# TOTAL AND DOUBLE-ACID EXTRACTABLE COPPER AND ITS ADSORPTION CHARACTERISTICS IN SELECTED SOILS IN KENYA

BY

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# DECLARATION

I, John Waithaka Ruguru, hereby declare that this thesis is my original work and has not been presented for a degree in any other University.

Signed 7-9-1992.

J.W. RUGURU

This thesis has been submitted for examination with my approval as University Supervisor

Signed Sep. 7, 1992.

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(University Supervisor)

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# TOTAL AND DOUBLE-ACID EXTRACTABLE COPPER AND ITS ADSORPTION CHARACTERISTICS IN SELECTED SOIL IN KENYA

## ABSTRACT

An investigation was conducted to determine the content and profile distribution of total copper (perchloric acid extractable) and double-acid (0.05N HCl + 0.025N $H_2SO_4$) extractable copper and its adsorption characteristics in surface and subsurface soils representing Andisols, Nitisols and Cambisols. The means of total copper in the A horizons of Kabete, Gituamba, Njoro and Naivasha soils were 26.8, 29.3, 3.3 and 8.9 ppm respectively and the means for the B horizons were 24.8, 31.3, 3.1 and 9.7 ppm respectively. Total copper was found to be generally uniformly distributed with depth. This uniformity was attributed to the low mobility of coper in soil. The means of the double-acid (DA) extractable copper in the A horizons of the same soils (i.e. Kabete, Gituamba, Njoro and Naivasha) were 0.08, 0.38, 0.18 and 0.09 ppm respectively and the means for the B horizons were 0.23, 0.39, 0.22 and 0.08 ppm respectively.

Total and DA-extractable copper contents were correlated with soil pH, organic carbon and CEC. There was no significant correlation between total copper and CEC, organic carbon, pH or DA-extractable copper. A significant non-linear relationship was found between DA-extractable copper and CEC in Naivasha soil ($r^2$=0.77). The copper adsorption maxima were 298 µg Cu/g for Naivasha soil, 284 µg Cu/g for Gituamba soil, 260 µg Cu/g for Kabete soil and 164 µg Cu/g for Njoro soil. The adsorption maximum was highly correlated to organic carbon and CEC except in Kabete soil.

# TOTAL AND DOUBLE-ACID EXTRACTABLE COPPER AND ITS ADSORPTION CHARACTERISTICS IN SELECTED SOIL IN KENYA

## 1.0 INTRODUCTION

### 1.1 The chemistry of copper

Copper is widely distributed geographically and geologically. The average amount of copper in the earth's crust is about 70 ppm (Hodgson, 1963). Copper frequently occurs as a primary sulphide mineral such as bornite ($Cu_5FeS_4$) or Chalcopyrite ($CuFeS_2$). Oxidised copper minerals are formed by weathering of sulphides and occur as oxides, hydroxides, carbonates, chlorides and silicates (Butts, 1964). Copper and sulphur form sulphides in which copper is in the +1 rather than +2 oxidation state due to the instability of copper (II) sulphide (Parker, 1981).

Copper (I) forms many slightly water soluble salts with anions $X^-$, in which copper (I) is stable. Such salts possess some degree of covalent bonding. The CuX species is often a weak electrolyte. Copper (II) salts, $CuX_2$, are usually much more soluble in water than the corresponding copper (I) salts and are stronger electrolytes.

### 1.2 Copper in soils

Copper in the earth's crust is most abundant in mafic and intermediate rocks and has a tendency to be excluded from carbonate rocks (Krauskopf, 1972). Copper forms several minerals of which the common primary minerals are simple and complex sulphides. These minerals are quite easily soluble in weathering processes and release copper ions especially in acid environment (Alina and Henryk, 1984).

The copper content of soils ranges from 1 to 3 ppm in soils where copper deficiency characteristically occurs to values of 200 ppm or more in soils where excessive copper has accumulated as a result of application of copper fungicides (Aubert and Pinta, 1977). Total copper content in soils depends on the copper concentration in parent rocks, humus, organic matter, clay and the pH. Basic or neutral pH soils which are rich in humus contain more copper than acid pH soils (Aubert and Pinta, 1977).

Copper is a very versatile trace cation and it shows a great ability to chemically interact with mineral and organic components of soils. 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 (Alina and Henryk, 1984). The low mobility of copper also means that it is not easily leached and when added to soil, it remains on the surface for a long period of time.

Generally copper remains isotopically exchangeable in acid soils and is fixed in complex forms in alkaline soils. Copper added to soil is easily sorbed by clays. Henkens (1961) found that copper penetration in a clay soil was about 2.5 cm during the year following application and had reached only 5 cm several

years latter. Menzel and Jackson (1950) showed that kaolinite is particularly active in sorbing copper as the
($CuOH^+$) ion.

Copper ions are held very tightly on both inorganic and organic exchange sites (McBride, 1981). According to Alina and Henryk (1984), the processes controlling fixation of copper by soil constituents are related to the following phenomena:

1. Adsorption
2. Occlusion and coprecipitation
3. Organic chelation and complexing
4. Microbial fixation.

Copper adsorption is strongly dependent on the pH. A common observation is that adsorption of copper ions increases as the pH increases (McLaren and Crawford, 1873 b). This pH-dependent copper adsorption is likely to be most important in soils a with large content of variable charge minerals (James and Barrow, 1981).

Occlusion, coprecipitation and substitution are involved in non-specific adsorption of copper (McBride, 1981). Non-diffusible fractions of soil copper are most probably incorporated in various mineral structures. 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 copper in non-diffusible form (Alina and

Henryk, 1984).

Soluble forms of copper in soils are of great importance in agronomic practice while total copper content of soils gives basic information for geochemical studies (Mitchell, 1955). Many kinds of organic substances form both soluble and insoluble complexes with copper, thus copper-binding capacities of soils and copper solubility are highly dependent on the kind and amount of organic matter in soils (Alina and Henryk, 1984). Copper is rapidly and strongly fixed by organic matter and copper deficiency is commonly found in organic soils. Such a deficiency is almost a feature of newly cultivated peat soils (Hesse, 1971). A beneficial result of this high affinity of organic matter for copper is that large quantities of copper can be fixed in a non-toxic form by soil organic matter.

An important aspect of copper and organic matter complexes involves binding with fulvic and humic acids. Schnitzer and Skinner (1966) reported log K values for Cu-fulvic acid complexes as 5.78 at pH 3.5 and 8.69 at pH 5.0. These fulvic acid compounds may be important as the soluble forms of organic copper. Humic acid is an important fraction for binding copper to organic matter in insoluble forms in the soil (Stevenson and Ardakani, 1972). The average stability constant (logK) for copper (II) ion with different humic acid sources was 8.7 (Stevenson, 1976).

Microbial fixation plays an important role in the binding of copper in certain surface soils. The amount of copper fixed by microbiomass is widely variable and is affected by such factors as metal concentration, soil properties and the growing season (Alina and Henryk, 1984).

The availability of soil copper to plants is relatively low, which is fortunate because only approximately 10 ppm of the dry weight of plants is copper, and excessive availability leads to stunted root systems (Woolhouse and Walker, 1981). Uptake of copper by plants is hindered by aluminium. Hiat et al (1963) showed that as little as 0.1 ug Al/g seriously reduced copper uptake by wheat.

Excess copper can be toxic to plants and this is liable to occur where copper compounds are applied as fungicides, particularly on acid soils. Copper also prevents uptake and translocation of iron thus inducing iron chlorosis. In soils contaminated with copper, liming or addition of peat are used as corrective measures. In deficient soils, copper fertilizers especially copper (II) sulphate ($CuSO_4 . 5H_2O$) are used.

Total levels of soil copper are of limited diagnostic value, except to identify extremely deficient soils with very low total copper concentrations (Lucas and Knezek, 1972). A host of chemical soil tests have been devised for estimating the ability of soils to supply copper for plant growth. The extractants used include water and dilute salts, acids and chelating agents. Acidic solvents such as HCl appear to extract copper from pools which are not available to plants (Martens, 1968).

Quantitative data on the content and distribution of cop

in Kenya soils are limited. Also not much study has been done

the behaviour of copper in Kenya soils. The objectives of th

investigation were:

(a) to study the distribution of total and double-ac ($0.05N\ HCl + 0.025N\ H_2SO_4$) extractable copper wi depth and to determine the relationship between doubl acid extractable copper and other soil chemic properties,

(b) to study the adsorption characteristics of copper the surface horizons of selected soils in Kenya.

# 2.0 LITERATURE REVIEW

## 2.1 Importance of copper in agriculture

Copper is essential for both plants and animals. In plants it participates in photosynthesis, assists in the assimilation of starch and nitrogen, enhances the stability of chlorophyll and stimulates respiration (Georgievskii, 1982). In animals it is essential for blood formation (Sauchelli, 1969).

A number of workers have observed crop responses to copper fertilization. Pinkerton et al (1964) were able to show that yellowing and die-back symptoms of wheat in Njoro were due to copper deficiency. Deficiency symptoms were also observed in maize, oats, barley, sorghum and some pasture grasses in Kenya (Wapakala, 1972). Adusyi (1971), working at Ruiru in Kenya observed coffee response to copper fertilization. In the Mbeya region of Tanzania, Mbonika and Uriyo (1984) found that wheat responded to copper fertilization.

## 2.2 Forms of soil copper

### 2.2.1 Mineral forms of copper

The average copper concentration in the earth's crust is about 70 ppm (Hodgson, 1963). The most common primary minerals of copper are simple and complex sulphides with strong covalent bonds formed between reduced copper ($Cu^{+}$) and sulphide ($S^{-2}$) anions. The copper sulphide structures are more covalent in nature than the silicate, oxides or carbonate structures. However, copper is capable of isomorphous substitution in ferromagnesian silicates, an excellent example being copper (II) ion replacement for manganese (II) ion in manganese garnets (Povarennyk, 1972).

While the predominant minerals of copper in the earth's crust are sulphides (largely in the +1 oxidation state), the metallic form of copper is also common in reducing environments. However upon exposure to the conditions at the earth's surface, $Cu^+$ and $Cu^0$ are oxidised to the +2 oxidation state. The flooding of soils may cause $Cu^+$, or even $Cu^0$, to become thermodynamically more stable than $Cu^{2+}$ (Lindsay, 1979), although this reduction process requires that the soil atmospheric level of oxygen be reduced to an extremely low concentration. In aerobic soil environments, the primary sulphide minerals are dissolved by weathering processes. The dissolution of chalcopyrite for example, can be written:

$$4CuFeS_2+17O_2+10H_2O \longrightarrow 4Cu^{2+}+4Fe(OH)_3+8SO_4^{2+} +8H^+$$

A number of secondary minerals of $Cu^{2+}$, including oxides, carbonates, silicates, sulphates and chlorides can then form, although all are relatively soluble. At low pH and under strong leaching conditions at the earth's surface, most of these minerals would not persist (McBride, 1981). It has been demonstrated that those copper minerals that are expected to be least soluble under conditions prevalent in the surface soils are much too soluble to control the very low observed activities of copper (II) ion in soil solution (Lindsay, 1979; McBride and Blasiak, 1979; Cavallaro and McBride, 1980).

(a) <u>Occluded and co-precipitated copper</u>

Since a relatively small fraction of the total copper in many soils is isotopically exchangeable (McLaren and Crawford, 1974; Kline and Rust, 1966) and chemical fractionation schemes generally show that the bulk of native copper in soil clays is only extractable by dissolution of the clays (McLaren and Crawford, 1973 a; Shuman, 1979), it is likely that a significant fraction of soil copper is occluded (i.e. buried) in various mineral structures. Calcareous soils, for example, have large fractions of non-diffusible copper in a form that is soluble in dilute acid (Kline and Rust, 1966). Non-diffusible copper cannot be adsorbed on surfaces and therefore is present as an impurity within carbonate minerals.

Non-calcareous soils contain fractions of copper which cannot be extracted by weak acids, but are solubilised by chemical treatments which dissolve iron and manganese oxides or layer silicate clays (McLaren and Crawford, 1973 a). This 'residual' copper which represents the bulk of the total in many soils exists in a largely non-diffusible form (McLaren and Crawford, 1974; Kline and Rust, 1966). Non-diffusible copper in soils may reside within oxide structures, since co-precipitation of $Cu^{2+}$ in aluminium and iron hydroxides occurs readily (McBride, 1978 a). An observed correlation between quantities of copper and manganese dissolved by the treatment of soil with oxalate suggests that copper associates more strongly with manganese oxides than iron oxides (McLaren and Crawford, 1973 a). Associations between copper and iron oxides have commonly been observed in soils (Mckenzie, 1975; Childs and Leslie, 1977), although no evidence was found for copper -manganese association in the same soils. Thus, data regarding Cu-Mn and Cu-Fe associations often appear to be contradictory. However, the abundance of iron relative to manganese may give copper a better opportunity to associate with iron-rich secondary mineral phases in soils despite a very strong affinity of manganese oxides for copper (McBride, 1981).

Since $Cu^{2+}$ is capable of isomorphous substitution in octahedral positions of layer silicate clays, a portion of the 'residual' copper that is released from soils by hydrofluoric (HF) acid treatment may originate from crystalline silicate clays, although crystalline oxides or primary mineral particles may contribute part of the HF-soluble copper (McBride, 1981).

### 2.2.2 Adsorbed forms of copper

#### (a) Adsorption on clays and oxides

Unlike many other metallic ions, $Cu^{2+}$ can be 'specifically' adsorbed by layer silicate clays, iron oxides, aluminium oxides, manganese oxides and organic matter. On layer silicates, $Cu^{2+}$ adsorption is not anomalous if the pH is maintained at relatively low value (<5) (McBride, 1981). Thus $Cu^{2+}$ and $Ca^{2+}$ have approximately equal preferences for exchange sites of montmorillonite at low pH (El-sayed et al, 1970). As the pH is raised, the layer silicate surfaces apparently promote hydrolysis of $Cu^{2+}$ with the accompanying release of protons (Farrah and Pickering, 1976 a, 1976 b), and the adsorbed copper becomes much less exchangeable.

