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DEPARTMENT OF CROP AND SOIL SCIENCES

A STUDY OF COPPER SORPTION IN SOILS AS INFLUENCED BY SOIL CHARACTERISTICS USING A LABORATORY COLUMN LEACHING TECHNIQUE

BY

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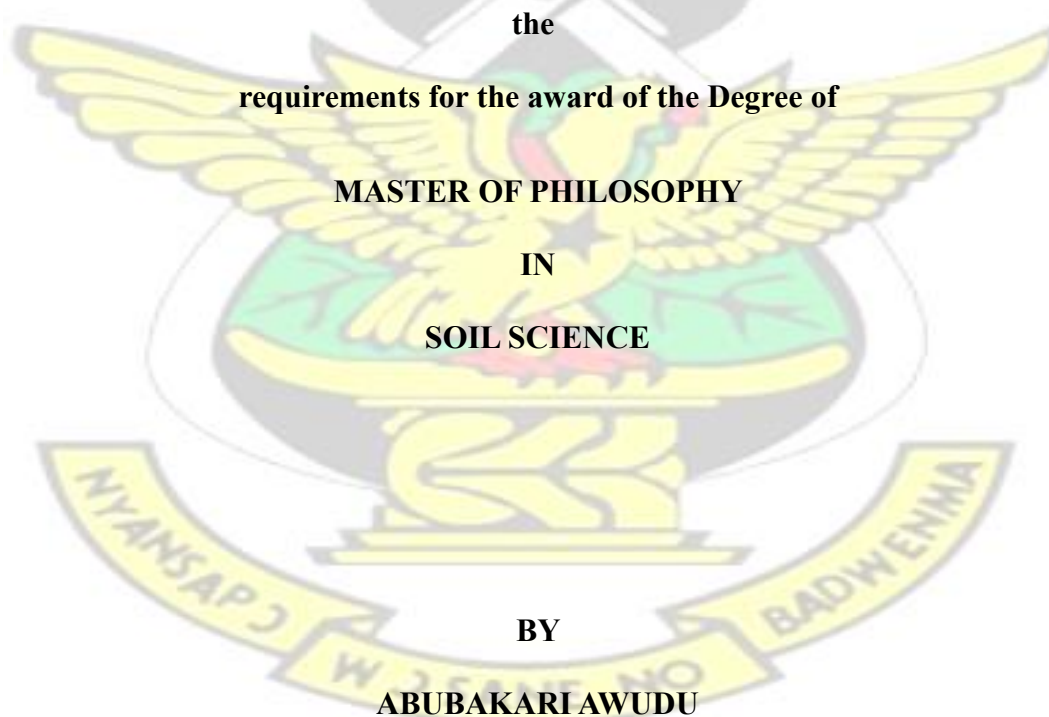
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BY

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DECLARATION

I certify that this thesis does not incorporate, without acknowledgement, any material previously submitted for a degree or diploma in any University; and that to the best of my knowledge and belief does not contain any material previously published or written by another person, except where due reference has been made in the text.

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ABSTRACT

Copper (Cu) is essential to plant metabolism, but when present in bioavailable forms at excessive levels, has the potential to become toxic to plants. It is frequently measured for regulatory decision making on toxicity levels in soils. Decisions on the utilization or containment of potential Cu toxicity require an understanding of its behaviour in the soil. Two experiments arranged in a Randomized Complete Block Design (RCBD), with four replications each, were therefore carried out separately, to assess the distribution of Cu in the soil as affected by selected soil characteristics. The treatments were 0.00, 12.33, 18.50 and 24.70 g/m^2 Nordox powder per column with an area of 81.04 cm^2. Two different soils, Nta and Temang soil series, (Gleyic Arenosol and Eutric Dysteric Gleysol, respectively.) made up of different parent materials were used for the studies. The study showed that Cu sorption increased with increasing soil organic matter content and confirmed soil organic matter as an important accumulator of Cu. This was further supported by the positive correlation between Cu and SOM with a correlation coefficient (r^2) of 0.999 and 0.996 under the Nta and Temang soil series respectively. Whilst the correlation between CEC and Cu sorption was positive in the Nta series, it was negative in the Temang series. Generally, copper sorption reduced with increasing soil depth along the soil column in both series. The increased contact time between the leaching solute and the top soil increased Cu sorption in the topsoil than the subsoil. The clay content did not show any regular pattern with Cu sorption. Copper sorption to the soil matrix increased with increasing pH in both soil types, but the effect was much more pronounced in the Nta series which generally recorded higher soil pH values than Temang series. Nta series adsorbed more Cu than the Temang series at all levels of Cu application. The increased sorption could be due to the relatively higher SOC content and pH of the Nta than Temang series. The results showed the annual Cu movement in the soil to be 4.17 and 4.58 cm y^{-1}

for the Nta and Temang series respectively. Also, copper would require about 40 and 76 years to reach the aquifer in Nta and Temang soil series, respectively. Continuous application of Cu-based fungicides to agricultural soils containing little amounts of organic matter should be exercised with caution as its accumulation may reach toxic levels. Continuous application of Cu may equally have serious groundwater contamination implications especially under low soil reaction conditions. Industries processing heavy metals can set up large column leaching apparatus to clean industrial effluents before disposing them into the environment.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Copper is extensively used in agriculture as a fungicide to protect coffee, cocoa, tea, banana, citrus, and other plants from major fungal leaf and fruit diseases such as blight, downy mildew, and rust (HSDB, 2008). Copper oxide is used as an active ingredient in various pesticides formulations and comes with various trade names such as Kocide 2000, Champion 80 WP, Nordox 75, Nordox Super 75 WG, Ridomyl Gold plus 65 WP and Ridomyl Gold plus 66 WP.

