To

My late Dad IBRAHIM AKOS and my Mum ASIBI.I.AKOS.

TITLE

ANALYSIS OF MICRONUTRIENTS IN AGRICULTURAL SOILS.

BY

AKOS NOEL IBRAHIM

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Supervisor: DR.A . A . FAROQ

CERTIFICATION

This is to certify that this dissertation is an original work undertaken by NOEL IBRAHIM AKOS and has been prepared in accordance with the regulations governing the preparation and presentation of dissertation in Federal university of technology, Minna.

DR.A.A.FAROQ	Date
[Supervisor]	
DR.E.R.SADIKU	Date
[HOD,Chemistry Department]	
External Examiner	Date

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A B S T R A C T

Analysis of the micronutrients [Fe, Cu,Zn and Mo] using the model PU 9100 atomic absorption spectrophotometer [AAS] has been carried out on soil samples taken from various farms around Minna Municipal.

The mixed acid extraction method was used for the bulk extraction of the micronutrients. The concentrations of the various micronutrients were found to vary between 1.68 and 3.75ppm for Iron; 0.26 and 3.50ppm for Copper; 0.61 and 1.55ppm for Zinc and 0.80 to 2.50ppm for Molybdenum.

The available forms of the various micronutrients analysed for were also determined. These also vary from farm to farm. For Iron the concentration was found to be between 1.28 and 3.53ppm; Copper 0.13 to 2.96ppm; Zinc 0.34 to 1.12ppm; and Molybdenum 0.60 to 2.08ppm.

The pH of the various soil samples were also determined using the Kent EIL 7045/46 pH meter.

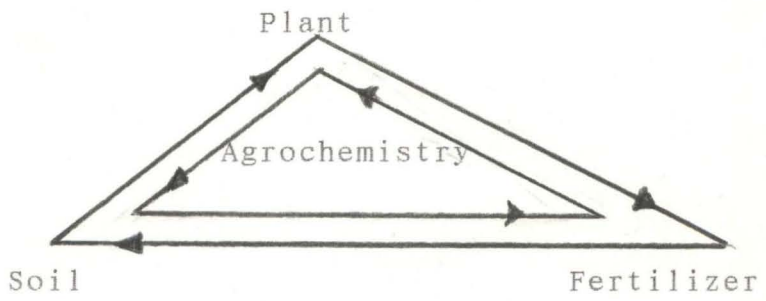
For most of the farms, the soils are alkaline in nature except for three farms located along Shiroro Dam Road and Chanchaga Area that are mildly acidic.

C H A P T E R O N E

1:0 INTRODUCTION.

Agricultural Chemistry is a scientific discipline concerned with the interaction of plants, soil and fertilizers in the cultivation of farm crops, the circle of nutrients in agriculture, and the application of fertilizers to improve the yield of crops, their quality and the fertility of soil[1].

Pryanishnikov[1] wrote that the objective of agro chemistry is to study the cycle of nutrients in agriculture and find ways to influence the chemical processes occurring in the soil and plants with a view to enhancing the yields of crops or varying their structure. Application of fertilizers is by far the most drastic way of altering this cycle. The use of organic and inorganic fertilizers form the basis of chemicalization of agriculture. The application of fertilizers increases the content of available nutrients in the soil, whereby the chemical composition of the later, its physical and other properties are changed.



Pryanishnikov Triangle[1].

Plants affect the physical properties of the soil by changing its porosity and improving its structure, while its chemical properties are altered as a result of the biological migration of some nutrients into the top layer, included by the vital activities of plants.

A reasonable effect on all soil properties is produced by the organic matter resulting from dying away of root system and decomposition of the crop residues left in the field after harvesting. In corporation of fertilizers into the soil changes the ratio and amounts of the individual nutrients present there, reaction of the soil solution (PH) and the composition of the absorbing complex, as well as activates many microbiological processes.

The theoretical and practical aspects of agrochemistry are studied using various approaches such as:

i. biological methods, including field, greenhouse and lysimeter experiments. These methods give insight into the role of individual nutrients in sustaining plants, their optimal ratios and amount of different crops and mechanism of their translocation into plants;

ii. laboratory methods of qualitative and quantitative analysis of soil plants and fertilizers;

iii. mathematical methods including statistical processing of experiment data and mathematical modelling of processes; and

iv. biophysical and microbiological methods.

By definition, essential elements are those without which plants cannot complete their development cycle and which cannot be replaced by other elements[1]

The nutrient elements present in a plant organism substantial quantities [from hundredths of a percent to several percent] are known as micronutrients, and those present in amounts ranging from thousandths to hundred thousandths of a percent are termed trace elements or micronutrients while elements present in even smaller amounts are referred to as ultramicronutrients[1].

Various biological groups of plants differ widely in their requirements for optimal concentrations of individual micronutrients. For example, maize and tobacco need greater amount of zinc, while grain crops require extra quantities of manganese[1].

The productivity of plants and uptake of micronutrients and micronutrients by them are directly dependent on the inorganic nutrient content in the soil. The presence of nitrogen, phosphorus and potassium in the nutrient medium determines to a great extent the plant growth rate and uptake of other inorganic nutrients by

plants. Increased uptake of nitrogen enhances the rate of absorption of P,, K, Ca, Mg, Cu, Fe, Mn and Zn by plants[1]. The effect of nitrogen on the uptake of the above nutrients is reversed by its excess amounts and depends on the form in which it is taken up. Excess P reduces the rate of absorption of Cu, Fe and Mg. In the presence of phosphates, plants take less zinc.

The soil is constituted by a soil phase, a liquid phase or soil solution and a gas phase or soil air. The solid phase is composed of inorganic and organic matter, and living organisms. Soils are both chemically and physically diverse, not only in composition, but in the dynamic changes that take place due to biological, environmental, and gravitational influences. Thus, micronutrients are just as diverse in their chemical and physical forms, which are expected to change due to perturbations of the system[2]. Much of the micronutrients associated with the solid phase are not available for plant uptake[2].

The soil solution is the central focus of soil chemistry, since it is from this medium that plants absorb nutrients and it is the center of all important soil chemical processes. The element concentrations in soil solution are in constant flux, influenced by a host of factors including moisture, pH, temperature, oxidation/reduction status, fertilizer additions, and plant uptake. Soil water content is most important, in that, wet conditions, elements dissolve or more by diffusion and with the water under

gravitational influence. As the soil dries, the ions in soil become more concentrated, and can precipitate or be adsorbed.

Most of the metallic micronutrients in soil solution are not in a free ionic form but are completed with both inorganic and organic ligands[2]. Therefore, the total content in solution is not as important as the chemical species [sposito, 1983], which to a great extent, determine plant availability. The micronutrients exist in solution as charged ions and, as such, are attracted to the charged surfaces of colloids.

Soil air has high carbon dioxide content and less oxygen content. The carbon dioxide content of the soil air depends on the rate of the gas exchange between the soil and the atmosphere[1].

The application of fertilizers to enhance maximum yield greatly alter the amount of race elements present in the soil. According to their chemical composition, all fertilizers are divided into organic and inorganic ones, and depending on their origin and sources, they may be commercial [nitrogen, phosphorus, potassium, compound, and micronutrient fertilizer] and domestic [manure, peat, ash etc][1].

Micronutrients are of great importance in plants, their absence is responsible for some plant diseases and often causes crops to perish. Application of appropriate micronutrients not only prevents

these diseases, but also ensure higher yields of better quality crops. They also enhance greater resistance of plants to diseases environmental conditions. They increase the chlorophyll content in leaves, improve photosynthesis and intensify the assimilating activity of the whole plant[3].

Micronutrients can affect crop production by either being deficient or in excess in the soil solution resulting in toxic effects. The margin of concentration between deficiency and toxicity limit is narrow for some micronutrients. As a result of this, difficulties are encountered in trying to correct deficiencies[4].

In general, crystalline and metamorphic rocks give rise to soils richer in trace elements than those over sedimentary rocks. Under non-intensive subsistence farming, micronutrients deficiencies were seldom recorded in the past because of the low rate of nutrient removal, burning of crop residues and the return of ashes and the effects of the fallow period. Under intensive and continuous cropping where large doses of fertilizers are applied, affecting soil pH and soil nutrient balance, the micronutrient disorders are much more pronounced and the frequency and severity of micronutrient may be expected to increase with the intensity of production[4].

Micronutrients are required by plant in small quantities, ranging from a few hundred grams to few kilograms per acre. Treatment for

micronutrient deficiencies usually involve either inclusion of small quantities of the appropriate carrier of the element in mixed fertilizer, or application of foliar sprays[5].

Table 1:1 General information about micronutrients[5].

Plant nutrient	Principal forms in soil.	Favorable soil condition	Forms assimilated by plants.	Fertilizer compounds	Methods of application.
Iron	Clay oxides	pH below 8.0	Fe^{2+}	$FeSO_4$ chelate	$FeSO_4$ orchelated Fe. Foliar sprays. Chelated iron to soil.
Manganese	Clay oxides	pH below 7.5	Mn^{2+} chelated	$MnSO_4$	Foliar spray
Zinc	Clay phosphate	pH below 8.0 Good structure	Zn^{2+} chelated	Zinc oxides $ZnSO_4$ chelate.	Foliar spray soil
Copper	Clay	pH below 8.0	Cu^{2+} chelated	$CuSO_4$ chelated. Glass frits.	Foliar spray soil
Boron	Soil minerals e.g Tourmaline	pH below 8.0	$B_4O_7^{2-}$ $H_2BO_3^-$	Borax Boric acid Glass frits.	Foliar spray soil
Molybdenum	Absorbed on feric oxides	pH above 6.0	MoO_4^{2-} $HMoO_4^-$	Sodium or ammonium molybdate	In mixed fertilizers. Foliar sprays.

1:2 Atomic absorption spectrophotometry [AAS].

AAS has become the most widely used single - element technique for the determination of metals. It is based on the absorption of radiation by neutral ground state atoms produced by an atomizer.

The typical instrumental configuration for an AAS is as shown in figure 1. The source is usually a hallow cathode lamp, although an electrodeless discharge lamp is often used for some elements [As, Se and Te] where the radiant power output of the hallow cathode lamp is low. The lamps are usually modulated at a 50% duty cycle by operation from a pulsed power supply. The atomizer is typically a flame or an electrothermal device[6].

A monochromator with a spectral bandpass of 0.1 to 2mm is required to isolate the resonance line of the element to be determined from lamp impurity and filler gas lines, and from the atomizer background emission.

The signal processor converts the photoanodic current from the photomultiplier tube [PMT] into a voltage. Amplification and demodulation circuitry extract the amplitude information from the carrier wave-form. Hardware or software logarithmic convertion is used to provide direct absorbance readout on a digital meter. [see figure 2].

1:3 Atomizers.

For AAS, the ideal atomizer would provide complete atomization of the element of interest irrespective of the sample matrix. For the lowest detection limits, the atomic vapour should not be highly diluted by the atomizer gas so that a large ground state neutral atom population is produced. Excitation of the analyte and other species should be minimal so that analyte and background emission noise is small. Although not ideal, flame and electrothermal atomizers have gained acceptance as reliable atomizers for AAS in many situations.[6]

1:4 Flame Atomizers

Combustion flames are still the most popular atomization sources for AAS. In most commercial AAS, a premixed, chamber-type nebulizer burner system is employed. The nebulizer is usually based on the concentric pneumatic design as shown in figure 3.

Nebulizer parts are fabricated with robust metals [e.g Pt-Ir ally, Ta, Pt] to enhance the chemical resistance to acidic solutions and other corrosive mixtures. Variable flow rate nebulizers allow solution flow rates to be reduced for solutions that would normally yield high absorbances.

The most popular flame provides higher atomization efficiencies and thus better detection limits for refractory elements such as Si, Al, Ti, V, Zr and the rare earths.

The burner control unit is designed for convenient and safe burner operation. Flow controllers with flow meters allow adjustment of the fuel/oxidant ratio, which is critical for some elements.

Due to potential flashback problems, a N_2O-C_2H_2 flame cannot be ignited directly. First, an air-C_2H_2 flame is lighted and then the N_2O flow is turned on and increased as the air flow is simultaneously decreased to zero. The procedure is reversed before extinguishing the flame. Many instruments provide push button flame ignition through activation of a small starter flame.

The burner is mounted on translational stages to allow the flame to be positioned so that the focused line source radiation passes through the middle of the flame at the desired burner height to maximise the absorbance.

The majority of AAS determinations are carried out by continuous aspiration of solution into a flame with a pneumatic nebulizer or by discrete sampling with an electrothermal nebulizer.