At trace levels in soils, $Cu^{2+}$ solubility may be controlled by specific interaction with hydrous oxide impurities in layer silicates rather than adsorption on the silicates (Jenne, 1968). Amorphous iron and aluminium hydroxides as well as crystalline oxyhydroxides readily adsorb $Cu^{2+}$ despite the presence of excess alkali metal ions (Kiniburgh et al, 1976; Forbes et al., 1976). In fact, with the possible exception of $Pb^{2+}$, $Cu^{2+}$ is the most strongly adsorbed of all the divalent transition and heavy metals on iron and aluminium oxides and oxyhydroxides (McBride, 1981). Since the mechanism of adsorption, unlike the loose electrostatic association observed on permanent charge clays, appears to involve formation of a direct surface Cu-O-Al or Cu-O-Fe bond (McBride, 1978a), the quantity of surface hydroxyl groups may determine the maximum level of chemisorption possible. Chemisorption of $Cu^{2+}$ on a crystalline mineral like gibbsite is likely to occur only at edges, where hydroxyls co-ordinated to single aluminium (III) ions exist.

In general, microcrystalline and amorphous oxides should have much greater capacities to chemisorb $Cu^{2+}$ than crystalline oxides with low surface areas (McBride, 1981). In some highly weathered soils, iron oxides are microcrystalline with particle sizes on the order of 100 Angstroms (Bigham et al., 1978). It is therefore reasonable to expect that oxides can play a significant role in specific adsorption of $Cu^{2+}$ by most soils as suggested by Jenne (1968).

Like iron and aluminium oxides, manganese oxides specifically adsorb $Cu^{2+}$ with the level of adsorption increasing as a function of pH (McLaren and Crawford, 1973 b). The affinity of synthetic manganese oxides for $Cu^{2+}$ is even stronger than that of iron or aluminium oxides (Mckenzie, 1980).

### (b) Adsorption on organic matter

Complexation by organic matter has long been recognised as an effective mechanism of $Cu^{2+}$ retention in soils. The $Cu^{2+}$ ion is directly bonded to two or more organic functional groups (mainly carboxylic, carbonyl and phenolic), so that the ion is immobilized in a rigid inner sphere complex (McBride, 1978 b). Trace levels of $Cu^{2+}$ in peats may also be strongly bound in porphyrin complexes (Goodman and Cheshire, 1973).

Although the isotopic exchangeability of $Cu^{2+}$ adsorbed on organic matter is lower than the exchangeability of $Cu^{2+}$ adsorbed on pure iron oxides, manganese oxides or layer silicates, organically bound copper (II) ion in soils is probably the largest contributor to the isotopically exchangeable (diffusible) fraction (McLaren and Crawford, 1974; Kline and Rust, 1966). The importance of organic forms of copper is demonstrated by the fact that alkali extraction techniques designed to remove most of the organic matter from mineral soils tend to solubilise a greater fraction of total soil copper than any other metal (Goodman and Cheshire, 1973 b). Organic solids serve the function of holding $Cu^{2+}$ in a kinetically available but thermodynamically stable (insoluble) form (McBride, 1981). Exchangeable and weak acid-extractable copper presents a small percentage of the total copper in most soils (McLaren and Crawford, 1973 a). This indicates that little $Cu^{2+}$ exists in unamended soils as exchange ions on permanent charge sites of clays or as specifically adsorbed forms on the external surfaces of layer silicates or oxides. The bulk of the copper is complexed by organic matter, occluded in oxides and substituted in primary or secondary minerals (McBride, 1981).

### 2.2.3 Solution forms of copper

A number of studies have produced evidence that the natural copper (II) ion in soil solutions at high pH does not exist as inorganic complexes but is largely complexed with soluble organics (Hodgson et al., 1965, 1966). The total complexed copper (II) ion in solution generally increases above pH 7 because of the greater solubility of soil organics at higher pH (McBride and Blasiak, 1979). On the other hand, the 'free' soluble copper (II) ion at higher pH is very much lower, commonly in the range of $10^{-9}$ - $10^{-6}$ M (McBride and Blasiak, 1979; Hodgson et al., 1965). Total native copper in soil solution is often about $10^{-6}$ - $10^{-7}$M (Bradford et al., 1971). The ratio of total dissolved copper to free (uncomplexed) copper (II) ion can therefore be greater than 100 (Hodgson et al., 1966).

Numerous studies using different techniques have all produced the conclusion that organic complexes are generally more important in soil solutions than inorganic complexes. It is expected that $Cu^{2+}$ will not adsorb on exchange sites of permanent charge clays in soils because of its much stronger affinity for organic or other sites of specific adsorption (McBride, 1981). Complexes of $Cu^{2+}$ with organic acids do not adsorb significantly on layer silicates clays because of their net negative charge (Bloomfield et al., 1976).

Unlike layer silicate clays, iron and aluminium oxides may show enhanced as well as inhibited adsorption of $Cu^{2+}$ in the presence of soluble organics. Because of the ability of oxides to adsorb organic acids including fulvic and humic acids by ligand exchange reactions (Parfitt et al., 1977a, 1977b), the presence of these organic substances on oxide surfaces may enhance adsorption of $Cu^{2+}$ if only a portion of the functional groups are involved in bonds to the surface. The remaining groups are then free to bond with $Cu^{2+}$, so that an oxide-organic-metal 'complex' is formed ( (McBride, 1981).

## 2.3 Fractionation of soil copper

McLaren and Crawford (1973 a, b; 1974) have distinguished five pools of soil copper:

(a) soil solution and exchangeable copper (soluble in 0.05M $CaCl_2$);

(b) copper weakly bound to specific sites (soluble in 2.5% acetic acid);

(c) organically bound copper (soluble in potassium pyrophosphate);

(d) copper occluded in oxide materials (soluble in acidic ammonium oxalate); and

(e) residual copper mainly in clay lattices (soluble in hydrofluoric acid).

These workers found that about one-fifth to one-half of the copper in 24 contrasting soil types was accounted for in organically bound forms.

## 2.4 Reactions of copper with organic matter

Organic substances of various types play a prominent role in the binding of copper in soils. A key role is played by humic and fulvic acids, which probably form highly stable complexes when copper is present in trace amounts (e.g. copper deficient soils). Fulvic acids are responsible for the formation of soluble complexes (Geering and Hodgson, 1969), while the humic acid fraction is responsible for the formation of insoluble complexes (Stevenson and Ardakani, 1972).

According to Stevenson and Fitch (1981) the formation of Cu-organic matter complexes would have the following effects in soil:

(1) the concentration of copper in soil solution can be lowered through complexation to clay-humus or by the formation of insoluble complexes with humic acids. Soluble ligands may be of considerable importance in transforming solid phase forms of copper into soluble forms.

(2) for conditions under which copper tends to precipitate (e.g., in calcareous soils), complexation will serve to maintain copper in soluble forms.

(3) when excess copper is present, complexation may reduce the concentration of $Cu^{2+}$ to a non-toxic level.

(4) natural complexing agents may be involved in the migration and transport of copper.

## 2.5 Copper content in soils and its distribution in soil profiles

Various workers have reported different values for soil copper contents. Mbonika and Uriyo (1984) reported that total copper in the Mbeya region of Tanzania ranged from 4.5 to 34 ppm. Viets and Lindsay (1970) reported that total copper in Colorado soils ranged between 2 and 92 ppm. Holmes (1943) compi analysis from a wide range of soils from the United Sta America and reported total copper in soil as ranging from 2 ppm. According to Bandyopandya and Adhikari (1988) soils i Bengal contained 19 to 36 ppm total copper. Nyandat and O (1976) in their survey of copper content in arable and areas of Kenya reported a range of 5 to 150 ppm total coppe contaminated soils, very high levels of soil copper ca obtained.

Copper is a rather immobile element and shows l variation in total content with depth (Hodgson, 1963). Ho movement of copper from highly leached surface horizons lower horizons has been observed in podzols (Alina and H 1984). Also, in forest soils, most of the copper accumula the organic-rich surface layer (Boggess, 1977). Of more int than the total copper is the 'available' copper as a functi depth. Copper extractable by weak acid usually varies with to a much greater extent than total copper (Swaine and Mit 1980), and is commonly higher in the organic-rich surface than in the lower horizons. Copper that is extractable by or EDTA generally decreases with depth in soil profiles whi chemically less labile forms of copper (e.g. occluded co increase with depth (Karim *et al.*, 1976).

## 2 6 Adsorption of copper

### 2 6.1 Theory of adsorption

Adsorption can be defined as adhesion in an extremely thin layer, of molecules, dissolved substances or liquids, to the surfaces of solids with which they come into contact (Boyd and Bernard, 1972). Adsorption of micronutrients can be described in quantitative or mathematical terms. Two adsorption isotherms, the Freundlich and the Langmuir, are the more widely applied in the adsorption of nutrients by soils.

The Langmuir equation has an advantage over the Freundlich equation in that an adsorption maximum can be obtained. The derivation of the Langmuir equation was based on three assumptions:

(a) a constant energy of adsorption which is independent of the extent of surface coverage;

(b) adsorption on specific sites with no interaction between adsorbate molecules; and

(c) maximum adsorption possible is that of a complete monomolecular layer on all reactive adsorbent surfaces.

A common form of the Langmuir equation is:

$$x/m = kbc/(1 + kc) \quad (1)$$

where,

$c$ = equilibrium concentration of adsorbate in question;

$x/m$ = the weight of adsorbate per unit weight of the adsorbent;

$k$ = a constant related to binding strength;

$b$ = the maximum amount of adsorbate that can be adsorbed.

The above equation is often rearranged to the linear form to permit easy verification of whether data conform to the Langmuir model,

$$c/x/m = 1/kb + c/b \qquad (2)$$

A plot of $c/x/m$ against $c$ yields a straight line with slope $1/b$ and intercept $1/kb$.

### 2.8.2 <u>The metal ions present in solution</u>

Copper ions tend to hydrolyse in solution to give, for example:

$$Cu^{++} + H_2O \rightleftharpoons CuOH^{+} + H^{+} \qquad (i)$$

and

$$CuOH^{+} + H_2O \rightleftharpoons Cu(OH)_2 + H^{+} \qquad (ii)$$

Polymeric forms also occur especially in concentrated solution and at high pH (James and Barrow, 1981). The pK of the first reaction is about 8 and this means that at pH 4 only about 0.01% of the copper ions in dilute solution are present as $CuOH^{+}$. However the proportion increases ten-fold for each unit increase in pH (James and Barrow, 1981). Thus adsorption is often observed to occur in a region in which the concentration of $CuOH^+$ ions, though small, increases ten-fold for each unit increase in pH (James and Barrow, 1981). Thus adsorption is often observed to occur in a region in which the concentration of $CuOH^+$ ions, though small, increases rapidly with the increasing pH (Mackenzie, 1980).

At high pH, copper ions may be removed from solution by precipitation of the oxide, the hydroxide or the hydroxy carbonate (James and Barrow, 1981). However, it has been shown several times by McBride and co-workers that the concentration of copper in soil is too low for such precipitates to be controlling the concentration (McBride, 1978 a, b; Cavallaro and McBride, 1978; McBride and Blasiak, 1979). Thus removal of copper from solution is not due to precipitation but adsorption.

### 2.8.3 Characteristics of adsorbents

A wide range of materials has been shown to be capable of adsorbing copper ions from solution. These include oxides of iron, manganese and silicon. An important property of these materials is that they have a variable charge (James and Barrow, 1981). At low pH the surface charge tends to be positive due to adsorption of protons; at high pH it tends to be negative due to loss of protons. The pH at which the material carries no net charge is an important characteristic of the material. For manganese oxides it is about pH 2 (Mckenzie, 1980) and thus in the middle range of pH, manganese oxides tend to bear a negative charge. For iron oxides it is about pH 8, and in the middle range of pH, the iron oxides tend to be positively charged. Adsorption also occurs on clays and, as Farrah and Pickering (1978 a) show, these materials may also have a variable charge. This variable charge is in addition to the fixed charge which may be present as a result of isomorphous substitution within the lattice.

### 2.6.4 Adsorption of copper by soil

Adsorption of copper in soils is very complicated and so understanding of the process has come mostly from the study of simplified systems (James and Barrow, 1981). From the general observation of increased adsorption of copper with increasing pH, it would be expected that increasing the soil pH would decrease the availability of copper to plants. However this has not always been the case. There is the possibility that the change in pH may affect the plant itself and thus mask the changes in the soil (Jarvis, 1981). It also happens that in soil, oxides usually bear a negative charge even at pH values at which the pure oxide is positively charged. This seems to be due to adsorption of organic matter and perhaps silicates (Jarvis, 1981). According to Mckenzie (1980) adsorption on negatively charged surfaces may be less sensitive to increases in pH than adsorption on positively charged surfaces. Another comment is that raising the pH of soil by liming stimulates mineralization of organic matter and this may cause release of copper.

A further characteristic of adsorption in soils, as distinct from adsorption on well crystallised oxides, is that a slow reaction following adsorption is more marked. As a result the adsorbed ligand becomes more tightly bound and less available to plants (James and Barrow, 1981).

Gituamba Agricultural Research Sub-station is in Murang'a district in Central Province. Its altitude is 2130m above sea level on the slopes of the aberdare mountains. The geology of this area consists of basalts and basaltic conglomerates of the Simbara Series (Siderius and Muchena, 1977). The mean annual rainfall at the station is 2005 mm and the mean annual temperature is 13°C. The soil reaction is acidic with an average pH ($H_2O$) of 4.8. The physiography of the area consists of rolling volcanic upland, hills and minor scarps. The main cash-crop in the area is tea. The dominant soil is a well drained, deep, dark-reddish brown clay with a humic A horizon. The soil contains amorphous clay which fixes phosphorus. According to FAO/UNESCO (1974) soil classification system, Gituamba soils are Humic Andosols.