Nordox 75 WG is a microfine red/brown copper fungicide with greater activity and adhesive properties for preventing cocoa blight diseases (CBD) and cocoa leaf rust (CLR) in coffee, early and late blight in potato and tomato and rust in French beans among other diseases. Biochemically Nordox 75 WG has competitive advantage over its counterpart fungicides because of its strong bonding to amino acid and carboxyl groups. It reacts with proteins and act as enzyme inhibitors. It is widely used either as ground or aerial application on vegetables and field crops to control black leaf spot (BLS), black rot and downy mildew as either ground or aerial application.

Copper may reach the soil directly via deliberate application (agrochemicals) or via indirect routes (i.e. waste water, sewage sludge, soil or air, and wet or dry deposition) (OECD, 2004). It must be noted that relatively few copper applications are made directly and exclusively to the target pest whiles most application methods rely on the use of an appropriate quantity of copper to the environment so that exposure to the target organism

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reaches effective levels. High levels of heavy metals are reported in the environment as a result of these activities and are therefore of great concern (Cooper *et al*., 1999). Although copper has known functions and are needed by plants as parts of coenzymes and enzymatic prosthetic groups, it is toxic to plants at high levels (Antosiewicz, 1992; Nedelkoska and Doran 2000).

Copper metal in excess concentrations can completely inhibit plant growth by interacting with the physiological and biochemical activities of plants (Baker, 1987). Copper binds tightly to organic soil particles (Kumar *et al*., 1995; Singh *et al*., 1997), which decrease its mobility in most soils and thereby reduce plant uptake (Salim *et al*., 1993; Kumar *et al*., 1995; Cooper *et al*., 1999). Copper is necessary for the growth of plants (Cook *et al*., 1997). It functions as a structural and catalytic component of several enzymes and proteins (Cook *et al*., 1997). Excess copper in the soil can however be toxic to plants which could lead to reduced growth, chlorosis and malformation of roots (Kjaer and Elmegaard 1996; Cook *et al*., 1997).

The amount of copper that is absorbed by plants and its toxicity depends on several factors, such as their nutritional status (Pahlsson, 1989), the exposure time and the concentration of copper in the soil (Pahlsson, 1989; Kjaer and Elmegaard, 1996), the species genotype (Pahlsson, 1989) and interaction of excess copper with other nutrients such as potassium, zinc, magnesium, and iron (Kjaer and Elmegaard, 1996; Cook *et al*., 1997). The latter may be due to either displacement or altered uptake of the elements in the soil by plants (Cook *et al.,* 1997). The alteration in uptake may come about through the competitive exclusion of other metals by copper at the uptake sites. Also, the observed levels of copper found in plants, most often than not, correlate with the levels present in

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the environment (Vesk and Allaway, 1997). Salim *et al*. (1993) found that concentrations of copper increased in radish plants when treated with an increasing concentration of this metal. The uptake of copper from the soil by plants is influenced by a variety of factors, including soil pH, temperature, ions, cation exchange capacity, organic matter content, the concentration of copper in the soil, and the plant species (Antosiewicz, 1992; Salim *et al*., 1993). Copper enters plant roots in the form of dissolved ions and move with the inflow of water apoplastically through the root hairs and into the cortex and are then translocated to the other parts of plants (Punz and Sieghardt, 1993).

Copper toxicity, therefore, has deleterious impacts on sustainable agriculture and environmental health. An in-depth study of its sorption would potentially contribute significantly to the proper use and management of copper based formulations in the farm enterprise.

1.2 Problem Statement and Justification

Despite constraining legislations with respect to the kind and amount of copper to apply, copper use still causes environmental contamination. The fate of copper in the soil, therefore, has major environmental and agricultural implications. Continuous application of copper in agriculture is being questioned due to human health and environmental concerns (Baker, 1990). It has been estimated that less than 0.1 % of the applied materials reach the target pest (Pimentel and Levitan, 1986), and the other fraction of the discharged chemical is dispersed in the environment. Considering the inherent toxicity and the possible deleterious effect of copper, an understanding of the distribution and partitioning of copper and its leaching potential would contribute significantly to the proper use and

management of copper-based formulations in agriculture. It will also be useful in the design and management of effluent disposal of industries processing heavy metals and land disposal systems for sewage sludge and city refuse containing heavy metals. It was in the light of these that this study was carried out.

1.3 Hypotheses

i. Soil characteristics will influence copper sorption and transport into the groundwater aquifers.

ii. The average time required for copper centre of mass to reach the groundwater aquifer will be affected by the selected soil chemical and physical properties.

iii. The selected soil physical and chemical properties will affect copper sorption at the various soil depths.

1.4 Main Objective

The main objective was to contribute to the knowledge and better understanding of copper accumulation, partitioning and transport through sorption studies in undisturbed soils towards a better management of copper based formulations in agriculture.

The specific objectives were to:
1. assess the impact of selected soil chemical and physical properties on Cu distribution and sorption.