1:5 Instrumentation

Most commercial AAS provide several features for convenience Normal operation requires that the photomultiplier tube [PMY] bias voltage be adjusted to very the PMT gain during the process of setting the readout absorbance to near zero option, the instrument automatically performs this adjustment when the appropriate front panel switch is activated. Thus, when sample is aspirated, the readout absorbance is nearly the true sample absorbance. For best accuracy, the blank absorbance should be recorded and subtracted from the measured sample absorbance[6]

A scale expansion control allow the measured absorbance to be multiplied by a known factor before displaying on the readout device. This is useful if measurements are limited by readout rather than noise. Scale expansion allows readout directly in concentration units.

The incorporation of a microprocessor into an AAS allows more convenient use of the features discussed above and provides additional versatility and automation capabilities.

1:6 Double - Beam System.

Most AAS double beam models are based on a design similar to the one shown in figure 4. With a double-beam system, the reference, beam does not pass through a "reference atomizer" to correct for blank absorption. Also, there is no compensation for drift and noise in the flame transmission characteristics[6]

This project is aimed at analysing the trace elements present in agricultural soils and acertain their levels in the soil. This will give a good knowledge of the soil fertility of the farms considered for the analysis.

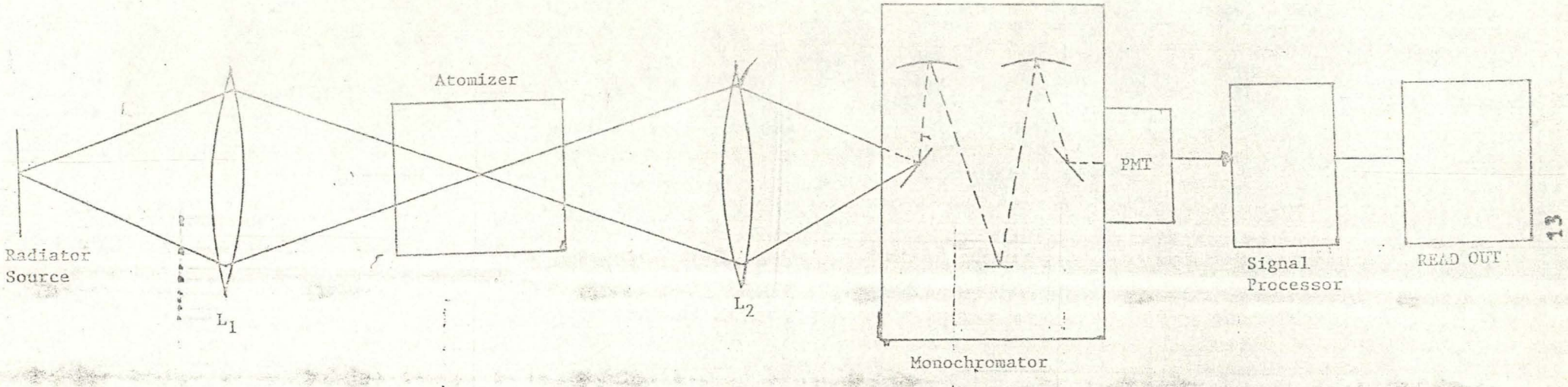


Fig. 1 Instrumental configuration for an AAS

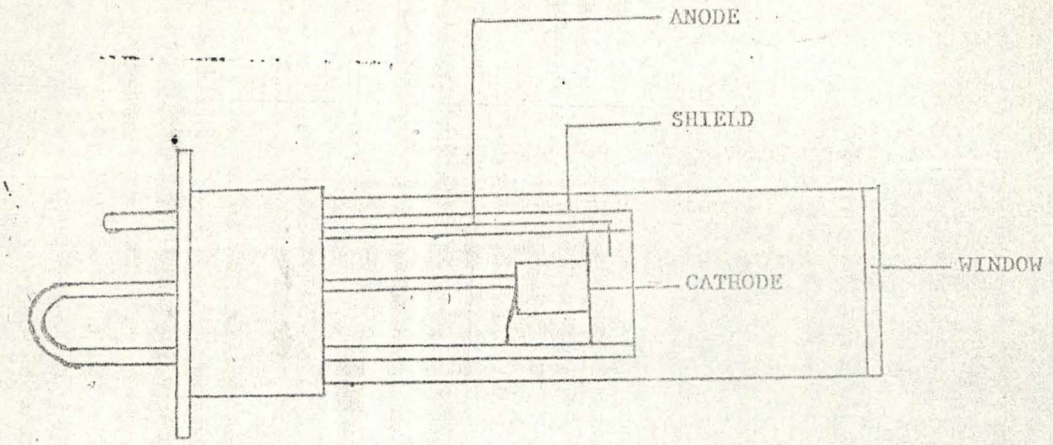


Fig. 2 HALLOW CATHODE LAMP

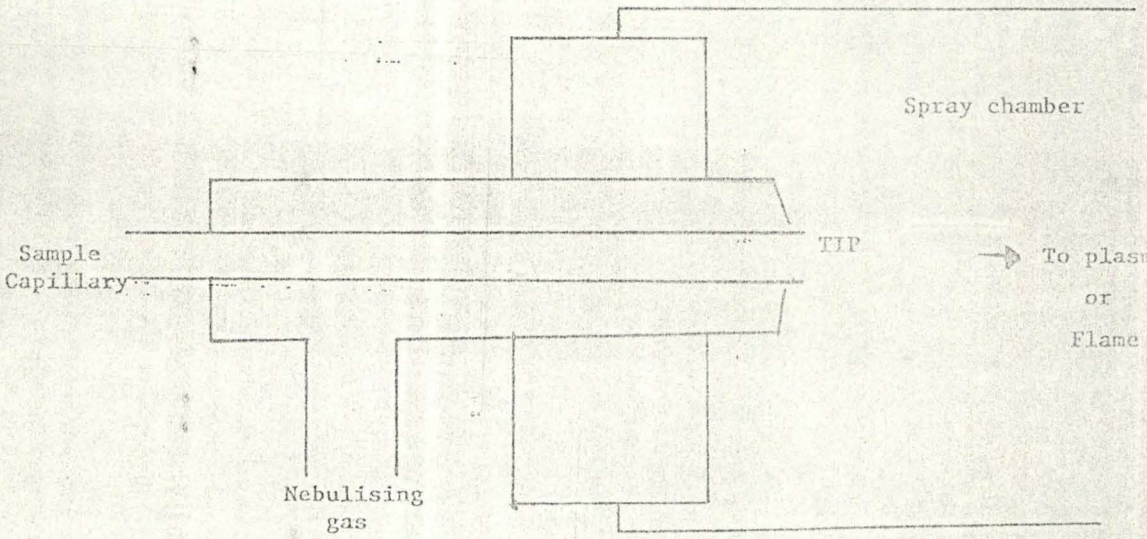


Fig. 3 NEBULIZER

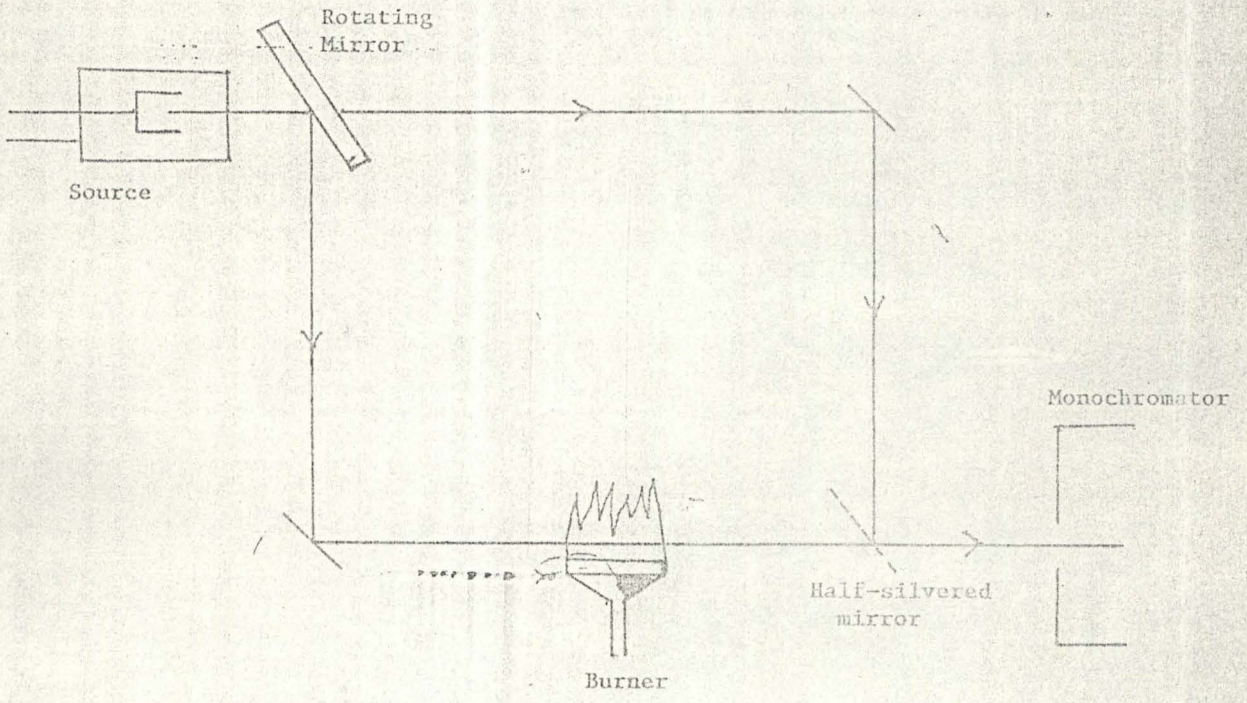


Fig. 4. AAS double-beam system

C H A P T E R T W O

LITERATURE REVIEW

2.0 INTRODUCTION

The soil is a natural body of animal, mineral and organic constituents differentiated into horizons of variable depth which differ from the material below in morphology, physical make-up, chemical properties and composition, and biological characteristics.[17]

In soil fertility, one is concerned with the ability of the soil to supply essential plant nutrients at a rate sufficient to sustain optimum growth of the plant. A balanced nutrition depends on the interaction between processes in the soil, in the root environment and processes internal to the plant linked to its growth and metabolism.

Any substance that is added to the soil to supply one or more plant nutrient and intended to increase plant growth is a fertilizer.[8] Responses to fertilizers vary greatly from year to year on many fields, even when the same crops are grown. There are many reasons. Variability due to irregularities in soil, site and crop, effect of weather, both on total yield and on the chemical availability and physical accessibility of nutrients in soil. Temperature and rain alter growth of roots, and therefore their efficiency in feeding

the crop. On most agricultural land, total supplies of micronutrients are determined at least as much by soil type as by fertilizer.

2.1 Micronutrients in fertilizers and manures.

Most ordinary fertilizers, both older dilute ones and the more concentrated materials based on ammonium nitrate and phosphate, do not contain substantial amount of micronutrients. Most claims that dilute fertilizers can correct element deficiencies are exaggerated.[8] Fertilizers made from naturally occurring raw materials sometimes contain appreciable quantities of micronutrients. Fertilizers containing a small concentration (about 10ppm) of a micronutrients and applied at a common rate (about 500kg/ha) will make little contribution to the micronutrient status of soils and will apply considerably less of the elements than may be removed by annual crop. Materials applied at rates of many tones/hectare, such as farm-yard manure, provide much greater quantities of micronutrients, approaching the amounts supplied as sprays to correct deficiencies in crops.[8]

2.2 Soil acidity and lime requirement.

The clay and organic matter in soils have negative electrical charges which attract and retain the positively charged cation of hydrogen, alluminium, calcium, potassium, magnesium and sodium.

These ions can be displaced by treating the soil with a strong solution of other cations and are therefore called exchangeable. In very acid soils, most of the negatively charged sites are occupied by hydrogen and some by alluminium. As more of the hydrogen is displaced by calcium the acidity is diminished and the pH rises.[8]

Soils become acid during prolonged cultivation and liming is necessary to maintain the soil pH in a desirable range.[9]

Several plant nutrients become less available at the extreme of pH values and other elements become available in toxic amounts, the pH value is often a guide in the diagnosis of fertility problems.

The soil pH s also used in the classification of soils. The average pH range of soils is from pH 3 to pH 10, but in humid regions the normal rang is from pH 5 to pH 7 and in arid region it is from pH 7 to pH 9. Acid sulphate soils may reach a pH value of 10 [9].