The National Plant Breeding Station is located 2km North-West of Njoro town in Nakuru District. The physiography of the area consists of flat to very gently undulating volcanic plain. The station is at an altitude of 2140m above sea level. The geology of the area consists of tuffs and volcanic ashes of late tertiary (Siderius and Muchena, 1977). The major crop grown in the area is wheat. The station has a mean annual rainfall of 938mm and a mean annual temperature of 15.8°C. The soil reaction is slightly acidic with an average pH ($H_2O$) of 6.3. The dominant soil is a well drained, deep, dark-reddish brown, friable clay with a humic top soil. According to FAO/UNESCO (1974) soil classification system, Njoro soils are Mollic Andosols.

The National Animal Husbandry Research Station is located 5 km north-west of Naivasha town in Nakuru District. The station is at an altitude of 1905m above sea level. The geology of the area consists of cambrian lake sediments with possible recent admixture of volcanic ash (Siderius and Muchena, 1977). The area has a dry climate with a mean annual rainfall of 825mm and a mean annual temperature of 17.3°C. The vegetation of the area is mainly grasses and shrubs. Most of the land is used for grazing. In this area farming is usually done with irrigation water from Lake Naivasha. The physiography of the area consists of flat to very gently undulating plain. The soil reaction is mildly to strongly alkaline. The average pH ($H_2O$) of the surface soil was 7.2. The dominant soils at the station are a dark-brown silt loam, a brown silt clay loam and a dark-brown clay. According to the FAO/UNESCO (1974) soil classification system, Naivasha soils are Orthic Solonetzs and Calcic Cambisols.

## 3.2 Soil sampling and sample preparation

Ten pits were dug in each of the four areas. Surface features like vegetation and slope were used to select the sites. The aim in selection of the sites was to ensure that there was variability in soil samples collected from the various pits. Variability was necessary for carrying out correlation studies. Each pit was 50 centimetres wide and 80 centimetres long; the depths varied between 30 and 150 centimetres.

## 3 4 Laboratory determination of copper

### 3 4.1 Total copper

The method used to determine total copper was a slight modification of the one described by Karim et al (1976). The modification effected was to omit HF in the digestion.

Under a fume chamber 10ml of concentrated $HNO_3$, 3ml of perchloric acid ($HClO_4$) and 3 drops of concentrated $H_2SO_4$ were added to a one-gram sample of soil (passing through a 0.5 mm sieve) in a digestion tube. The soil-acid mixture was allowed to stand overnight. The following day the tubes were placed in a block digester and the mixture was heated until it was almost dry. The contents of the tubes were allowed to cool to room temperature and then concentrated HCl was added to redissolve the copper in the sample. After allowing the contents to stand for one-hour, the residue was brought to 100-ml volume with redistilled water. Total copper in the solution was determined on a model 2380 Perkin-Elmer Atomic Absorption Spectrophotometer (AAS).

To calculate the amount of total copper in soils, the following formula was used:

$$\text{total Cu } (\mu g \text{ Cu/g soil}) = \frac{\text{AAS reading (ppm)} \times 100}{\text{Weight of sample (g)}}$$

### 3.4.2 Double-acid extractable copper

The method used to determine double-acid extractable copper is described by Dale and Amacher (1982). 5g of air-dry soil (passing through a 0.5mm sieve) was weighed into a 50 ml extraction bottle. 25mls of the double-acid (0.05N HCl + 0.025N $H_2SO_4$) was then added. The soil-acid mixture was shaken in a mechanical reciprocating shaker for 15 minutes. The suspension was then filtered by gravity through a Whatmann no. 42 filter paper. The filtrate was analyzed for copper by an Atomic Absorption Spectrophotometer (AAS).

The following formula was used to calculate the amount of double-acid extractable copper in soils:

$$\text{DA extractable copper } (\mu g\ Cu/g\ soil) = \frac{\text{AAS reading (ppm)} \times 25}{\text{Weight of sample (g)}}$$

### 3.4.3 Copper adsorption

To obtain adsorption isotherms, 5 concentrations of copper (II) chloride ($CuCl_2$) ranging from 2 to 10 ppm copper were used. The method used has been described by Harter (1979). 25ml of each solution was mixed with 0.25g of soil (passing through a 1mm sieve) in a centrifuge tube. The soil-solution mixture was shaken overnight in a mechanical reciprocating shaker at room temperature (20-22°C). The following day, the samples were centrifuged and then filtered. The copper in solution was determined by an Atomic Absorption Spectrophotometer. The difference between initial amount of copper in solution and that remaining after the reaction period was assumed to have been adsorbed by the soil. From the adsorption data, adsorption maxima were calculated using the Langmuir equation.

# 4.0 RESULTS AND DISCUSSIONS

## 4.1 Soil pH

The pH of Kabete soil ranged from 5.8 to 6.9. The soil can therefore be regarded as slightly acidic. The above pH range is optimum for the growth of most crops. In Gituamba soil, the pH varied from 4.3 to 5.4. This soil is strongly acidic compared with the other three soils. The soil is known to be high in exchangeable aluminium and very low in exchangeable bases. According to Siderius and Muchena (1977) the soil has a base saturation of only 3%. Aluminium ions hydrolyse in solution to release hydrogen ions and this lowers the pH. In Njoro soil the pH ranged from 5.8 to 6.8. This was quite similar to the range observed for Kabete soil. The Naivasha soil was slightly acidic to alkaline with the pH ranging from 6.1 to 8.0. Since Naivasha is a dry region, bases accumulate in the soil due to lack of sufficient water for leaching. As a result, the soil pH rises. The pH data for the four soils are shown in Tables I (a-d).

Tables I (a-d). Soil pH for Kabete, Gituamba, Njoro and Naivasha soils measured in water (1:2.5)

Table Ia. Soil pH for Kabete soils

| Pit No. | Horizon | Depth (cm) | pH ($H_2O$) |
|---|---|---|---|
| 1 | A | 0-23 | 6.8 |
| 2 | A | 0-31 | 6.6 |
| 3 | A | 0-20 | 6.9 |
| 4 | A | 0-20 | 6.3 |
| 5 | A | 0-13 | 6.5 |
| 6 | A | 0-16 | 6.5 |
| 7 | A | 0-25 | 6.0 |
| 8 | A | 0-10 | 6.1 |
| 9 | A | 0-20 | 5.8 |
| 10 | A | 0-26 | 6.1 |

**Table Ib  Soil pH for Gituamba soils**

| Pit No. | Horizon | Depth (cm) | pH ($H_2O$) |
|---|---|---|---|
| 1 | A | 0-38 | 5.1 |
| 2 | A | 0-16 | 4.8 |
| 3 | A | 0-24 | 4.9 |
| 4 | A | 0-13 | 4.3 |
| 5 | A | 0-25 | 5.4 |
| 6 | A | 0-20 | 4.4 |
| 7 | A | 0-17 | 4.6 |
| 8 | A | 0-24 | 5.1 |
| 9 | A | 0-15 | 4.8 |
| 10 | A | 0-20 | 4.7 |

**Table Ic. Soil pH for Njoro soils**

| Pit No. | Horizon | Depth (cm) | pH ($H_2O$) |
|---|---|---|---|
| 1 | A | 0-15 | 6.5 |
| 2 | A | 0-20 | 5.8 |
| 3 | A | 0-11 | 6.4 |
| 4 | A | 0-27 | 6.8 |
| 5 | A | 0-20 | 6.4 |
| 6 | A | 0-15 | 6.4 |
| 7 | A | 0-18 | 6.4 |
| 8 | A | 0-17 | 6.3 |
| 9 | A | 0-17 | 6.1 |
| 10 | A | 0-30 | 6.2 |

**Table Id. Soil pH for Naivasha soils**

| Pit No. | Horizon | Depth (cm) | pH ($H_2O$) |
|---|---|---|---|
| 1 | A | 0-23 | 8.0 |
| 2 | A | 0-27 | 7.6 |
| 3 | A | 0-30 | 7.5 |
| 4 | A | 0-27 | 6.9 |
| 5 | A | 0-20 | 6.1 |
| 6 | A | 0-27 | 7.2 |
| 7 | A | 0-27 | 6.8 |
| 8 | A | 0-31 | 8.8 |
| 9 | A | 0-21 | 8.0 |
| 10 | A | 0-13 | 6.7 |

## 4.2 Organic carbon

Tables II (a-d) show the organic carbon contents of the four soils. These were obtained using the Walkley - Black method (Walkley, 1947). Kabete samples had on average an organic carbon content of 4.2%. The range was from 3.2 to 6.3%. Gituamba soil had the highest amount of organic carbon. This ranged between 3.2 and 10.7% while the average was 7%. The high amounts in this soil can be attributed to the dense growth of vegetation which benefits from the high rainfall in the area. This vegetation adds to the organic carbon content of soil upon decay. The organic carbon in Njoro soil ranged between 2.2% and 8.3% while the average was 4.1%. The vegetation in this region and Kabete is less dense than in Gituamba. This means that less organic matter is added into these soils upon decay of the vegetation and so their organic carbon contents are lower. Naivasha Animal Husbandry Research Station is located in a semi-arid area which supports a sparse vegetation. As a result organic carbon is low in this soil.

Table II (a-d). **Organic carbon content for Kabete, Gituamba, Njoro and Naivasha soils**

**Table IIa. Organic carbon content for Kabete soils**

| Pit No. | Horizon | Depth (cm) | Organic carbon (%) |
|---|---|---|---|
| 1 | A | 0-23 | 4.5 |
| 2 | A | 0-31 | 3.7 |
| 3 | A | 0-20 | 3.9 |
| 4 | A | 0-20 | 4.3 |
| 5 | A | 0-13 | 3.8 |
| 6 | A | 0-18 | 3.2 |
| 7 | A | 0-25 | 4.7 |
| 8 | A | 0-10 | 6.3 |
| 9 | A | 0-20 | 3.3 |
| 10 | A | 0-28 | 4.4 |

**Table IIb. Organic carbon content for Giluamba soils**

| Pit No. | Horizon | Depth (cm) | Organic carbon (%) |
|---|---|---|---|
| 1 | A | 0-38 | 8.3 |
| 2 | A | 0-16 | 9.3 |
| 3 | A | 0-24 | 7.9 |
| 4 | A | 0-13 | 10.7 |
| 5 | A | 0-25 | 3.3 |
| 6 | A | 0-20 | 5.2 |
| 7 | A | 0-17 | 4.6 |
| 8 | A | 0-24 | 5.2 |
| 9 | A | 0-15 | 9.4 |
| 10 | A | 0-20 | 6.1 |

Table IIc. Organic carbon content for Njoro soils

| Pit No. | Horizon | Depth (cm) | Organic carbon (%) |
|---|---|---|---|
| 1 | A | 0-15 | 5.2 |
| 2 | A | 0-20 | 2.7 |
| 3 | A | 0-11 | 8.3 |
| 4 | A | 0-27 | 3.7 |
| 5 | A | 0-20 | 2.2 |
| 6 | A | 0-15 | 4.3 |
| 7 | A | 0-18 | 3.5 |
| 8 | A | 0-17 | 4.3 |
| 9 | A | 0-17 | 3.1 |
| 10 | A | 0-30 | 3.9 |

**Table IId. Organic carbon content for Naivasha soils**

| Pit No. | Horizon | Depth (cm) | Organic carbon (%) |
|---|---|---|---|
| 1 | A | 0-23 | 5.1 |
| 2 | A | 0-27 | 1.9 |
| 3 | A | 0-30 | 9.2 |
| 4 | A | 0-27 | 6.6 |
| 5 | A | 0-20 | 3.7 |
| 6 | A | 0-27 | 3.2 |
| 7 | A | 0-27 | 4.4 |
| 8 | A | 0-31 | 0.8 |
| 9 | A | 0-21 | 1.2 |
| 10 | A | 0-13 | 2.9 |

Kabete

## 4.3 Cation Exchange Capacity (CEC)

The average CECs for Kabete and Njoro soils were 24.8 and 19.6 meq/100g respectively. The ones for Gituamba and Naivasha soils were 29.9 and 27.3 meq/100g respectively. According to Siderius and Muchena (1977) Gituamba and Naivasha soils contain much amorphous clay. Amorphous clay and organic matter are known to have a large amount of pH-dependent charge. Since the determination of CEC was done at pH 7, the high CECs of Gituamba and Naivasha soils may be due to an increase in pH-dependent charge. Since Gituamba soil is also high in organic carbon and therefore organic matter, its CEC is higher. Kabete soil has a clay content of 72% in the surface horizon while Njoro soil has about 44% (Siderius and Muchena, 1977). Since the two soils have comparable organic matter contents, the higher CEC of Kabete soil may be due to its higher clay content. The CEC data for the four soils are shown in Tables III (a-d).

