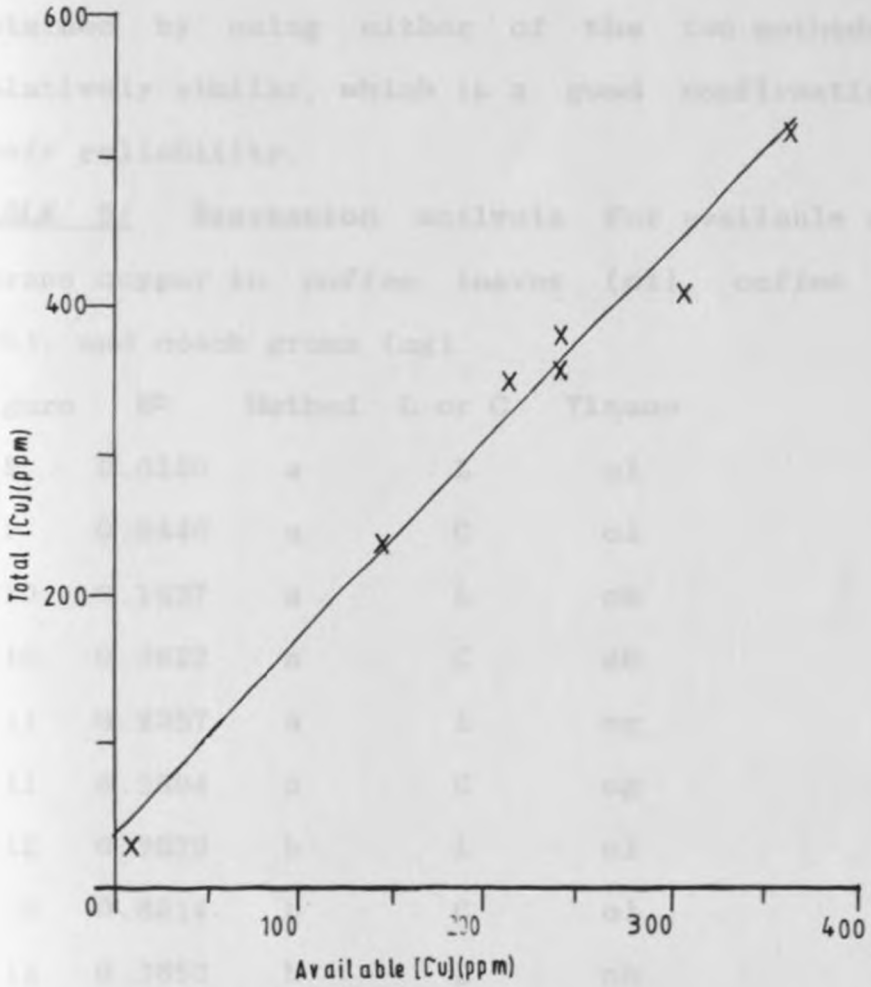


Fig. 4.8: Total versus available [Cu] (ppm) `method c'

in table 3 support this deduction in that the trend in the column for total copper versus the column for available copper under method (a) is poor. The other two methods, b and c had good linear correlation with total copper content in the soil. They may thus be the more reliable methods for extracting unbound copper from the soil. The copper concentrations obtained by using either of the two methods were relatively similar, which is a good confirmation of their reliability.

TABLE 5: Regression analysis for available copper versus copper in coffee leaves (cl), coffee beans (cb), and coach grass (cg)

Figure	R^2	Method	L or C	Tissue
4.9	0.0190	a	L	cl
4.9	0.8446	a	C	cl
4.10	0.1637	a	L	cb
4.10	0.3622	a	C	cb
4.11	0.2357	a	L	cg
4.11	0.3604	a	C	cg
4.12	0.7079	b	L	cl
4.12	0.8814	b	C	cl
4.13	0.3653	b	L	cb
4.13	0.7027	b	C	cb
4.14	0.7270	b	L	cg
4.14	0.7611	b	C	cg
4.15	0.6880	c	L	cl

Figure	R^2	Method	L or C	Tissue
4.15	0.8574	c	C	cl
4.16	0.3495	c	L	cb
4.16	0.6577	c	C	cb
4.17	0.6651	c	L	cg
4.17	0.7090	c	C	cg

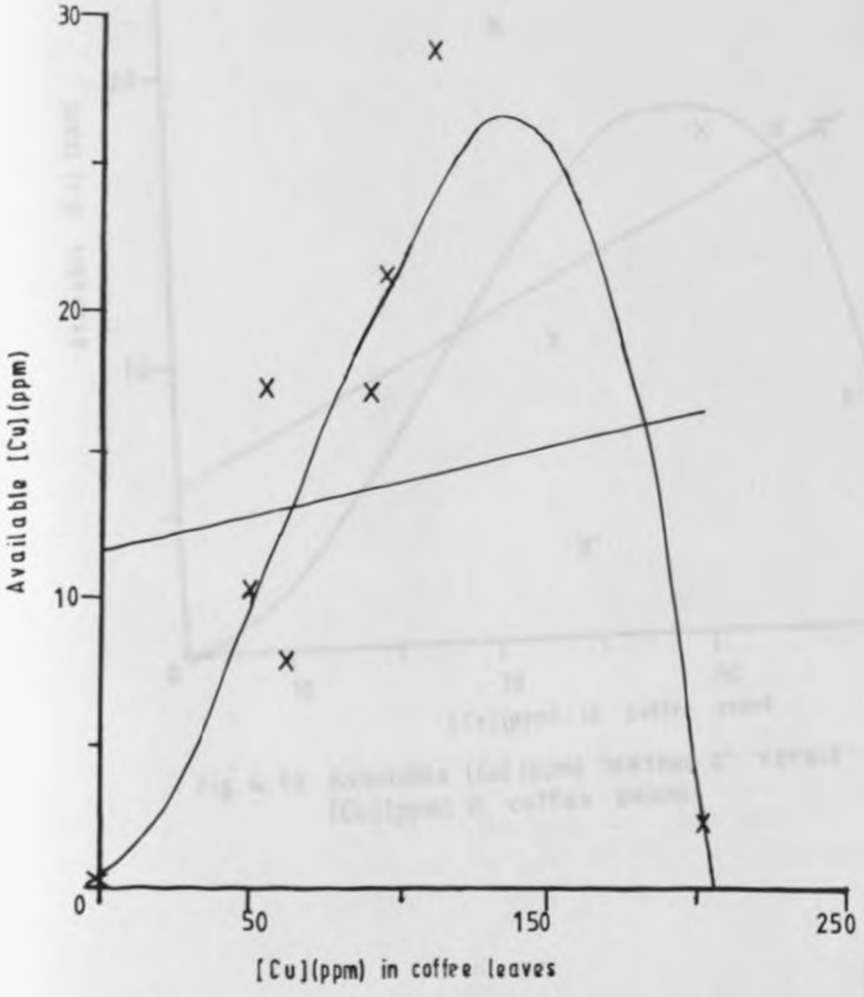


Fig. 4.9:
Available [Cu](ppm) method a versus [Cu](ppm) in coffee leaves

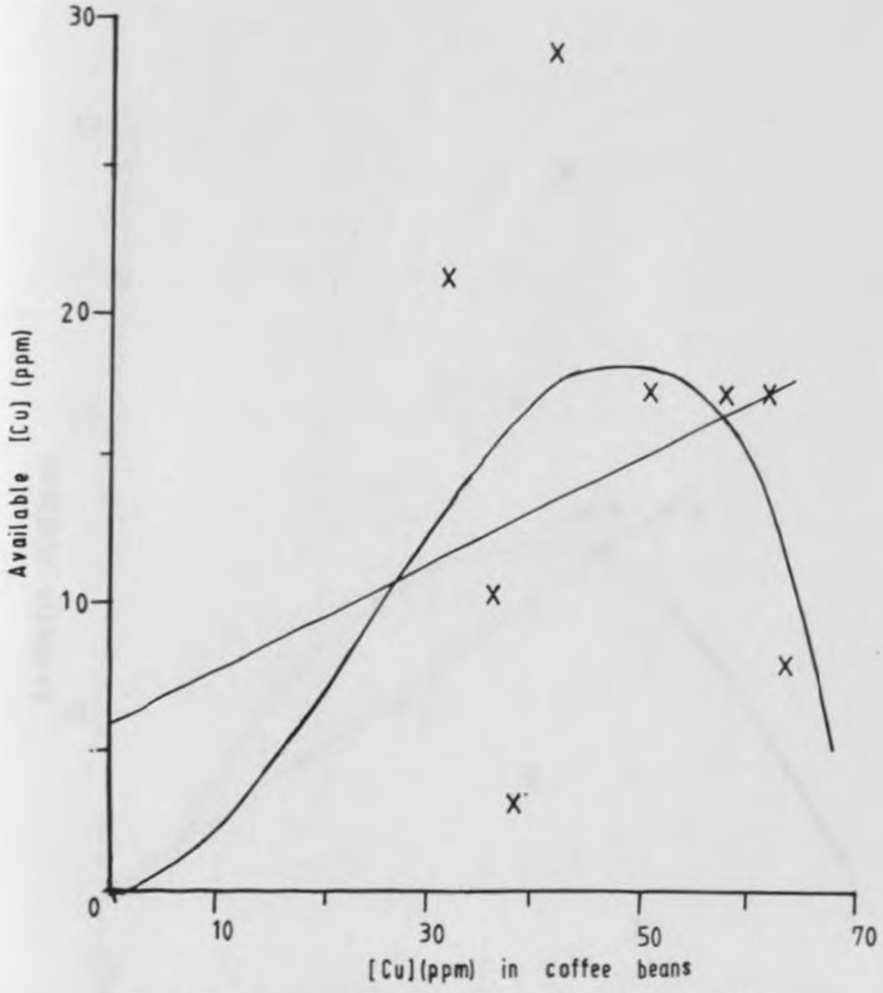


Fig. 4.10 : Available [Cu] (ppm) 'method a' versus [Cu](ppm) in coffee beans.

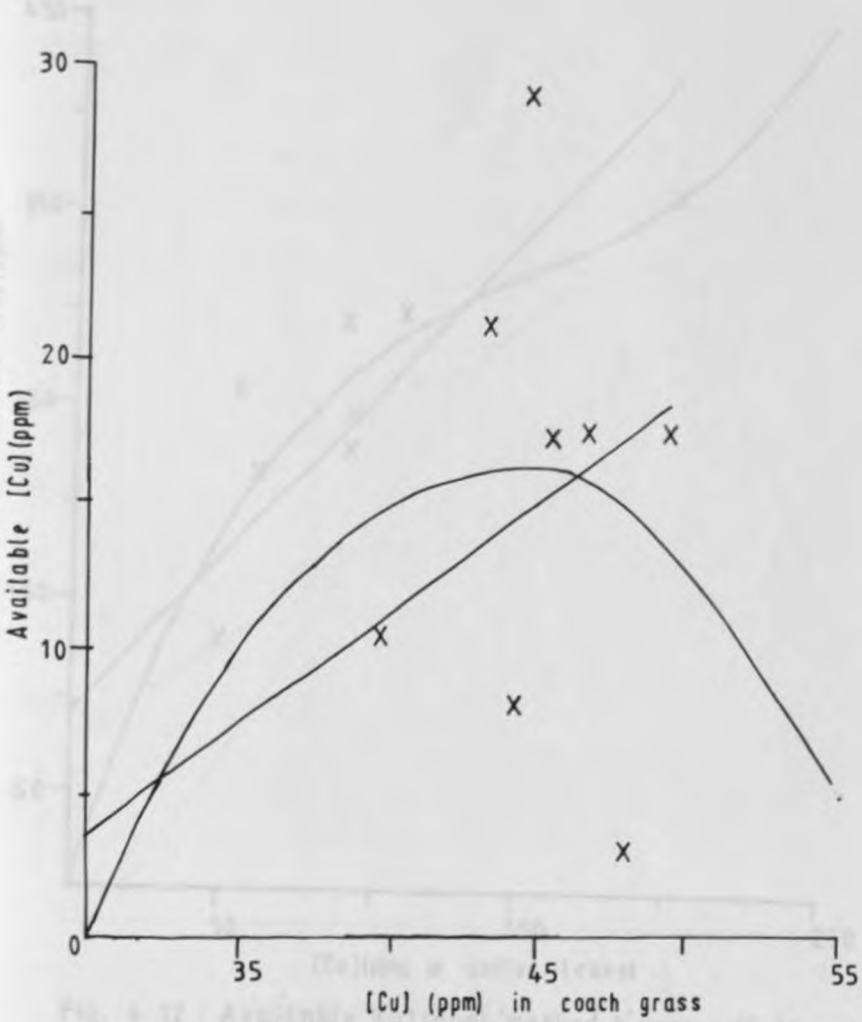


Fig. 4.11: Available [Cu] (ppm) 'method a' versus [Cu] (ppm) in coach grass.

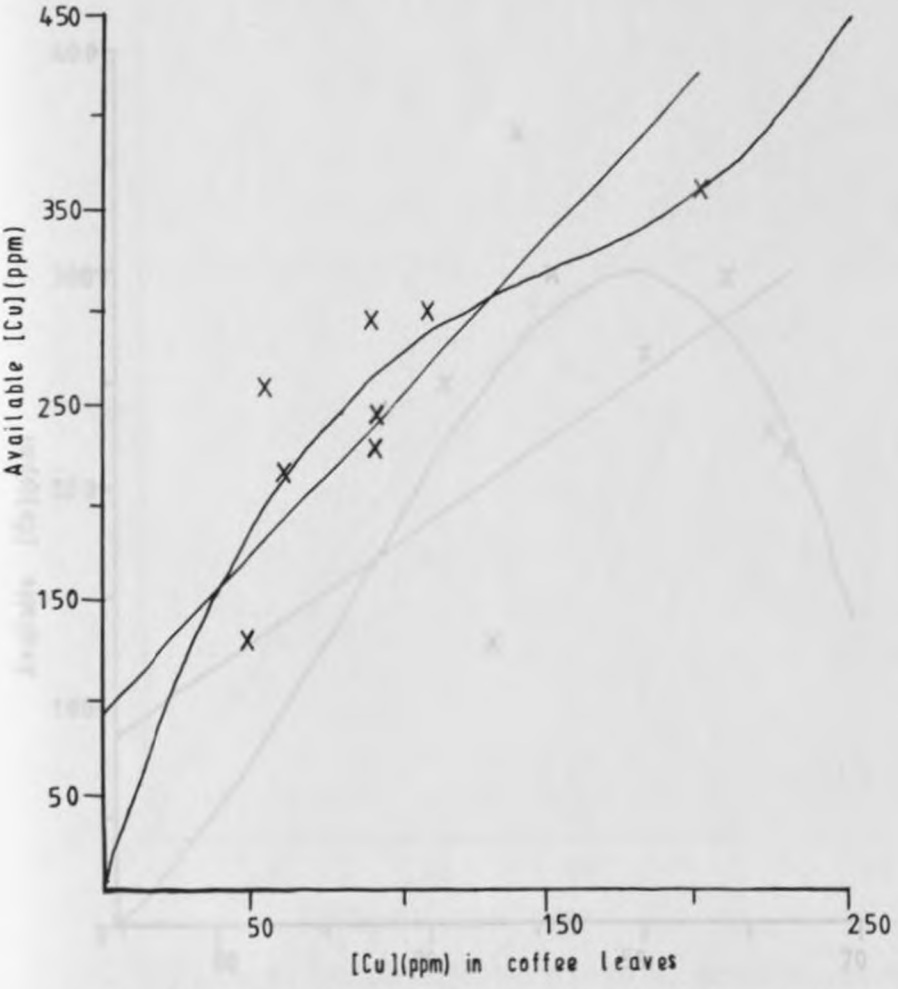


Fig. 4 12 : Available [Cu](ppm) `method b´ versus [Cu](ppm) in coffee leaves.