Until fairly recently, most of the soil fertility work in the West African Savanna has been centered on N and P, the two limiting nutrients. With the increasing shift toward intensive continuous cultivation., trace element deficiencies are beginning to limit crop yields.[11] subsequent to the confirmation, through field studies of B, Mo and Zn responses of some savanna crops, considerable interest has been generated in the micronutrient fertility of the area. [12,13] The total content of an element in a given soil is no

more that an inventory, which does not provide any reliable indication about the availability of that nutrient element. In soil fertility evaluation, therefore, emphasis is often rightly placed on the plant-available component and on those secondary soil factors that influence availability of plant uptake or both. Various soil factors such as pH, organic matter, clay fraction and moisture content are usually associated with plant availability of Mn and Cu.[14,15] The Nigerian savanna soils are generally well drained coarse-textured inceptisols and utisols low in organic matter and exchange properties. The inherent natural fertility of the soils is therefore generally low.

As would be expected the amounts of Cu and Mn extracted differ with the extracting solution. Evaluation of several micronutrient soil test methods showed that 0.1M EDTA IN NH_4 OAc pH 7, O.IN HCl, and O.O5N HCl + O.O25N H_2SO_4 (DA) were the most suitable extracting reagents for plant available Cu and Mn in the semiarid West African Savanna.[10] It was also reported that O.IN HCl extracted Cu and Mn than did the O.IM EDTA-NH_4OAc extractant.[16]
However, working with the humid derived savanna and forest soils of southern Nigeria, contrasting results were obtained.[17]

The heterogeneity of soils makes it difficult or impossible to distinguish small alterations with time in the concentration of nutrients in the soil by means of repeated soil sampling and analysis. Such alterations may be harmless in a short perspective

but may be risky in the long run. A more sensitive method to reveal weak current time trends is to establish the degree of imbalance between supply and removal of the element of interest. If steady state conditions prevail, nutrients concentration in the soil remain unchanged. These nutrients increase with time if more is supplied than removed; if the opposite applies they decrease. The rate of change may be estimated if the annual imbalance is related to the soil contact.

Trace elements are removed from agricultural soils by crops and by leaching, and they are added in applied fertilizers and by atmospheric deposition. By quantifying these fluxes the degree of imbalance can be revealed, and alterations in concentrations and quantities can be estimated to direction and rate.[18]

It is important to recollect that rainwater is in effect, a dilute solution of carbonic acid (H_2CO_3). Consequently, in a region of humid climate where percolation of rain-water is persistent, the nutrient ions which are detached are carried away into the drainage water in the form of carbonates. The carbonic acid molecules exchange their hydrogen for mineral ions they pass through the clayhumus complex and then continue to more downwards as carbonate salts.

It is clear, therefore, that unless replacement takes place, either through the further weathering of rock minerals or by decay of

organic matter, ultimately the clay-humus complex could become completely hydrogen saturated by this leaching process. This rarely happens because, when a high amount of acidification has been achieved, the clay itself begins to decompose and the aluminium ions released there from displace some of the exchangeable hydrogen.[19]

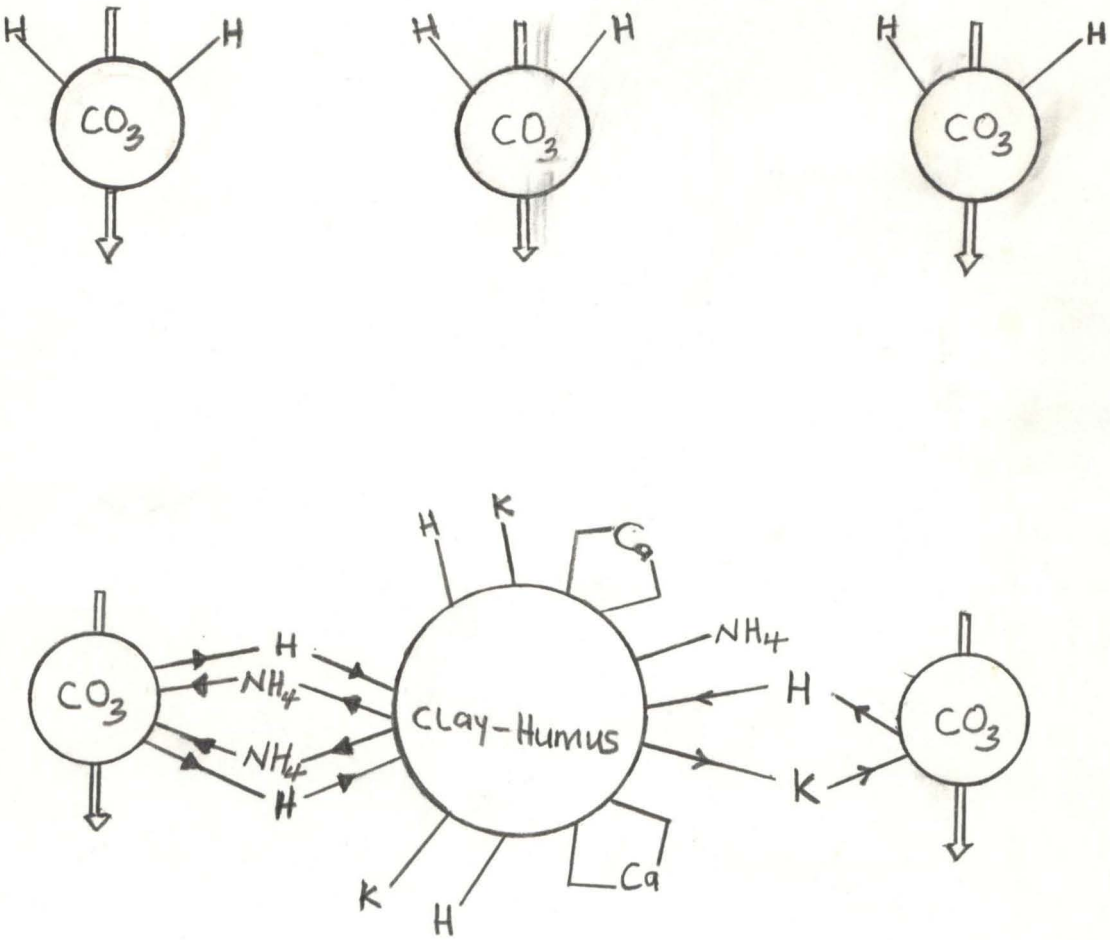


Fig 5: Diagrammatic representation of the leaching of nutrient ions by percolating carbonic acid.[19]

2.3 Boron

Boron is essential for the growth of pollen tubes. It is essential for seed and cellwall formation. It also forms sugar/borate complexes associated with sugar translocation. Boron is important in protein formation. The deficiency of Boron generally stunts plant growth-the growing point and younger leaves first. Boron deficiency is noticed when rosetting and death of terminal bud in Alfalfa are observed. For cotton the deficiency is observed when ringed or bonded leaf petioles, with dieback of terminal buds causing rosetting effect at the top of the plant is noticed.[20]

Boron occurs in the earth crust mainly as borax, $Na_2B_4O_710H_2O$. It also occurs adsorbed on surfaces of clays and hydrous iron and aluminium oxides and as boric acid, H_3BO_3, $H_2BO_3^-$ and $B(OH)_4$[21-23]. The total Boron content of typical Nigerian soils was reported to range between 1.20 and 1.50ppm on sandstone and 0.48 to 12ppm on basement complex with a mean of 1.12 and 2.75ppm has been given for soils of south-western Nigeria savanna zones for available Boron[25], while Bamjoko et al (1981) reported a range of 0.13 to 0.21ppm for soils derived from sandstone at 0-20cm, and 0.23 to 0.81ppm for soils from basement complex. Wide variations exist both in the nutrient element requirement of plants and its uptake. The Boron content of root crops and legumes are the highest followed by fruits and vegetables while cereals and hays are poorest in Boron. It was therefore suggested that the measurement of B uptake should

be on the plant materials rather than directly measuring extractable B levels in the soil.[26,17] The literature indicates B deficiency problem which was first identified by staff of the cotton breeding section at Samaru in 1969.[28]

It has been observed that the range between upper and lower limits for B useful to plants is very narrow. Values ranging from O.1 to 1.5ppm and which vary in relation to plant variety have been indicated.[29] Wide spread deficiency of Boron in farmers fields in Nigeria (in some localities very severe) was reported in 1974; being below the critical minimum O.1-O.2ppm of hot-water-soluble Boron.[30] However, values of hot-water-soluble Boron at which deficiency may be expected vary according to crop and soil. Similarly, toxicity of Boron varies according to crop and soil, the acceptable upper limit for sensitive crops being about 2ppm Boron.[4]

2.4 Copper

Copper occurs in soil principally as Cu^{2+} ion, adsorbed by clay minerals or tied up by organic matter.[21,31] Contents in the earths crust vary according to the nature of the parent rock. A range of 1.6 to 140ppm with a mean of 26.4ppm for the total copper content of basement complex soils of the tropical dry rainforest of southwestern Nigeria was obtained.[32] The observed that copper content increased with depth in most of the profiles examined, and which coincided with increase in clay content.

Available copper is that extractable by DTPA, (diethylenetriaminepentaacetic acid), EDTA or dilute HCl, depending on soil properties other extractants have also used. Dilute HCl has been found unsuitable for dry soils with high pH or high organic carbon content.[33] It has however been used successfully on acid soils.[34] The DTPA soil test developed by Lindsay and Norvell (1978) has been used extensively for the estimation of available copper, but NH_4HCO_3 - DTPA mixture has similarly been found to be effective in extracting substantial amounts of copper from soils (Saltanpour and Schwals 1977). For semiarid savanna soils of Nigeria, Lombin (1983) reported a range of 0.54 to 1.69ppm with a mean of 1.03ppm, and 0.49 to 1.50ppm dilute HCl - and DTPA - extractable Cu respectively.[10] He indicated a strong relationship between copper levels and organic matter levels and Cu and clay fractions.

For 77 colarado soils, Lindsay and Norvell (1978) reported a range of DTPA - extractable Cu of 5 to 26ppm with a mean of 16.5ppm.[35] Increasing the shaking time and the concentration of DTPA increased the amount of Cu extracted. pH change on the other hand had little or no effect while an increase in temperature by $10.^0C$ caused an increase of 24 percent in extractable Cu.

It has been reported that there have been very few serious attempts to determine the amounts and relative proportions of soil copper. Previous workers have either concentrated solely on measuring total or extractable copper or have concerned themselves with one

reasonably well defined fraction such as exchangeable and soluble copper or copper (and other trace elements) associated with the free oxide fraction of soil.[36-39]

Grimme (1967) in his copper fractionation scheme ignores altogether the more suitable forms of soil copper.[40] Soil samples used for the study were selected to include ranges of pH, organic matter, free oxides, clay and total copper contents since these properties were expected to exert the greatest influence on the behaviour of copper in soils.[41]

Preliminary experiments showed that variation in temperature has a significant effect on the amount of copper extracted by some reagents. To overcome this, the first three extractions were carried out in a constant temperature cabinet set at 30.^{0}c. The times for extraction were more than adequate to ensure equilibration at this temperature.[41]

2.5 Iron.

Iron is taken up by plant roots as Fe^{2+} and it can be transported to root surfaces as iron chelates. Iron deficiency is common in calcareous soils and soil solutions high in HCO_3 ion concentration due to the high pH values associated with the presence of these ions. Fe chlorosis may be observed also in acid soils where high levels of Mn or p, Zn and Cu are present.[42] Increase in HCO_3^- ion

concentration usually due to increased CO_2 pressure would, in calcareous soils decrease Fe availability or its inactivation within the plant by increasing solubility of calcium phosphate and hence the concentration of Ca^{2+} and PO_3^{4-} ions.[43,44]

Increase of Fe deficiency in Nigerian soils have been reported by some workers.[45,46] Large responses to Fe application by maize in the forest and savanna zones of southwestern Nigeria have been reported.[45] In another report, it was observed that Fe among other micronutrients was essential for large yields of maize in Nigeria.[47]

A critical level of 4.8ppm NH_4HCO_3 - DTPA-extractable Fe has been reported for sorghum (Havlin and Saltampour 1981). These authors listed the advantages of the NH_4HCO_3-DTPA soil test, which was developed for the simultaneous extraction of Cu, Fe Mn and Zn.[35]

2.6 Manganese.

Manganese exists in soil in the form of insoluble oxides of trivalent and tetravalent Mn, exchangeable and water - soluble divalent Mn, as organically bound Mn, and reducible Mn; all of which are in a state of equilibrium with one another.[2] The level of exchangeable, water-soluble and easily reducible Mn in soil is important factor for a satisfactory Mn nutrition of crops and should be of the order of 0.2 to 5.ppm, 2 to 3ppm and 25 to 65ppm respectively.[21]

In Nigeria, a range of extractable Mn of 10 to 1000ppm was reported with a mean of 319.9ppm in the 0-15cm top soil.[48] It was also indicated that double acid HCl/H_2SO_4 and EDTA-extractable Mn ranged from 12.5 to 53.9ppm with a mean of 31.6ppm, and from 1.40 to 47.1ppm with a mean of 24ppm respectively.[10] This assertion confirmed the findings of Kayode and Agboola (1981) who observed that Mn did not limit the yield maize in all the locations investigated in the country.