2. establish the relative susceptibility of selected soils to copper toxicity towards selecting disposal sites for copper laden sludge or refuse.
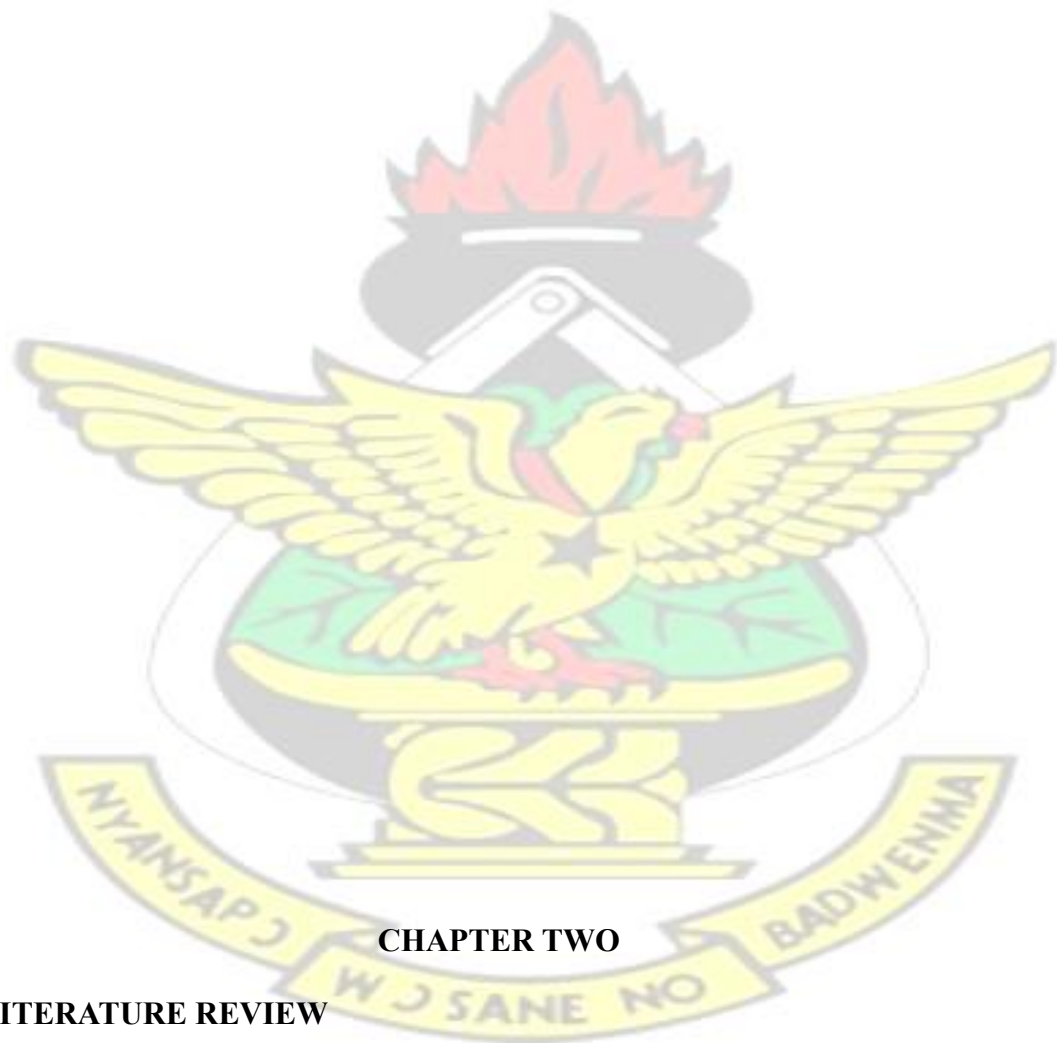
CHAPTER TWO

2.0 LITERATURE REVIEW

2.1. Sources of heavy metals in soil

Elements having approximate atomic weight between 63 and 200 are classified as heavy metals (NCSU Water Quality Group, 2006). Heavy metals in the environment originate

from various sources; including pollution of the atmosphere by motor vehicles, urban and industrial wastes, mining and smelting of non – ferrous metals, and some contributions from agricultural sector; involving the use of agricultural fertilizers and pesticides (Alloway, 2004). Sharma *et al*. (2009) reported that most of these metals in the soil are mainly the result of contamination by industrial emissions, with some contamination arising from the use of sewage sludge added to soil. These metals in the environment, depending on their quantities and source of deposition, may pollute the land or water.

Other sources include the decomposition of plant and animal detritus, precipitation or atmospheric deposition of airborne particles from volcanic activity, wind erosion, forest fire smoke, plant exudates and oceanic spray (Kennish, 1992). Additionally, surface runoff from mining operations, combustion of fossil fuels may end up polluting the air atmosphere with metal particulates that eventually settle to the land surface. Urban storm water runoff may often contain metals from roads and atmospheric fallout (Connel *et al*., 1984).

2.1.1. Sources of copper

Copper is a reddish metal with a face – centred cubic crystalline structure. It reflects both red and orange light, absorbs other frequencies in the visible spectrum, due to its band structure (http://www.Lenntech.com/periodic/elements/Cu.htm). The various sources of copper in the environment are industrial copper use, vehicle fluids leaks and dumping, vehicle brake pads and architectural and marine antifouling coatings of copper (Sharma *et al*., 2009). Copper oxide is used as an active ingredient in various pesticides formulations and comes with various trade names such as Kocide 2000, Champion 80

WP, Nordox 75, Nordox Super 75 WG, Ridomyl Gold plus 65 WP and Ridomyl Gold plus 66 WP.