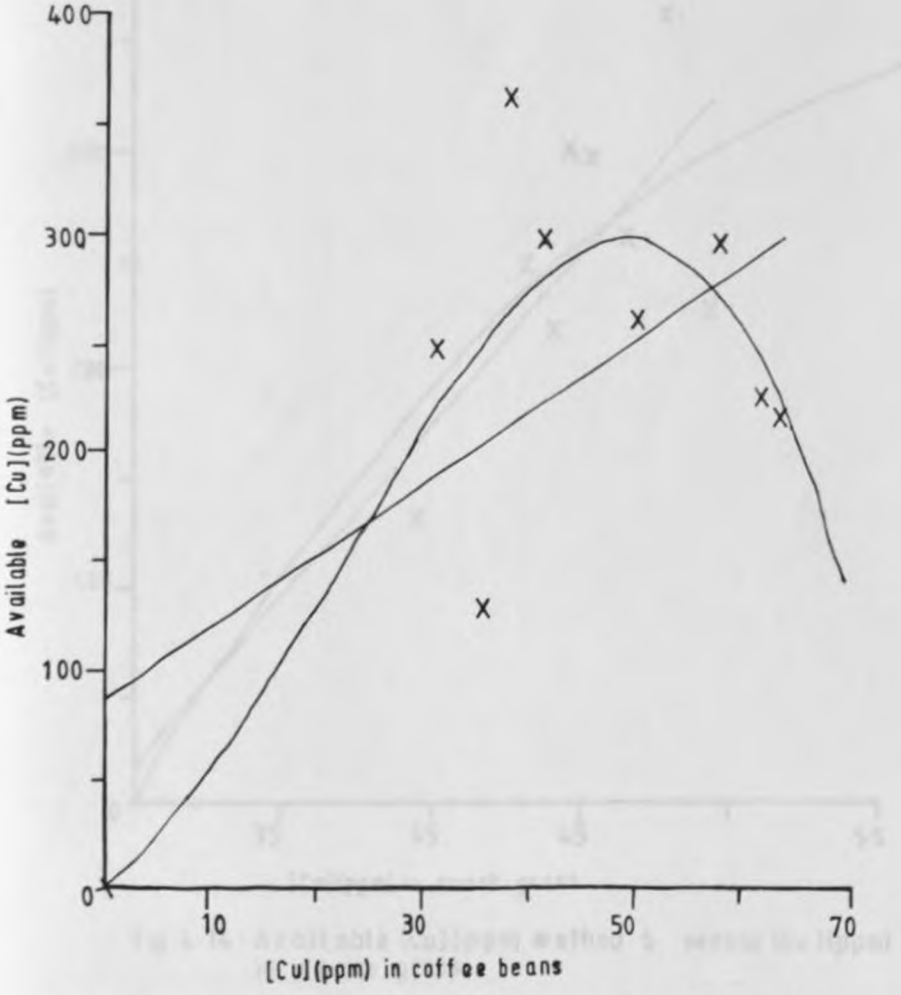


Fig. 4.13: Available [Cu](ppm) method b versus [Cu](ppm) in coffee beans

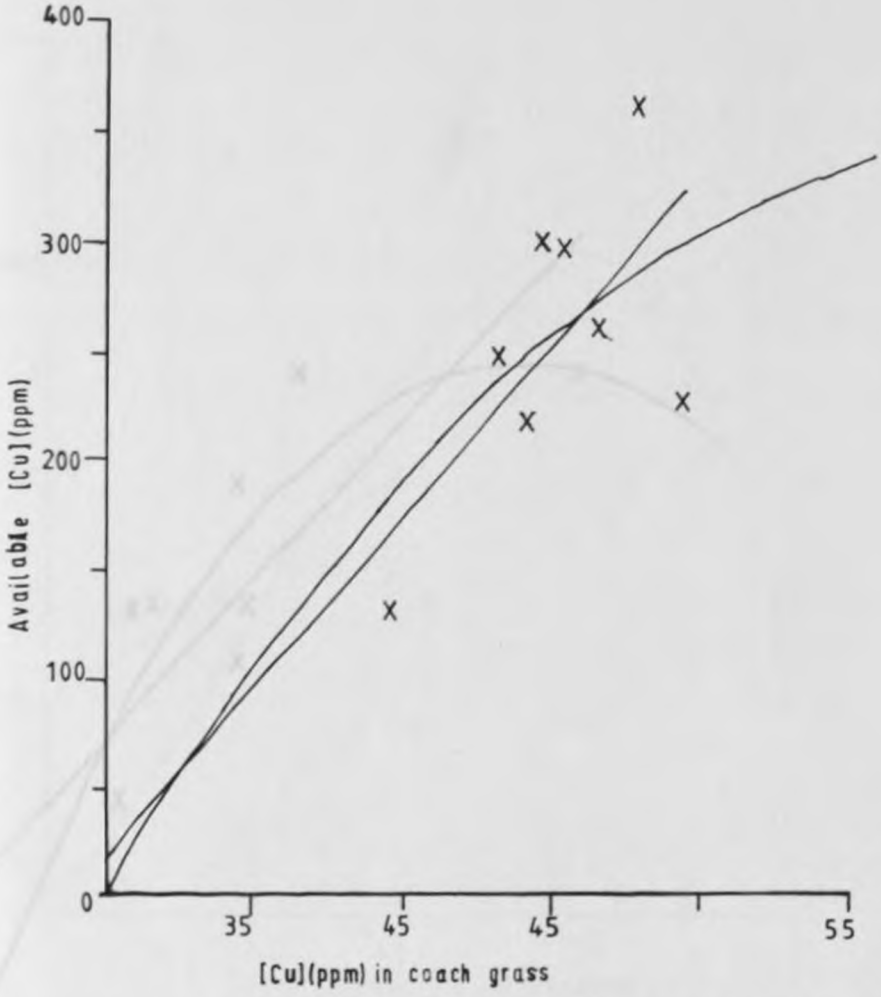


Fig. 4.14: Available [Cu](ppm) method b versus [Cu](ppm) in coach grass

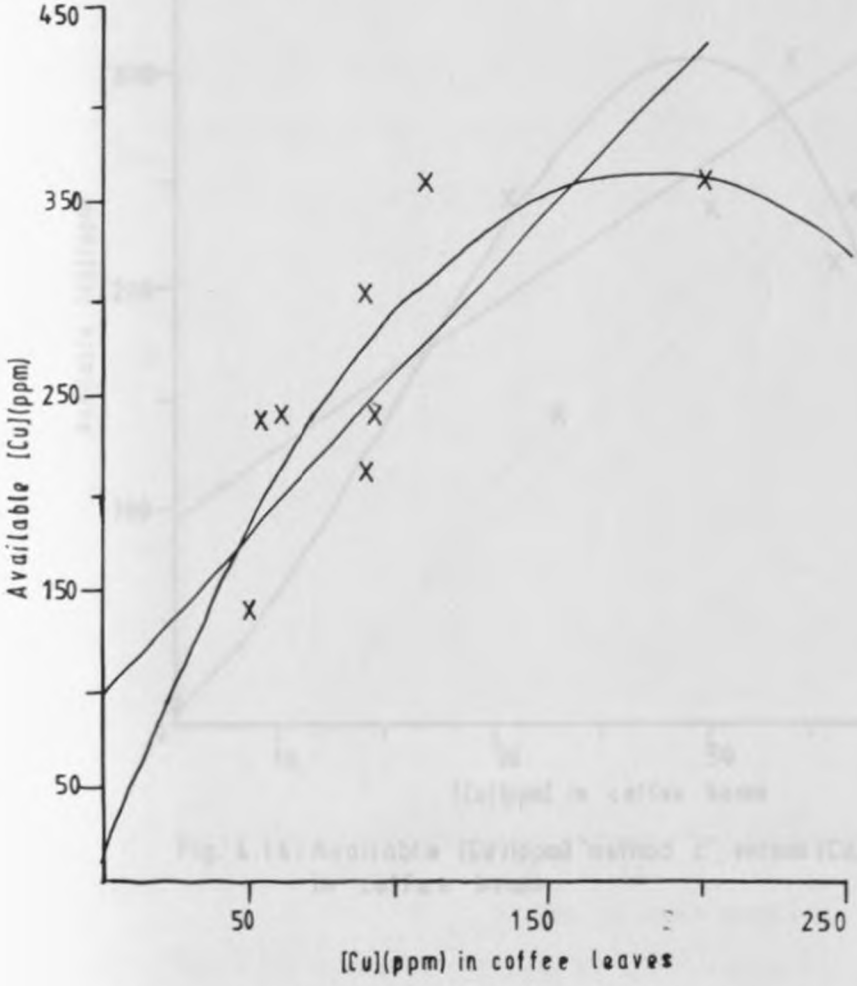


Fig. 4.15: Available [Cu](ppm) method c versus [Cu](ppm) in coffee leaves

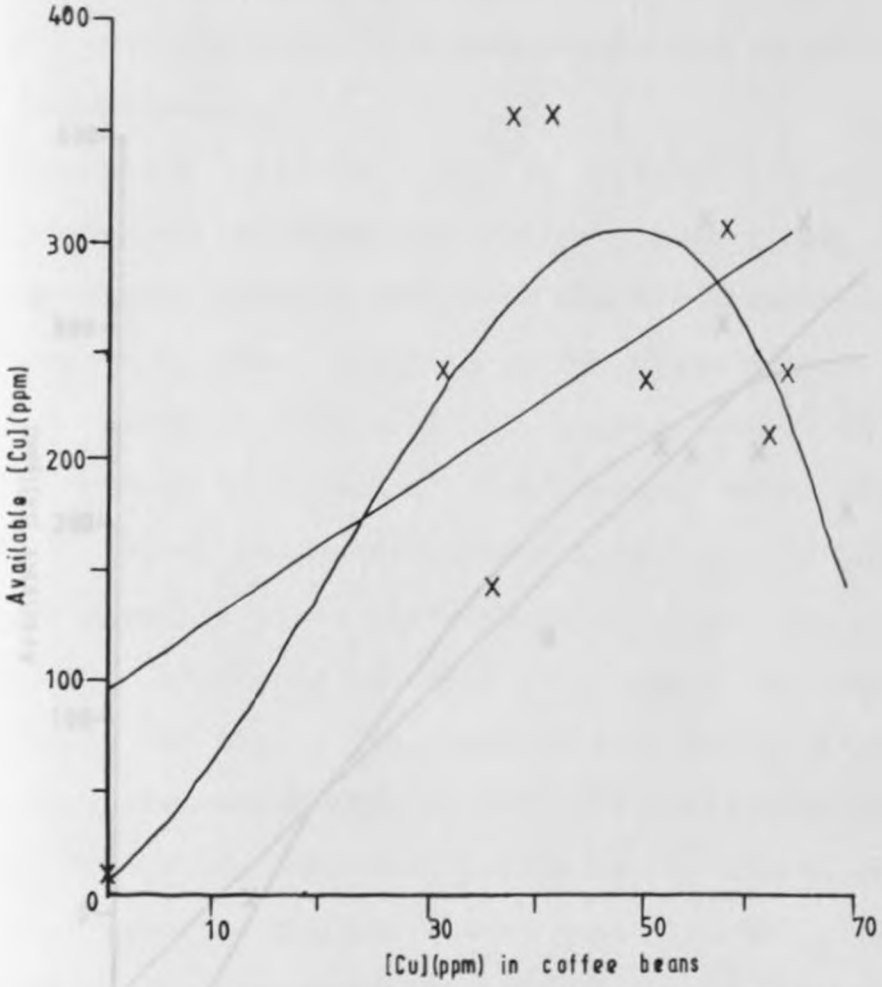


Fig. 4.16: Available [Cu](ppm) 'method c' versus [Cu](ppm) in coffee beans.

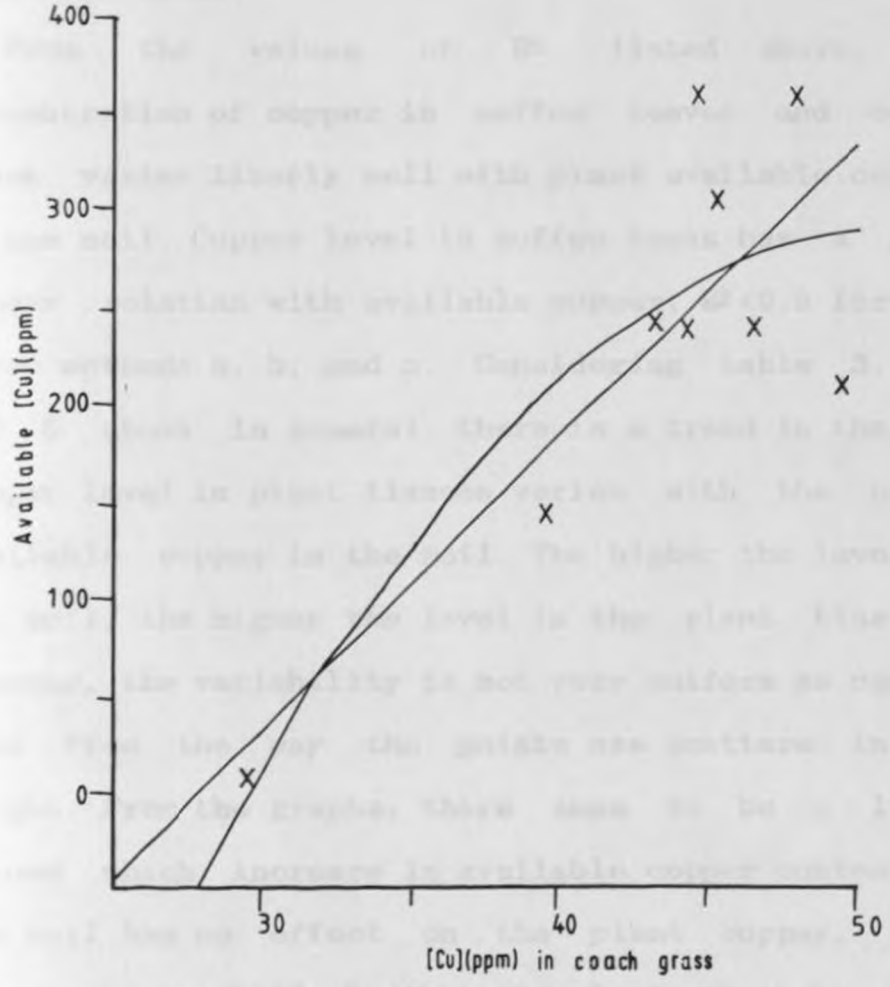


Fig. 4.17: Available [Cu](ppm) method c versus [Cu](ppm) in coach grass.

Of all the three methods, values obtained using method (a) poorly correlated with copper levels in plant tissues (R^2=0.0190 and R^2=3622 except for one extreme R^2=0.8446). The copper level obtained using the other two methods (b and c) had a good linear correlation (between R^2=0.6651 and R^2=0.7270) with copper level in plant tissues, except for copper level in coffee beans.

From the values of R^2 listed above, the concentration of copper in coffee leaves and coach grass varies linerly well with plant available copper in the soil. Copper level in coffee beans has a poor linear relation with available copper, R^2<0.5 for the three methods a, b, and c. Considering table 3, 4, and 5 above in general, there is a trend in the way copper level in plant tissues varies with the plant available copper in the soil. The higher the level in the soil, the higher the level in the plant tissues. However, the variability is not very uniform as can be seen from the way the points are scattered in the graphs. From the graphs, there seem to be a limit beyond which increase in available copper content in the soil has no effect on the plant copper. The reason here could be that the plants stop absorbing copper after having taken their maximum. As such, since the plant has taken enough, it cannot absorb any

further even if the soil can provide more.

Regression analysis was also done for the comparison of total copper in the soil with copper in plant tissues. The results of the analysis are tabulated below:-

Table 6 Regression analysis for total copper versus copper in plants

Figure	R^2	L or C	Tissue
4.18	0.7034	L	cl
4.18	0.8852	C	cl
4.19	0.3752	L	cb
4.19	0.7105	C	cb
4.20	0.7385	L	cg
4.20	0.7727	C	cg

The trend here is similar to that for available copper versus copper in plant tissues. This was expected because there was a good linear relation between available copper and total copper (Figs. 7 and 8 on page 86 and 87).

4.4 Copper content in the plant tissues

According to table 3, the range of copper concentration in coach grass is quite small (between 25.56 ppm and 49.44 ppm. The total copper content in the soil samples taken from a non-coffee area (30.48 ppm) is almost equal to the concentration in coach grass