Tables III (a-d). Cation exchange capacity for Kabete, Gituamba, Njoro and Naivasha soils

Tables IIIa. Cation Exchange Capacity for Kabete soil samples

| Pit No. | Horizon | Depth (cm) | CEC (meq/100g) |
|---|---|---|---|
| 1 | A | 0-23 | 25.6 |
| 2 | A | 0-31 | 23.8 |
| 3 | A | 0-20 | 22.0 |
| 4 | A | 0-20 | 26.0 |
| 5 | A | 0-13 | 24.4 |
| 6 | A | 0-18 | 24.4 |
| 7 | A | 0-25 | 26.4 |
| 8 | A | 0-10 | 28.8 |
| 9 | A | 0-20 | 22.8 |
| 10 | A | 0-28 | 24.4 |

**Table IIIb. Cation Exchange Capacity for Gituamba soil samples**

| Pit No. | Horizon | Depth (cm) | CEC (meq/100g) |
|---|---|---|---|
| 1 | A | 0-38 | 33.0 |
| 2 | A | 0-16 | 37.2 |
| 3 | A | 0-24 | 28.8 |
| 4 | A | 0-13 | 42.0 |
| 5 | A | 0-25 | 18.4 |
| 6 | A | 0-20 | 22.4 |
| 7 | A | 0-17 | 25.6 |
| 8 | A | 0-24 | 23.2 |
| 9 | A | 0-15 | 38.2 |
| 10 | A | 0-20 | 25.8 |

**Table IIIe. Cation Exchange Capacity for Njoro soil sample.**

| Pit No. | Horizon | Depth (cm) | CEC (meq/100g) |
|---|---|---|---|
| 1 | A | 0-15 | 23.2 |
| 2 | A | 0-20 | 12.8 |
| 3 | A | 0-11 | 30.4 |
| 4 | A | 0-27 | 18.6 |
| 5 | A | 0-20 | 13.2 |
| 6 | A | 0-15 | 21.2 |
| 7 | A | 0-18 | 19.2 |
| 8 | A | 0-17 | 18.0 |
| 9 | A | 0-17 | 15.6 |
| 10 | A | 0-30 | 22.8 |

Table IIId. Cation Exchange Capacity for Naivasha soil samples

| Pit No. | Horizon | Depth (cm) | CEC (meq/100g) |
|---|---|---|---|
| 1 | A | 0-23 | 33.2 |
| 2 | A | 0-27 | 33.6 |
| 3 | A | 0-30 | 42.0 |
| 4 | A | 0-27 | 28.4 |
| 5 | A | 0-20 | 22.0 |
| 6 | A | 0-27 | 25.2 |
| 7 | A | 0-27 | 29.8 |
| 8 | A | 0-31 | 25.6 |
| 9 | A | 0-21 | 15.2 |
| 10 | A | 0-13 | 18.4 |

## 4.4 Content and profile distribution of total and double-acid extractable copper

Table IV shows the means and the ranges of total and double-acid extractable copper in soil samples from the A and B horizons for each soil. The results indicate that Gituamba and Kabete soils can be classified together as soils of high total copper contents while Njoro and Naivasha are soils of low total copper contents. The differences in copper contents within a given area may be due to such factors as vegetation and management

The parent materials underlying the soils may be the major contributor to differences in copper contents observed between soils. Both Gituamba and Kabete soils are high in total copper Gituamba soils are underlain by basalts while Kabete soils are underlain by trachytes (Siderius and Muchena, 1977). Nyandat and Ochieng (1976) found that soils underlain by the above types of rocks were high in total copper. Njoro and Naivasha soils are underlain by volcanic ash (Siderius and Muchena, 1977). Both of these soils had low levels of total copper. Nyandat and Ochieng (1976) found that soils underlain by volcanic ash had low levels of total copper.

Soil samples from Gituamba had the highest amounts of double-acid extractable copper. Although soil samples from Njoro were the lowest in total copper, they were not the lowest in double-acid extractable copper. Soil samples from Naivasha had more total copper than those from Njoro. However the opposite was true for double-acid extractable copper. These results indicate that total copper and double acid extractable copper are not correlated (see Table V).

Many of the soils profiles sampled showed little variation in total copper contents with depth (see Appendix I). As such the A and B horizons in most profiles had comparable amounts of total copper (Table IV). Swaine and Mitchell (1960) also found that trace elements are distributed quite uniformly from horizon to horizon. Hodgson (1963) attributed the uniform distribution of copper in soil profiles to its low mobility.

However, Karim *et al* (1976) did not find a uniform profile distribution of copper. According to their observations, soils with medium and coarse-textured surfaces had less copper in the surface than in the sub-surface horizons. The converse was also true for soils with clayey surfaces. The explanation they gave for this observation is that copper was moving from the A horizon and was being immobilised in the more clayey B horizon. In the soils with clayey surfaces, the higher copper contents in the A horizon was attributed to the accumulation of copper in organic matter and reduced leaching losses of copper from the clayey surface horizons.

Double-acid extractable copper was distributed uniformly between the A and B horizons for soil profiles in Njoro, Naivasha and Gituamba. In the Kabete profiles, there was an obvious increase of double-acid extractable copper in the B horizons. This is shown by the higher average amount of double-acid extractable copper in the B horizon as compared to the A horizon (Table IV). The Kabete soil profiles have a B horizon with an illuvial accumulation of clay, i.e., a Bt. It seems that in the A horizon copper is mainly bound by organic matter and is not easily extracted by double-acid. In the B horizon which has more clay, copper is mainly bound by the clay and a greater proportion of this copper is extractable by double-acid.

## 4.5 The relationship between total copper and soil chemical properties

Correlation coefficients were determined for the relationship between total copper, soil pH, organic carbon, double-acid extractable copper and CEC (Table V). For all the soils investigated no significant correlation was found between total copper and any of the above soil chemical properties. Nyandat and Ochieng (1976) found a similar result and concluded that total copper in soils depends on the parent material from which the soil is derived rather than on soil chemical properties.

Table V. **Correlations between total copper and other so chemical properties**

Kabete soil

| Soil property | Correlation coefficie |
|---|---|
| pH | -0.3085 n.s |
| Organic carbon (%) | -0.0550 n.s |
| CEC (meq/100g | 0.1846 n.s |
| Extractable copper (ppm) | 0.3768 n.s |

Gituamba soils

| Soil property | Correlation coefficie |
|---|---|
| pH | 0.0801 n.s |
| Organic carbon (%) | 0.3328 n.s |
| CEC (meq/100g) | 0.4171 n.s |
| Extractable copper (ppm) | -0.0943 n.s |

Njoro soils

| Soil property | Correlation coefficien |
|---|---|
| pH | 0.3878 n.s |
| Organic carbon (%) | 0.6093 n.s |
| CEC (meq/100g) | 0.6106 n.s |
| Extractable copper (ppm) | 0.3841 n.s |

Naivasha soils

| Soil property | Correlation coefficien |
|---|---|
| pH | 0.0910 n.s |
| Organic carbon (%) | -0.0357 n.s |
| CEC (meq/100g) | -0.1060 n.s |
| Extractable copper (ppm) | 0.1352 n.s. |

n.s = not significant

## 4.6 The relationship between double-acid extractable copper and soil chemical properties

The relationships between double-acid extractable copper and soil pH, organic carbon and CEC were evaluated. No significant correlation was found between double-acid extractable copper and any of the above soil chemical properties (Table VI). However a highly significant non-linear relationship was found between double-acid extractable copper and CEC in Naivasha soils ($r^2 = 0.77$) (Fig 1). The lack of correlation between double-acid extractable copper and CEC or organic carbon suggests that double-acid does not remove copper from cation exchange sites or the organically bound copper.

A significant correlation between double-acid extractable copper and total copper was expected since other extractants have been shown to extract copper that is correlated to total copper. Nyandat and Ochieng (1976) found EDTA-extractable copper to be correlated with total copper in a wide range of Kenya soils while Karim et al (1976) found DTPA-extractable copper in soils from Louisiana (U.S.A.) to be correlated with total copper. Therefore it is likely that EDTA and DTPA extract certain groups bound with copper which double acid cannot extract.

Table VI. Correlations between double-acid extractable copper and other soil chemical properties

Kabete soil

| Soil property | Correlation coefficient |
|---|---|
| CEC (meq/100g) | 0.2818 n.s |
| Organic carbon (%) | 0.3870 n.s |
| pH | -0.4547 n.s |

Gituamba soil

| Soil property | Correlation coefficient |
|---|---|
| CEC (meq/100g) | -0.3060 n.s |
| Organic carbon (%) | -0.3778 n.s |
| pH | -0.2808 n.s |

Njoro soil

| Soil property | Correlation coefficient |
|---|---|
| CEC (meq/100g) | -0.0881 n.s |
| Organic carbon (%) | -0.0757 n.s |
| pH | 0.0263 n.s |

Naivasha soil

| Soil property | Correlation coefficient |
|---|---|
| CEC (meq/100g) | -0.5055 n.s |
| Organic carbon (%) | -0.2488 n.s |
| pH | 0.4748 n.s |

n.s. = not significant

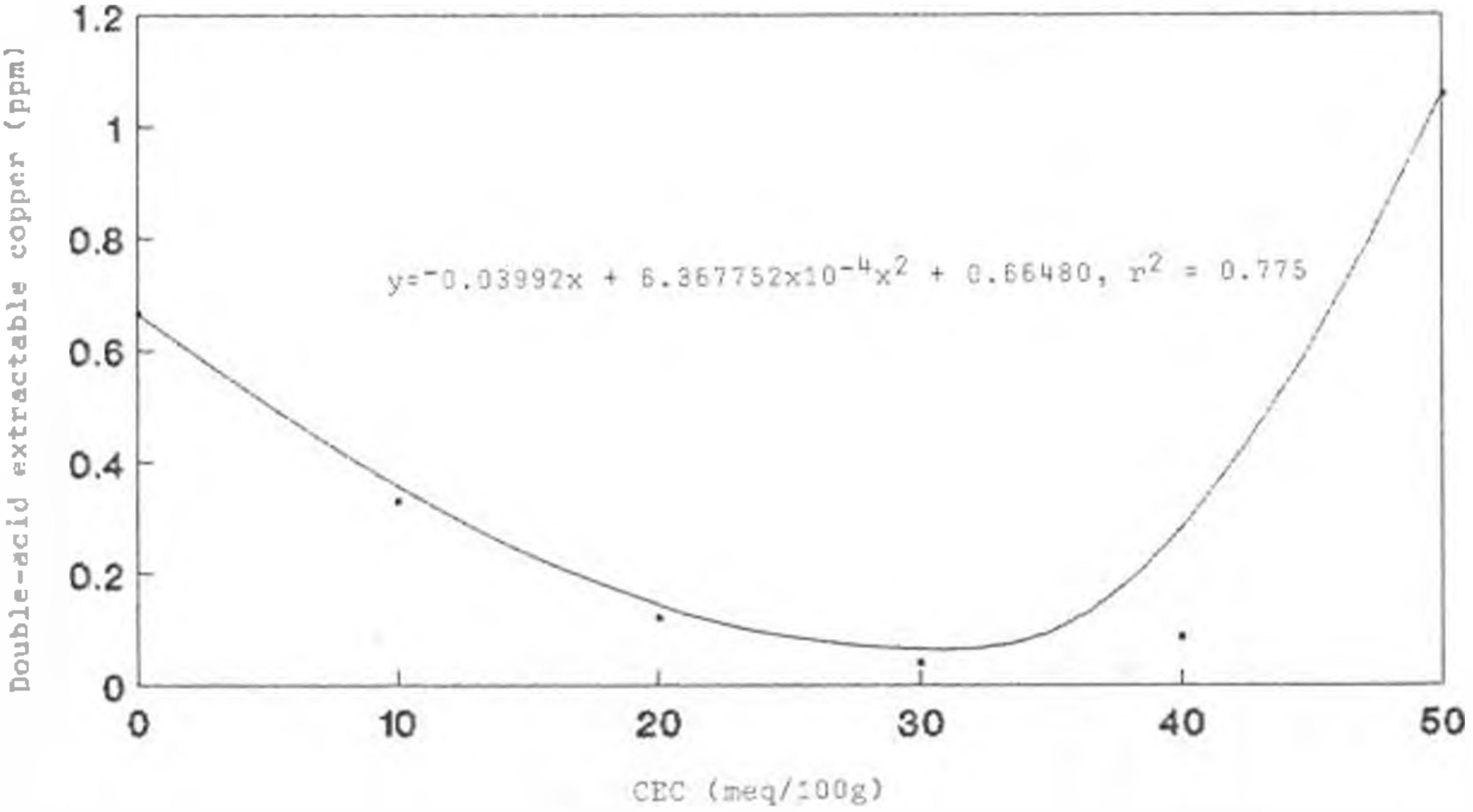

Fig 1. The relationship between double-acid extractable copper and CEC in the surface horizon of Naivasha soil.

## 4.7 Adsorption of copper by soil

Adsorption isotherms were plotted for soil samples from the four areas. Only the surface horizons were sampled for the study of adsorption in all the soils. For a majority of the soil samples, replotting the adsorption data according to the Langmuir equation gave linear graphs indicating satisfactory agreement with this theoretically derived equation. From such graphs, the adsorption maxima were calculated. The adsorption maxima were then correlated with pH, CEC, double-acid extractable copper and organic carbon (Table VII).

Table VII. **Correlation between copper adsorption maxima and other soil chemical properties**

Kabete soil

| Soil property | Correlation coefficient |
|---|---|
| pH | 0.2254 n.s |
| Organic carbon (%) | 0.2282 n.s |
| CEC (me /100g | 0.2677 n.s |
| Extractable copper (ppm) | 0.5002 n.s |

Gituamba soil

| Soil property | Correlation coefficient |
|---|---|
| pH | -0.0831 n.s |
| Organic carbon (%) | 0.9256 *** |
| CEC (me /100g) | 0.9182 *** |
| Extractable copper (ppm) | -0.4694 n.s |

Njoro soil

| Soil property | Correlation coefficient |
|---|---|
| pH | 0.2421 n.s |
| Organic carbon (%) | 0.8851 *** |
| CEC (me /100g) | 0.7853 ** |
| Extractable copper (ppm) | -0.2078 n.s |

Naivasha soil

| Soil property | Correlation coefficient |
|---|---|
| pH | 0.2128 n.s |
| Organic carbon (%) | 0.8406 ** |
| CEC (me /100g) | 0.8958 *** |
| Extractable copper (ppm) | -0.3103 n.s. |

*** - significant at 0.1%

** = significant at 1%

n.s = not significant

### 4.7.1 Copper adsorption by Kabete soils

Figure 2 is an adsorption curve for Kabete soil. Figure 3 is the corresponding Langmuir adsorption isotherm. The mean copper adsorption maximum as calculated from the Langmuir equation was 280 µg Cu/g soil. This mean was for 10 samples from ten profiles in the area. No significant correlations were found between the copper adsorption maximum and CEC, pH, organic carbon or double-acid extractable copper. The lack of correlation with CEC (r=0.27) suggests that the adsorption of copper via the normal cation exchange mechanism is not an important process in this soil. The lack of corre-lation between copper adsorption maximum and organic carbon (r=0.23) indicates that soil constituents other than organic matter are important in the binding of copper in this soil.