2.7 Molybdenum.

Molybdenum exists in soils as the oxides of Mo^{6+}, Mo^{5+} and Mo^{4+}, the first of which is the form available to plants, but the others may be transformed into it. Mo^{6+} in turn is readily reduced in alkaline medium to MoO^{2}_{4-} the form believed to be a primary source of Mo to plants.[21] The solubility of Mo is principally influenced by soil pH and increases as the pH increases.[31] This is in contrast to other micronutrients such as Mn, Co, B, Ni Fe, Cu and Zn, which become less soluble and available with increasing soil pH. Mo contents in plants vary considerably according to the factors affecting uptake and ranges from less than 0.1 to over 200ppm in dry matter.[31]

Lombin (1985) reported $(NH_4)_2C_2O_4$ - extractable Mo values of less than 0.10ppm for 24 soil samples, 0.10 to 0.15ppm for 21 samples and between 0.16 to 0.20ppm for 5 samples. Organic matter, low pH

and clay content were identified as factors affecting Mo availability in the savanna zone.

2.8 Zinc.

The forms in which Zinc occurs in soil include water-soluble Zinc, non-exchangeable or fixed zinc.[31,49] Acid sandy soils low in total Zinc, neutral or basic soils, especially calcareous soils: soils with a high content of fine clay and silt, and soils high in available P have been listed to be associated with zinc deficiencies.

Ondo State soils were reported to contain 1.3 to 63ppm (mean 9.0ppm) total zinc.[48] It was also reported that soils of southwestern Nigeria contained a total Zn range of 6,0 to 100 μgg-1 (mean 30.8 μgg-1).[32] The zinc content was observed to increase with depth in most of the profiles examined and coincided with increase in clay with depth.

In a multiple regression analysis. It was observed that the best prediction for zinc uptake by plants was a combination of 0.1m HCl-extractable Zn, pH, organic matter and silt plus clay fraction.[47] Zinc has been studied using salts and in some cases, acids for exchangeable forms.[50] White (1957) used 5N NH_4Cl at pH 8.0 for Zn.[26] A 0.05M $CaCl_2$, 1M NH_4OAc and 1N $MgCl_2$ have been used for exchangeable Zn, Cu and Mn.[51-53] Magnesium chloride solution has been

found suitable as a predictor of Zn uptake.[54,55] The colloidal fractions of soils play especially important roles in retaining and releasing microelements to plants. It is reported that organic matter chelates Zn in soils.[56] Both clays and Fe and Al oxides adsorb Zn and are relatively similar in retention.[57,58] Clay type has a profound influence on microelements adsorption.[50]

CHAPTER THREE

EXPERIMENTAL

3.0 SAMPLING PROCEDURE

Samples were taken from farms located along Bida and Shiroro dam roads; Chanchaga, Tudun-Fulani settlements and Federal University of Technology Bosso campus, Minna. These farms were mapped out into uniform past cropping areas and assigned an identification mark. Random samples over each farm were collected to give a composite sample. All the soil samples used for the analysis were collected in plastic sample bottles to avoid contamination from metals. In order to obtain a representative sample, both surface and sub soil were collected and thoroughly mixed[20]

3:1 SAMPLE PREPARATION.

The soil samples were dried on a sheet of paper and all large lumps crushed. The mixed acid method of digestion was employed for the analysis[59] This method involves the dissolution of the soil samples with concentrated perchloric and nitric acids [ratio 3:4]. This also decomposes the organic compounds in the soil.

3:2 EXPERIMENTAL PROCEDURE.

For each experiment about 2.00g of air-dried soil was accurately weighed into a beaker. 20cm^3 concentrated nitric acid was carefully measured and added to each soil sample. It was allowed to stand for

at least one hour after which 15cm^3 perchloric acid was added[59]. The mixture was then digested on a hot plate till it turned yellow or white. The residues were washed with dilute hydrochloric acid and filtered. The filtrate obtained was used for determining the micronutrients present using atomic absorption spectrophotometer[59]. The results are tabulated in table 4:10

3:3 SOIL pH DETERMINATION.

10g of air-dried soil was accurately weighed into a beaker. Distilled water was added and allowed to stand for 30 minutes. It was stirred occasionally with a glass rod. The electrodes of the pH meter were inserted into the partly settled suspension and the pH measured. The result are tabulated in table 4:11.

3:4 DETERMINATION OF AVAILABLE FORMS.

The extracting solution was prepared as per reference 35. The solution consist of diethylenetriaminepentaacetic acid [DTPA], hydrated calcium chloride and triethanolamine [TEA]. The resulting solution was adjusted to pH 7.30 using I:In hydrochloric acid.

10g of air-dried soil was placed in a conical flask, and 20cm^3 extracting solution was added. Each flask was covered with stretchable parafilm and secured upright on a horizontal shaker with a stroke of 8.0cm with a speed of 120 cycles/minute. After

shaking for 2 hours the suspensions were filtered by gravity through whatman filter paper. The filtrates were analysed to determine Zn, Fe, and Cu using AAS [35]. The results are tabulated in table 4:12.

For the determination of molybdenum the 10g of air-dried soil was transfered into a bottle and 200cm^3 Tamm's reagent was added. The bottle was stoppered and shaken. This mixture was then filtered and the filtrate used for the determination. The results are tabulated in table 3:3

CHAPTER FOUR

RESULTS AND DISCUSSION

4:0 ANALYSIS OF RESULTS.

In this research, the micronutrients in agricultural soils were quantitatively analysed using the model PU 9100 series AAS. The pH values of the various soil samples were also determined using the pH meter and determination of the available forms was also carried out. It should be noted here that most of the farms used for the analysis are solely managed by the peasant farmers in those localities except two farms that are managed by the Niger State Forestry Management Board. These farms are located along Shiroro dam road. For the farms in F.U.T. Bosso Campus, Minna, only farm A is managed purely by the School of agriculture for experimental purposes. The others are intermittently given out to local farmers for dry season farming. As a result of this, fertilizer application is also carried out in these farms without any specialist advice just like the other farms as at the time of the research.

Results obtained for the various analysis are as shown in the tables below.

4.1 Table 4:10 Concentration of micronutrients.

SAMPLE LOCATION		CONCENTRATION IN PPM			
F.U.T. Bosso Campus Minna		Fe	Cu	Zn	Mo
	A	3.60	1.00	1.50	2.20
	B	3.40	0.40	1.00	2.50
	C	3.20	0.37	1.24	1.76
	D	3.10	0.31	0.96	1.00
Bida Road farms	E	3.75	0.47	0.91	1.51
	F	3.75	3.50	1.00	1.56
	G	3.00	0.58	0.70	1.13
	H	2.55	0.38	0.89	1.16
Tudun-Fulani area farms	I	3.30	0.33	0.97	1.68
	J	3.18	0.28	0.61	1.59
	K	3.56	0.36	0.91	1.10
	L	2.81	0.30	0.68	1.05
Shiroro dam road farms	M	3.48	0.72	1.35	1.78
	N	2.57	0.48	0.94	1.57
	O	2.55	0.32	0.86	0.98
	P	3.57	0.56	1.55	1.07
Chanchaga area farms	Q	2.56	0.74	0.61	1.12
	R	2.79	0.51	0.85	1.08
	S	1.75	0.61	0.98	0.83
	T	1.68	0.26	0.88	1.03

4.2 Table 4:11 pH values of soil samples.

SAMPLE LOCATION		pH
F.U.T Bosso Campus, Minna farms	A	7.52
	B	8.99
	C	9.40
	D	9.34
Bida road farms	E	7.24
	F	8.76
	G	9.04
	H	10.15
Tudun-Fulani area farms	I	9.05
	J	7.53
	K	9.73
	L	7.96
Shiroro dam road farms	M	6.78
	N	7.06
	O	6.84
	P	8.47
Chanchaga area farms	Q	6.85
	R	7.70
	S	8.53
	T	7.65

4.3 Table 4:12 CONCENTRATION OF AVAILABLE FARMS

SAMPLE LOCATION		CONCENTRATION IN PPM			
		Fe	Cu	Zn	Mo
F.U.T Bosso campus, Minna	A	3.05	0.81	1.02	2.00
	B	2.95	0.29	0.81	2.08
	C	2.77	0.28	1.21	1.50
	D	2.90	0.23	0.70	0.78
Bida road farms	E	3.12	0.29	0.80	1.06
	F	3.53	3.96	0.86	1.27
	G	2.25	0.40	0.47	0.88
	H	2.50	0.24	0.54	0.95
Tundun-Fulani area farms	I	3.01	0.22	0.63	1.40
	J	2.86	0.15	0.37	1.24
	K	3.30	0.27	0.61	0.67
	L	1.15	0.13	0.31	0.83
Shiroro dam road farms	M	2.98	0.53	1.05	1.33
	N	2.06	0.28	0.61	1.21
	O	2.20	0.25	0.49	0.72
	P	3.10	0.37	1.02	0.77
Chanchaga area farms	Q	2.09	0.62	0.37	0.89
	R	2.37	0.45	0.49	0.91
	S	1.36	0.48	0.58	0.60
	T	1.28	0.21	0.45	0.70

The distribution of the various elements in the farms is as shown in figures A to H, and the appendix shows the calibration curves.