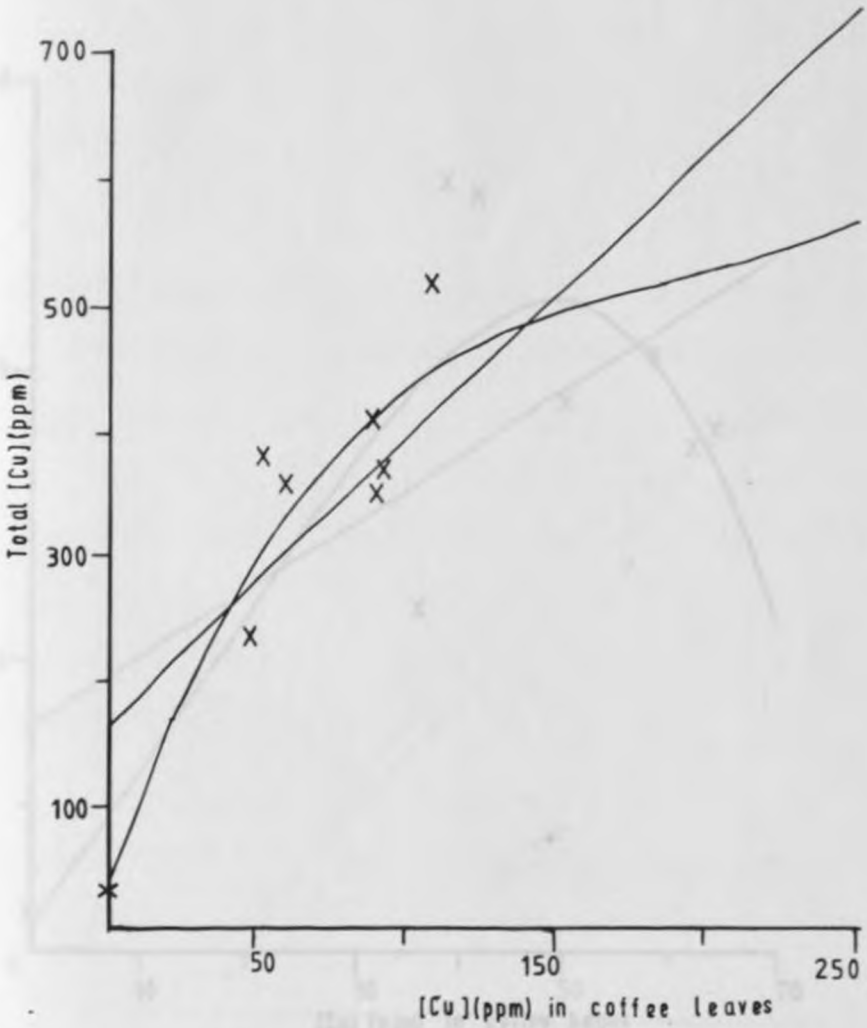


Fig. 4.18: Total [Cu](ppm) versus [Cu](ppm) in coffee leaves

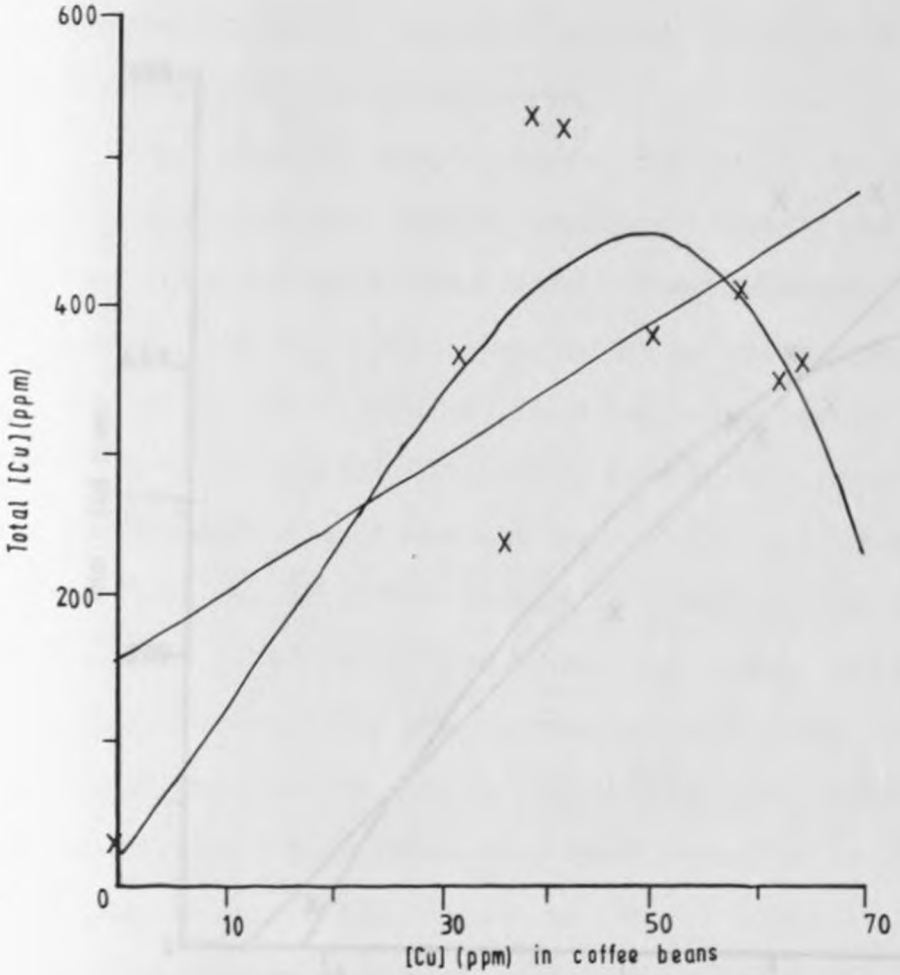


Fig. 4.19: Total [Cu] (ppm) versus [Cu] (ppm) in coffee beans

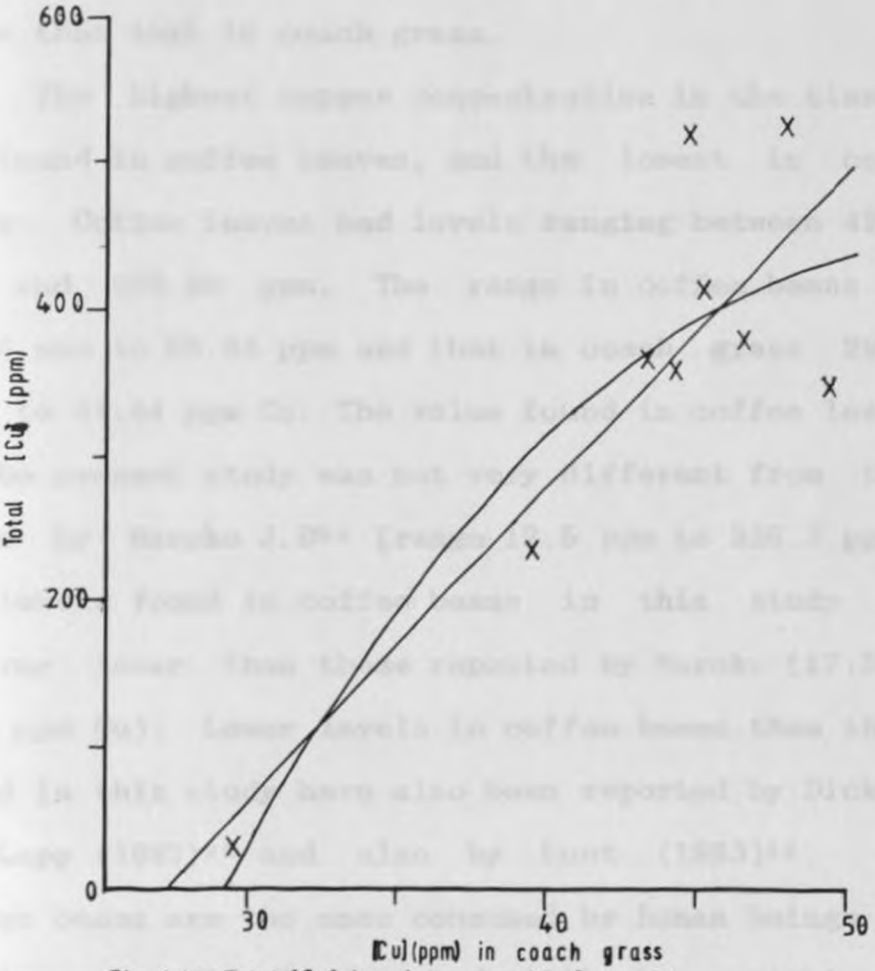


Fig. 4.20: Total [Cu] (ppm) versus [Cu] (ppm) in coach grass

from the same area. The reason here could be that the soil nutrients keep on getting removed without replacement. The removal of soil nutrients is done when the nappier grass is cut for livestock every time it reaches a given height. Thus the nutrients absorbed by the nappier grass are never recycled back to the soil. The same reason could account for the available copper in the soil around this area being lower than that in coach grass.

The highest copper concentration in the tissues was found in coffee leaves, and the lowest in coach grass. Coffee leaves had levels ranging between 49.77 ppm and 200.50 ppm. The range in coffee beans was 31.36 ppm to 63.84 ppm and that in coach grass 29.56 ppm to 49.44 ppm Cu. The value found in coffee leaves in the present study was not very different from that found by Maroko J.B[94] [range 12.5 ppm to 336.3 ppm]. The levels found in coffee beans in this study are however lower than those reported by Maroko (17.8 to 25.5 ppm Cu). Lower levels in coffee beans than those found in this study have also been reported by Dickson and Lepp (1983)[95] and also by Lunt (1983)[96]. The coffee beans are the ones consumed by human beings and the low copper levels detected in the beans might mean that there is no danger of copper contamination for human consumption. In this study, the coffee bean was analysed wholly (top peel, husk, mucillage and inner

bean unseperated). The innermost bean if analysed seperately would be expected to have lower copper concentration than the whole bean. This would even qualify the coffee more fit for human consumption, since only the innermost bean is used in beverage. The outer covers if analyed seperately might have had higher copper levels than those found for whole beans. A study of copper levels in potato peels versus peeled potato (to be discussed later) showed that the peels had a higher copper content than the peeled potato.

It has been reported that absorbed copper is mostly concentrated in coffee branches than in other tissues[97]. In table 3, the highest levels of copper (sample number 5 and sample number 6) were obtained in samples taken from around coffee stems that had dried out. The same results (highest copper levels) had been obtained on previous samples colleccted around dry coffee stems (Table 1). The dry coffee stems were in different coffee farms and the fact that the soils around them had higher copper levels than soils from other areas in the coffee farms indicates that high copper levels had contributed to the drying out. The other possibility discussed earlier (use of the areas for spraying equipments) can also not be ruled out.

High copper content in the soil can affect plants by impaired uptake of other nutrients.

Tolerable copper limits for mature coffee plants have not been established, and as such, it is not easy to determine the toxic limit for the plants. However, Vasudeva and Rotageri (1980)[98] have reported tolerable levels for young seedlings. Presence of high levels of copper in soils might render such soils unsuitable for sensitive crops.

Also included in this study were seven coffee farms in a region where alot of copper based fungicides are used for prevention of coffee leave rust. The major aim was to establish the relation between soil pH and the copper content in the soil. The samples were taken from two depths, top soil(0 to 15 cm) and subsoil (15 to 45 cm). The results of this study are shown in table 7 below.

TABLE 7: TOTAL COPPER CONTENT (Tt) VERSUS AVAILABLE (Av) [EDTA EXTRACTABLE] COPPER IN THE TOP SOIL [(Ts) 0-1 FOOT] AND THE SUB SOIL [(Ss) 1-2 FEET] FROM 7 FARMS ALONG RUTUI RIVER. ALL VALUES ARE IN PPM (micrograms per gram)

SAMPLE	TSpH	TSTt	TSAv	SSpH	SSTt	SSAv
5A	4.15	890.40	198.50	4.24	71.92	30.15
5B	3.51	425.70	235.40	3.97	73.22	32.41
5C	4.12	436.30	306.50	4.66	47.23	28.65
5D	3.77	389.50	229.40	4.71	28.85	22.36
6A	3.50	351.10	197.40	4.38	31.61	23.24
6B	3.69	370.50	211.10	4.14	50.34	24.28
6C	4.25	319.00	196.50	4.40	18.20	10.12
6D	3.47	358.60	206.10	3.81	28.64	10.58
7A	3.67	258.70	144.60	4.10	88.59	40.08
7B	4.31	267.90	141.90	4.20	86.99	61.05
7C	4.03	218.50	130.20	4.01	48.80	22.54
7D	3.91	120.40	64.04	4.02	50.00	26.01
8A	3.83	279.60	145.40	3.75	99.00	107.30

SAMPLE	TSpH	TSTt	TSAv	SSpH	SSTt	SSAv
8B	3.58	219.10	107.80	3.55	119.40	37.95
8C	3.58	129.60	59.47	3.60	69.34	21.83
8D	3.84	259.40	149.30	3.82	99.21	41.23
9A	3.38	189.50	85.35	3.40	189.30	93.46
9B	3.76	139.50	61.35	3.74	129.90	55.55
9C	3.76	159.10	63.78	3.85	139.80	51.59
9D	3.71	149.30	61.41	3.34	149.70	67.54
10A	6.16	170.20	80.41	6.29	160.70	76.78
10B	4.15	192.70	75.33	4.11	182.10	83.05
10C	4.57	151.50	57.26	3.82	181.10	80.92
10D	4.01	150.00	62.41	3.78	170.60	76.75
11A	4.68	550.20	300.90	4.62	200.60	60.47
11B	6.31	771.20	122.20	3.73	339.10	168.20
11C	4.67	749.80	518.30	5.50	240.90	100.10
11D	4.63	530.00	360.70	5.42	217.30	92.17

TABLE 7B: Averages per farm for the Data in Table 7. The values given are copper concentrations in parts per million ±Standard Deviation (n=4 in all cases).

SAMPLE	TSpH	TSTt	TSAv	SSpH	SSTt	SSAv
5	3.89	535.50	242.40	4.40	55.31	28.39
	±0.31	±237.40	±45.64	±0.35	±21.31	±4.31
6	3.73	349.80	202.80	4.18	32.20	17.05
	±0.36	±22.06	±7.00	±0.28	±13.39	±7.76
7	3.98	216.40	120.20	4.08	68.59	37.42
	±0.27	±67.46	±37.95	±0.09	±22.18	±17.48
8	3.71	221.90	115.50	3.68	96.75	52.09
	±0.15	±66.51	±41.77	±0.13	±20.63	±37.80

SAMPLE	TSpH	TSTt	TSAv	SSpH	SSTt	SSAv
9	3.65 ±0.18	159.40 ±21.65	67.97 ±11.64	3.59 ±0.25	152.20 ±26.04	67.03 ±18.88
10	4.72 ±0.99	166.10 ±19.99	68.85 ±10.82	4.50 ±1.20	173.60 ±10.10	79.37 ±3.14
11	5.07 ±0.83	650.30 ±127.80	325.50 ±163.60	4.82 ±0.83	249.50 ±62.01	105.20 ±45.33

The reagent used for extracting the available copper was 0.5M EDTA all along. In each farm, four samples were taken from different sections. The farms are represented by sites (5-11) in table 7 and 7B above.

Figs. 4.21 and 4.22 ahead) show that there is a strong linear relationship between total copper and available copper in the soil for both top-soil and sub-soil. The results in the table show that pH is higher for the sub-soils than for the top soil. For the top-soil, the pH range between 3.38 and 6.31. For the sub-soil the pH ranges between 3.34 and 6.29. The results also show that concentration of copper in the top-soil is far much higher than the concentration of copper in the sub-soil. Thus the concentration of copper decreases with depth as already reported previously (table 1).

Figs. 4.23 to 4.26 show that as the concentration of copper in the soil increases, the pH decreases upto a minimum value and then starts increasing. The pH values found in