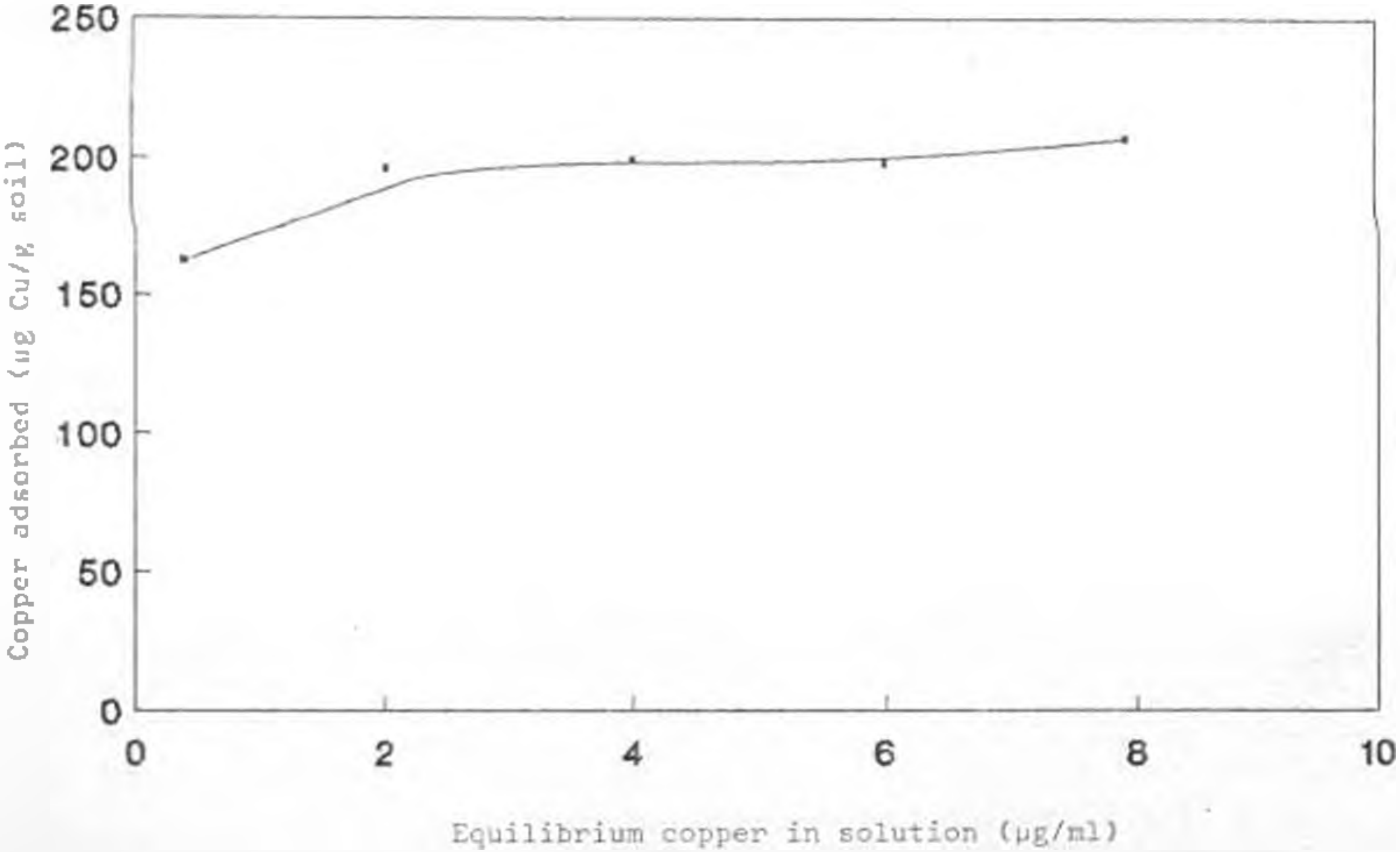

Fig 2. Copper adsorption curve for Kabete soil.

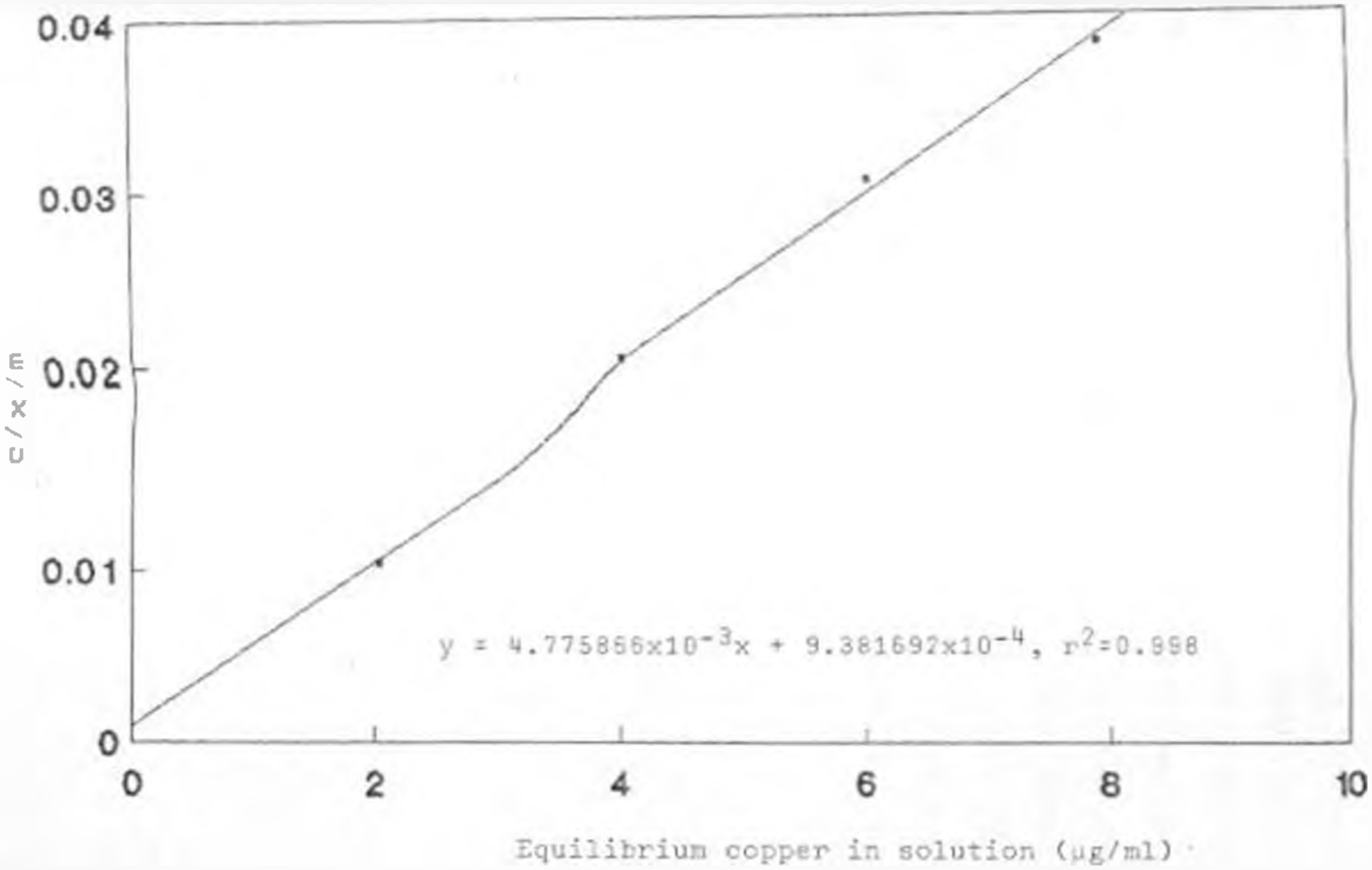

Fig 3. Sorption isotherm
for kabete soil.

### 4.7.2 Copper adsorption by Gituamba soil

Figures 4 and 5 are an adsorption curve and a Langmuir adsorption isotherm respectively for Gituamba soil. Figures 6 and 7 are an adsorption curve and a Langmuir adsorption isotherm for the sample adsorbing most copper. Highly significant correlations were found between adsorption maximum and CEC ($r=0.82^{***}$) and between adsorption maximum and organic carbon ($r=0.93^{***}$) (Table VII). The highly significant correlation observed between CEC and organic carbon ($r=0.96^{***}$) (Appendix IIb.), indicates that organic matter is an important contributor to CEC in this soil. It is also likely that adsorption of copper in this soil is mainly by organic matter.

### 4.7.2 Copper adsorption by Gituamba soil

Figures 4 and 5 are an adsorption curve and a Langmuir adsorption isotherm respectively for Gituamba soil. Figures 6 and 7 are an adsorption curve and a Langmuir adsorption isotherm for the sample adsorbing most copper. Highly significant correlations were found between adsorption maximum and CEC (r=0.92***) and between adsorption maximum and organic carbon (r=0.93***) (Table VII). The highly significant correlation observed between CEC and organic carbon (r=0.95***) (Appendix IIb.), indicates that organic matter is an important contributor to CEC in this soil. It is also likely that adsorption of copper in this soil is mainly by organic matter.

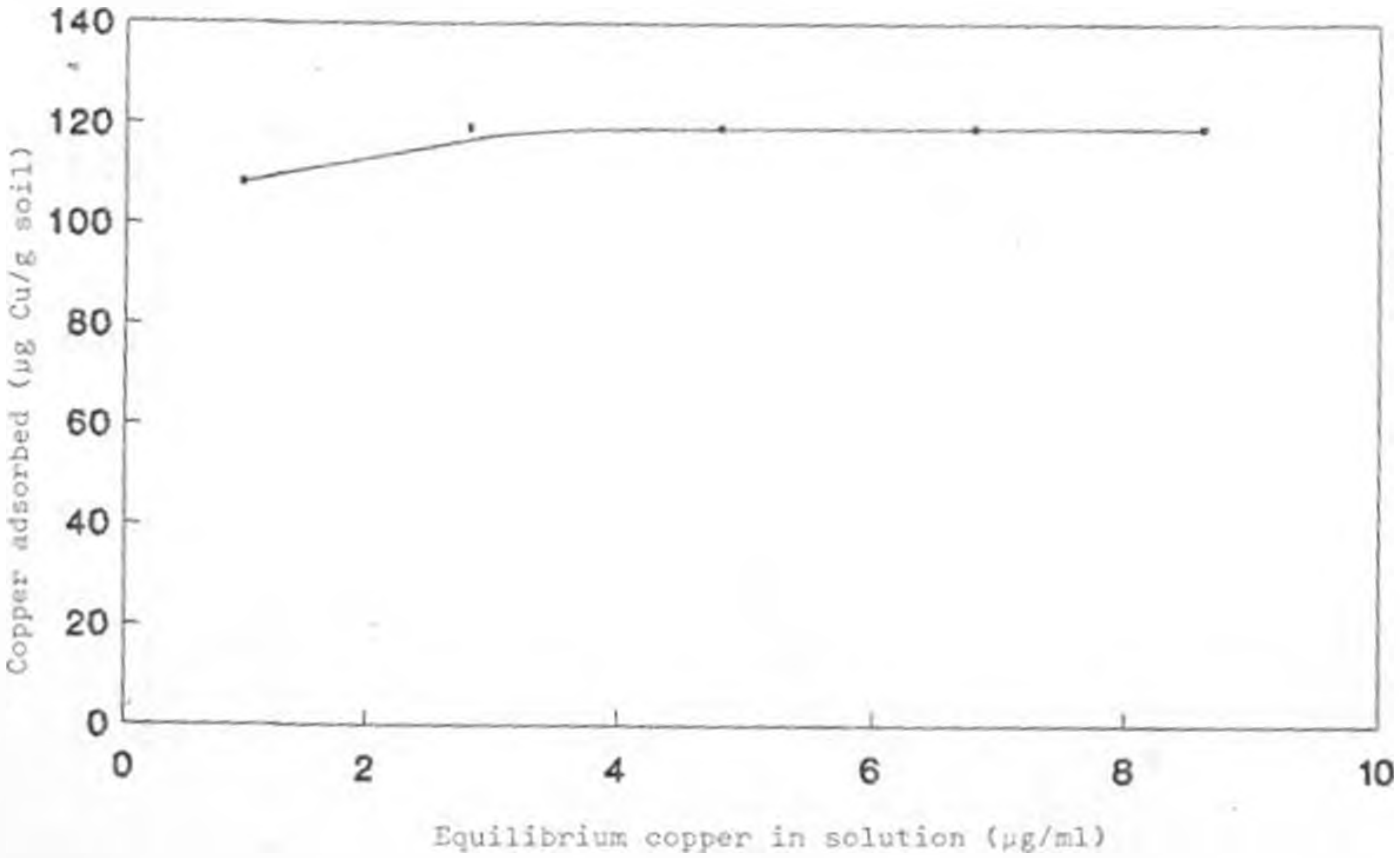

Fig 4. Copper adsorption curve
for Gituamba soil.