Table 2.1: Fertilizer sources of copper

Source	Formula	Percent Copper
Copper Chelate	$Na_2CuEDTA$	13
Copper Sulphate	$CuSO_4.5H_2O$	25
Cupric Oxide	CuO	75
Cuprous Oxide	Cu_2O	89

Source: Schulte and Kelling (1999)

2.2. Effect of copper on health and environment

2.2.1. Effect of copper on health

Although copper can be taken in small amounts in the range of 1-2 mg daily dietary intake basis to maintain good health, high levels of copper can be harmful to health (Sharma *et al.,* 2009). Long – term exposure to copper can cause irritation of the nose, mouth and eyes. It can also cause headaches, diarrhoea, stomach ache, dizziness and vomiting. (www.lenntech.com /periodic/elements/cu.htm). Exposure to very high levels can damage the liver and kidney and may lead to death. Copper reacts with other elements to form compounds such as copper sulphate that is harmful to humans. Toxic response in humans has been observed at 11 mg/kg. Copper sulphate is corrosive to the skin and eyes. It is readily absorbed through the skin and can produce a burning pain and itching due to skin contact. (www.lenntech.com/periodic/elements/cu.htm). Eye contact with copper may result in conjunctivitis, inflammation of the eyelid lining, cornea tissue deterioration, and clouding of the cornea (Extonet, 1996). Long – term effects are more likely in individuals

with „Wilson‟s disease‟, a condition that causes excessive absorption and storage of copper. „Wilson‟s disease‟ is an inherited genetic disorder characterized by the body‟s inability to properly excrete copper, leading to accumulation of copper in the tissues which may cause liver disease and mental retardation (www.copperinfo.co.uk/health).

2.2.2. Effect of copper on the environment

Copper is a very common substance that occurs naturally in the environment and spread through the environment through natural phenomena. It may also be released through anthropogenic activities in mine sites, industrial settings, landfills and waste disposal (www.lenntech.com/ periodic/ elements/cu.htm).

In soil, most copper compounds will settle and be bound to either water sediments or soil particles. Water soluble copper compounds form the largest threat to humans.

Usually water – soluble copper compounds occur in the environment after application of copper based chemicals in agriculture. Copper is a metal and therefore, does not break down in the plants and animals when found in their system. On soils polluted with copper, only a limited number of plants have a chance of survival. (www.lenntech.com /periodic/ elements/cu.htm). Copper can also interrupt the activities of microorganisms and earthworms in the soil with adverse consequences on the decomposition of organic matter and nutrient availability to plants (www.lenntech.com/periodic/ elements/cu.htm).

2.3. Symptoms and visual evidence of copper toxicity in plants

The most widespread visual evidence of copper toxicity is a reduction in plant growth as toxicity increases (Sharma *et al*., 2009). Interveinal foliar chlorosis is a common initial symptoms of copper toxicity (Taylor and Foy, 1985; Zhu and Alva, 1993). The chlorosis usually comes in the form of cream or white spots or lesions (Lee *et al*., 1996a; O‟Sullivan *et al*., 1997). With increasing exposure, leaf tips and margins can become necrotic (Taylor and Foy 1985; Yau *et al*., 1991). Yau *et al*. (1991) reported that in an acute Cu toxicity, leaves may become wilted before eventually becoming necrotic. It can also be associated with purpling of foliage (Choi *et al*., 1996) but this is not apparent in all species (O‟Sullivan *et al.,* 1997). The toxicity of copper can also affect both root growth and form often before any effect on the above – ground growth (Minnich *et al*., 1987). Copper toxicity manifests in short, blunt-tipped radicles and dark brown/black coloration of dicot seedlings with a disposition to fungal attack (Patterson *et al.,* 1983).

The toxic action of metals of which copper is no exception can be seen both at the macro – scale on growth reduction or stunted growth and foliar symptoms. The effects of metals can be seen automatically as cellular symptoms at a smaller scale. Symptoms at both macro and cellular are side effects of the direct mode of action. The direct mode of action of copper is on plant metabolism. Increase in the concentration of any metabolite can demonstrate either increased production or decreased utilization by the reaction for which it is a substrate or product (Burke *et al*., 1990). Also at elevated Cu concentration, where root symptoms were apparent but not growth reduction, total chlorophyll contents and chlorophyll a to b ratios were reduced but there was no effect on net photosynthesis (Rousos *et al*., 1989). At higher external Cu concentrations where growth was depressed,

lower chlorophyll contents (Luna *et al*., 1994; Ouzounidou *et al*., 1992; 1994), a reduced photosynthetic capacity including an inhibitory effect on photosynthesis II (Arellano *et al*., 1995; Baron *et al*., 1995), and an increase in the breakdown of carotenoid (Luna *et al*., 1994) occurred. A side effect of copper inhibiting photosynthesis is an increase in the production free radicals and therefore an increase in rate of leaf senescence due to oxidative damage (Luna *et al*., 1994). It has also been demonstrated that the toxic action of copper is substitution of Cu^{2+} for Mg^{2+} in chlorophyll molecules, thus reducing photosynthesis (Kupper *et al*., 1996).

Although very little research have been undertaken to understand the effects of copper toxicity on transpiration and water budgets within plants, Rousos *et al*. (1989) found that, at low Cu toxicity in *Brassica oleracea* var *Capitata* (Cabbage), root symptoms were expressed but growth had not decreased and no effect on water transpiration was apparent. Copper toxicity has a significant effect on enzyme production and metabolism. Excess copper has been found to inhibit ATPase activity in the plasma membrane of *Zea mays* roots (Kennedy and Gonsalves, 1989). However, the authors suggested that this was an indirect effect of Cu toxicity resulting from the leakage of K ions. Also copper toxicity has also been shown to inhibit acid phosphatase activity in antioxidative enzymes as a result of Cu mediated oxidative damage (Luna *et al*., 1994; Weckx and

Clijsters, 1996; Savoure *et al*., 1999). *In-Vitro* studies have also shown that, the cells of *Helianthus annus* roots had a decrease in its mitotic index with a corresponding increase in mitotic abnormalities as the Cu supply increased (Chakravarty and Srivastava, 1992).