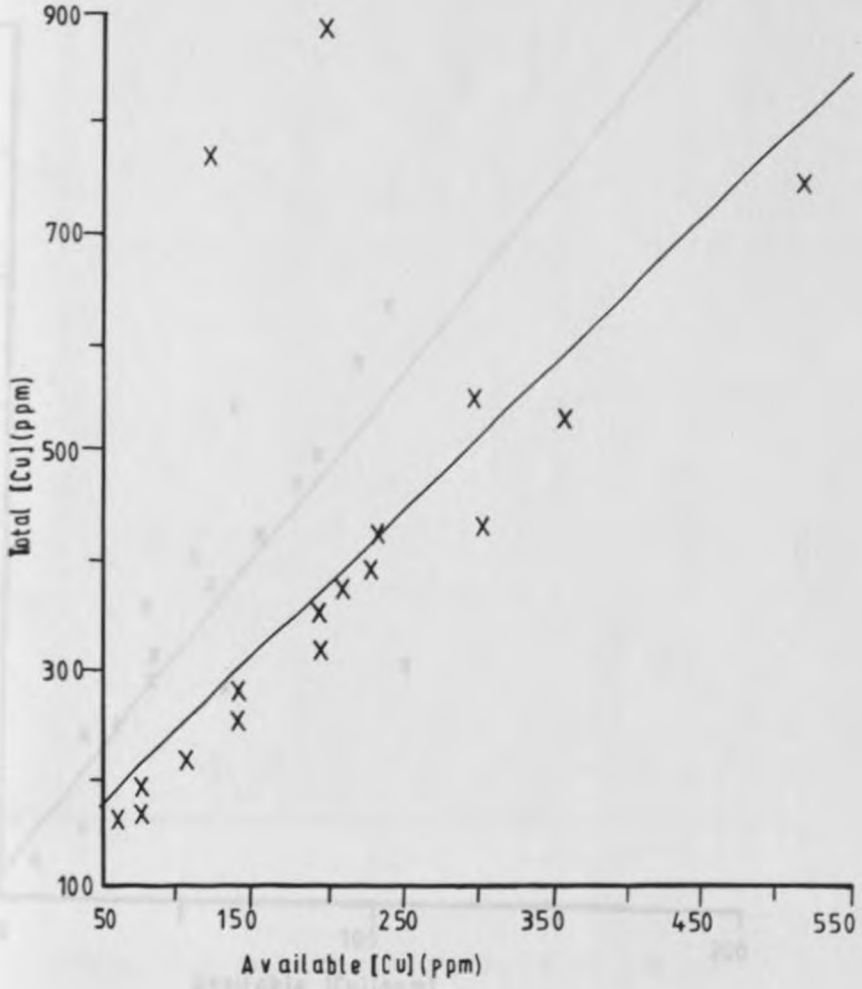


Fig. 4 21: Total versus available [Cu] (ppm) for top soil

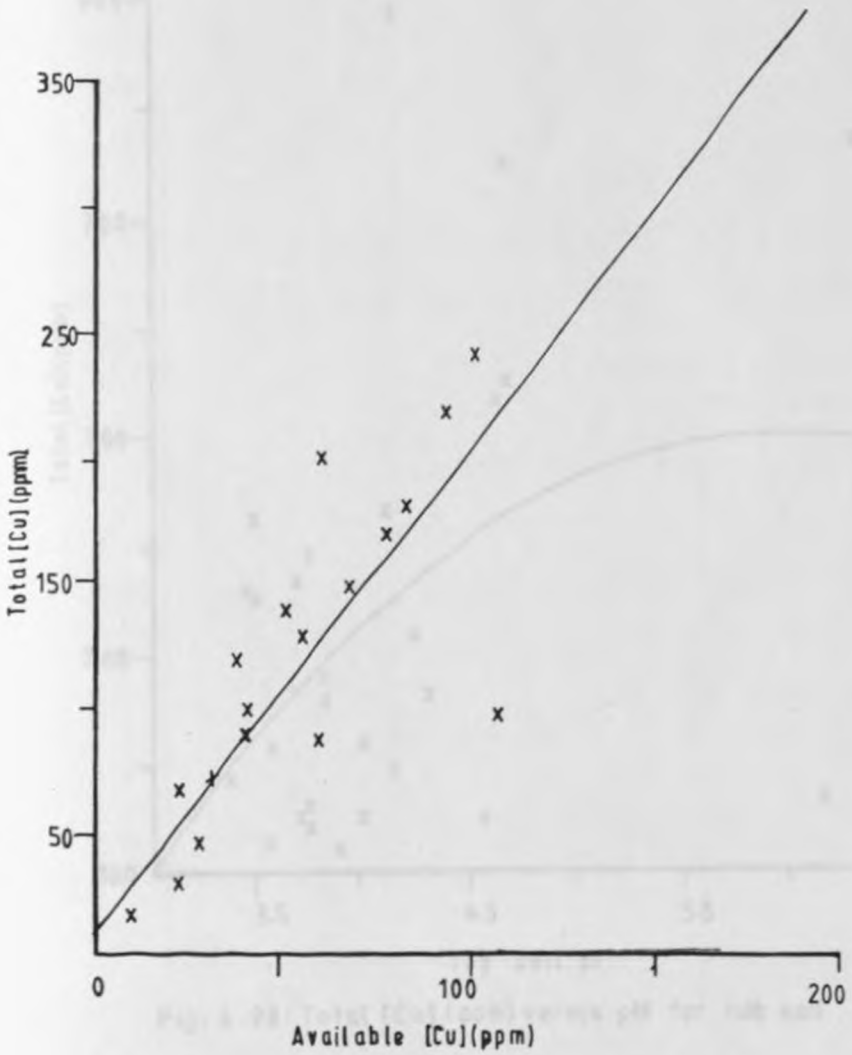


Fig.4.22:Total versus available [Cu](ppm) for sub soil

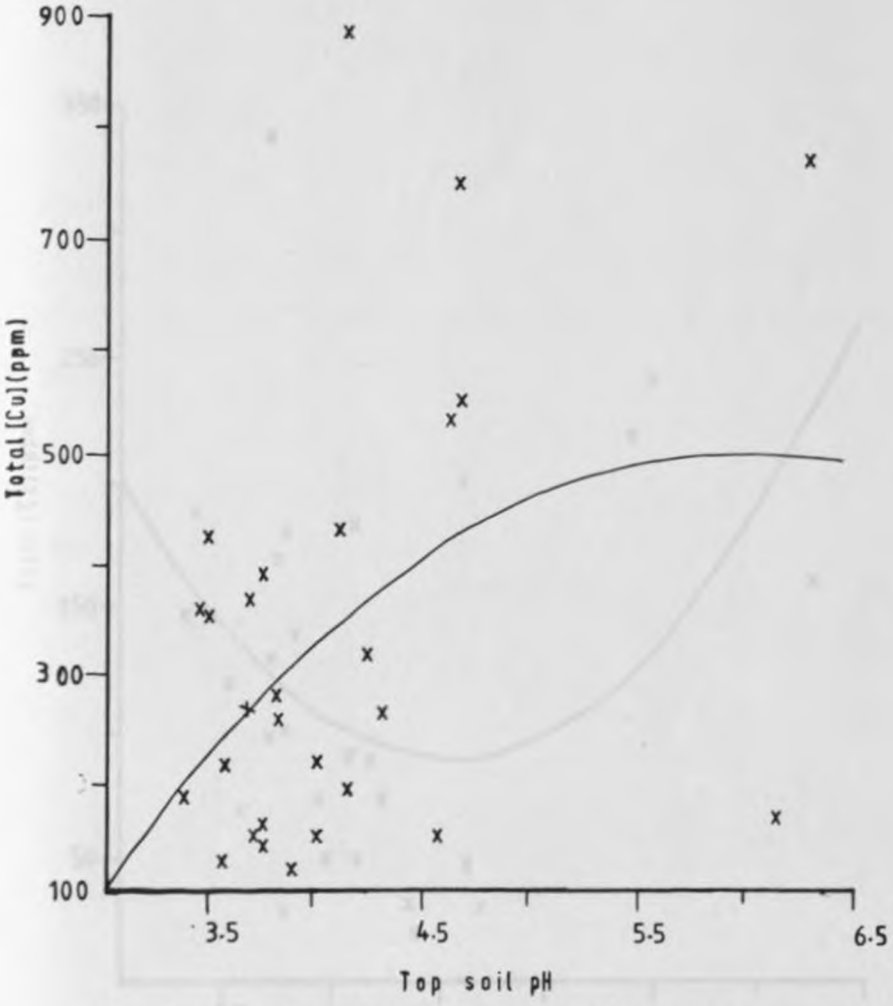


Fig. 4.23: Total [Cu] (ppm) versus pH for sub soil

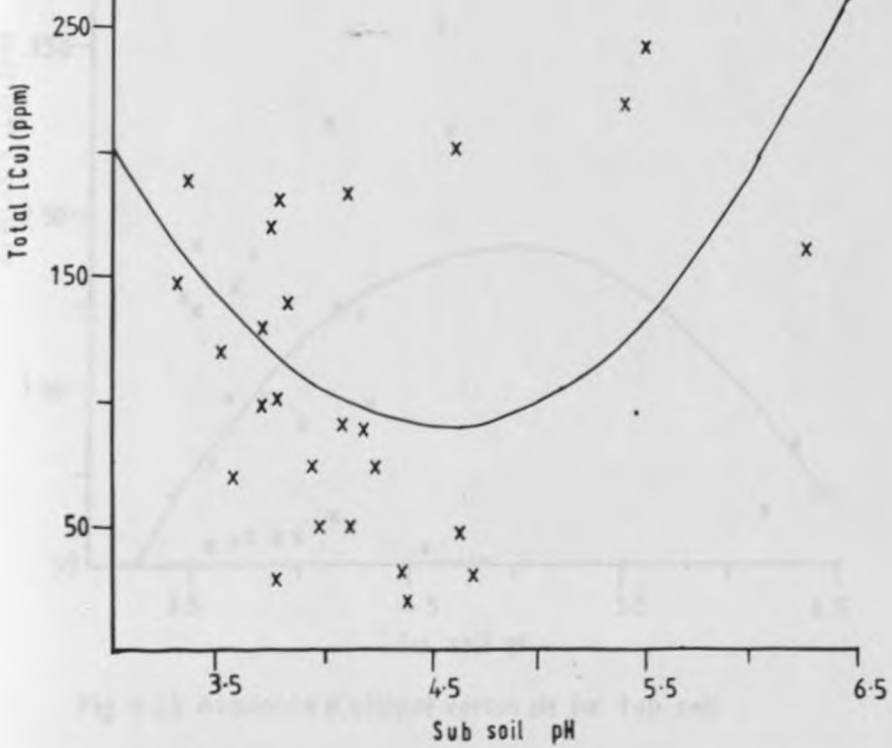


Fig. 4.24: Total [Cu](ppm) versus pH for sub soil

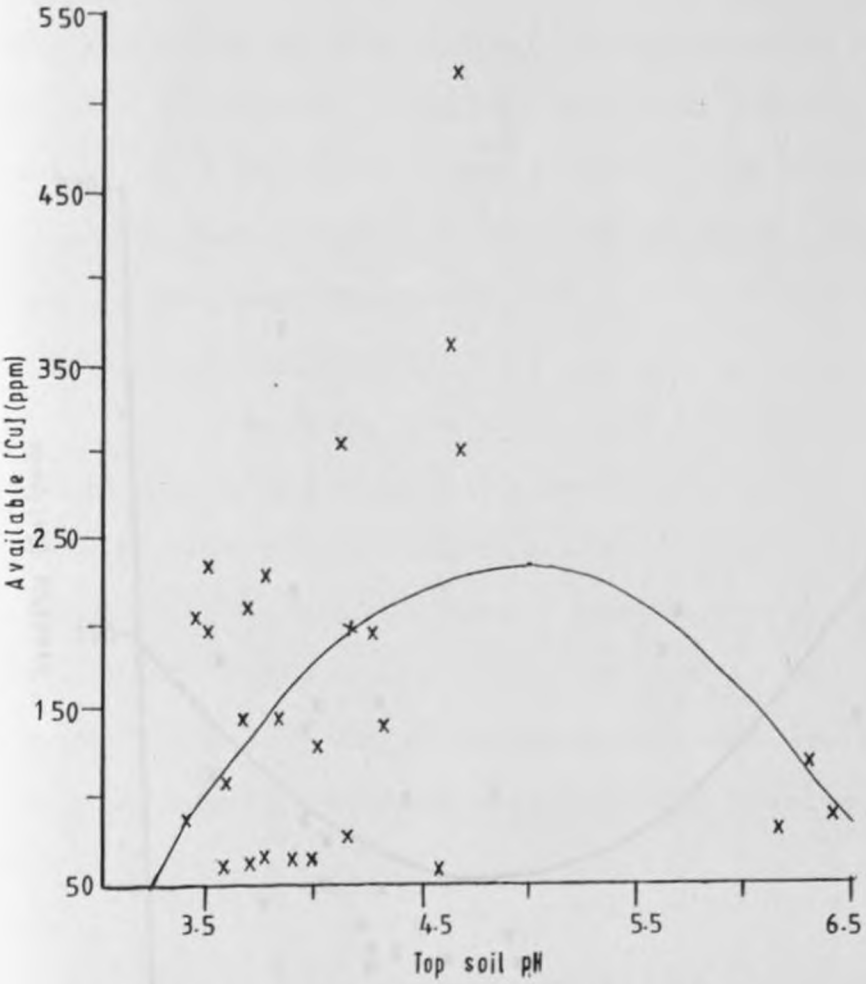


Fig. 4.25: Available [Cu](ppm) versus pH for top soil

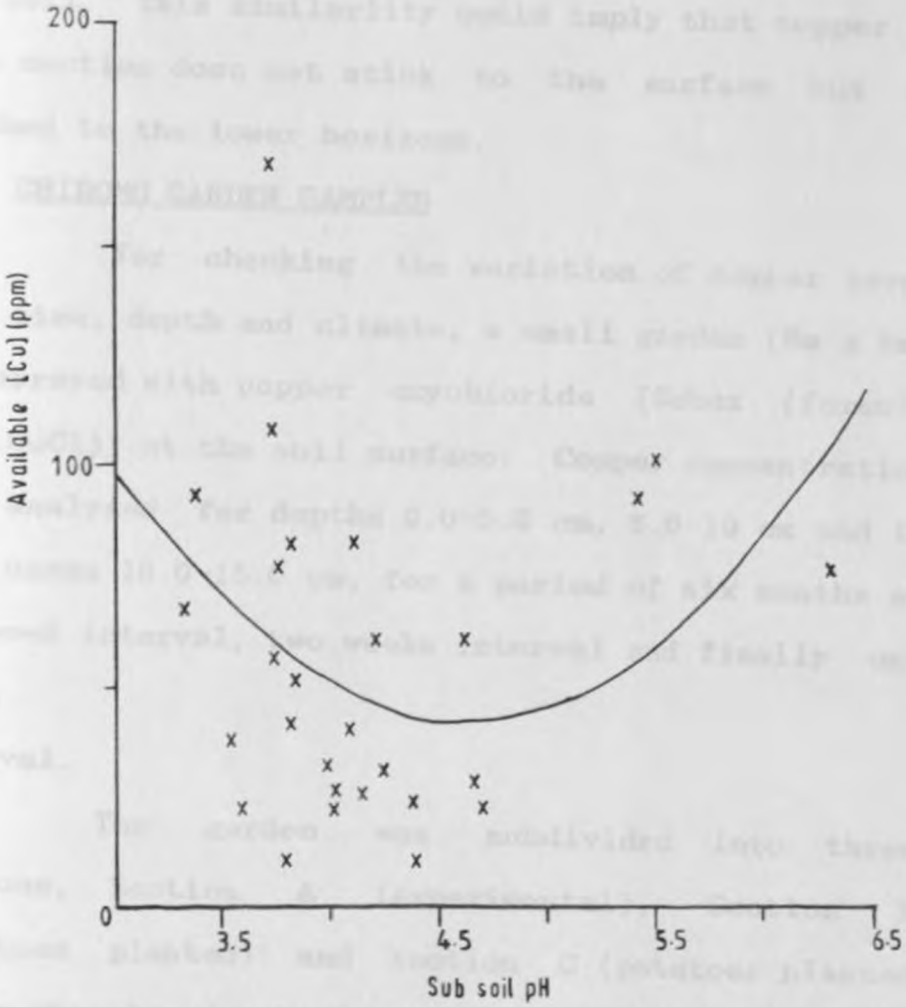


Fig. 4.26: Available [Cu](ppm) versus pH for sub soil

this study are similar to those reported for most agricultural soils (between 4 and 8)[99]. It is also reported in the same reference that "the more acid a soil is, the more mobile will become such elements as iron, manganese, zinc, copper and other minor elements. In fact this seems to be the case in this study. Samples having the lowest pH values (e.g. sample 9A and 9D in the table) have copper levels which are relatively similar for both top-soil and sub-soil. This similarlity could imply that copper in this section does not stick to the surface but is leached to the lower horizons.

4.5 CHIROMO GARDEN SAMPLES

For checking the variation of copper level with time, depth and climate, a small garden (6m x 6m) was sprayed with copper oxychloride [Cobox (formula CuOH.CuCl)] at the soil surface. Copper concentration was analysed for depths 0.0-5.0 cm, 5.0-10 cm and in some cases 10.0-15.0 cm, for a period of six months at one week interval, two weeks interval and finally one month

interval.

The garden was subdivided into three sections, Section A (experimental), Section B (potatoes planted) and section C (potatoes planted but no spraying done) as indicated in fig 3.3 in the previous chapter. The climatic data obtained during

the period is given in table 9.

Table 8 below shows the levels of copper obtained at different depths and time for the three subsections in the garden.

TABLE 8: SOIL SAMPLES FROM CHIROMO GARDEN DEPTH 1 = 0 to 5 cm; DEPTH 2 = 5 to 10 cm; DEPTH 3 = 10 to 15 cm

TABLE 8 (a) SECTION A

WEEK	DEPTH 1	DEPTH 2	DEPTH 3
0	40.93	----	----
	±28.71a	----	----
1	28.08	8.34	----
	±2.77b	±1.78b	----
2	22.68	13.41	----
	±10.16b	±2.55b	----
3	36.70	14.29	----
	±5.00b	±1.12b	----
4	28.43	13.68	----
	±5.22b	±1.21b	----
6	26.51	12.75	----
	±16.68b	±4.73b	----
8	22.72	10.46	----
	±0.04	±0.04	----
12	22.71	10.40	10.43
	±0.01	±0.01	±0.02
16	22.64	16.74	16.13
	±1.81	±0.02	±0.99
20	21.57	8.79	10.70
	±0.00	±0.06	±0.03

TABLE 8 (b) SECTION B

WEEK	DEPTH 1	DEPTH 2	DEPTH 3
0	61.39 ±27.96b	---- ----	---- ----
1	36.69 ±0.16	27.39 ±0.02	---- ----
2	21.84 ±1.32	11.08 ±0.01	---- ----
3	32.24 ±0.07	10.57 ±0.01	---- ----
4	33.10 ±1.18	12.75 ±0.01	---- ----
6	36.97 ±0.04	12.05 ±1.26	---- ----
8	11.77 ±5.91	12.42 ±0.03	---- ----
12	16.61 ±0.04	12.43 ±0.01	12.42 ±0.02
16	23.26 ±1.05	15.57 ±1.05	17.13 ±0.69
20	15.78 ±1.42	14.98 ±0.35	18.44 ±0.00

TABLE 8 (c) SECTION C

WEEK	DEPTH 1	DEPTH 2	DEPTH3
0	7.19 ±3.50	---- ----	---- ----
1	6.46 ±0.02	8.00 ±1.35	---- ----
2	6.44 ±0.01	8.73 ±0.01	---- ----
3	6.97 ±1.26	8.42 ±0.00	---- ----

WEEK	DEPTH 1	DEPTH 2	DEPTH3
4	8.42 ±0.00	9.15 ±1.26	---- ----
6	8.45 ±0.01	8.42 ±0.02	---- ----
8	12.45 ±0.02	12.45 ±0.02	---- ----
12	12.45 ±0.01	12.47 ±0.01	10.40 ±0.02
16	15.02 ±0.04	13.82 ±1.05	11.52 ±0.01
20	15.23 ±0.023	12.68 ±0.00	12.05 ±0.00

KEY for table 8
All the values given under Depth 1, 2 and 3 are concentrations in micro-grams per gram (ppm).
Each sample was analysed in triplicate (n=3) and the recorded value is the average ±standard deviation.
Letter (a) is for the samples whereby an average of 12 replicate samples is recorded (n=12). Letter (b) implies that n=6. n=3 elsewhere.