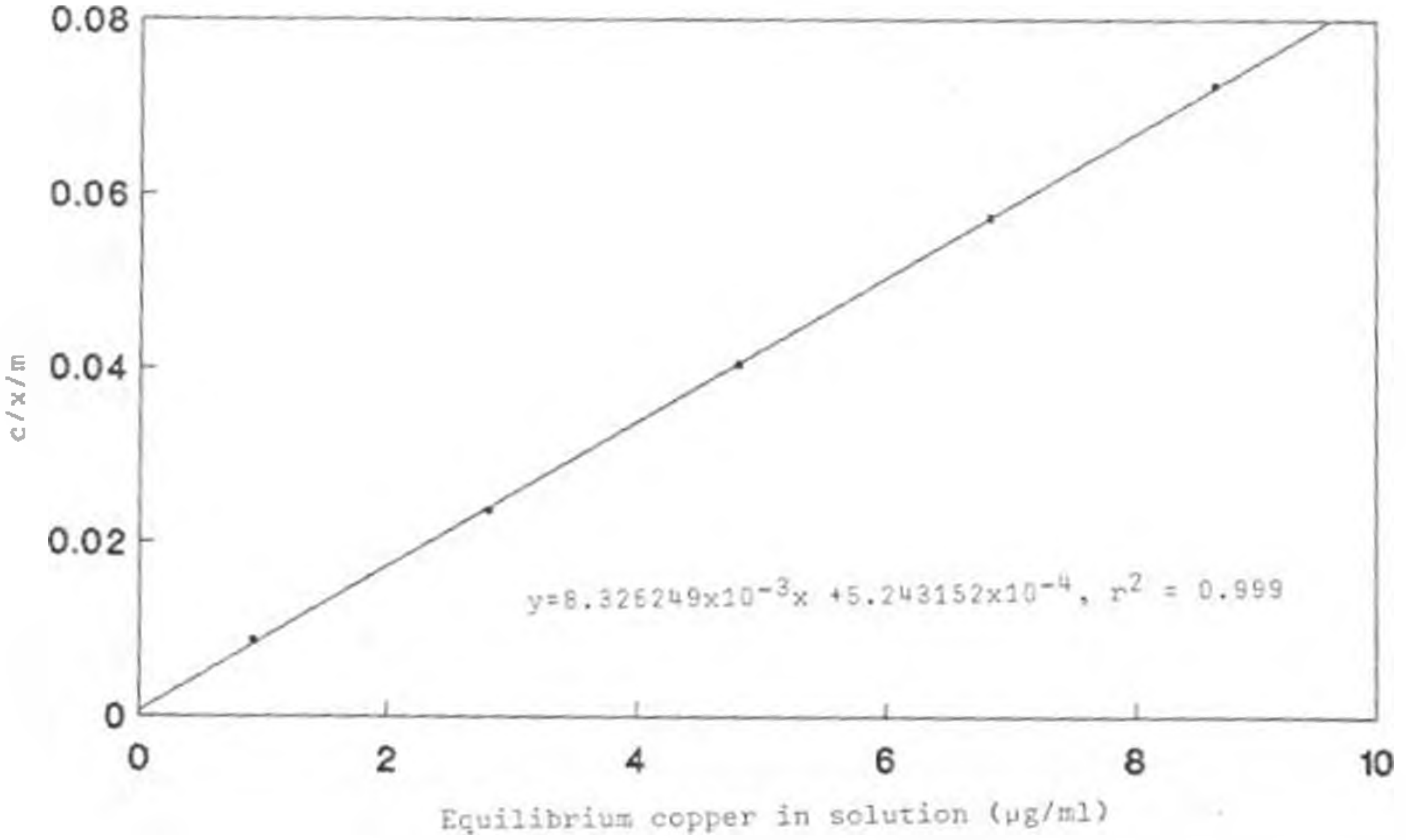

Fig 5.Sorption isotherm for Gituamba soil.

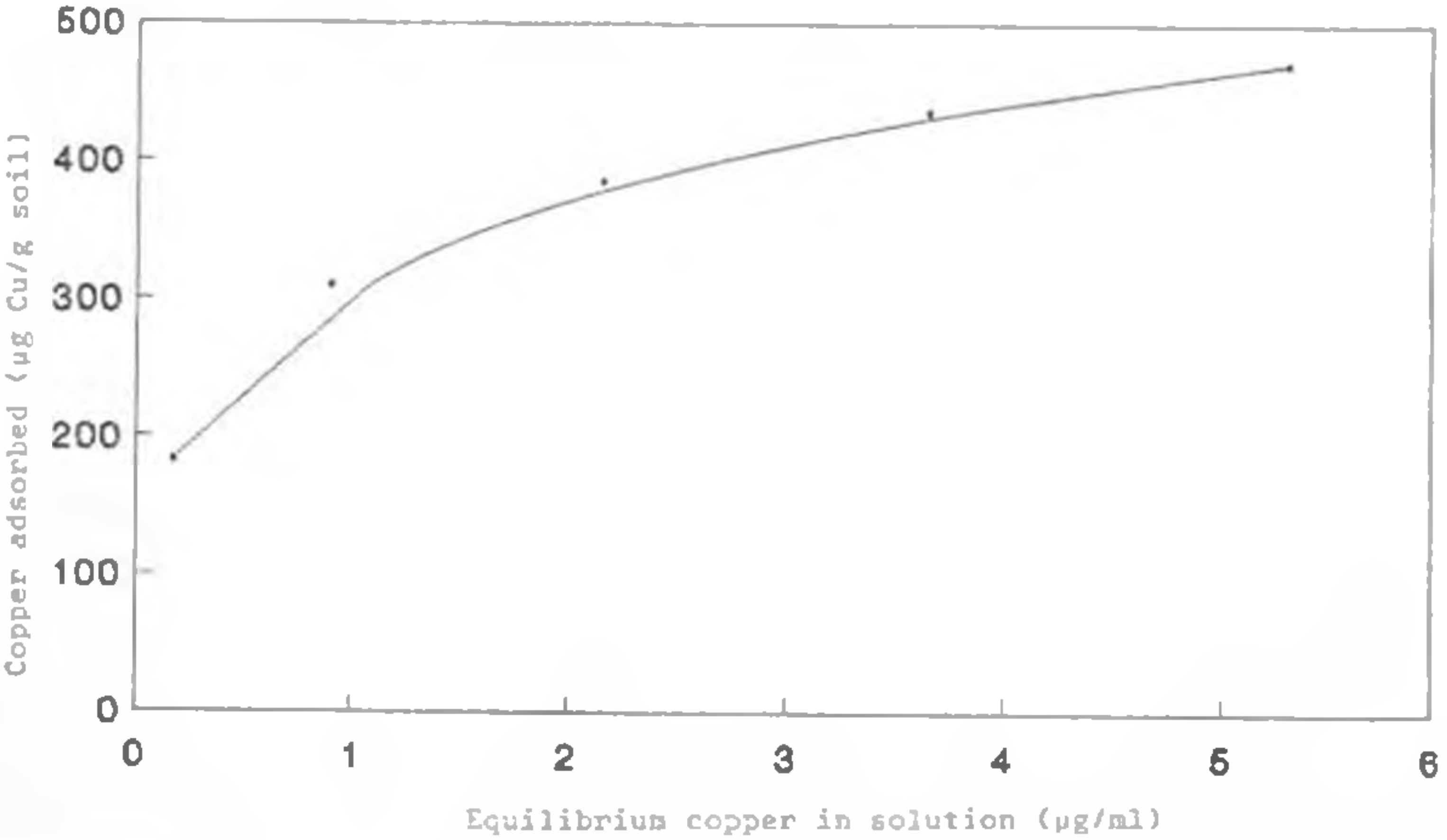

**Fig 6. Copper adsorption curve for** ***Gituamba sample adsorbing the highest amount of copper.***

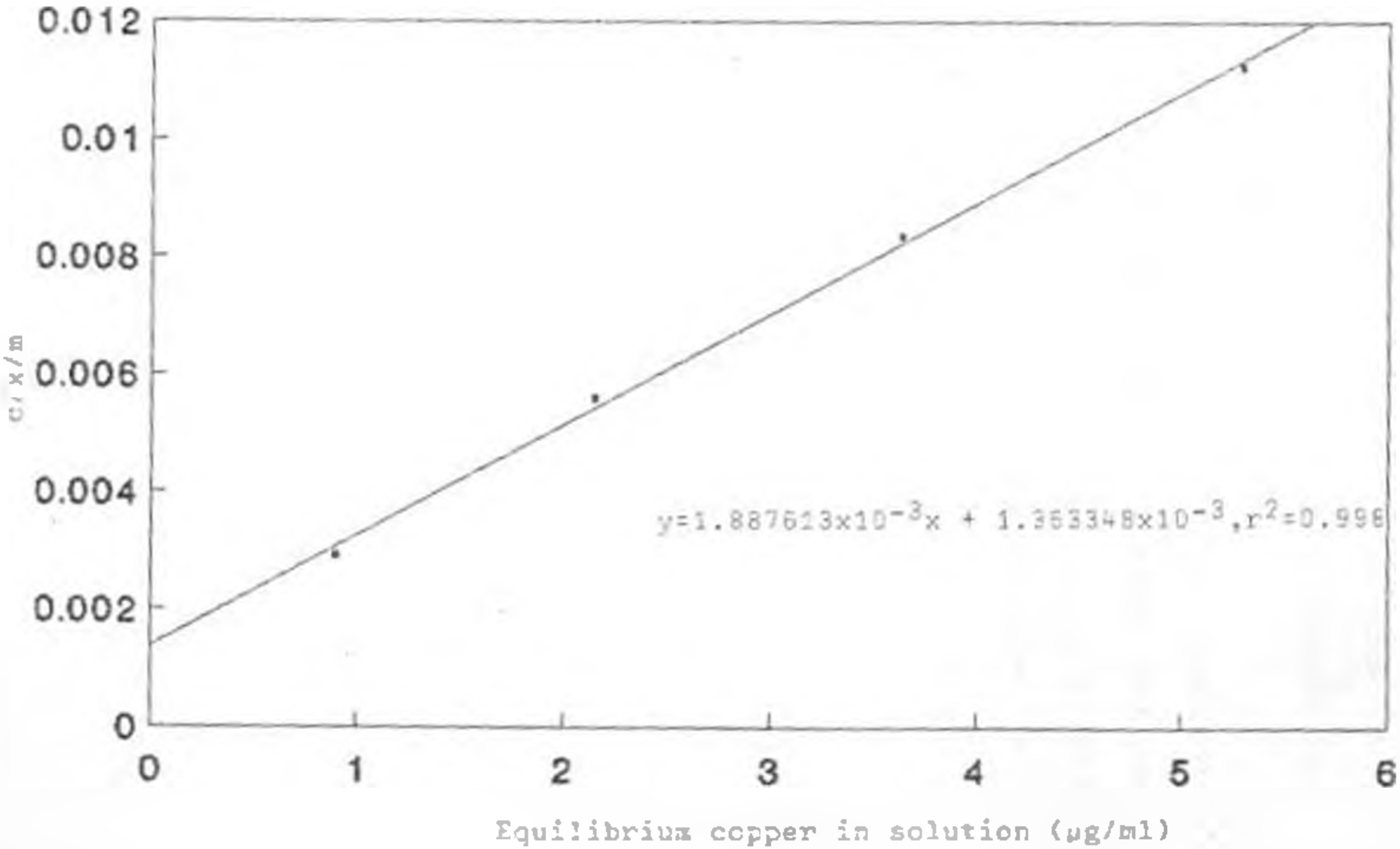

Fig 7.Sorption isotherm corresponding to fig.6.

### 4.7.3 Copper adsorption by Njoro soil

Figures 8 and 9 are an adsorption curve and the corresponding Langmuir adsorption isotherm for a soil sample from Njoro. The mean adsorption maximum for this soil was 164 µg Cu/g soil. The mean was for 10 samples from ten different profiles in the area.

Significant correlations were found between adsorption maximum and organic carbon (r=0.89***) and between adsorption maximum and CEC (r=0.80**). This indicates that organic matter is very important in the binding of copper in this soil.

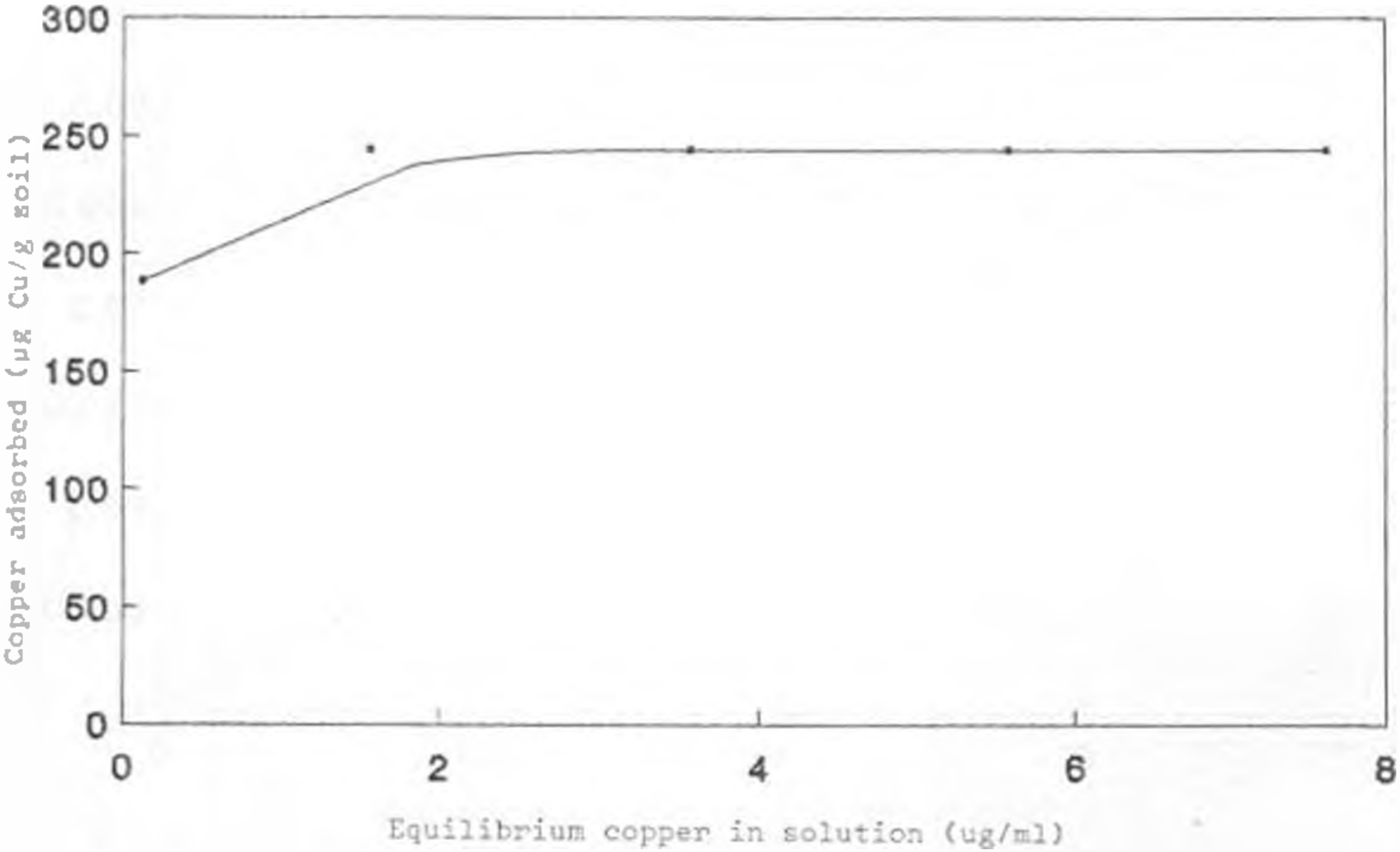

Fig 8. Copper adsorption curve for Njoro soil.