It is quite likely that different plant species may have evolved different spectrum of mechanisms to tolerate excess copper and that even within plant species more than one mechanism could be in operation. Plants have both constitutive (utilised by sensitive and tolerant phenotypes) and adaptive (utilise by tolerant phenotypes only) mechanisms to withstand excess copper (Meharg, 1994). One mechanism of lessening the toxicity effects of copper is preventing excess copper from entering the plants. The two main ways in which plants could do this, is by either precipitating or by complexing copper in the root environment. Plants are able to precipitate metals by increasing pH of its rhizosphere or by excreting anions such as phosphate. While there is large body of circumstantial evidence suggesting a pH mediated tolerance mechanism, it is unlikely to be a major tolerance mechanism (Taylor, 1991).

Research has shown that there is a significant complexation of copper at the cell wall – plasma membrane interface. A significant proportions of Cu accumulate the cell wall – plasma membrane interface tolerance and it has been hypothesized that this could be the site of metal tolerance (Sharma *et al*., 2009). For an instance, 60 % of Cu in the roots of *Lolium multiflorum* (Italian rye grass) was bound by the cell membrane and plasma membrane (Iwasaki *et al*., 1990). Also, *Minuatia verna* ssp. *hercynica* growing on heavy metal contaminated medieval mine dumps has high concentration of Cu in the cell walls (Neumann *et al*., 1997). In comparison, no accumulation of Cu was detected in the cytoplasm suggesting strong use of exclusion by the Cu adapted subspecies. Plant cation exchange capacity (PCEC) has also proved useful in metal complexing. PCEC is largely determined by the exchange sites in cell wall (Horst and Marchner, 1978). Sensitive cultivars have been shown to have much lower cell wall CECs than tolerant cultivars

(Masion and Bertsch, 1997). It has been suggested that tolerant cultivars use the high CEC to complex metals at the cell wall and thereby preventing entry to the cell.

2.4 Sorption and its related terminologies

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from *absorption*, in which a substance diffuses into a liquid or solid to form a solution. The term *sorption* encompasses both processes, while *desorption* is the reverse process. Adsorption (herein referred as sorption) is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification (http://en.wikipedia.org/wiki/Adsorption)

Similar to surface tension, sorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favourable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption. Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behaviour of real gases. Chemisorption is a type of adsorption whereby a

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molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption (http://en.wikipedia.org/wiki/Adsorption).

Once in the body of the soil, chemical molecules partition between the aqueous and solid phases of the soil. The degree to which a chemical molecule prefers one phase over the other will affect every aspect of it in soil. Many chemical compounds are, thus, strongly sorbed onto the plants or on to clay particles and organic matter in the soil. Sorption, therefore, determines whether the chemical will persist or not, be transported and become a pollutant or not (especially to groundwater), and often, whether, it will be efficacious or not (Cohen *et al*., 1986; Wauchope *et al*., 2002). Soil sorption is characterized by a partition constant K, conventionally with a subscript "d" (for „distribution") (Hamaker and Thompson, 1972). It is defined as the ratio of the quantity of molecules adsorbed to the quantity of molecules in solution at equilibrium. Presently, octanol/water partition coefficients (K_{ow}) and organic carbon partition coefficients (K_{oc}) values are critical parameters typically related to sorption and desorption processes (Cheng, 1990).

2.5. Factors affecting Cu^{2+} availability and sorption in soil

Soil has the ability to immobilise introduced chemicals like heavy metal ions. The immobilisation is mainly due to sorption properties which are determined by physicochemical properties of the soil, such as, amount and type of clay and organic fraction, pH, water content, temperature of the soil and properties of the particular metal

ion (Stevenson, 1992)**.** Clay particles are usually negatively charged. This is a very important factor influencing sorption properties of the soil.

2.5.1. Soil properties

The soil properties which affect copper availability includes, Clay content, Soil reaction (pH), Organic matter among others.

2.5.1.1. Minerals

The mineral adsorbents involved in the adsorption of Cu^{2+} are clay (silicate minerals), oxides and hydroxides (Calvet, 1989). Clay surfaces are mainly hydrophilic because of hydroxyl groups and exchangeable cations. Barriuso *et al.* (1994) reported that adsorption of copper on clay minerals is likely to occur on the external surface of clay particles rather than in the interlamillar space and increases with specific clay surface. Clay and hydrous oxides determine copper availability mainly by specific adsorption to surface hydroxyl groups (Miller *et al*., 1987; Pampura *et al*., 1993), non-specific adsorption (exchange) (Kalbasi *et al*., 1978; Basta and Tabatabai, 1992), coprecipitation (Martinez and McBride, 1998), and precipitation as the discrete copper oxide or hydroxide (Martinez and McBride, 1998). Therefore, increasing clay and hydrous oxide contents in the soils provides more sites for adsorption of copper.

2.5.1.2. Soil pH

Soil pH is an important indicator of the chemical processes that occur in the soil, and therefore may serve as a guide to likely deficiencies and/or toxicities (Slattery *et al*. 1999).