TABLE 9 WEATHER DATA FOR NAIROBI BETWEEN JANUARY AND JUNE 1990

JANUARY 1990

DATE	RH	TEMP1.	TEMP2.	RFALL	SS
19	40.75	28.0	15.0	0.0	10.20
20	61.46	26.5	14.2	1.5	7.60
21	54.00	23.9	13.6	0.0	8.30
22	57.31	23.4	11.7	0.0	7.45
23	52.46	28.3	14.6	0.0	8.20
24	58.62	26.8	14.7	0.0	0.00
25	51.62	26.5	11.7	0.0	0.00
26	54.00	26.4	14.4	0.0	0.00
27	53.62	27.2	14.7	0.0	0.00
28	47.23	28.0	14.7	0.0	0.00
29	46.08	28.6	13.7	0.0	0.00
30	47.00	26.0	15.4	0.0	0.00
31	46.17	26.7	12.2	0.0	0.00

FEBRUARY 1990

DATE	RH	TEMP1.	TEMP2.	RFALL	SS
1	43.00	26.9	14.7	0.0	6.50
2	55.85	27.8	15.3	0.0	8.19
3	54.69	27.5	15.5	0.0	9.04
4	54.00	27.7	15.8	0.0	9.25
5	41.33	28.5	15.5	0.0	9.27
6	46.85	29.9	12.5	0.0	9.20
7	51.46	29.3	16.0	0.0	8.75
8	53.69	29.9	15.3	0.0	9.07
9	58.54	31.3	15.6	0.0	3.55
10	53.23	29.6	11.1	0.0	9.41
11	53.92	29.7	16.0	0.0	10.25
12	52.47	30.8	15.7	0.0	10.10
13	48.62	29.6	17.0	0.0	9.00
14	49.15	28.8	14.4	0.0	9.31
15	47.54	30.3	14.8	0.0	10.54
16	57.00	27.8	15.6	0.0	4.18
17	57.15	28.1	14.0	0.0	9.10
18	49.69	29.3	13.0	0.0	6.50
19	42.75	28.5	15.8	10.2	2.09
20	61.46	21.2	14.5	0.1	0.00
21	54.00	26.7	11.9	3.1	5.44
22	57.31	24.3	14.5	0.0	0.30
23	52.46	26.9	14.0	11.9	5.12
24	58.62	26.1	15.6	0.0	5.40
25	51.62	27.8	12.8	0.0	10.31
26	53.00	25.5	15.0	7.7	0.08
27	46.88	26.5	14.4	0.0	1.80
28	47.19	28.7	13.6	0.0	7.90
29	51.62	27.8	12.0	8.0	0.00

MARCH 1990

1	52.06	26.7	15.7	0.0	6.90
2	52.69	27.8	15.0	0.0	3.70
3	51.95	27.1	14.8	0.0	8.90
4	49.00	28.2	15.6	8.0	4.70
5	55.06	25.0	12.8	0.0	2.30
6	61.13	25.8	13.5	14.2	1.40
7	46.44	27.3	13.8	26.5	6.60
8	53.69	25.4	13.7	0.0	5.60
9	50.88	26.0	12.4	3.8	10.00
10	53.38	26.1	14.3	0.0	8.70
11	48.88	26.5	15.0	0.0	7.40
12	56.08	27.3	15.0	0.0	9.60
13	57.28	25.8	12.0	61.9	2.70
14	62.04	26.7	14.3	65.3	4.70
15	61.20	26.2	13.7	0.0	7.30
16	56.76	25.7	14.8	0.9	8.10
17	61.56	23.5	12.8	14.2	3.50
18	61.68	23.7	14.6	0.0	6.80

DATE	RH	TEMP1.	TEMP2.	RFALL	SS
19	60.07	25.5	14.5	1.2	9.10
20	61.52	25.1	13.8	10.9	4.50
21	56.04	27.0	14.4	0.0	6.70
22	56.96	26.5	15.5	5.9	8.20
23	63.72	24.9	15.3	0.0	0.00
24	60.28	24.8	14.5	0.0	5.10
25	53.84	25.6	16.0	0.0	9.60
26	53.72	27.3	16.1	0.0	8.80
27	54.48	0.0	15.8	0.0	8.10
28	53.96	27.8	0.0	0.7	7.80
29	58.12	27.4	15.7	0.0	9.30
30	62.96	24.5	16.0	0.0	1.10
31	60.68	24.4	13.8	0.8	6.90
APRIL 1990					
1	55.00	28.6	15.3	39.2	8.80
2	60.68	27.8	15.0	24.0	6.30
3	64.76	20.8	14.0	1.9	1.60
4	54.48	25.9	12.5	9.0	9.40
5	55.28	27.2	14.6	15.8	9.00
6	63.20	22.9	14.1	0.0	0.00
7	58.36	25.2	14.5	2.3	1.20
8	64.76	24.8	15.0	0.0	1.80
9	66.92	24.0	14.6	69.9	3.00
10	63.76	22.3	13.6	0.0	1.30
11	64.92	21.5	14.3	0.0	2.70
12	70.04	26.0	15.2	3.0	0.00
13	57.24	27.3	14.4	0.0	6.40
14	60.04	26.8	14.8	7.8	5.50
15	60.64	28.1	15.1	1.0	3.20
16	59.84	21.1	15.1	20.8	6.50
17	59.40	26.3	14.3	0.8	6.80
18	58.40	28.6	14.7	0.0	4.30
19	56.48	26.0	16.5	0.0	7.40
20	56.00	26.0	15.0	0.0	7.60
21	54.00	26.5	15.3	0.6	10.30
22	62.64	26.9	15.0	48.7	5.30
23	63.20	26.4	15.0	3.4	1.70
24	62.40	24.1	15.0	4.5	2.00
25	59.68	23.7	14.7	0.0	7.50
26	58.44	24.1	14.7	0.0	0.00
27	61.80	23.7	15.0	0.0	3.00
28	58.40	24.1	14.8	0.0	10.00
29	55.72	23.2	12.3	0.0	9.60
30	52.24	26.2	15.2	0.0	9.60
MAY 1990					
1	54.72	25.8	15.5	0.0	9.80
2	53.28	26.4	15.0	0.0	8.60
3	53.44	27.0	14.5	0.0	10.30
4	55.16	27.1	14.8	0.0	8.80

DATE	RH	TEMP1.	TEMP2.	RFALL	SS
5	52.92	21.3	15.5	0.0	9.50
6	52.36	28.2	3.0	0.0	10.90
7	43.54	29.0	15.7	0.0	9.50
8	58.68	25.6	17.0	0.2	7.10
9	63.00	26.0	14.4	89.1	3.70
10	58.28	27.6	14.5	0.0	7.70
11	58.84	27.6	14.5	0.0	7.00
12	58.92	26.0	13.9	7.1	4.00
13	62.48	23.7	14.9	6.0	5.00
14	61.8	25.1	14.7	14.4	4.10
15	55.16	23.9	13.8	0.0	6.40
16	64.64	26.8	13.4	0.0	6.50
17	67.64	24.6	11.7	0.0	8.00
18	68.56	25.7	12.5	0.5	9.60
19	74.00	26.6	14.4	0.0	8.70
20	79.20	24.4	14.0	0.0	4.00
21	81.88	23.8	14.2	1.9	0.90
22	76.12	24.5	13.7	40.0	4.00
23	79.08	23.6	14.0	0.0	2.70
24	75.08	24.2	13.8	1.2	2.80
25	74.72	0.0	13.5	13.6	7.00
26	79.96	0.0	14.3	6.2	3.20
27	75.84	23.8	13.0	0.0	4.40
28	83.68	23.3	13.2	1.0	2.70
29	73.70	30.0	13.0	0.0	4.50
30	73.40	23.2	13.2	0.0	6.30
31	65.12	0.0	11.7	0.0	4.80
JUNE 1990					
1	71.32	22.5	13.5	0.0	5.00
2	75.76	27.3	13.2	0.0	5.00
3	75.24	0.0	13.5	0.0	2.30
4	69.36	22.6	12.5	0.0	5.20
6	72.88	0.0	11.9	0.0	2.90
7	79.16	19.7	13.0	0.0	0.20
8	76.88	0.0	12.2	0.0	1.10
9	73.56	21.5	10.9	0.0	1.20
10	64.16	23.2	11.5	0.0	6.40
11	67.96	23.4	12.5	0.0	4.70
12	62.56	24.7	11.2	0.0	8.10
13	62.41	0.0	11.9	0.0	2.00
14	65.92	21.3	11.7	0.0	2.60
15	66.24	22.3	11.5	0.0	4.40
16	61.64	23.3	11.5	0.0	7.10
17	60.64	25.1	9.9	0.0	10.50
18	66.80	23.8	10.5	0.0	5.80
19	77.72	20.8	11.5	0.0	1.10
20	64.32	25.7	9.0	0.0	7.20
21	65.31	25.3	11.3	0.0	6.00
22	71.04	25.2	12.9	0.0	6.50
23	78.56	25.9	13.2	3.6	5.30
24	73.40	23.8	11.2	0.0	8.50

DATE	RH	TEMP1.	TEMP2.	RFALL	SS
25	69.60	22.9	12.0	0.0	6.70
26	56.28	25.0	6.5	0.0	9.60
27	58.36	27.1	7.8	0.0	9.60
28	72.88	25.5	8.7	0.0	5.30
29	65.80	28.0	11.8	0.0	6.50
30	75.48	26.5	13.5	17.3	6.50

KEY:
RH = Relative Humidity (%)
TEMP.1 = Temperature Maximum (°C)
TEMP.2 = Temperature Minimum (°C)
RFALL = Rainfall (mm)
SS = Sunshine (Hours)

A hand sprayer was used for spraying the garden, ensuring maximum possible uniformity in the distribution of the fungicide on the plot. Before spraying, the level of copper in the whole garden for the surface soil was found to be 6.44 ppm. Immediately after spraying, several soil samples were taken from the surface. These samples showed a wide range of concentrations of copper (between 27.35 ppm and 87.89, for section A (average 40.93 ppm); 35.89 ppm and 86.89 ppm for section B, (average 61.39 ppm). The copper concentration found for the unsprayed section C was 7.19 ppm, which was slightly higher than the level found before the spraying had been done. The level being higher for the unsprayed area was a clear indication that some spray had found way to that section, mostly due to being blown by the wind.

During the first few days after starting the garden, the climate was quite dry and it had not rained for several weeks previously. As such, the

areas where potatoes had been planted (B & C) were watered daily until the rains started.

For area A, the results in table 8 show that the copper concentration at the surface was decreasing slowly though not uniformly. Within the first twenty one weeks, the copper level in this area fell from 40.93 ppm to 21.57 ppm. The minimum concentration (about 23 ppm) was attained after eight weeks and this value tended to remain constant. Thus there was no significant change in surface copper concentration for area A within the final twelve weeks. The graph in fig. 4.27 was drawn to show the trend of concentration versus time in area A.

It would have been expected that, after the rains started, leaching took place and as such the concentration in the soils from a deeper horizon would increase. This was actually the case within the first three weeks where the levels increased from 8.34 ppm to 15.89 ppm at 5.0 to 10.0cm depth. However, from the fourth week onwards, the level of copper within the depth of 5 cm to 10 cm tended to remain constant. The graph in fig. 4.28 was drawn to show the trend in concentration for depth 5 cm to 10 cm with time in area A. For leaching to take place, the element has to be in solution form. Thus any free copper ions on the surface were expected to dissolve during rains and

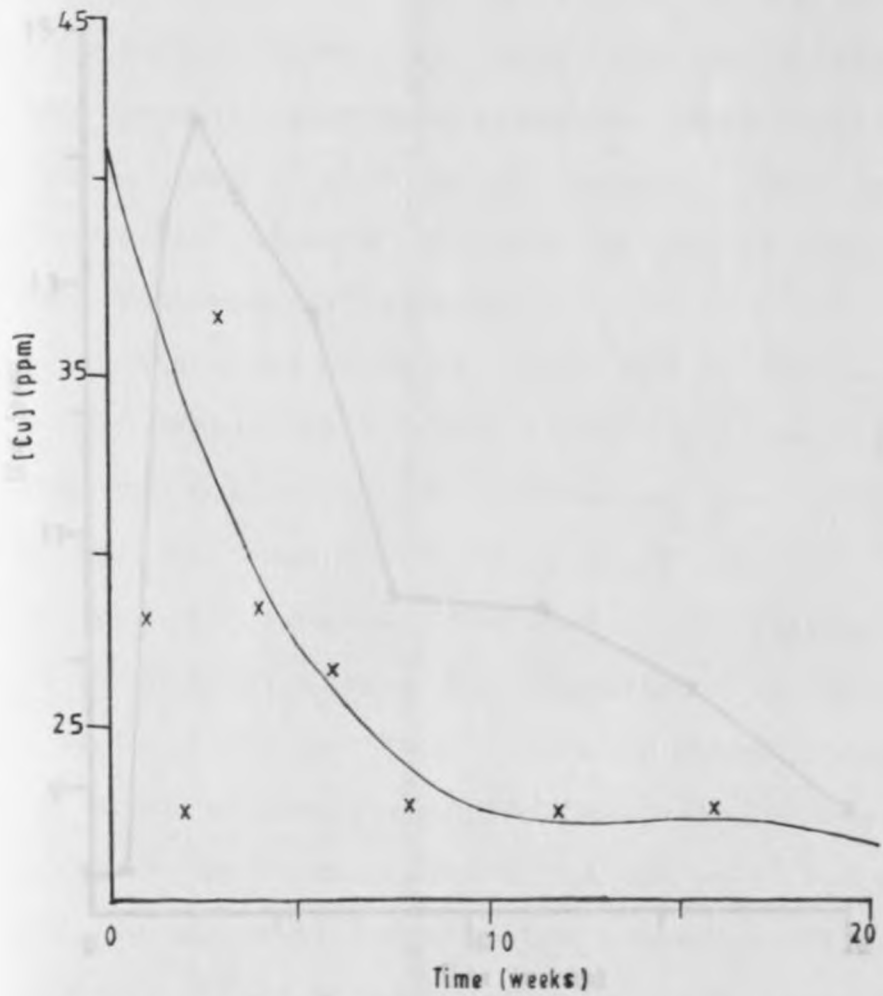


Fig. 4.27 : [Cu] (ppm) versus time(weeks) for area A 0 to 5 cm depth.

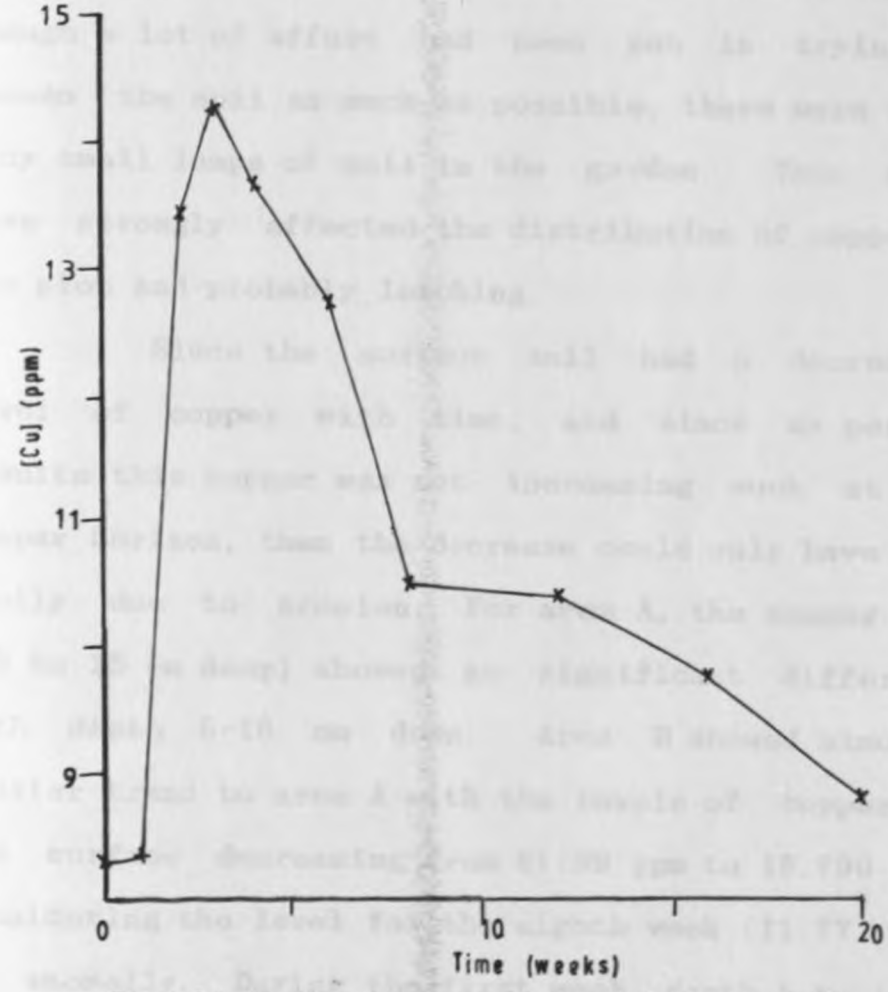


Fig. 4.28 : [Cu] (ppm) versus time(weeks) for area A
5 to 10 cm depth.

be leached in the soil. However, the soil in question was not free from organic matter or any other complexing agents and as such copper could have got bound at the surface and fail to leach. But still, some could still find way to deeper horizons. The soil texture is a factor that can affect the leaching of elements. For instance , it would be difficult for solutions to get inside a rock. The plot in question was cultivated on a virgin ground that had not been tilled previously to the knowledge of the writer. Though a lot of effort had been put in trying to loosen the soil as much as possible, there were still many small lumps of soil in the garden. This might have strongly affected the distribution of copper in the plot and probably leaching.

Since the surface soil had a decreasing level of copper with time, and since as per the results this copper was not increasing much at the deeper horizon, then the decrease could only have been mostly due to erosion. For area A, the deeper soil (10 to 15 cm deep) showed no significant difference with depth 5-10 cm down. Area B showed almost a similar trend to area A with the levels of copper in the surface decreasing from 61.39 ppm to 15.798 ppm; considering the level for the eighth week (11.77 ppm) an anomally. During the first week, depth 5 to 10 cm down showed quite a high level of copper, 27.39 ppm.

Since this area had been watered on a daily basis, including the day copper was sprayed, much copper might have leached down even before getting bound by the surface materials. The watering was done using a hose pipe of a half inch (1.27 cm) diameter, and if droplets fell on a loose ground, they could penetrate far down thus taking much of the surface constituents deeper.

In the area B, leaching seems to have played a bigger role than in area A since the concentration of copper showed an increase at the deeper horizons within the last three weeks. Figs. 4.29 and 4.30 show the trends in this area. The unsprayed area (C) had copper levels which were relatively low and constant throughout the period. The levels ranged between 7.19 ppm and 15.23 ppm. The high concentrations towards the final weeks might be due to deposition of copper from the sprayed areas during runoff. Also, the fungicide Triadimefon {1-[4-chlorophenoxy]-3,3-dimethyl-[1H-1,2,4-triazol-1-yl]-2-butanone}[100] trade name (Bayleton) that was used to prevent leaf bright in the potatoes might have had some copper which would also raise the levels. This was later found to be the case when the fungicide was analysed and found to have 156 ppm copper. Figs. 4.31 and fig. 4.32 show the variation in copper concentration with time for area C.