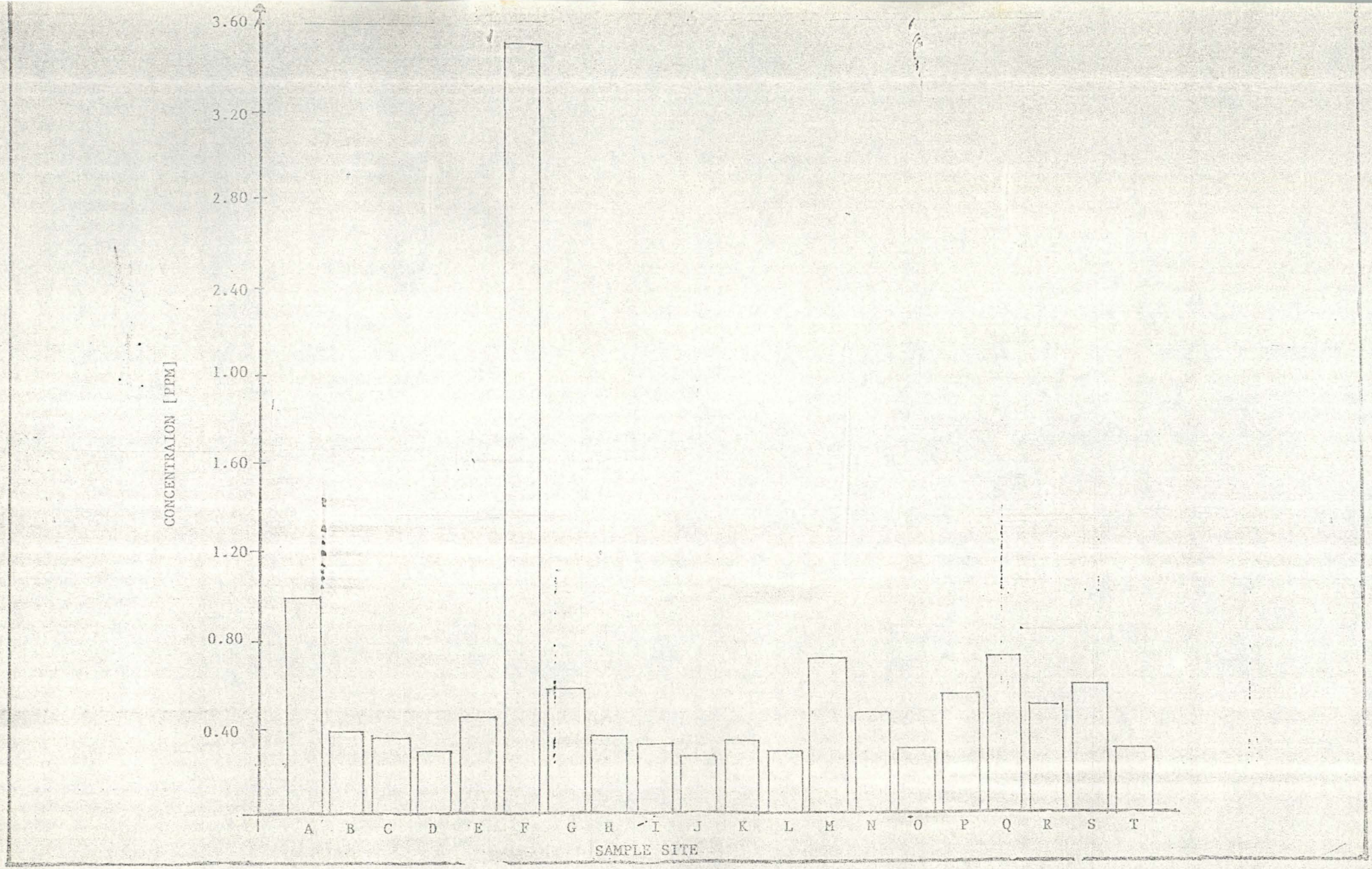


Figure A: copper distribution

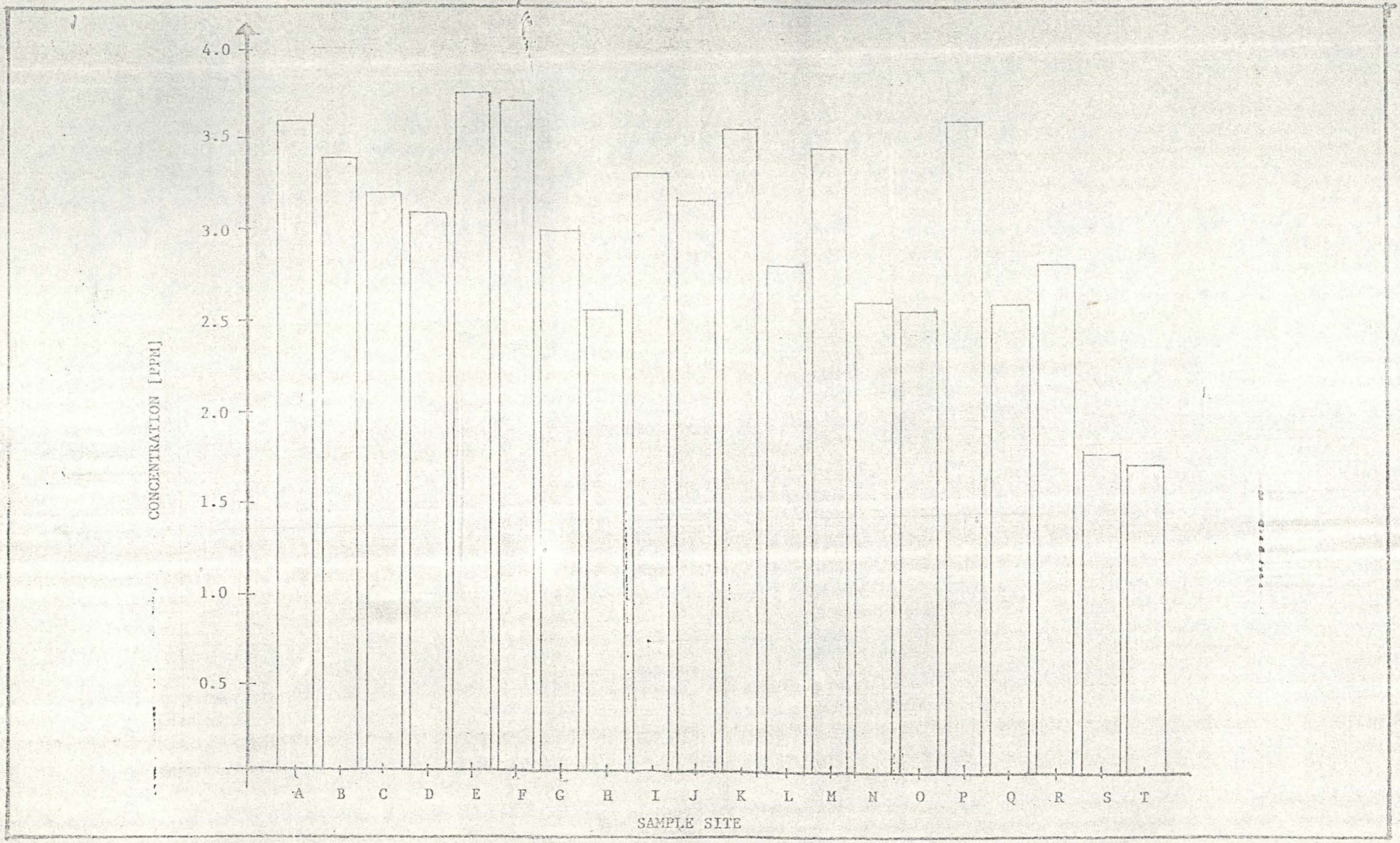


Figure B: Iron distribution

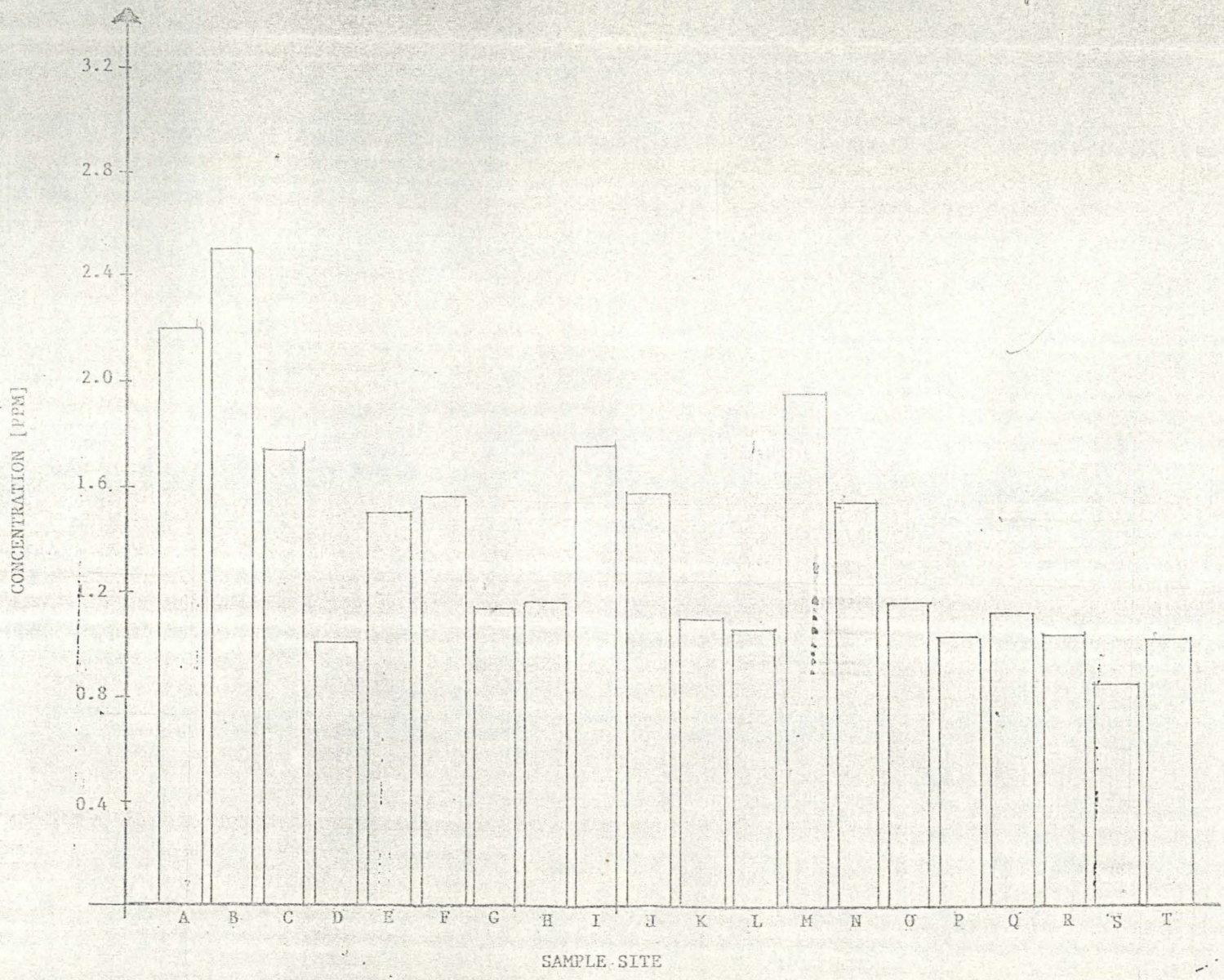


Figure C: Molybdenum distribution

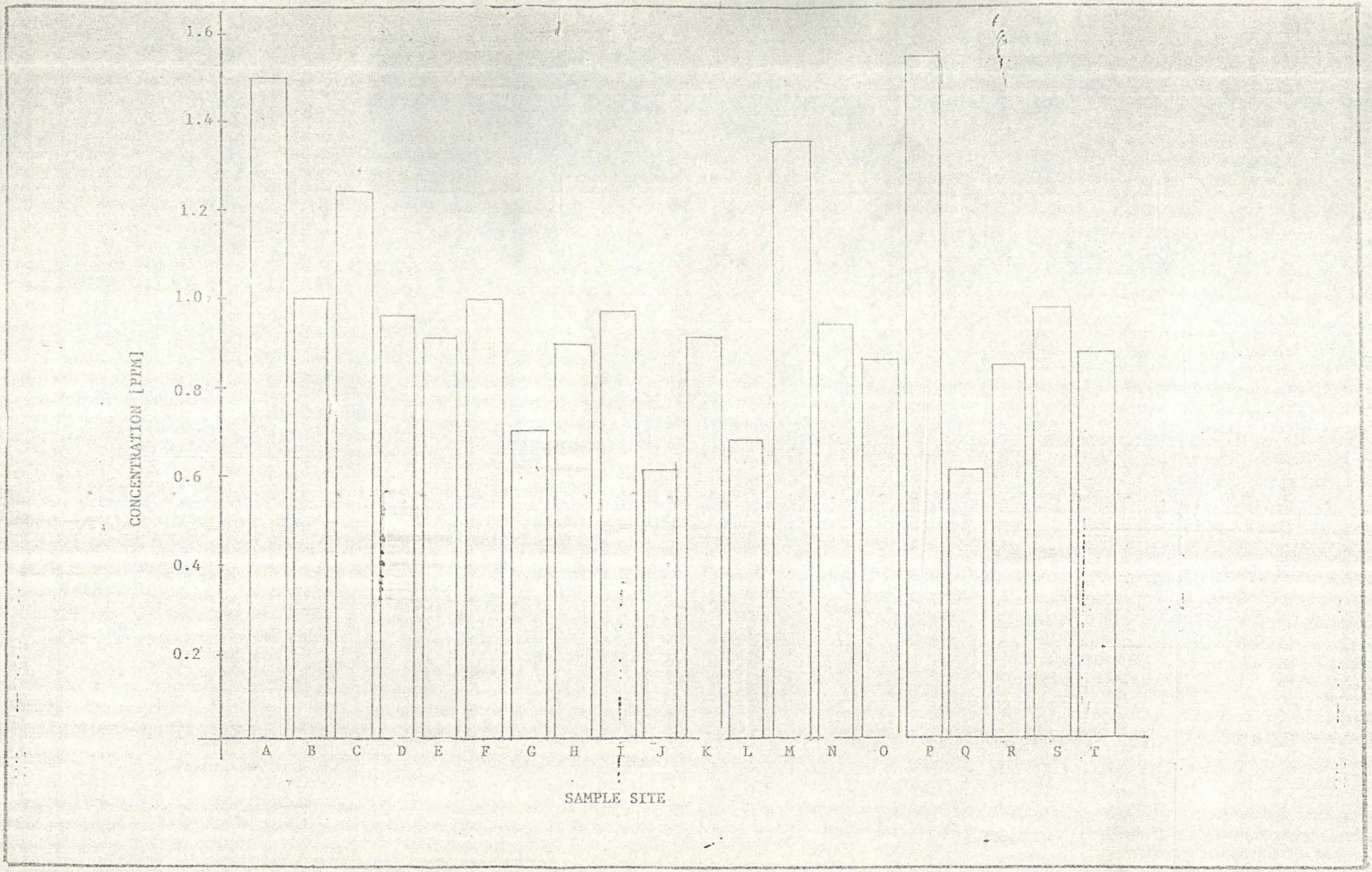


Figure D: Zinc distribution