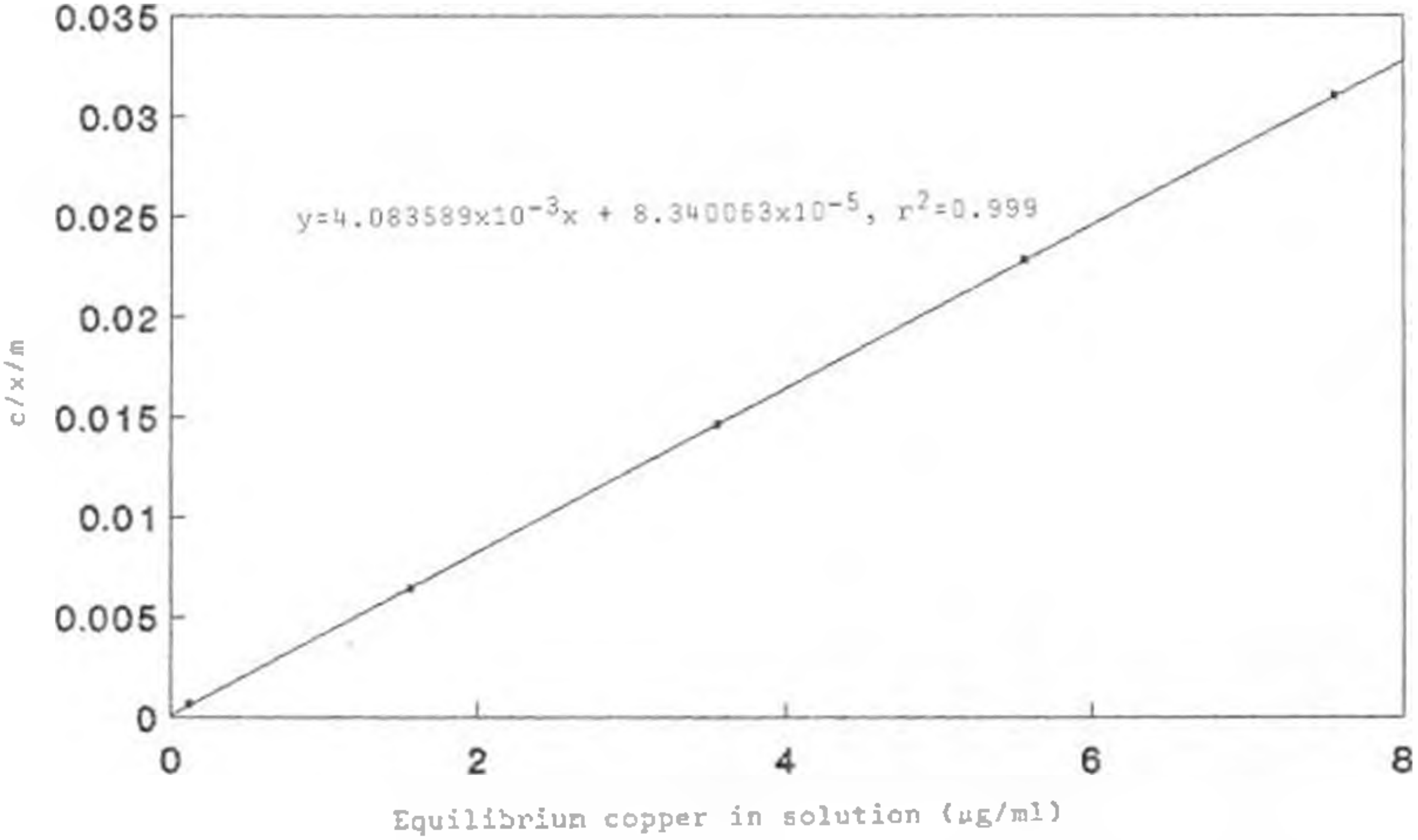

**Fig 9. Sorption isotherm for Njoro soil.**

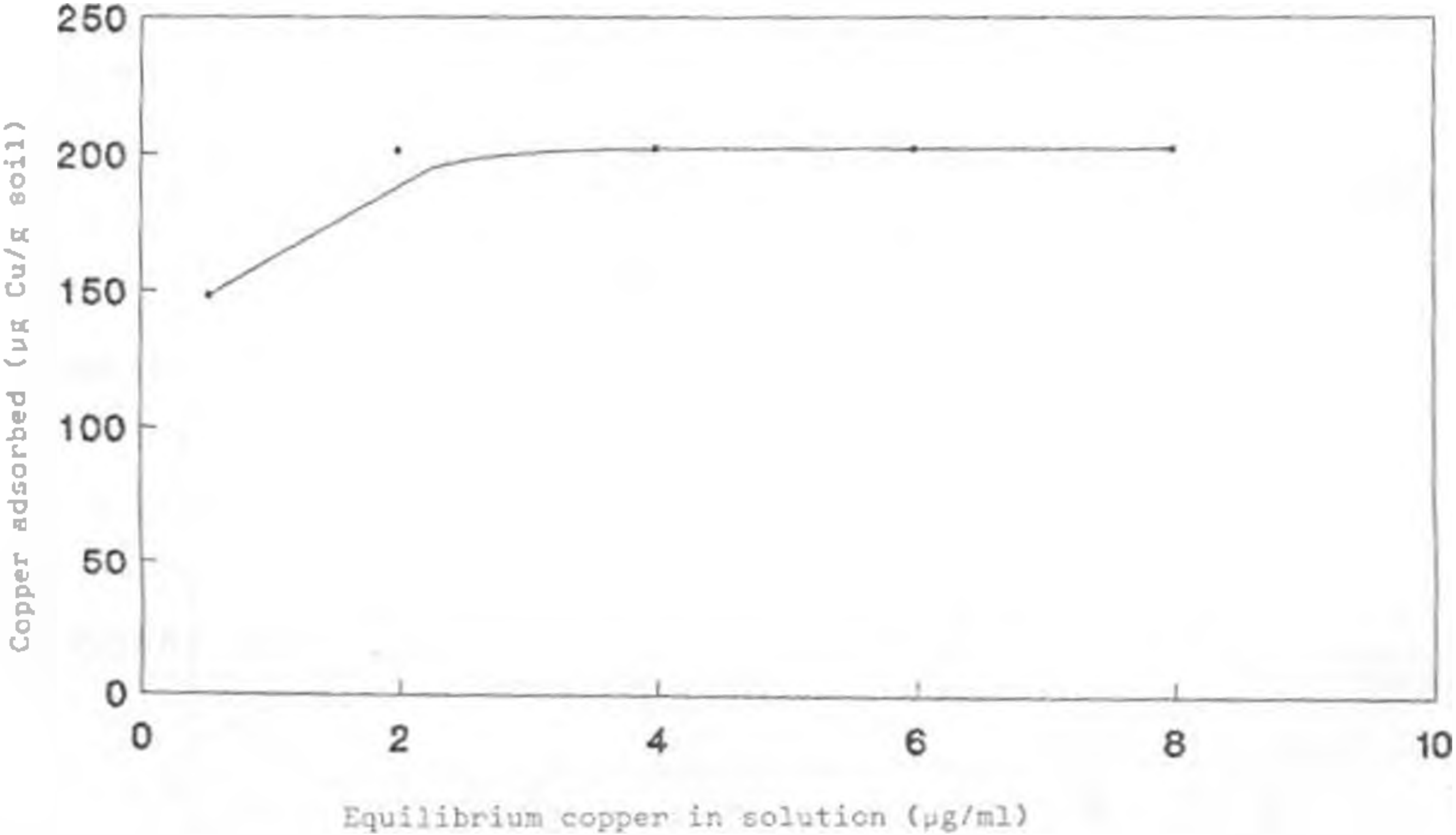

Fig 11. Copper adsorption curve for Naivasha sample adsorbing the lowest amount of copper.

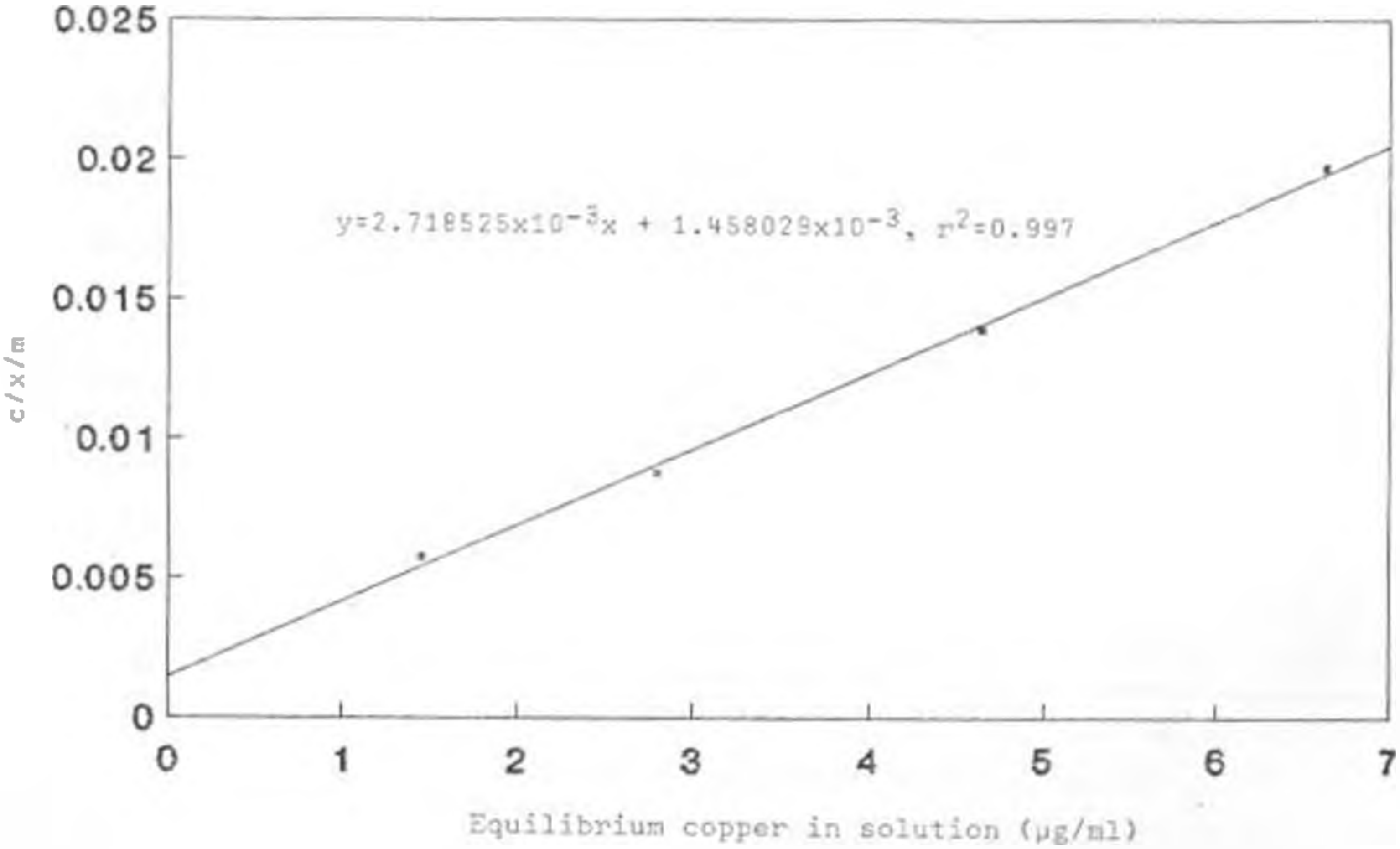

Fig 12. Sorption isotherm corresponding
fig.10.