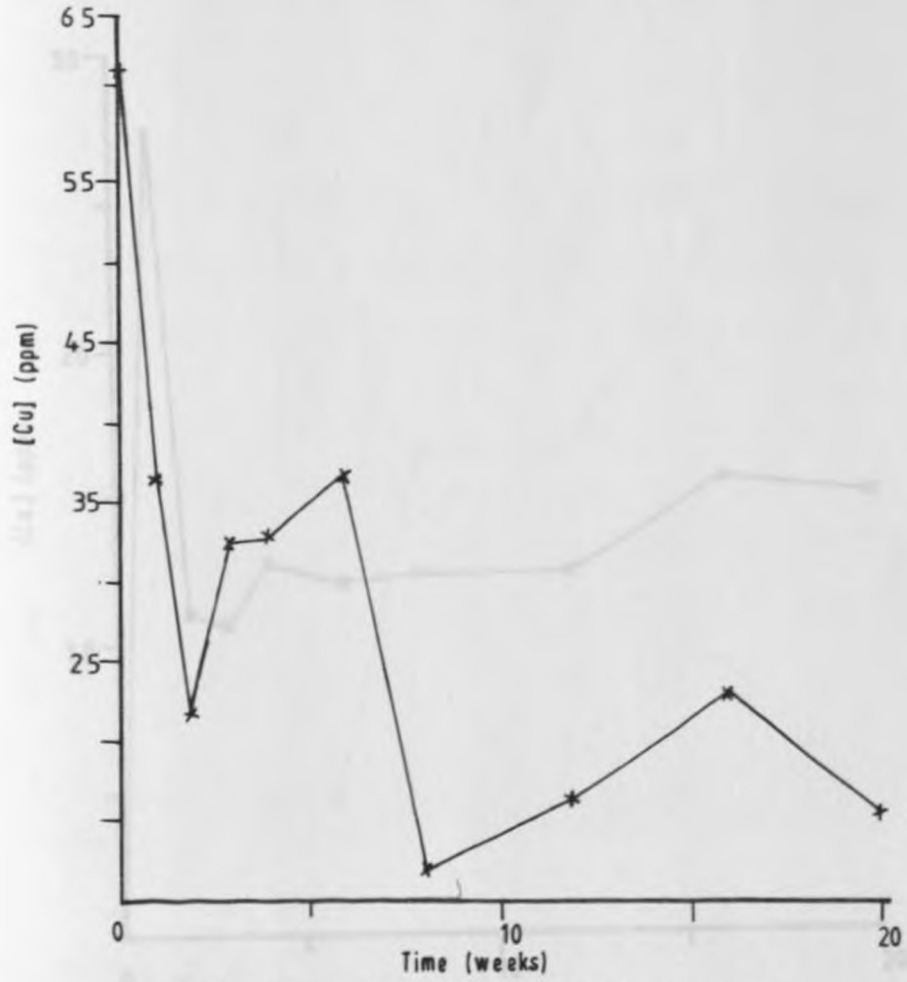


Fig 4:29: [Cu] (ppm) versus (weeks) for area B
0 to 5 cm depth.

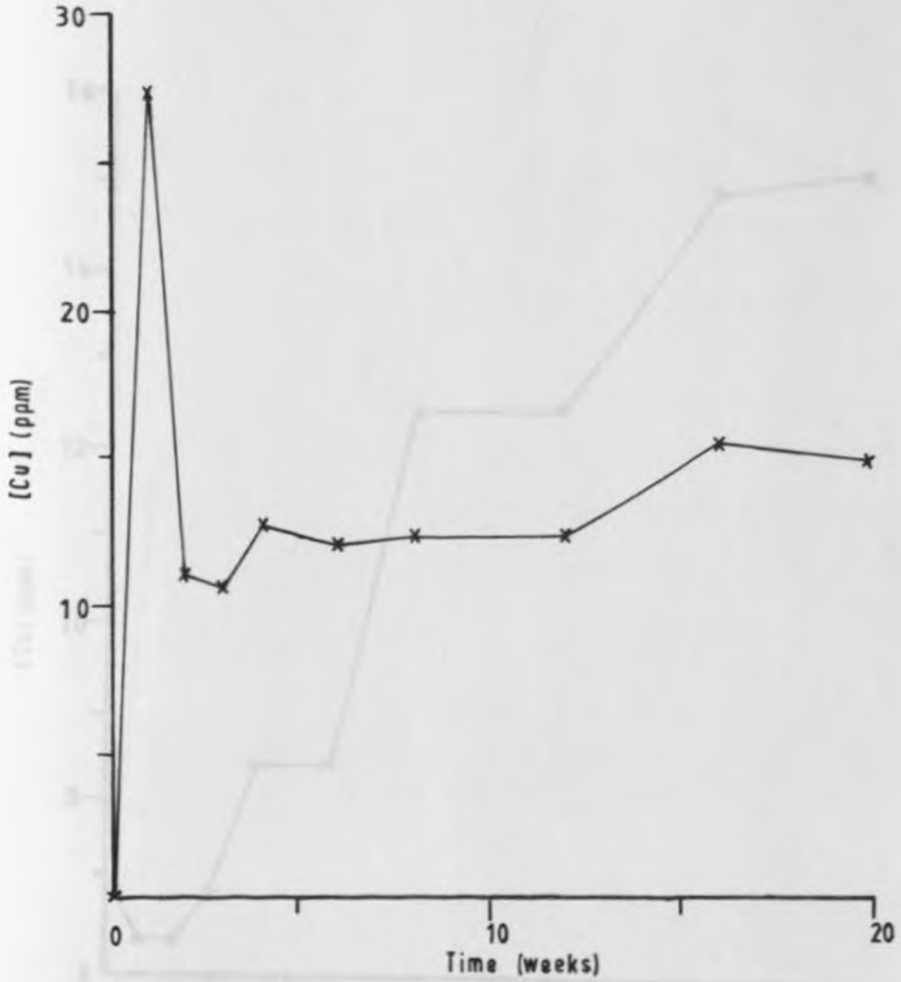


Fig. 4.30: [Cu](ppm) versus time(weeks) for area B 5 to 10cm depth.

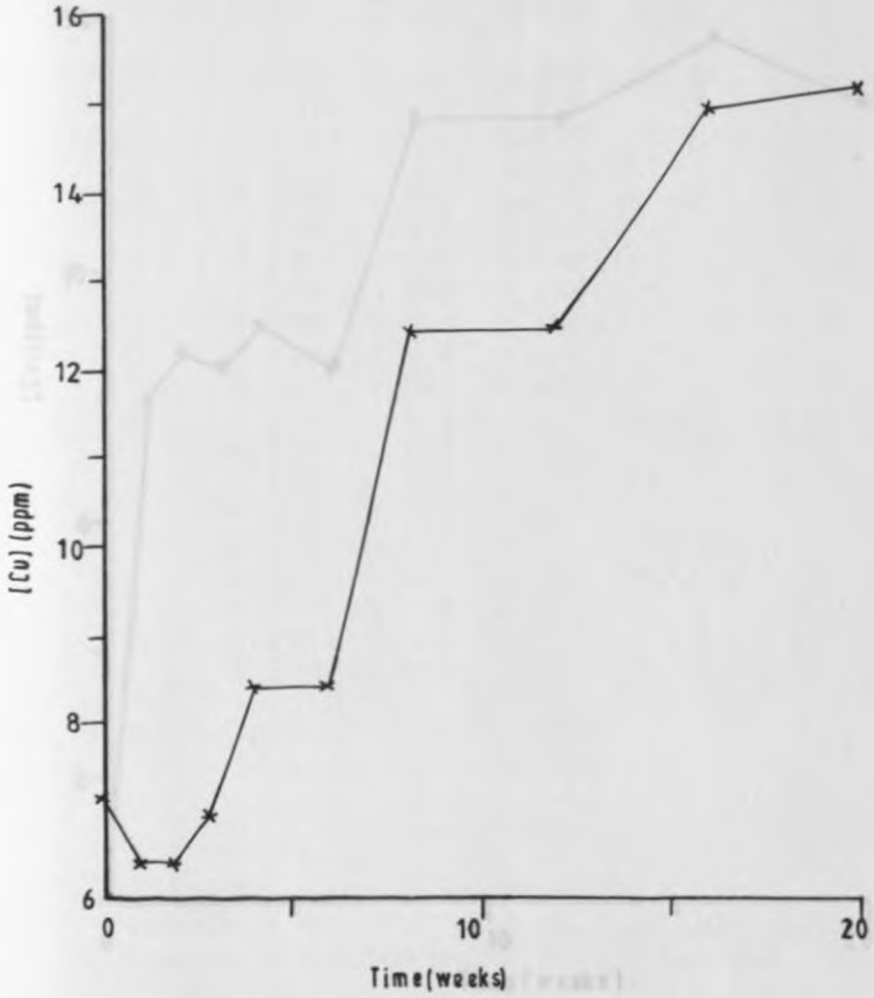


Fig. 4.31 : [Cu] (ppm) versus time (weeks) for area C 0-5cm depth

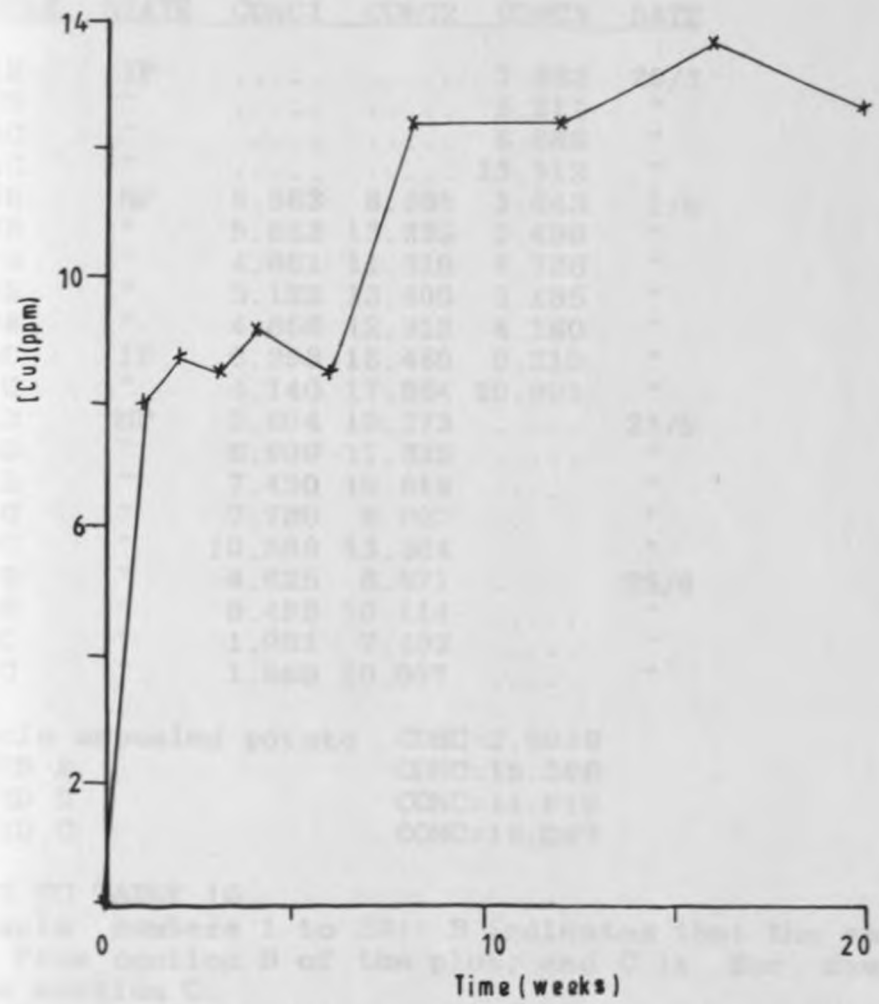


Fig. 4.32: [Cu] (ppm) versus time weeks for area C 5 to 10cm depth.

4.6 POTATOES

The potatoes planted in areas B and C on second February 1990 were also analysed, and the results are as shown in table 10 below.

TABLE 10 Concentration (micrograms per gram) of copper in potato tissues.

SAMPLE	STATE	CONC1	CONC2	CONC3	DATE
1B	IP	.....	.....	7.292	29/3
2B	"	.....	.....	5.211	"
3C	"	.....	.....	6.689	"
4C	"	.....	.....	13.312	"
5B	MP	5.683	6.695	1.643	1/5
6B	"	5.683	13.235	3.498	"
7B	"	4.661	11.810	4.726	"
8B	"	3.122	13.400	2.185	"
9B	"	4.656	12.813	4.160	"
10C	IP	8.253	16.480	9.310	"
11C	"	4.140	17.864	10.901	"
12B	MP	2.604	10.273	.....	23/5
13B	"	6.909	11.335	.....	"
14B	"	7.430	10.819	.....	"
15C	"	7.780	6.020	.....	"
16C	"	10.889	13.304	.....	"
17B	"	4.625	6.871	.....	25/6
18B	"	9.488	10.114	.....	"
19C	"	1.991	7.403	.....	"
20C	"	1.989	10.077	.....	"

Whole unpeeled potato	CONC=2.6039
WEED A	CONC=15.386
WEED B	CONC=14.818
WEED C	CONC=19.097

KEY TO TABLE 10

Sample numbers 1 to 20:- B indicates that the sample was from section B of the plot, and C is for samples from section C.

STATES:- IP represents immature plant (the potato leaves were green during harvest time); MP implies the potato plant was mature for harvesting (the leaves were dried out).

CONC1 represents concentration in peeled potato

CONC2 represents concentration in potato peels

CONC3 represents concentration in potato leaves.

DATE represents the time at which the plant was

Potatoes were planted in two sections of the garden, B and C. Potatoes planted in Section C were meant to be controls i.e. the soil surface had not been sprayed with copper oxychloride.

After 4 weeks, the potato leaves emerged from the ground. When most of the plants had branches of about 8 cm long, the potatoes were sprayed with Bayleton (Triadimefon $C_{14}H_{16}N_3O_2$) fungicide to prevent bacterial bright. The LD50 = 363 $mgKg^{-1}$ for the fungicide in female plants. Its water solubility is 260 mgl^{-1} [101]

4.6.1 Leaves

Green leaves sampled two months after planting gave an average of 6.25 ppm for the area B (sprayed) and an average of 10.00 ppm Cu in area C (unsprayed). The plants in area B had grown faster and were healthier than those in area C. The leaves in area B had started yellowing, a condition that signifies maturity of the potato. At such a stage of development, the leaves stop being physiologically active and it has been established that levels of metal ions are low during such a stage[102]. The leaves from area C were very green, at a stage where physiological activity is optimum and levels of metal ions high. Two months later, most of the plants had their branches dried out due to maturity of the potatoes. The dried up branches sampled had copper

concentrations ranging between 1.64 ppm and 4.73 ppm. It was expected that higher concentrations of copper would be obtained in plants from the area that had been sprayed i.e. area B. However, that was not found to be the case. Some plants in area C had higher copper levels in the leaves than those from area B. This could have been due to the state of maturity at which the leaves were sampled as explained above. Another possibility could be that copper concentration in potato leaves is independent of how much the soil contains. This possibility can be supported by the fact that the copper content in plant shoots does not exceed a certain threshold value, though there is a pattern of relationship between copper in the soil nutrient solution and copper in the plant tissues[102].

The concentration of copper in green leaves was generally far much higher than that in dried out leaves. This was in agreement with the above phenomenon of physiological activity. For the green leaves, the lowest copper concentration was 5.21 ppm whereas the highest copper concentration for mature leaves was 4.73 ppm. Efforts to try and find out where the copper goes after the plant has dried were fruitless, and as such further investigation is called for here.

4.6.2 Potato Tubers

The tubers were first peeled (1 mm peel) and the peeled tuber analysed separately from the peels. In general, the concentrations of copper in these plant parts were non-dependent upon the area from which the plant was harvested (sprayed or unsprayed). For the peeled potatoes, those which were mature (ready for harvest) had copper concentrations ranging between 1.99 ppm to 10.89 ppm. Those plants that were harvested before maturity ranged between 4.14 to 8.25 ppm Cu. The peels had far much higher copper concentration than the inner peeled potato. They ranged between 6.02 ppm and 13.40 ppm for the mature plants; and between 16.45 ppm to 17.86 ppm for the immature plants.

As had been the case for the leaves, the immature plants had higher copper levels in tubers than the mature plants. According to these results, most copper is concentrated on the peels. As such, it may pose no danger for human to eat potatoes harvested from an area with high levels of soil copper, since the peels are thrown away and only the inner bit is eaten. However, it may be a danger to other domestic animals, e.g. cows which end up being given the peels as a part of roughage. One tuber was analysed whole (i.e. without peeling) and was found to have 2.60 ppm copper.

Also analysed was a weed (datura species) for the purpose of checking whether there could be a difference between the sprayed area and the unsprayed area. The weeds from the sprayed area had 15.39 ppm copper and 14.82 ppm Cu. The weed from the unsprayed area had 19.10 ppm Cu. It was expected that the weeds from the sprayed area should have had more copper than those from the unsprayed area. In all cases only one breed of weed was sampled and at the same stage of growth. The number of weed samples analysed were not enough for any conclete conclusion to be made here.

4.7 WATER SAMPLES

The water samples that were analysed gave the results shown in tables 11 and 12 below. During the sampling session, the pH of a small quantity of sample from each site was not adjusted in the field. The pH values recorded below are for such samples.