For this reason, among others, Dragun (1998) provided guidelines for interpreting soil pH values for environmental evaluation. The equilibrium between copper metal speciation, solubility, adsorption and exchange on solid phase sites is intimately connected to soil solution pH (Olomu *et al*., 1973; Sauve *et al*., 1997). Hence, numerous studies have found soil pH to have a large effect on copper metal bioavailability (Mcbride *et al*., 1997). Reddy (1995) found that Cu^{2+} concentration increased from 37 to 95 % as the pH of the soil increased. Other studies have found little relationship between soil pH and Cu concentration in the soil solution (Jeffery and Uren,

1983; Sauve *et al*., 1997). The reason for this is the strong affinity of OM for Cu (Norvell, 1991). Thus, the amount of organic matter could be a more important determining factor on Cu solubility than pH.

2.5.1.3. Organic matter

Soil organic matter originates from crop residues, microbial biomass and organic amendments enrichment. It has a very heterogeneous composition and contains both hydrophilic and hydrophobic groups (Calvet *et al*., 2005). Copper ions can be complexed by organic matter and therefore altering their availability to plants. The carboxyl (COO^-) groups in both solid and dissolved organic matter form stable complex with copper metal (Baker and Senfts, 1995). Copper ions form strong coordination complex with organic matter (Stevenson, 1976; 1991). Hence, Cu^{2+} is often bound to the soil organic matter fraction and soil organic matter could be the most important soil factor in determining Cu bioavailability (del Castilho *et al*., 1993). Sauve *et al*. (1997) showed that in a range of Cu contaminated soils, greater than 98 % of the copper in the soil solution was bonded to

organic complexes. Miller *et al*. (1987) reported that Cu applied as sewage sludge was retained in the soil solution in greater quantities than Cu applied as a sulphate because it was bonded to the organic carbon in the sludge.

2.5.1.4. Oxidation and Reduction

The Oxido – reduction (redox) conditions of a soil play a role in the availability of copper in soil. The redox condition of a soil is affected by several factors; such as soil waterlogging and compaction among others. The redox condition in the soil affects the availability of copper in the soil by affecting the proportion of particular metal species and by affecting the solubility of copper (Patrick and Jugsujinda, 1992; Evangelou, 1998).

It is reported that most copper in the soil are present in the divalent form with the monovalent forms being highly unstable (Knezek and Ellis 1980; Whitehead, 2000). Hence, copper is said to be significantly reduced under low redox conditions (Whitehead, 2000).

2.5.2. Physico – chemical properties of a compound influencing sorption
2.5.2.1. Surface, volume, and branching

The absorption of copper increases with volume and the degree of branching which is correlated to the surface area (Mamy and Barriuso, 2005). The molecular volume is related to water solubility (Calvet, 1989), and the degree of branching encodes intermolecular accessibility (Kier and Hall, 2000).

2.5.2.2. Electronic structure

The nature of atoms of functional groups determine the electronic structure of a species that governs the type of interaction of an element with soils (donor – acceptor electron, hydrogen bonds) (Calvet, 1989). The different substitutions and their spatial arrangement in the molecule have an effect on the adsorption by influencing the reactivity of functional groups that participate in the bond interactions (Liu *et al.*, 2000).

2.5.2.3. Ionization

Ionization determines the charge of a species and depends on its electronic structure. In general, the sorption of cation is strong on negatively charged surfaces like clays, oxides, hydroxides and humic substances. On the contrary, anions are not adsorbed on these surfaces, but their sorption is dependent on soils with high positive charges, like tropical soils (Mamy and Barriuso, 2007).

2.5.2.4. Hydrophilic and hydrophobic balance

The hydrophilicity of a species is defined by its water solubility and the hydrophobicity by their octanol/water partition coefficient. The adsorption of a substance decreases when their water solubility increases because of their high affinity for the water phase, and conversely the adsorption increases with the hydrophobicity of the substance (Mamy and Barriuso, 2007). It also depends on the hydrophilic/hydrophobic balance of the phosphorus groups balance of the soil adsorbents. The sorption of ionisable molecule like copper involves high – energy binding adsorption phenomena (ionic and coordination

bindings, complex formation with metals in solution or at the solid – liquid interphase) that balance the effects of high solubility (Tao and Lu, 1999).

2.6. Behaviour of copper in soils

The total amount of copper in soils is made up of 5 major „pools‟ classified according to the physico – chemical behaviour of copper. The pools are: soluble forms in the soil solution which usually forms very low concentration, stable organic complexes in the humus, copper sorbed by hydrous oxides of Manganese and Iron, metal adsorbed on the clay – humus colloidal complex and the crystal lattice – bound copper in soil minerals which is only released on weathering.

The total copper concentration in the soil solution are in the range of $0.01 – 0.6$ μM, which is very low when compared to the total soil copper content of $25 – 40$ mg/kg soil (Sharma *et al.*, 2009). This is so because of the high affinity of copper to sorption (Loneragan *et al*., 1975). The retention of copper in soils is mainly due to the adsorption, which is the passage of a solute from an aqueous phase to the surface of a solid adsorbent (Calvet, 1989). These solid adsorbents are the different soil constituents. Several adsorption mechanisms are possible including; hydrogen bonding, ion exchanges, interaction with other metallic cations in the soil, polar interactions, charge transfers, London – Vander Waals dispersion forces and hydrophobic effects (Calvet *et al.*, 2005). As the soil constituents contain polar and ionisable groups, the adsorption of Cu can involve several of these mechanisms. The process of adsorption and desorption are said to be antagonistic. Desorption is inversely related to adsorption, being small when adsorption is great (Mamy and Barriuso, 2007). In certain cases, hysteresis is observed in

the adsorption and desorption mechanism. Hysteresis can be due to the irreversible adsorption, physical entrapment of copper in organo – mineral aggregates (Mamy and Barriuso, 2007).