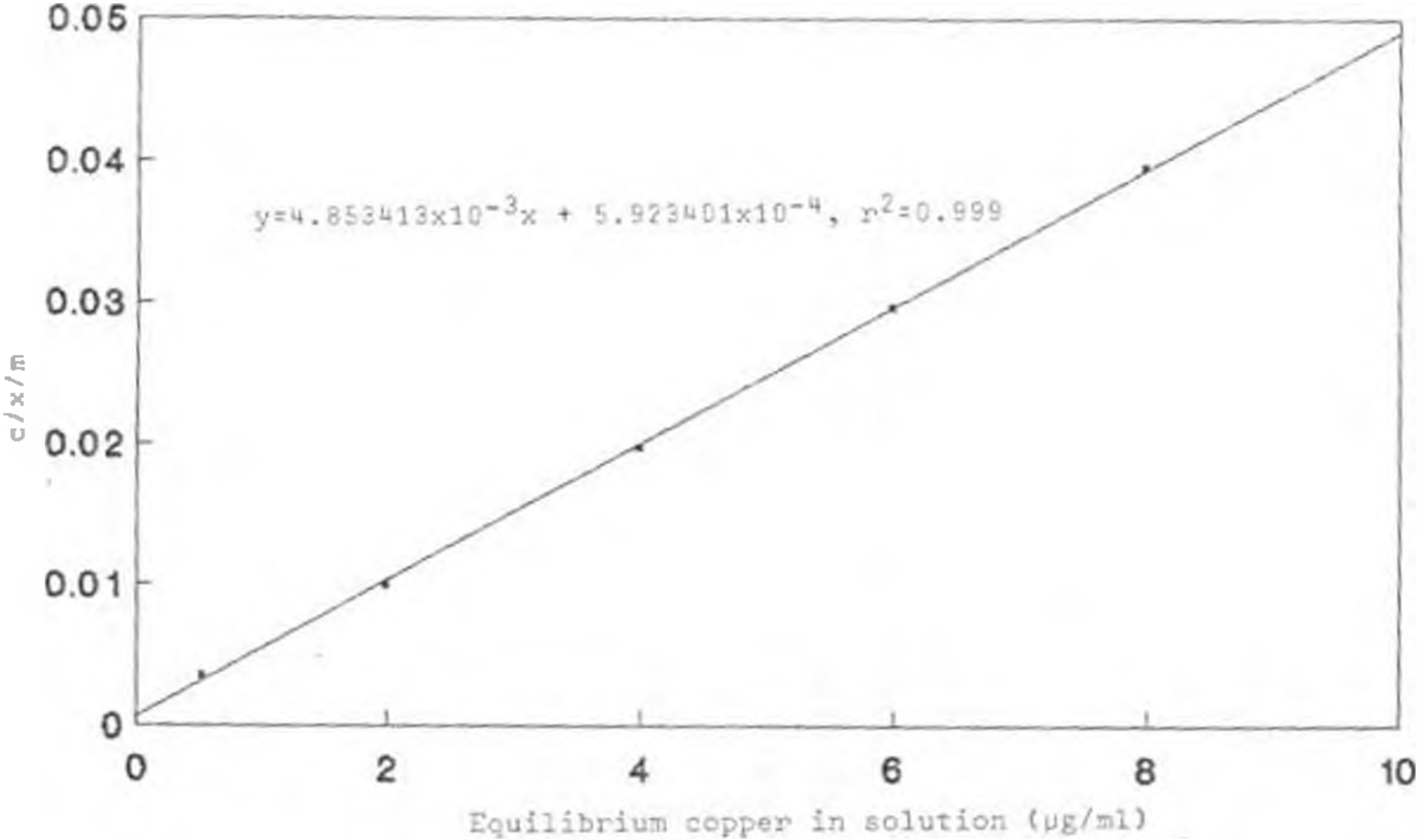

Fig 13. Sorption isotherm corresponding to fig. 11.

### 4.7.5 Comparison of adsorption maxima among the soils

Table VIII shows the means and the ranges of adsorption maxima for soil samples from the four areas. Soil samples from Njoro adsorbed on average the least amount of copper while those from Naivasha adsorbed the most copper. The high pH of Naivasha soil may be one of the factors causing increased adsorption. According to Mckenzie (1981) copper adsorption increases with increase in pH.

Adsorption of copper by Kabete soil, though uncorrelated to either CEC or organic carbon, was quite high. The lack of correlation between the adsorption maximum and CEC suggests that copper adsorption may not be through the normal cation-exchange mechanism. The lack of significant correlation between copper adsorption maximum and organic carbon is an indication of the importance of copper adsorption by substances other than soil organic matter. The high clay content of this soils which is about 70% (Siderius and Muchena, 1977) may be responsible for the high copper adsorption maximum.

The soil samples from Njoro had on average the lowest adsorption maximum. Since this adsorption maximum was highly correlated with organic carbon, it seems that adsorption of copper in this soil is mainly by organic matter. Kabete soil had on average a pH and organic carbon content similar to that of Njoro. The higher adsorption maximum of Kabete soil relative to Njoro soil is probably due to the high clay content of the former. Gituamba soil had a higher adsorption maximum than Njoro soil since its organic carbon content was also higher. Both soils had a similar clay content of above 40% in the surface horizon (Siderius and Muchena, 1977).

Table VIII. The means and the ranges of adsorption maxima for the surface soil sample (A horizon) from the four areas

| Soil | Adsorption maximum (µg Cu/g soil)<br>Mean | Range |
|---|---|---|
| Kabete | 260 | 153.7-333.4 |
| Gituamba | 264 | 113.2-529.8 |
| Njoro | 164 | 121.8-278.5 |
| Naivasha | 289 | 144.4-623.3 |

For all the soils, the CECs were much higher than the adsorption maxima (Table IX). This indicates that copper is not very effective in displacing other cations from cation exchange sites.

Table (IX) A comparison of the adsorption maxima with the CECs

| Soil | mean adsorption maximum (meqCu/100g soil) | mean CEC (meq/100g) |
|---|---|---|
| Kabete | 0.81 | 24.84 |
| Gituamba | 0.83 | 29.95 |
| Njoro | 0.51 | 19.80 |
| Naivasha | 0.93 | 27.32 |

## 5.0 CONCLUSIONS

Gituamba soil was strongly acidic with the pH ranging between 4.3 and 5.4. Njoro and Kabete soils had similar pHs. The pH for Kabete soil ranged between 5.8 and 6.9 while that of Njoro soil ranged between 5.8 and 6.8. These two soils can be said to be slightly acidic. Naivasha soil was slightly acidic to alkaline with the pH ranging between 6.1 and 8.0. Of the four areas, Gituamba is the wettest while Naivasha is the driest; consequently the areas have low pH and high pH respectively.

Organic carbon content was highest in Gituamba soil and lowest in Naivasha soil. In all the soils the organic carbon content was positively correlated with the CEC. This is an indication that organic matter is an important contributor to the CEC of these soils. The slight correlation between organic carbon and CEC observed on Naivasha soil is an indication that other constituents, presumably amorphous clays, are likely to be important contributors to the CEC of this soil.

The distribution of total copper with depth was found to be generally uniform for the soils used in this study. This uniformity was attributed to the low mobility of copper in soils. There was more double-acid extractable copper in the B horizon (0.23 ppm) than in the A horizon (0.08 ppm) of Kabete soil although there was more total copper in the A horizon (26.6 ppm) than in the B horizon (24.6 ppm) of this soil. One can conclude from this observation that copper is more weakly held in the B than in the A horizon in Kabete soil. Althou Njoro soil had the lowest total copper content, double ac extractable copper in the same soil was higher than Naivasha soil. From this observation we can conclude that greater proportion of copper in Njoro soil is more weakly he than in the Naivasha soil.

The complete lack of correlation between total copper an the soil chemical properties determined leads one to conclud that total copper content in the soils most probably depends on the parent materials from which the soils were derived.

The adsorption maxima in all the soils were found to be much lower than the CECs. This indicates that copper ions are not very effective in displacing other cations from the cation exchange sites. From this observation, it can be suggested that adsorption of copper through the normal cation exchange mechanism in which $Cu^{2+}$ ion would displace another positive ion, for example $Ca^{2+}$ from the cation exchange sites in soils, may not be very important. It is likely that copper is mainly adsorbed through forming bonds with soil constituents such as organic matter and clays rather than simply replacing other cations as usually happens in cation exchange reactions between, for example one $NH_4^+$ for one $Na^+$ or $2NH_4^+$ for one $Ca^{2+}$.

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# APPENDICES

Appendix 1a. Distribution of total and double-acid extractable copper with depth in selected pits at Kabete

| Pit No. | Horizon | Depth (cm) | total copper (ppm) | Extractable copper (ppm) |
|---|---|---|---|---|
| 3 | A | 0-20 | 15.8 | 0.05 |
| | AB | 20-53 | 15.8 | 0.05 |
| | Bt | 53-100 | 15.8 | 0.05 |
| 5 | A | 0-13 | 19.0 | 0.05 |
| | AB | 13-35 | 19.0 | 0.15 |
| | Bt | 35-55 | 18.0 | 0.10 |
| 10 | A | 0-28 | 25.3 | 0.10 |
| | AB | 28-57 | 25.3 | 0.35 |
| | $Bt_1$ | 57-81 | 22.2 | 0.30 |
| | $Bt_2$ | 81-109 | 25.3 | 0.40 |

Appendix 1b. Distribution of total and double-acid extractable copper with depth in selected pits at Gituamba

| Pit No. | Horizon | Depth (cm) | total copper (ppm) | Extractable copper (ppm) |
|---|---|---|---|---|
| 4 | A | 0-13 | 25.3 | 0.15 |
| | BA | 13-42 | 28.5 | 0.15 |
| | B | 42-620 | 25.3 | 0.15 |
| 5 | A | 0-25 | 38.0 | 0.25 |
| | C | 25-50 | 38.0 | 0.15 |
| 8 | A | 0-20 | 28.5 | 0.45 |
| | BC | 20-53 | 28.5 | 0.35 |
| | CB | 53-85 | 25.3 | 0.40 |
| 9 | A | 0-15 | 57.0 | 0.45 |
| | AB | 15-56 | 57.0 | 0.05 |
| | Bw | 56-76 | 60.2 | 0.05 |
| 10 | A | 0-21 | 19.0 | 1.00 |
| | AB | 21-51 | 19.0 | 0.00 |

Appendix 1c. Distribution of total and double-acid extractable copper with depth in selected pits at Njoro

| Pit No. | Horizon | Depth (cm) | total copper (ppm) | Extractable copper (ppm) |
|---|---|---|---|---|
| 1 | A | 0-15 | 6.3 | 0.45 |
| | C1 | 15-34 | 9.5 | 0.60 |
| | C2 | 34-47 | 9.5 | 0.25 |
| | C3 | 47-66 | 9.5 | 0.30 |
| 2 | A | 0-20 | 1,3 | 0.20 |
| | C | 20-30 | 1.3 | 0.20 |
| 6 | A | 0-15 | 3.2 | 0,20 |
| | Bw | 15-36 | 3.2 | 0.05 |
| 7 | A | 0-18 | 1.3 | 0.15 |
| | Bw | 18-48 | 1.3 | 0.05 |
| 8 | A | 0-17 | 1.3 | 0.10 |
| | B1 | 17-38 | 3.2 | 0.05 |
| | B2 | 38-63 | 3,2 | 0.10 |
| 9 | A | 0-17 | 3.2 | 0.10 |
| | B1 | 17-34 | 3.2 | 0.05 |
| | B2 | 34-55 | 1.3 | 0.10 |

Appendix 1d. Distribution of total and double-acid extractable copper with depth in selected pits at Naivasha

| Pit No. | Horozon | Depth (cm) | Total copper (ppm) | Extractable copper (ppm) |
|---|---|---|---|---|
| 2 | A | 0-27 | 3.2 | 0.05 |
| | B | 27-48 | 3.2 | 0.05 |
| 5 | A | 0-20 | 3.2 | 0.05 |
| | B1 | 20-30 | 3.2 | 0.05 |
| | B2 | 30-80 | 3.2 | 0.15 |
| 10 | A | 0-13 | 12.7 | 0.10 |
| | B1 | 13-44 | 12.7 | 0.00 |
| | B2 | 44-78 | 15.8 | 0.10 |
| | CB | 78-115 | 15.8 | 0.10 |

Appendix IIa **Correlations among soil chemical properties in Kabete soil**

| Correlations | Adsorption maximum | CEC | Organic C | pH | Extractable Cu |
|---|---|---|---|---|---|
| Adsorption maximum | 1.0000 | 0.2677 n.s | 0.2282 n.s | 0.2254 n.s | 0.5002 n.s |
| CEC | 0.2677 n.s | 1.0000 | 0.8434** | -0.3199 n.s | 0.2818 n.s |
| Organic C | 0.2282 n.s | 0.8434** | 1.0000 | -0.2068 n.s | 0.3819 n.s |
| pH | 0.2254 n.s | -0.3199 n.s | -0.2068 n.s | 1.0000 | -0.4547 n.s |
| Extractable Cu | 0.5002 n.s | 0.2818 n.s | 0.3819 n.s | -0.4547 n.s | 1.0000 |

Appendix IId. Correlations among soil chemical properties in Naivasha soil

| Correlations | Adsorption maximum | CEC | Organic C | pH | Extractable Cu |
|---|---|---|---|---|---|
| Adsorption maximum | 1.0000 | 0.8958*** | 0.8406*** | 0.2128 n.s | -0.3103 n.s |
| CEC | 0.8958*** | 1.0000 | 0.6773* | 0.1687 n.s | -0.4798 n.s |
| Organic C | 0.8406*** | 0.6773* | 1.0000 | -0.0513 n.s | -0.2244 n.s |
| pH | 0.2128 n.s | 0.1687 n.s | -0.0513 n.s | 1.0000 | -0.6625 n.s |
| Extractable Cu | -0.3103 n.s | -0.4798 n.s | -0.2244 n.s | 0.6625 n.s | 1.0000 |

*** = significant at 0.1%

** = significant at 1%

* = significant at 5%

n.s= not significant