TABLE 11 Rutui river water samples

SAMPLE	DEPTH	pH	CONC
W11	A	5.42	9.375
W12	A	5.55	4.074
W13	C	5.46	4.074
W21	A	7.09	4.074
W22	B	7.11	4.174
W23	C	7.12	18.750
W31	A	7.19	20.000

SAMPLE	DEPTH	pH	CONC
W32	B	7.11	8.148
W33	C	6.79	8.148
W41	A	7.08	nd
W42	B	4.99	4.074
W43	C	7.20	4.074
W44	A	7.31	4.074

TABLE 12 Ruiru river water samples

SAMPLE	DEPTH	pH	CONC
W1i	A	6.77	6.250
W1ii	A	7.06	4.074
W2i	A	6.25	6.830
W2ii	B	7.26	nd
W3i	A	7.35	nd
W3ii	A	7.40	6.250
W3iii	B	7.33	4.074
W4i	A	7.19	8.148
W4ii	A	7.28	4.074
W4iii	C	7.41	nd

KEY TO TABLE 11 AND TABLE 12:

CONC represents concentration in parts per billion (ppb).

DEPTH A represents the surface of the river; B represents the middle of the river (about 1 metre

depth); C represents the river bed.

nd implies not detected.

Generally, the concentration of copper in the river water samples was low, ranging between 4.074 ppb and 20.0 ppb. The pH of the water samples immediately after collection ranged between 4.99 and 8.15.

For Rutui River, samples taken from the source had the lowest concentration of copper (W11-W13). However, the difference in concentration with distance downstream from the source was quite negligible. The highest copper concentration (20 ppb) was detected in a sample collected at a low river speed region. This site was next to the drainage of a coffee factory called Rutui Coffee Factory. In the same site, samples collected at the middle depth and near the river bed had a low level of copper. According to the results, the level of copper increased downstream even though at a small rate. It was expected that the increase in concentration with distance downstream would be quite large. This would be the case due to the fact that coffee farms are situated in areas downstream. Also the river drains coffee factory waste which is expected to have a substantial amount of copper from washing of the beans. However, according to the results, the increase of copper concentration downstream is very

small and does not reflect the expectation above. For copper from the farms to reach the rivers, there has to be erosion taking place. Most of the farms along the river slope towards the river. As such, the eroded materials during runoff end up in the river.

When there is runoff, the volume of water in the rivers is usually very large and a lot of dilution of the dissolved materials takes place. During this time, the river also moves at a higher speed than usual, thus giving little room for deposition of materials. Thus elements existing or imported by rain from the farms are swept away to lakes or oceans. This could be the only best explanation as to why the copper levels were quite low in the river water.

No purification was done to the water samples prior to analysis. Whole samples (water and all particles trapped in it) were acid digested and analysed. Thus the results reflect the total copper content of the water. Usually, the people who use river water just use it the way they tap it from the river (without any treatment) either for feeding livestock or for domestic purpose. Subjecting the water to any purification prior to analysis would thus not be a good indicator of what is contained in the water that people use.

These results show that the copper level has not reached the toxic limit for domestic purposes.

4.8 SEDIMENTS

Tables 13 and 14 show the concentrations of copper in sediments collected along the rivers.

TABLE 13

SEDIMENT SAMPLES COLLECTED ALONG RUTUI RIVER

DIST	0.00	0.00	0.01	3.00	3.00
CONC	9.58	9.58	27.22	41.94	40.67
STDE	0.00	0.00	0.00	0.04	0.00

DIST	3.00	6.00	6.00	6.00
CONC	37.85	23.03	25.46	35.63
STDE	0.01	0.58	0.01	0.00

KEY:
DIST=Distance from the source of the river in kilometres;
CONC=Concentration of copper in parts per million (ppm);
STDE=Standard Deviation (n=3 in each case).

TABLE 14
SEDIMENT SAMPLES COLLECTED ALONG RUIRU RIVER

DIS	0.00	1.00	3.00	3.40	6.00	6.40	10.00
CON	6.75	10.47	9.64	19.49	20.98	17.57	14.41
SDE	0.00	0.01	0.54	0.04	0.64	0.29	0.02

KEY:
DIS=Distance downstream from Ruiru Dam in kilometres;
CON=Concentration OF copper (ppm);
SDE=Standard Deviation (n=3 in each case).

According to the results, there is an increase in concentration of copper with distance

though some samples far downstream had lower copper levels than some samples upstream. The highest copper level in sediments was 41.94 ppm. The sample having this was taken from a coffee factory drain near the river and as such a high value was expected. The lowest level of copper of Rutui River sediments was 9.58 ppm. This sample was obtained from the source of the river. Most samples averaged around 28 ppm of copper. For Ruiru River, the sediment from the dam (source) had the lowest copper level (6.75 ppm).

4.9 ACCURACY AND PRECISION

Accuracy and precision are two important factors in any analytical work. The accuracy of an analysis refers to its correctness and is determined by the absolute error involved, 'absolute error' being the difference between the observed value and the accepted value. Precision refers to the reproducibility of an analytical result. The measures of precision are the 'mean deviation',the relative mean deviation', and the 'coefficient of variation (relative standard deviation)', which can be computed statistically[103].

The reliability and quality (accuracy), of the results obtained and the procedure used in this thesis was checked by analysis of certified materials. The certified reference materials distributed by International Atomic Energy Agency (IAEA) were

analysed using the same procedure as for the samples. The copper concentration obtained for Lake sediment Sl-1/1979 was 26.4±0.9 ppm ($mgKg^{-1}$). This value is not far from the mean IAEA value 30.0±5.6 $mgKg^{-1}$ [104]. The literature value is given as 28 ppm[105]. The concentration obtained for soil-5 was 81.7±8.5 ppm Cu, which also was not very different from the IAEA value 77.1±4.7 $mgKg^{-1}$ [106].

These reference materials were each analysed in triplicate, taking 0.25 g portions.
Standard Deviation was used as the measure of precision in this thesis. The formula used to find the Standard Deviation was

$$SDE=\{[\text{sum of } d^2]/(n-1)\}^{1/2}$$ [107].

Where d = deviation of a value from the mean

n = number of values averaged

4.10 Some World limits for copper

According to the Codex Alimentarius Commission[108], the maximum acceptable load for man is 0.5 $mgKg^{-1}$, body weight. In Kenya Subsidiary Legislation, (1978), the exemption limit cited for marine freshwater animal products is 100 $mgKg^{-1}$ of copper. Austrarian, National Health and Medical Research Council (NHMRC) has recommended a value of 10

$mgKg^{-1}$ for foodstuffs in general. According to WHO[109], a daily copper intake rate of 2.1 mg is adequate for adults.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

Pesticides are used in order to boost food production, by destroying the pest or the pathogen. Their toxicity can however be exerted in unwanted directions, thus affecting the user, the consumer and the ecosystem in which the pesticides are used. Strict adherance to precautions by the user to is highly called for, inorder to reduce the dangers associated with pesticide toxicity.

Copper based fungicides are mostly used against coffee diseases such as leave rust, coffee berry disease etc. The fungicides are applied on the surface of the coffee leaves and berries. In the process of application, the fungicides can spread in the surrounding environments, such as on the soil surface and on food crops growing near the area of application.

There are several analytical techniques that can be used to monitor the levels of pesticides in the environment. For copper, Atomic Absorption spectrometry is a good technique since it is simple, quick, cheap, accurate and precise. The accuracy of the method has been demonstrated in this study by the fact that certified materials anaysed showed results within the limits approved for those materials by the

International Atomic Energy Agency (IAEA). This has also proved the procedure used for sample preperation reliable.

The copper level found in river water was below the maximum allowable limits by the world health organization. Copper is expected to find its way from the coffee farms to the rivers through soil erosion. During such a time, the volume of water is usually large and at a high speed, and hence much of the copper that finds way to the river is carried far downstream. Thus the copper has little chance of accumulating in the river water. This could be the reason behind river water having a low copper concentration.

In the coffee farms studied, the concentration of copper ranged widely. Farms that are well mananged had a higher copper content than those which were poorly mananged. Flat sections of the coffee farms had a higher copper content than sloping sections. The sloping sections are more prone to soil erosion than the flat sections, thus copper is expected to accummulate mostly on the flat sections. The concentration of copper was higher for the top soils than for the sub soils. This is expected because the soil surface is the direct recipient of the fungicides during application. The top soil copper content was found to be proportional to the sub soil copper

content, implying that the copper in the sub soil is part of the top soil copper that has leached depthwise. Soils in sections near the river banks have a lower copper content than those in sections far away from the river banks. Materials deposited in such sections are carried away by the river when it overflows, hence reducing their levels. Sediments have a lower copper level than the soils. The most likely reason is that the river water dissolves the copper on the sediment and washes it away.

The total copper content in the soil was found to be proportional to plant available copper content. This could mean that bound copper (unavailable to plants) gets unbound according to the content in the soil. Binding of the unbound copper cannot be a good explantion here since the binding depends on the availability of complexing materials in the soil. Total copper being proportional to available copper is a usefull factor in that a person willing to compare any parameter with copper content in the soil can use either of the two (total copper or available copper).

The highest copper concentration was found in soils around dead coffee plants. The high copper level around such plants could have been the cause to the death of the plants, either due to intoxication or due to causing impaired intake of other nutrients. A more

convincing conclusion could be drawn here if the dead plants were available for analysis.

Coffee leaves have a higher copper level than the other tissues analysed in the present study. The coffee bean had a very low copper concentration.

In the potato, the stem and leaves were found to have higher copper concentration than the tubers. For the potato tubers, the peels had a higher copper concentration than the peeled potato tubers. The peeled tuber is the part used as food and its having very low copper levels proves it fit for human consumption in terms of copper.

5.2 RECOMMENDATIONS

1) Pesticide levels in the environment (animal tissues, foodstffs, plants, water, air, etc) should be continously monitored.

2) Environmentally benign methods of pest control (eg use of predators, etc.) should be encouraged.

3) Use of disease resistant breeds (eg Ruiru-11 coffee breed which is resistant to coffee berry disease) should be encouraged. Reseach on other disease resistant breeds needs be carried out.

4) Soils from all agricultural areas should be analysed for all elements that have an impact to plant growth and human health.

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A P P E N D I X

Appendix 1

i. The weight (Wt g), volume (V ml), absorbance (ABS) and concentration (conc ppm) for Rutui River samples The concentration was calcurated using the formula: Conc=(((ABS - Y-intercept)/gradient)XVolume/weight).

Row	WT	Vf	ABS1	CONC
1	2.5004	250	1.4E-2	33.664
2	2.5011	250	1.4E-2	33.654
3	2.5004	250	1.4E-2	33.664
4	0.2541	20	2E-2	39.14
5	0.2506	20	2E-2	39.687
6	0.2515	20	2E-2	39.545
7	2.5017	250	1.5E-2	36.321
8	2.4999	250	1.5E-2	36.347
9	2.503	250	1.5E-2	36.302
10	2.5004	250	5E-3	9.5796
11	2.5	250	5E-3	9.5811
12	2.4998	250	5E-3	9.5819
13	2.5003	250	5E-3	9.58
14	2.5008	250	5E-3	9.5781
15	2.5006	250	5E-3	9.5788
16	2.6011	250	1.2E-2	27.216
17	2.6005	250	1.2E-2	27.222
18	2.6007	250	1.2E-2	27.22
19	0.2514	20	1.6E-2	31.044
20	0.252	20	1.6E-2	30.97
21	0.2511	20	1.6E-2	31.081
22	0.2519	20	5.4E-2	111.73
23	0.253	20	5.4E-2	111.25
24	0.2526	20	5.4E-2	111.42
25	0.2501	20	2E-2	39.766
26	0.2502	20	2E-2	39.75
27	0.25	20	2E-2	39.782
28	0.2504	20	1.9E-2	37.581
29	0.2504	20	1.9E-2	37.581
30	0.2502	20	1.9E-2	37.611
31	0.2496	20	2.1E-2	41.991
32	0.2501	20	2.1E-2	41.907
33	0.25	20	2.1E-2	41.923
34	0.2498	20	1.6E-2	31.243
35	0.2515	20	1.6E-2	31.031
36	0.2502	20	1.6E-2	31.193
37	0.2503	20	1.4E-2	26.903
38	0.2519	20	1.4E-2	26.732

COPPER ANALYSIS B

Row	Wt2	Vf2	ABS2	CONC
1	0.4981	40	1E-2	9.3873
2	0.503	40	1E-2	9.2959
3	0.5025	41	1E-2	9.5378
4	0.5013	44	1E-2	10.26
5	0.5025	40	1E-2	9.3051
6	0.5	40	1E-2	9.3517
7	0.2509	20	1.6E-2	19.519
8	0.2519	20	1.6E-2	19.441
9	0.251	20	1.6E-2	19.511
10	0.4979	42	1.6E-2	20.655
11	0.5002	42	1.6E-2	20.56
12	0.5025	41	1.7E-2	21.719
13	0.4994	40	1.5E-2	17.904
14	0.4993	43	1.4E-2	17.414
15	0.4996	43	1.4E-2	17.404
16	0.4987	41	1.8E-2	23.638
17	0.501	46	1.6E-2	22.482
18	0.5007	40	1.8E-2	22.969
19	0.2507	20	1.3E-2	14.43
20	0.2513	20	1.3E-2	14.396
21	0.2511	20	1.3E-2	14.407
22	0.2493	20	1.9E-2	24.777
23	0.2516	20	1.9E-2	24.551
24	0.25	20	1.9E-2	24.708
25	0.2509	20	1.4E-2	16.119
26	0.2509	20	1.4E-2	16.119
27	0.2507	20	1.4E-2	16.131
28	0.2508	20	1.4E-2	16.125
29	0.2501	20	1.4E-2	16.17
30	0.251	20	1.4E-2	16.112
31	0.25	60	9.4E-2	458.02
32	0.2529	60	9.4E-2	452.77
33	0.2503	60	9.4E-2	457.48
34	0.2507	20	9.9E-2	160.76
35	0.2508	20	9.9E-2	160.69
36	0.2508	20	9.9E-2	160.69
37	0.251	80	8.2E-2	526.69
38	0.2509	80	8.2E-2	526.9
39	0.251	80	8.2E-2	526.69
40	0.2497	60	5.8E-2	274.08
41	0.2526	60	5.8E-2	270.93
42	0.2501	60	5.8E-2	273.64
43	0.2491	20	1.9E-2	24.797
44	0.2497	20	1.9E-2	24.737
45	0.2497	20	1.9E-2	24.737

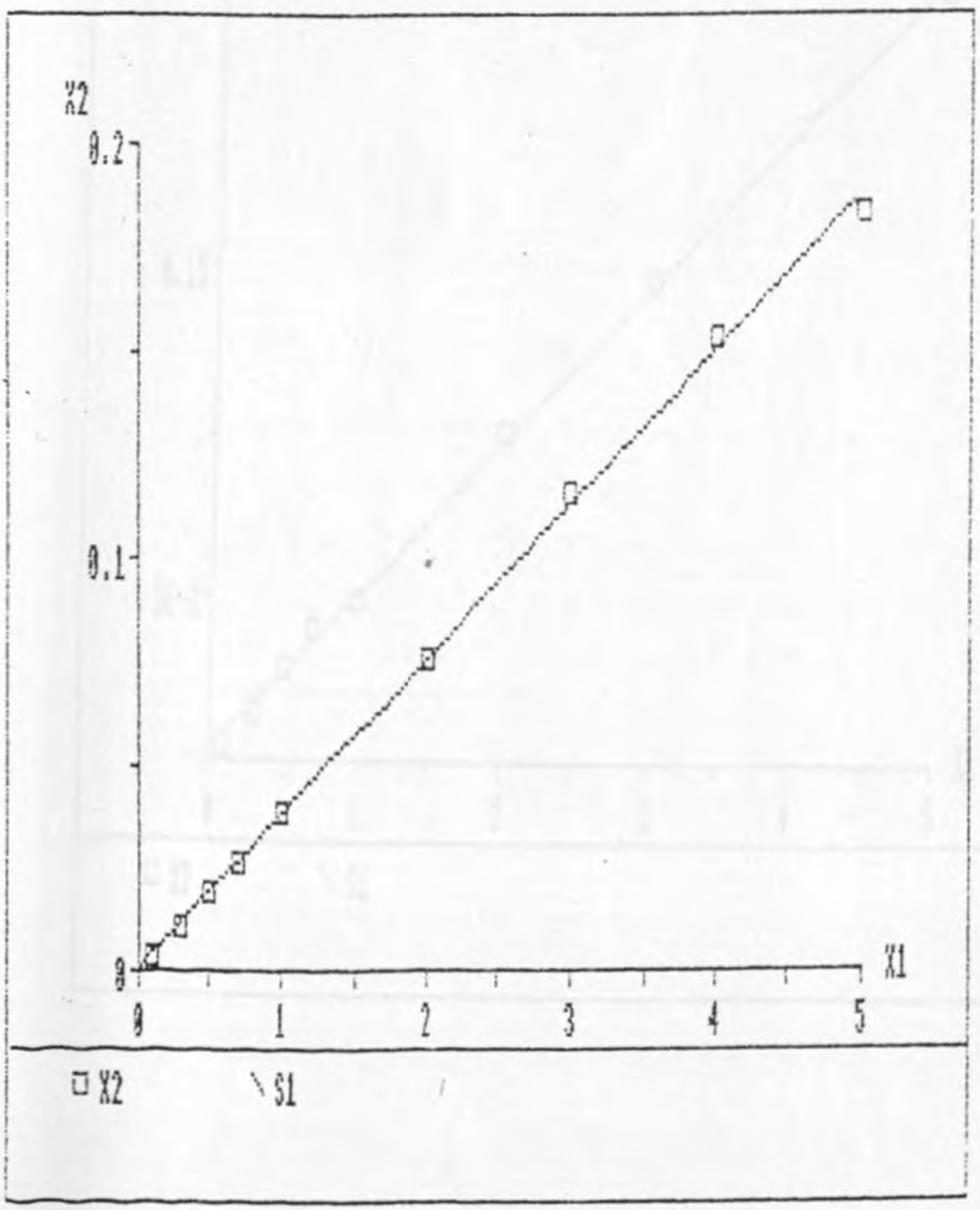
:
COPPER ANALYSIS C
:

Row	Wt3	Vf3	ABS3	CONC3
1	0.5011	40	1.7E-2	28.421
2	0.5017	40	1.7E-2	28.387
3	0.5012	40	1.7E-2	28.415
4	0.5003	40	2E-2	33.593
5	0.501	40	2E-2	33.546
6	0.5005	40	2E-2	33.58
7	0.5002	40	1.5E-2	25.053
8	0.4999	40	1.5E-2	25.068
9	0.4998	40	1.5E-2	25.073
10	0.5007	40	1.1E-2	18.198
11	0.5008	40	1.1E-2	18.194
12	0.5	40	1.1E-2	18.223
13	0.5014	40	2.6E-2	43.751
14	0.502	40	2.6E-2	43.699
15	0.501	40	2.6E-2	43.786
16	0.5006	40	2.6E-2	43.821
17	0.5011	40	2.6E-2	43.777
18	0.5013	40	2.6E-2	43.76
19	0.501	40	2.2E-2	36.959
20	0.501	40	2.2E-2	36.959
21	0.5008	40	2.2E-2	36.974
22	0.4996	40	0.14	239.01
23	0.5	40	0.14	238.82
24	0.4999	40	0.14	238.86
25	0.4999	40	3.5E-2	59.275
26	0.5002	40	3.5E-2	59.24
27	0.5007	40	3.5E-2	59.181
28	0.5004	40	3.5E-2	59.216
29	0.4991	40	3.5E-2	59.37
30	0.5	40	3.5E-2	59.264
31	0.5002	40	2E-2	33.6
32	0.4999	40	2E-2	33.62
33	0.5	40	2E-2	33.613
34	0.4998	40	1.6E-2	26.784
35	0.4999	40	1.6E-2	26.779
36	0.5	40	1.6E-2	26.773
37	0.2508	20	8E-3	13.051
38	0.2503	20	8E-3	13.077
39	0.2511	20	8E-3	13.036
40	0.2503	20	1.1E-2	18.201
41	0.2504	20	1.1E-2	18.194
42	0.25	20	1.1E-2	18.223
43	0.2493	20	9E-3	14.845
44	0.2507	20	9E-3	14.762
45	0.2502	20	9E-3	14.791
46	0.2506	20	6E-3	9.6498
47	0.2495	20	6E-3	9.6923
48	0.2499	20	6E-3	9.6768
49	0.2497	20	9E-3	14.821
50	0.2499	20	9E-3	14.809
51	0.2502	20	9E-3	14.791
52	0.2493	20	4E-3	6.2705

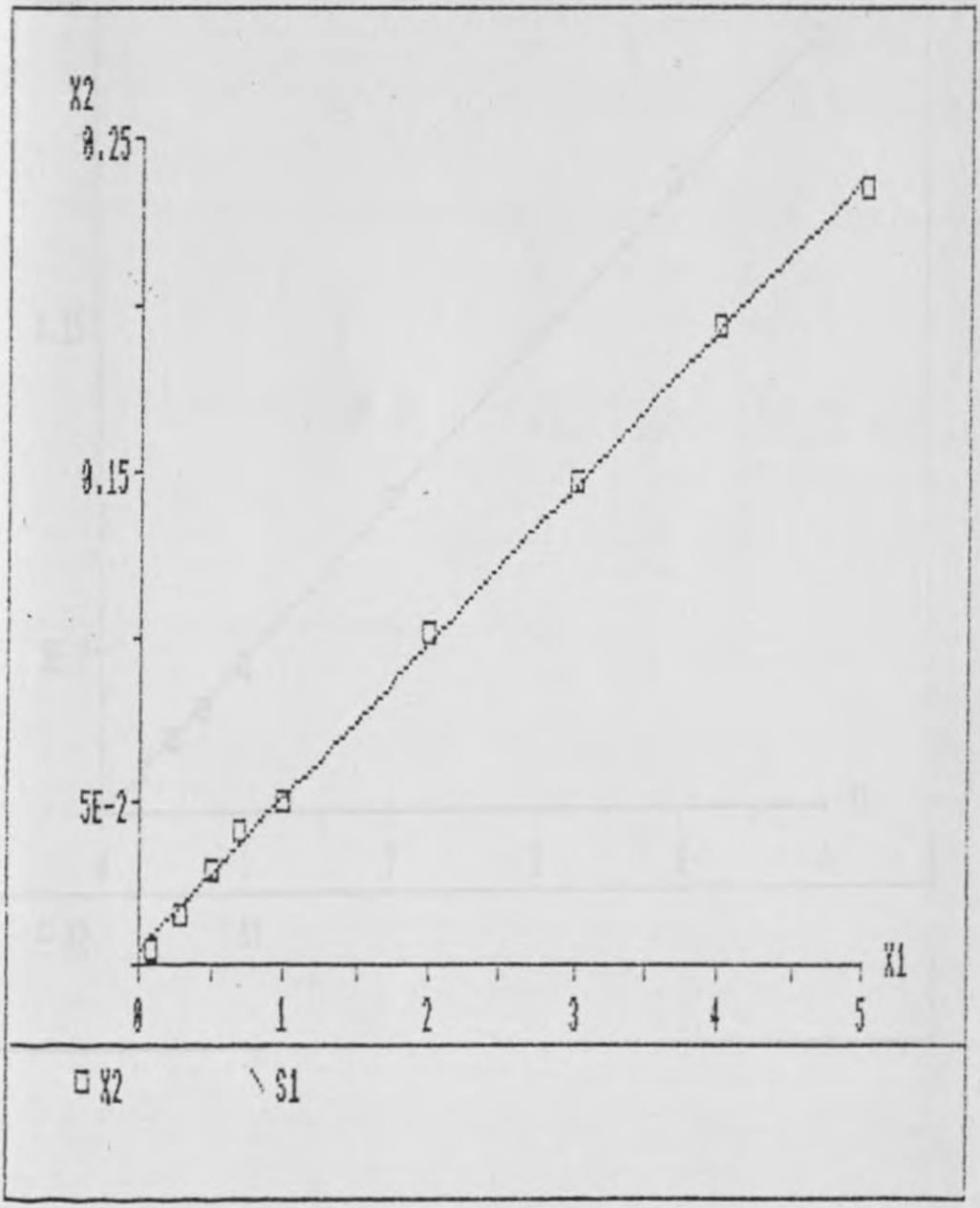
53	0.2502	20	4E-3	6.2479
54	0.2501	20	4E-3	6.2504
55	0.2496	20	8.2E-2	139.86
56	0.2499	20	8.2E-2	139.69
57	0.2497	20	8.2E-2	139.8
58	0.2496	20	2.2E-2	37.093
59	0.2498	20	2.2E-2	37.063
60	0.25	20	2.2E-2	37.033
61	0.2496	20	4E-3	6.2629
62	0.2496	20	4E-3	6.2629
63	0.2498	20	4E-3	6.2579

ii. Callibration graphs used in the determination of copper concentrations [X1 is the concentration of copper standards (ppm) and X2 is the absorbance obtained using AAS]

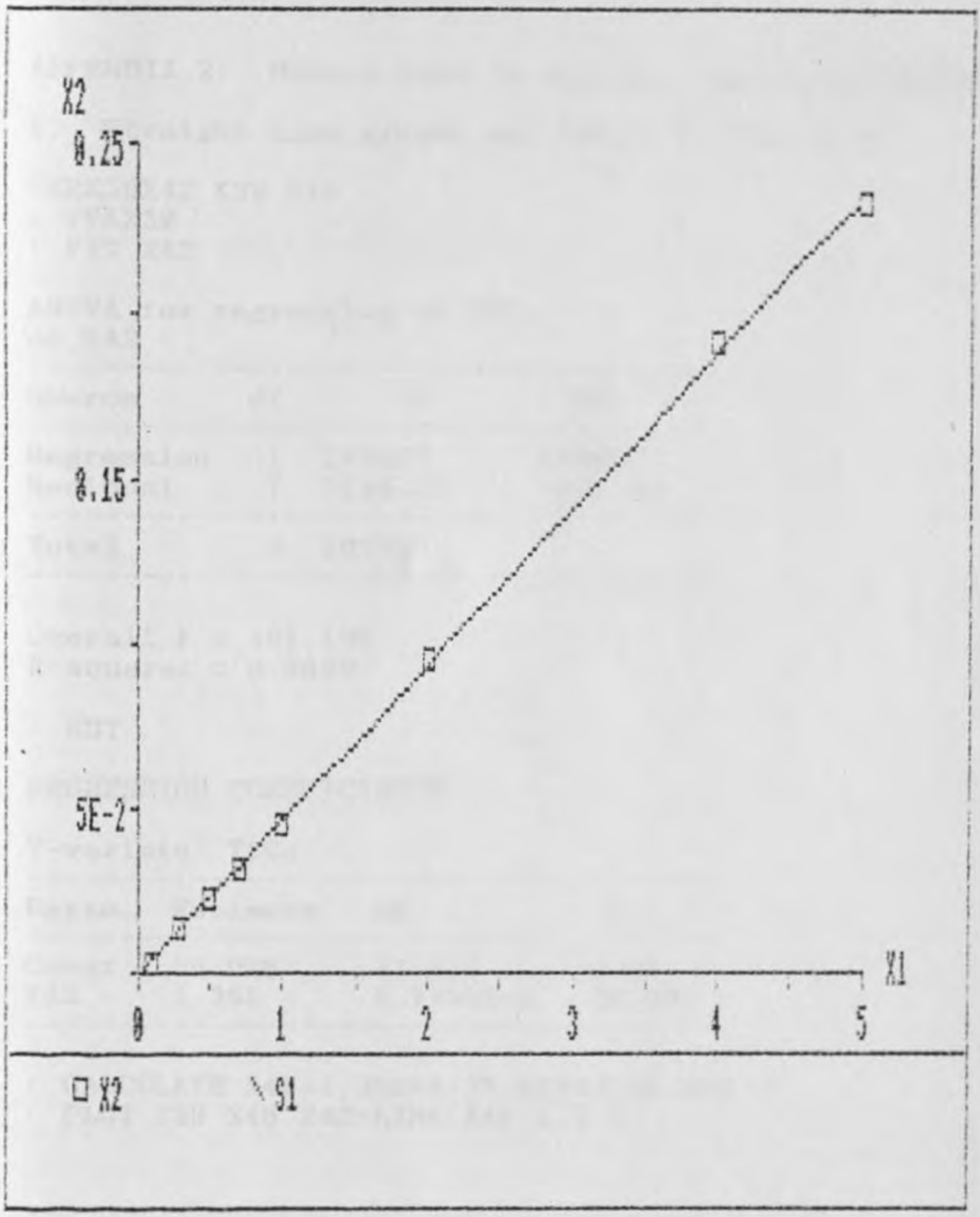
ANALYSIS 1



ANALYSIS 2



ANALYSIS 3



APPENDIX 2: Models used in drawing regression graphs

i. Straight line graphs eg. Graph 7, Fig. 4.8

```
TERX39X42 X39 X42
: YVAX39
: FIT X42

ANOVA for regression of TtCu
on X42
```

Source	df	SS	MS
Regression	1	178607	178607
Residual	7	3116.35	445.192
Total	8	181723	

```
Overall F = 401.190
R-squared = 0.9829

: EST

REGRESSION COEFFICIENTS

Y-variate: TtCu
```

Param.	Estimate	SE	t
Const	35.028	17.435	2.01
X42	1.358	6.7798E-2	20.03

```
: CALCULATE X48=1.358*X+35.02842+35.028
: PLOT X39 X48 X42:LINE X48 1 1 1
```

ii. smooth curve eg. Graph 27 next page.

```
X27=X1*X1
: X28=X1*X27
: TERX1X5X27X28
: YVAX5
: FITX1

ANOVA for regression of ADp2
on WEEK
-------------------------------------
Source      df      SS        MS
-------------------------------------
Regression   1   4.51377     4.51377
Residual     8   44.3999     5.54999
-------------------------------------
Total        9   48.9137
-------------------------------------

Overall F = 0.813
R-squared = 0.0923

: ADDX27

Residual S.S.          = 33.4605
Residual d.f.          = 7
Increase in Reg.S.S.   = 10.9394
Increase in Reg.d.f.   = 1
F-ratio for change     = 2.289
on (1,7) d.f.

: ADDX28

Residual S.S.          = 18.9658
Residual d.f.          = 6
Increase in Reg.S.S.   = 14.4947
Increase in Reg.d.f.   = 1
F-ratio for change     = 4.586
on (1,6) d.f.

: REF

ANOVA for regression of ADp2
on WEEK X27 X28
-------------------------------------
Source      df      SS        MS
-------------------------------------
Regression   3   29.9479     9.98262
Residual     6   18.9658     3.16097
-------------------------------------
Total        9   48.9137
-------------------------------------

Overall F = 3.158
R-squared = 0.6123
```

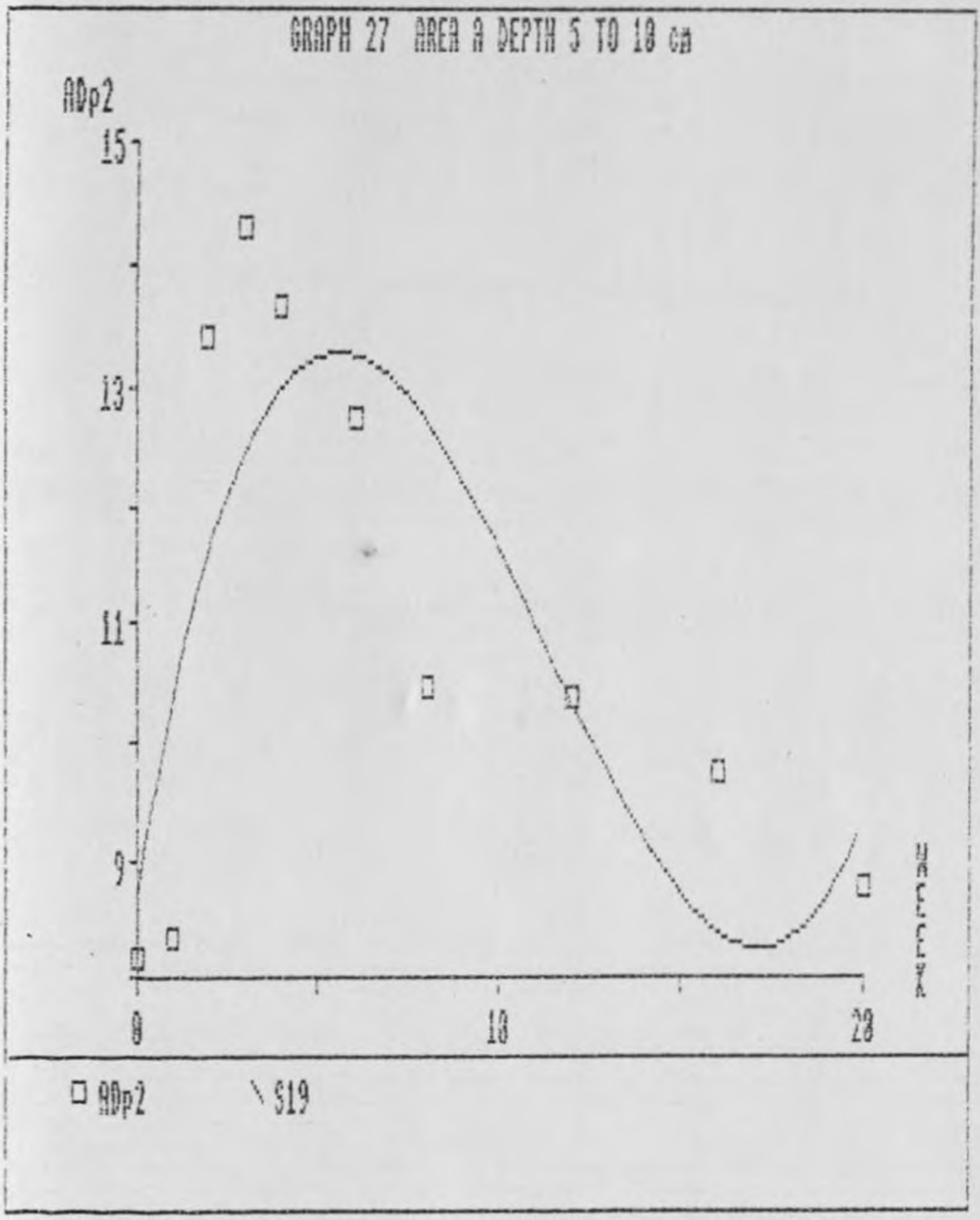
```
: EST

REGRESSION COEFFICIENTS

Y-variate: ADp2
----------------------------------------
Param.   Estimate    SE            t
----------------------------------------
Const    8.6973      1.3727        6.34
WEEK     1.8462      0.71568       2.58
X27      -0.21977    8.9889E-2     -2.44
X28      6.453E-3    3.0135E-3     2.14
----------------------------------------

: ENTS19
S19: 8.6973+X*(1.8462+X*(-0.21977+X*(6.453E-3 )))
: USES20

  S20 : plox5S19x1;TIT"GRAPH 27  AREA A DEPTH 5 TO 10 cm"
```


GRAPH 27 AREA A DEPTH 5 TO 10 cm
ADp2
15
13
11
9
0
10
20
ADp2
S19