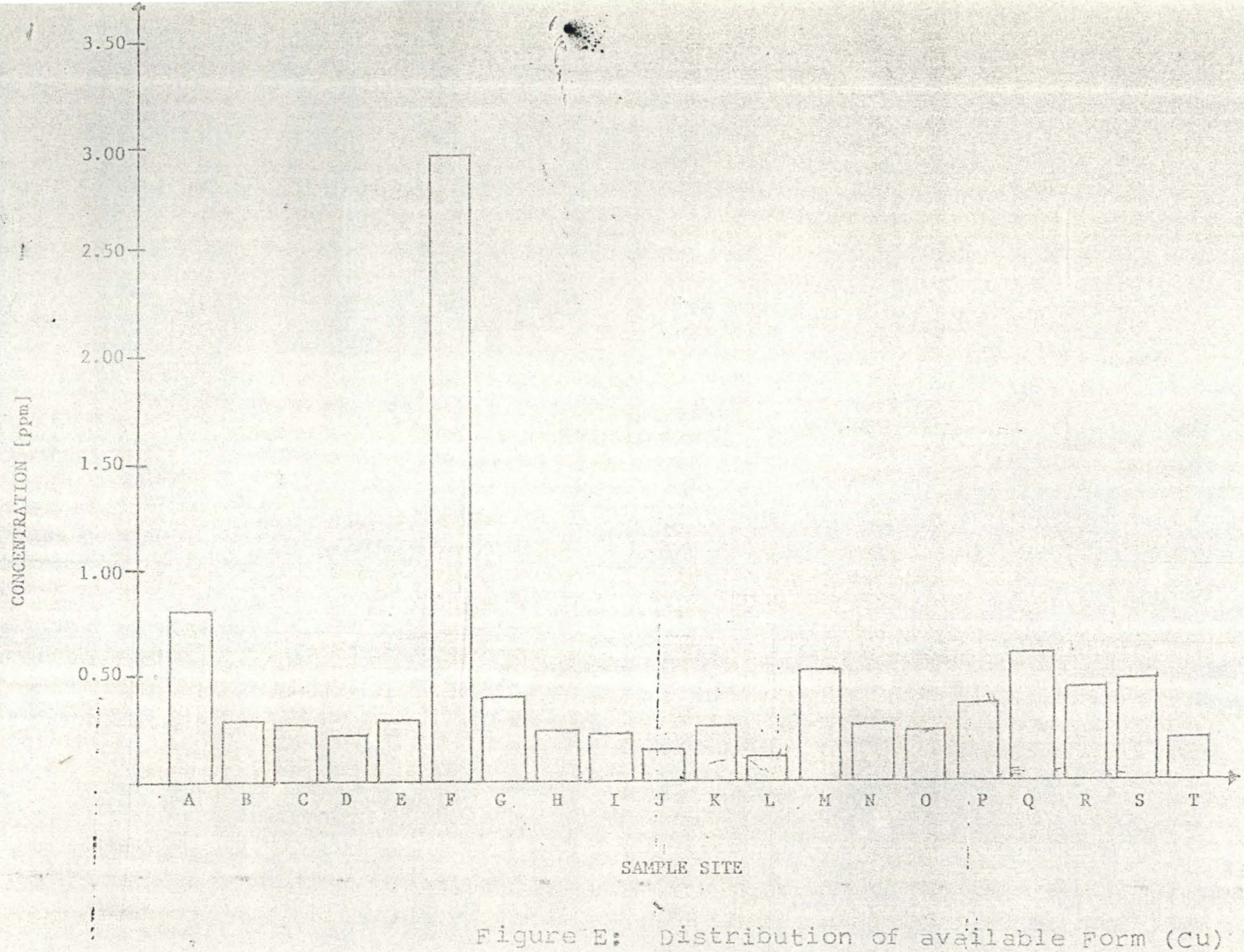


Figure E: Distribution of available Form (Cu)

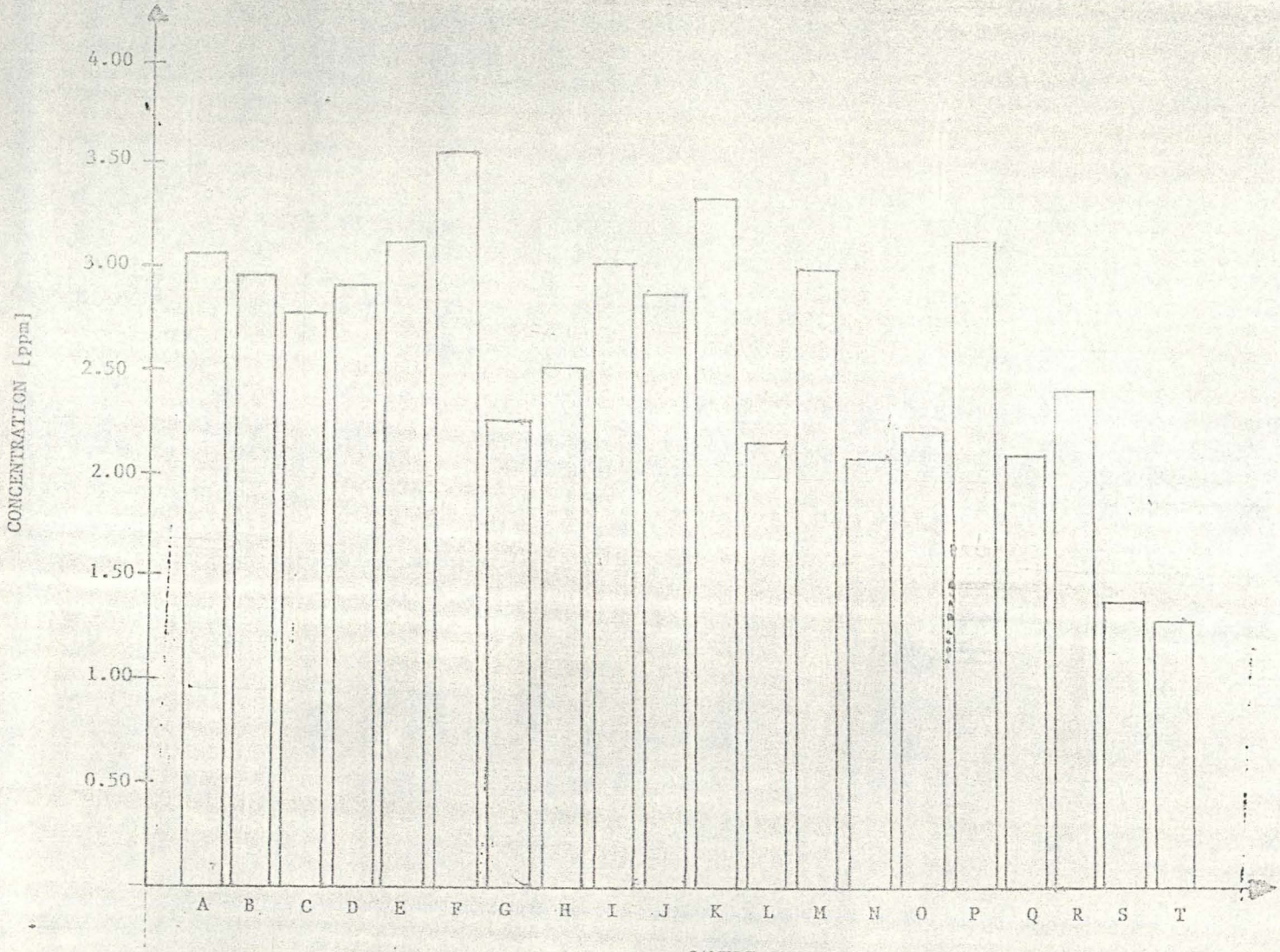


Figure F; Distribution of available Form (Fe)

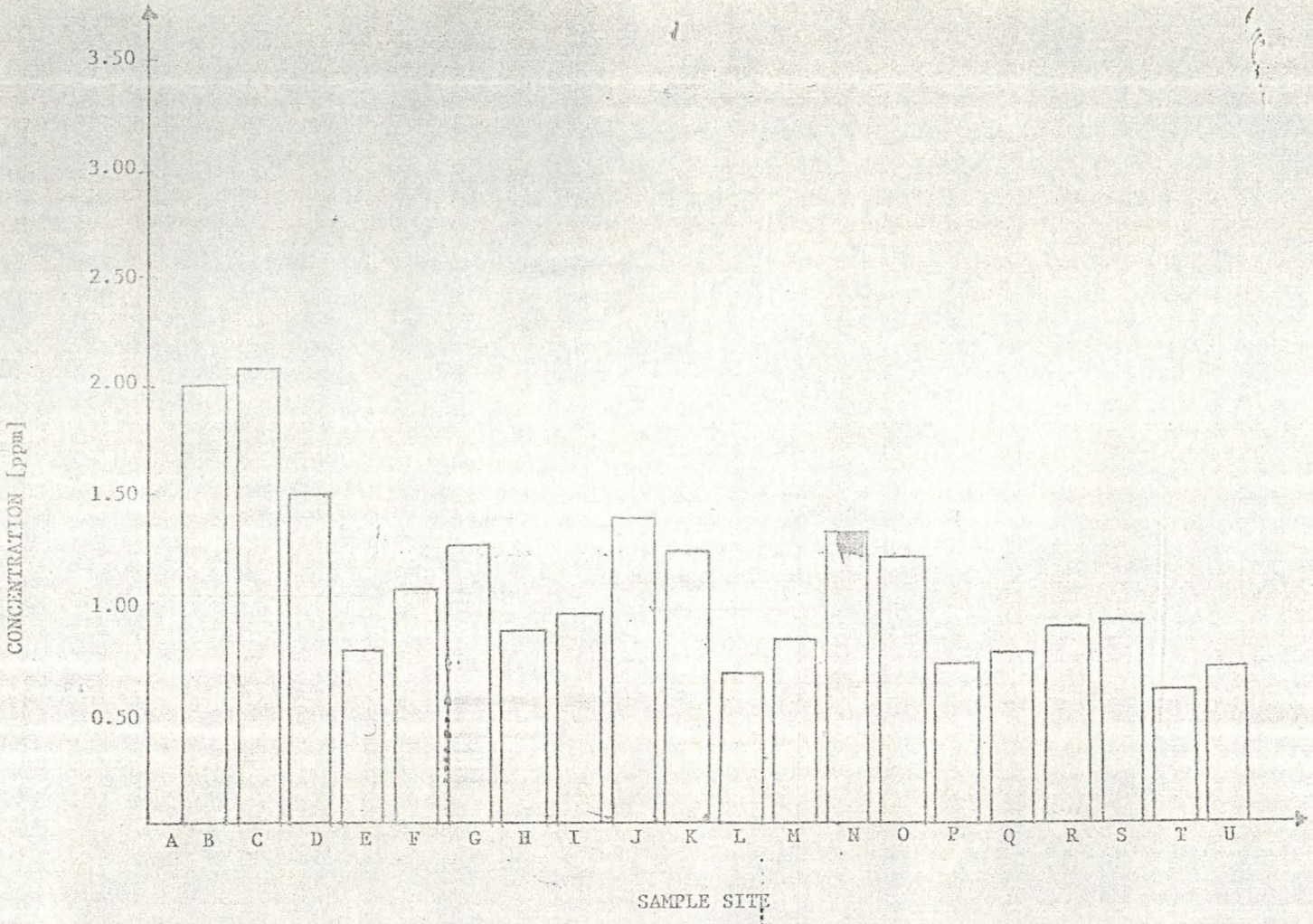


Figure G: Distribution of available Form (Mo)