2.7. Copper and nutrient availability

Copper in the soil can bind strongly to organic matter, clay minerals and hydrated oxides of iron, aluminium and manganese (Schnitzer, 1969). This phenomenon may reduce the concentration of these nutrients in the soil or complex them to become unavailable to plants. The amount of nutrients such as zinc, manganese and iron decreased following continuous application of copper in Bordeaux mixture (Savithri *et al*., 2003). In a similar manner, available phosphorus content of the soil decreased following fungicide application at both surface and subsurface layers, (Cooper *et al.,* 2009). This may be due to increasing base saturation of the soils with lime – containing fungicide residues, perhaps encouraging fixation or immobilization of available phosphorus (Caudhuri, 1964). Akinnifesi *et al*. (2006) similarly observed that increasing copper content of soils in cocoa plantations reduced the amounts of phosphorus available to plants and caused nutrient imbalance. Copper has been found to suppress rates of nitrogen fixation by bacteria rhizobium at relatively high Cu levels of 235 ppm (OMRI, 2001).

2.8. Effect of copper on soil fauna

Detrimental effects of elevated copper concentration were observed on mycorrhizal associations (Georgieva *et al*., 2002) and microbial population and functions (Dumestre *et al*., 1999). In some orchards, most animal life in soil, including large earthworms have

been eliminated by the extensive use of copper containing fungicide (Extoxnet, 1996; Norgrove, 2007). It has been reported that earthworms are more susceptible to heavy metals such as copper than most other groups of soil invertebrates (Bengtsson and Rundgren, 1992; Reinecke *et al*., 1997), exhibiting chronic toxic responses at Cu concentration of less than 16 mg/kg (Helling *et al*., 2000).

Copper is a relatively non – specific bactericide and fungicide, and can kill naturally occurring microorganisms on leaves as well as those that have been applied as biocontrol including *Bacillus spp*. and *Trichoderma spp*. (OMRI, 2001). Cu also suppresses rates of nitrogen fixation by the bacteria Rhizobium under similar conditions as stated above (OMRI, 2001).

2.9. Methods of sorption measurement

Several methods are in use. These include batch equilibrium, centrifugation, filtering, laboratory column experiments and lysimeters.

2.9.1. Batch experiments

In batch experiments, the retention of a species of interest is measured with soil suspensions, according to the OECD 106 guideline (OECD, 2008a). A volume of an aqueous solution containing a species of interest is added to a mass of dry sieved soil in glass centrifuge tubes. The soil suspension is shaken mechanically for 24 hours in darkness and then centrifuged. The 24 hour duration is the time needed to reach equilibrium between the adsorbed species and species in solution. The amount of species retained on the solid adsorbent is calculated as the difference between initial species

concentration in solution and centrifuged supernatant concentration. In general, the smaller the concentration, the greater the adsorbed amount per unit mass of soil. The distribution coefficients between soil and soil solution is then calculated according to the Freundlich (Kf) model:

$$Kf = Qs/Ce^{nf} ` \tag{2.1}$$

Where, Qs (mg/kg) is amount of species adsorbed in soil at equilibrium concentration, Ce (mg/L) is the species concentration in the supernatant solution, and nf is an empirical coefficient. At linear isotherm, nf = 1. One of the demerits of this method is that, the adsorption of the species of interest on the surface of the flask used for the experiment has to be determined (Calvet, 1989). There is also an overestimation of the amount of species sorbed due to the intensive shaking of soil – species solution (Walker and Jurado – Exposito, 1998). This leads to dispersion of soil structure and a higher availability of sorption sites. (Walker and Jurado – Exposito, 1998).

2.9.2. Centrifugation

This method involves the preparation of the soil sample at a particular soil moisture treated with the species of interest, incubated, and then centrifuged to collect the soil solution which is directly analysed for its concentration. (Walker and Jurado – Exposito, 1998).

2.9.3. Filters

Gaillardo and Dur (1995) developed an original method using remoulded soil samples that were placed in Petri dishes to give a 3 – 4 mm thick soil layer at controlled water content.

The soil solution was sampled with a glass microfiber filters laid on the soil surface. The volume of the soil solution and the dissolved species retained in the filters are determined. This method also proved useful for undisturbed soil samples.

2.9.4. Laboratory soil column experiment

The laboratory soil column experiment, also known as the laboratory flow through (or Column) method, is one of the most commonly used methods (Relyea, 1982). In this method a solution containing a known amount of a contaminant is introduced into a column. The soil column allows a study of Cu retention in dynamic conditions. The column is filled with disturbed or undisturbed soil and a solution of known species applied to the surface of the column then water flow is imposed though rainfall simulation or pressure head control (Pot *et al*., 2011). A special advantage of the laboratory column experiment is that it allows the possibility to determine the vertical distribution of a substance in the soil core. That is, if recovery in the leachates is incomplete (Benoit *et al*., 2000; Vincent *et al*., 2007). This method was used in the study.

2.9.5. Lysimeters

In this method, an undisturbed soil block or cylinder is embedded in an inert container with its bottom permeable to drainage water or leachate. One of the outstanding features of Lysimeters is its capability to monitor mass fluxes of water and chemicals under field climatic conditions and representative crop practices (Saison *et al*., 2008). The distribution of the chemical in the soil can be determined. Compared to laboratory experiments, outdoor Lysimeter studies are closer to field environmental conditions, also there is no significant disturbance of the soil structure, but the major limitation is the fact that certain

variable experimental conditions such as environmental and climatic parameters are not controlled (OECD, 2008b).