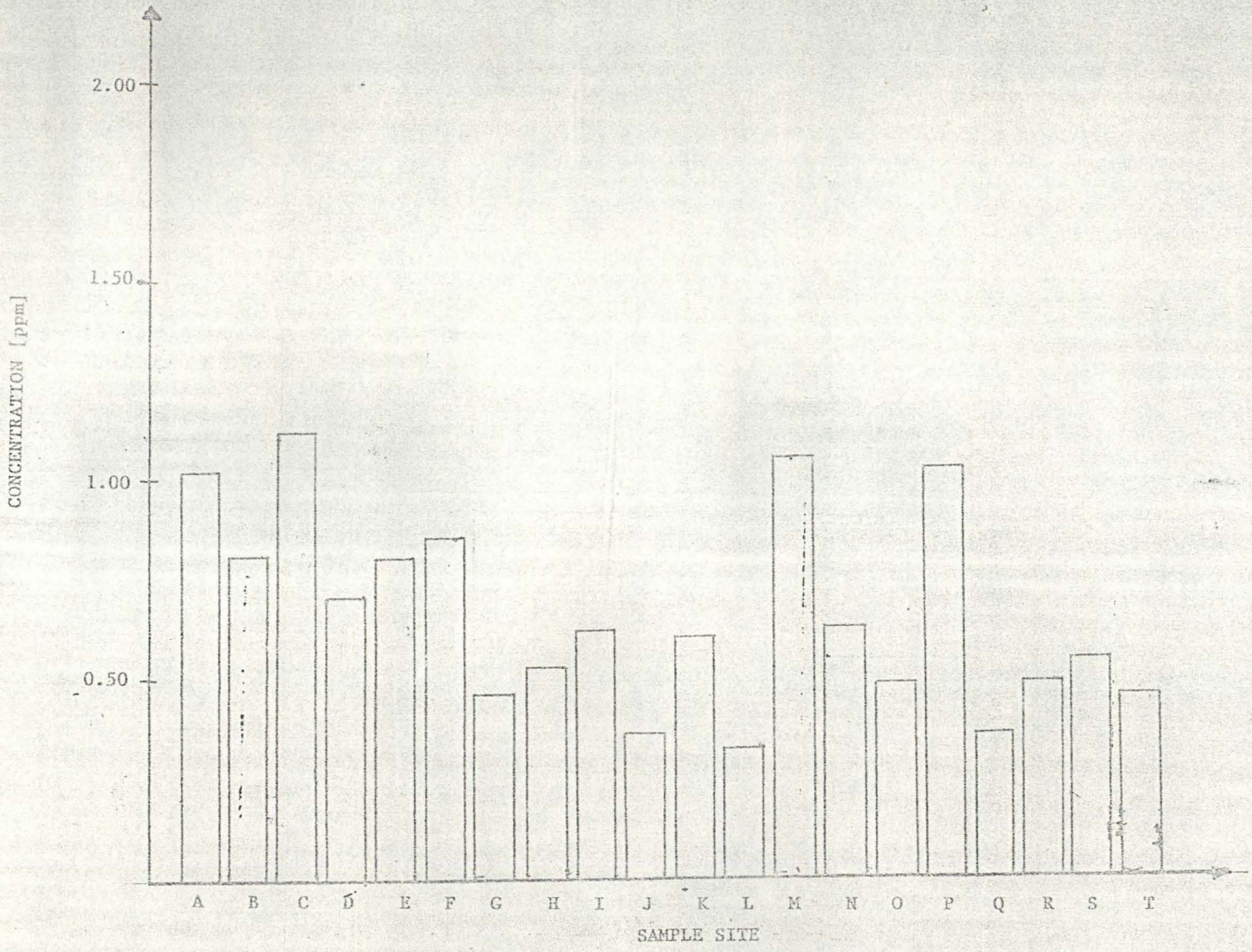


Figure Figure H: Distribution of available Form (Zn)

4:5 SOIL pH

Most of the soil analysed were found to be alkaline in nature except for three farms that are fairly acidic. The soil samples that were found to be acidic were taken from a forest vegetation. This agrees with the results obtained as compared to the locations where the soil samples were collected.

Liming may not be required for most of the farms except for farms M and O along Shiroro dam road and Q in Chanchaga area. Liming is usually carried out to raise the pH value of the soil, hence it is not necessary to add more lime to most of the farms.

Previous studies have shown that Maize, Guinea corn, Rice, Millet, Yams and Groundnut grow best under alkaline soils provided other conditions are satisfied. These are crops that are commonly cultivated in the localities where soil samples were obtained for the analysis. The soil pH values obtained from the analysis are good for the cultivation of such crops except the three farms mentioned earlier.

4:6 MICRONUTRIENTS

The requirement for micronutrients vary from plant to plant. Some require a higher concentration of a particular nutrient than the others. The release of micronutrients in the soil depend on the soil pH and other factors mentioned earlier.

4:6:1 COPPER

Looking at the result, it appears a significant amount of copper is available. A concentration of 0.26ppm to 3.50ppm was obtained for the various farms. This quantity is fairly enough especially for the farm with concentration of 3.50ppm

Mixed crop farming is mostly practiced on a yearly basis in most of the farms considered for the analysis and fertilizer is usually applied during each planting season. This may fairly affect the level of copper in the soil. The rate of removal of copper from the soil depends to a great extent on the type of crops cultivated on the farmland.

In most of the farms considered for the analysis crops like Yams, Maize, Guinea corn, Groundnut, Millet, Rice are usually cultivated. These are crops that require copper for healthy growth. Necessary steps should be taken to raise the level of copper in farms that do not have sufficient quantity as revealed by the results.

Among typical deficiency symptoms of copper in plant are chlorosis and leaf distortion. These symptoms occur preferentially in young shoot tissues. The decrease in photosynthetic electron transport with copper deficiency decreases the rate of carbon dioxide fixation, and the concentration of starch and soluble carbohydrate in plants during vegetative growth is responsible for low dry matter production. Reduction of fruit or seed yield also occurs with copper deficiency. In legumes, copper deficiency depresses modulation and the nitrogen - fixation rate, leading to nitrogen deficiency[2].

However, it was not possible to find out whether the crops cultivated in these farm-land has copper deficiency since the analysis were carried out during the dry season.

4:6:2 IRON.

Iron as an element is characterised by easy change of the oxidation state [$Fe^{III} \rightleftharpoons Fe^{II}$]. The main oxidation state of iron in plants is the ferric form [Fe(lll)][2]. The ferrous form [Fe(ll)] and the highly toxic free Fe^{2+} are normally below the detection level in plants, but can reach values upto 20% of the total iron under certain circumstances [Manchold et al; 1968; Goodman and Dekock, 1982]. Iron activates a number of enzymes and plays a role in the synthesis of ribonucleic acid.

From the current study the amount of iron detected varies from farm to farm. The lowest being 1.68ppm and the highest being 3.75ppm in the soil samples analysed. This quantity is significant considering the type of crops cultivated in the farms. Mixed cropping is practiced in the farmlands where soil samples were collected.

Iron deficiency will result in a decrease in the concentrations of chlorophyll in and other light harvesting pigments [carothene and Xanthophyll], as well as in the activities of electron carriers of both photosystems[2]. This may result in low yield of crops that depend on the absorption of iron for such processes. Nevertheless, these deficiencies present may hardly be observed because of the application of fertilizer and manure before and during the planting season.

4:6:3 MOLYBDENUM.

Molybdenum exist in plants as an anion, primarily in its highest oxidised form, Mo [IV], and also as Mo [IV]. The functions of molybdenum in plants are related to electron transfer reactions.

From the current study, the amount of molybdenum detected ranges from 8.0 to 2.50ppm. This quantity is sufficient for some crops like Yams, Rice, Guinea corn, but insufficient for legumes. Compared with other micronutrients, the molybdenum requirement of plant is the lowest and depends on the form of nitrogen supply. Due

to the high molybdenum concentrations of root nodules of legumes, crops that rely on nitrogen fixation have a higher molybdenum demand than other species[2]. As a result of this, such legumes if planted in these farms will give low yield.

Molybdenum has a striking effect on pollen formation. Tasseling, anthesis, and development of anthesis in corn are inhibited by molybdenum deficiency. Poor and delayed flowering and reduced viability of the pollen grains may also explain the reduction in fruit formation in Mo deficiency melon plants growing on acid soils. The risk of premature sprouting of grains on corn cobs is increased when the molybdenum concentrations in the grains fall. Molybdenum in involved in nitrogen fixation as such its requirement for root nodules in legumes is particularly high.

It has been reported that heavy phosphate application increases molybdenum uptake while heavy sulphur application decreases it[8]. Superphosphate and NPK fertilizers are the common fertilizers applied in these farms. As a result molybdenum is made more available for the plant uptake. This may account for the low level detected in the soils analysed. Due to the regular application of fertilizers in these farms, deficiency symptoms may hardly be observed in the plants cultivated in these farms.

4:6:4 ZINC

The element zinc is not subject to valency change and exist in plants only as Zn[II]. As a mineral nutrient, Zinc mainly functions as a divalent cation by coupling enzymes with corresponding substrate and forming tetrahedral chelates with different organic compounds including polypeptides[2].

The amount of Zinc detected in the various soils analysed varies from one farm to the other. The lowest amount detected is 0.61ppm while the highest is 1.5ppm. This quantity is not enough considering the type of crops cultivated.

Yams and potatoes are among common crops grown in the farms analysed. It is reported that these type of crops require a reasonable quantity of Zinc to give good yield[2]. The low level of Zinc can be attributed to the crops cultivated in these farms as the rate of removal is greater than replacement.

In Zinc deficient plants, metabolic changes are manifold and quire complex, and include changes in metabolism of carbohydrates, proteins, auxins, and impaired membrane integrity. It is reported that only with extreme zinc deficiency, net photosynthesis in inhibited, presumably due to disturbed chloroplast structure and inhibited photosynthesis electron transfer[2].

To arrest the deficiency of these micronutrients in general specialist advice on methods of fertilizer and manure application should be employed, and good management practices be employed to reduce the loss of these nutrients through leaching and other ways.

Also, to achieve any significant success in minimising or effectively correcting problem of micronutrient deficiencies requires a thorough knowledge of the micronutrient needs of the various plants and crops grown. The research scientist and technologist should show greater attention and much interest in this area. This will require backing by the private sector, especially those in Agro-Allied industries and also the government as regards funding. It is hoped that with such combined efforts the problem of micronutrient deficiency and poor crop yield will be properly addressed.

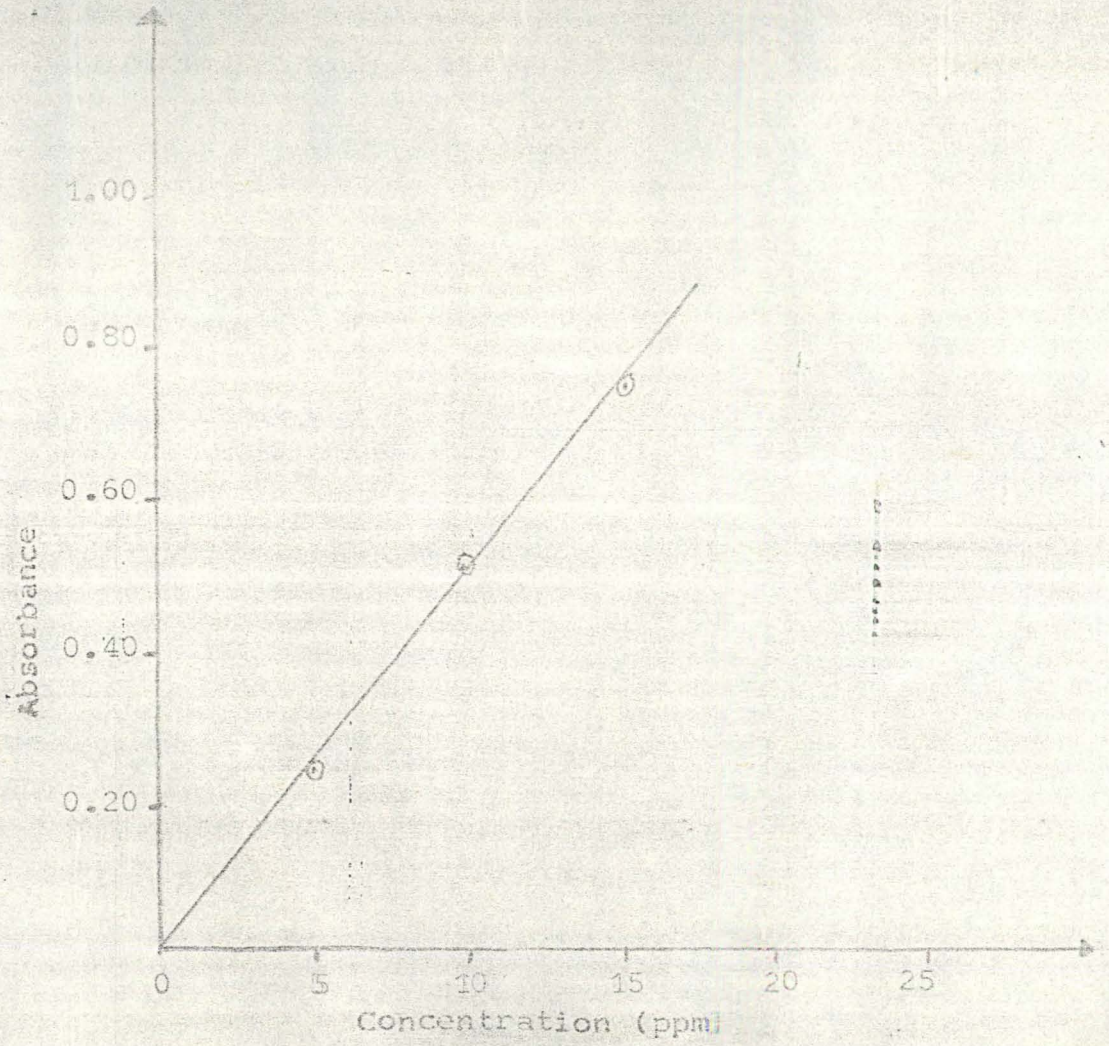


Fig 1 Calibration curve for copper

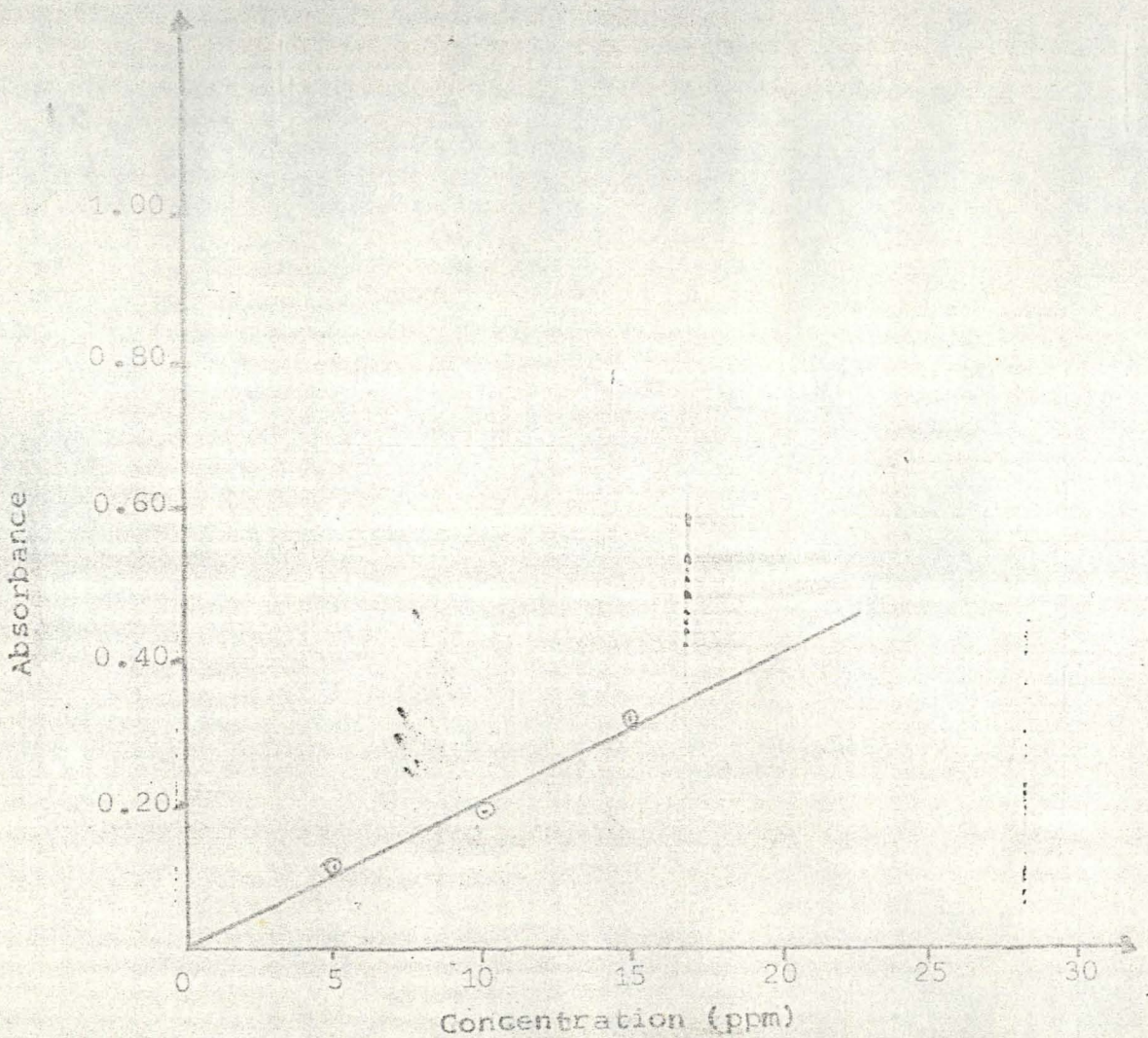


Fig 2: Calibration Curve for Iron

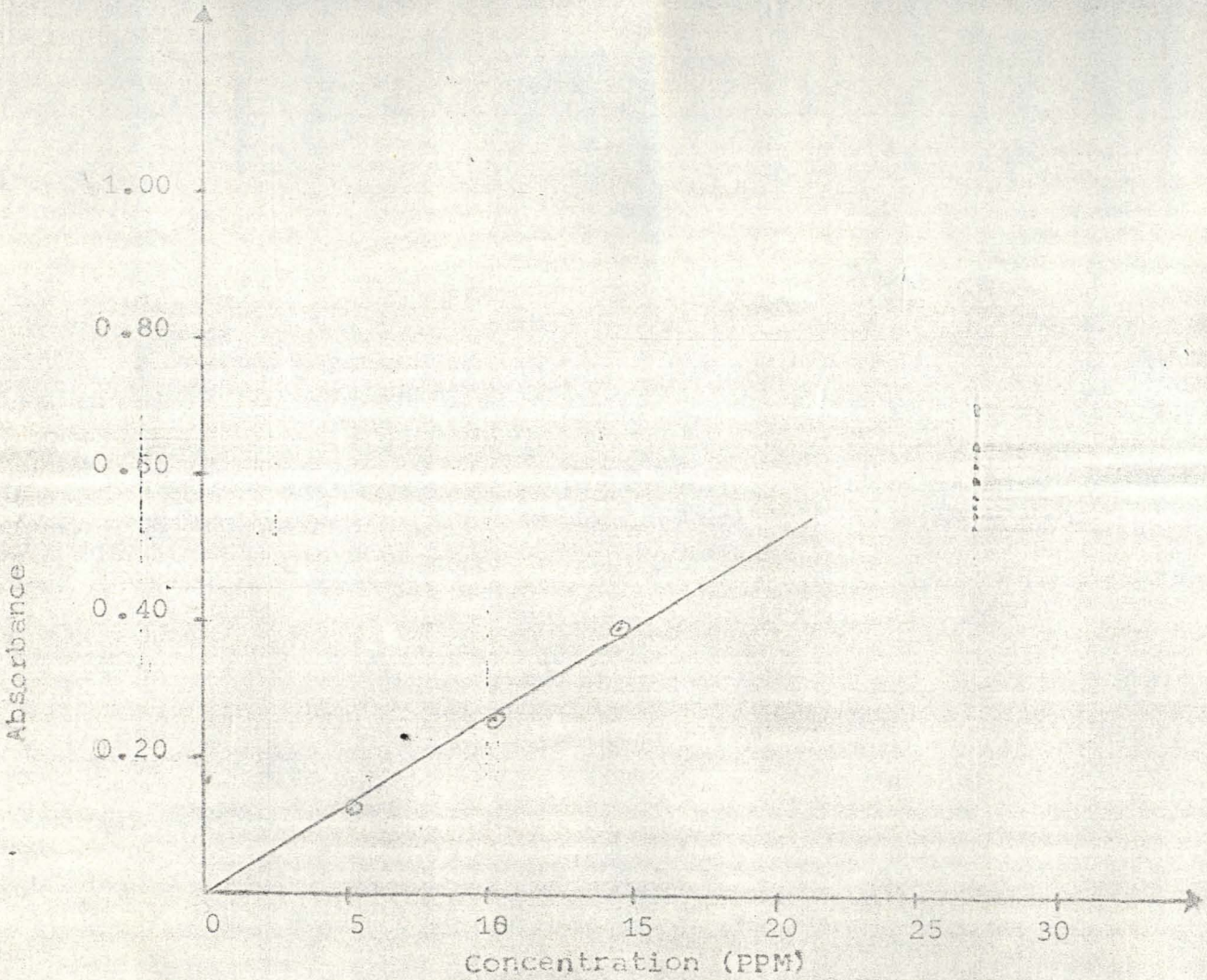


Fig 3: Calibration Curve for Molybdenum

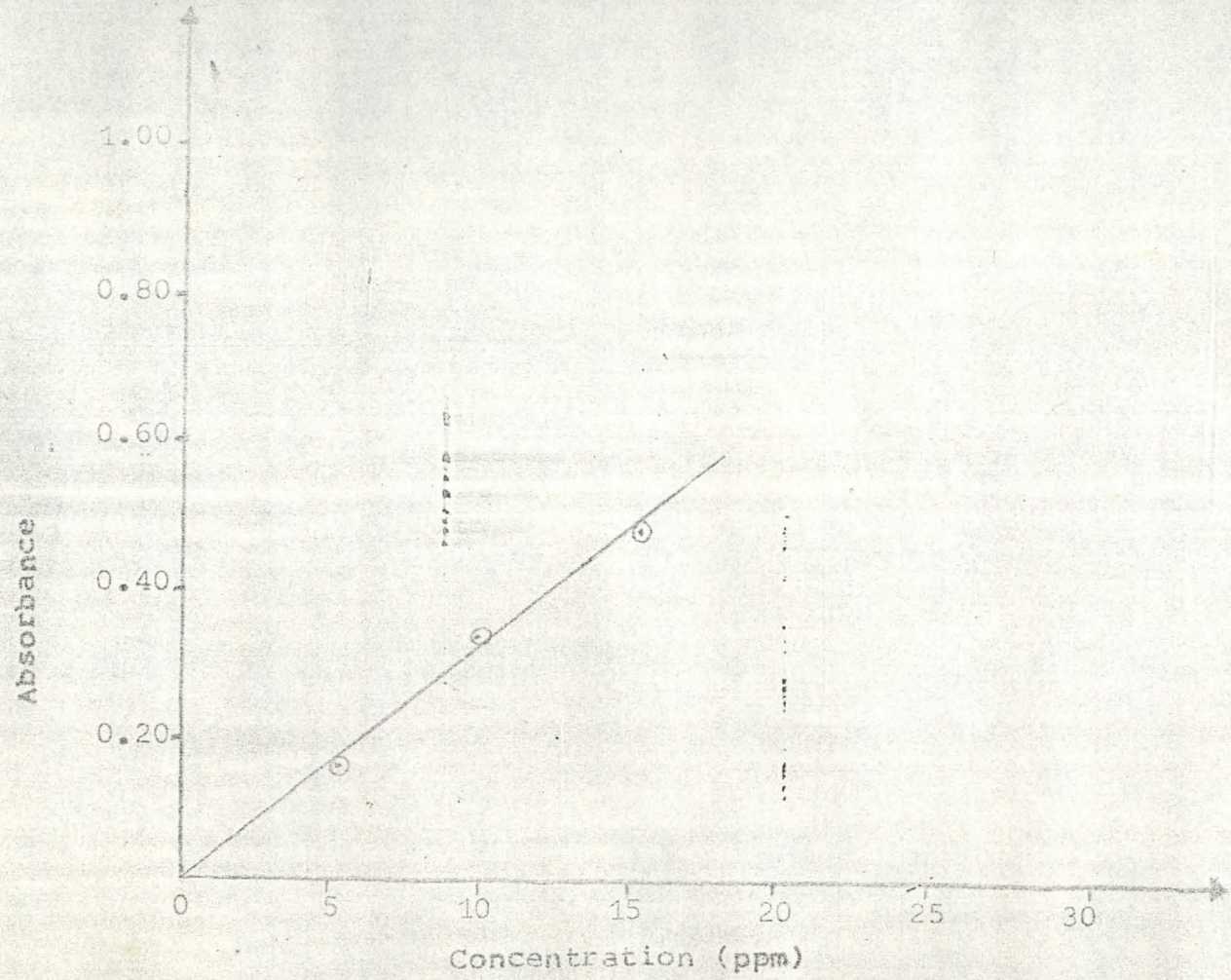


Fig 4: Calibration Curve for Zinc

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