<div align="center">CHAPTER THREE</div>

3.0 MATERIALS AND METHOD

3.1 Study area

The study was carried out at the Soil Science Laboratory of the Department of Crop and Soil Sciences at the Kwame Nkrumah University of Science and Technology (KNUST), Kumasi. The soils used belong to the Nta and Temang series, classified as Gleyic Arenosol and Eutric-Dystric Gleysol, respectively. The Temang series was sampled from a Forest reserve whereas Nta was under a forb regrowth mainly *Panicum maximum*. The former was at the Bobiri Forest Sanctuary at Kubease and the latter at the Electrical Engineering backyard at the KNUST, both in the moist semi-deciduous forest zone of Ghana. The rainfall regime is bimodal averaging 1450 mm per annum. The soils are the most extensively cultivated soil to vegetables. The physical and chemical properties are presented in Chapter four.

3.2 Soil sampling

The laboratory column leaching method was used for the experiment. The nonsectionable columns consisted of polyvinyl chloride (PVC) pipes with an inner diameter of 10.16 cm and a height of 60 cm. The 20 PVC pipes used in sampling each of the two soil types were bevelled at the lower end to provide a cutting edge to minimize penetration resistance during field core sampling. The sampling depth was 30 cm leaving an extra height of 30 cm to the brim. This extra 30 cm height served to receive the „spike" solution. Smaller

core samplers, 10x10 cm (Plate 1) were also used to take soil samples for initial physico-chemical analyses.

Plate 1: PVC pipes inserted into the soil for sample collection

3.3 Preparation of soil columns

The soils were saturated in 0.01M CaCl$_2$ "artificial rain", equilibrated and allowed to drain freely under gravity for a period of 48 h to attain field capacity before the treatments were imposed. This is shown in Plate 2.

Plate 2: Saturation in artificial rain, equilibration and prepared Cu^{2+} solution for column spiking.

3.4 Experimental treatments

The source of Cu was Nordox 75 % WG of high purity (99.4 %). It contained 86 % cuprous oxide with an equivalent amount of 75 % metallic copper. The treatments were 0.00, 100, 150 and 200 mg Nordox powder per column with an area of 81.04 cm^2, which is equivalent to 0.00 g/m^2, 12.33 g/m^2, 18.50 g/m^2 and 24.70 g/m^2 respectively. The Nordox powder was mixed with 10 mL of distilled water and applied at the surface of the soil columns and allowed to stay overnight. The next day the surface of the soil columns were covered with a filter paper (Whatman No. 42) in preparation for the application of the artificial rain to minimize disturbance of the surfaces of the soil column. Based on the inner diameter of the soil column (10.16 cm) and the average annual rainfall of the agroecological zones (1450 mm) of the study areas, 924.43 mL "of artificial rain" (simulated from a dropping funnel) was used to leach each soil column at a flow rate of

10 mL per minute. The leachates were collected at 30 minutes intervals. After the leaching process, the soil was extruded from the PVC pipes following a day of free drainage and was sectioned into segments of 0-10 cm, 10-20 cm and 20-30 cm.

Each soil segment and the leachate were then analyzed for the test substance, Cu.

Plate 3: Inserted filter paper after spiking, leaching process and extruded soil after leaching.

3.4 Depth to groundwater

The assessment of the depth to groundwater was necessary to facilitate the determination of the rate of movement of copper and the time to reach the groundwater. A survey using a 10 m long Line Level was used to determine the depth to groundwater at the sampling point. The depth to the groundwater was the vertical distance between the sampling point and the surface of the stream at the valley bottom. As shown in Plate

4 below.

Plate 4: Determination of the vertical distance from the point of soil sampling to the ground water.

3.5 Preparation of standard copper solutions

One gram Cu wire was weighed and transferred into a 1 L flask, followed by the addition of 30 mL of HNO_3, and made up to a liter with distilled water. The flask was stoppered and shaken to produce 1000 µg/mL Cu solution. One milliliter of the 1000 µg/mL Cu solution was dilluted to 100 mL to obtain 10 µg/mL standard Cu solution.

3.5.1 Working solution

The working solution was prepared by pipetting 2, 3, 4, 5, 6, 7 mL of 10 µg/mL of the standard Cu solution into a 50 mL flask and made to volume with DTPA solution to obtain 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4 µg/mL Cu. Fresh standards were prepared every fortnight.

3.5.2 Standard curve for copper

The standards were flamed on an Atomic Absorption Spectrophotometer (AAS) at a wavelength of 324.8 nm. A graph of the value of absorbance against the known concentration of Cu was plotted to obtain the standard curve.

3.5.3 Determination of copper ions in soil segments

At the end of the leaching experiment, the soil columns were extruded and sectioned into three segments of 0-10 cm, 10-20 cm and 20-30 cm. These segments were analyzed by weighing 10 g of the soil sample into a 100-mL narrow-mouthed polypropylene bottle. Twenty millilitres (20 mL) of extraction solution (DTPA) was added and the bottle stoppered. It was then shaken for 2 hours at room temperature ($25^{\circ}C$). This was followed by filtering the content into polypropylene bottle. A blank solution without soil as control was prepared. Copper content was then determined by atomic absorption spectrophotometry.

Calculation

Content of copper in the sample (mg/kg) = C µg/mL x 2 (dilution factor).

where:

Dilution factor = 2.0 (soil sample taken = 10.0 g and DTPA used = 20 mL); absorbance reading on AAS of the soil extract being estimated for copper and concentration of copper as read from the standard curve for the given absorbance of copper = C µg/mL.

3.5.4 Determination of copper ions in the leachate

Copper metals in leachate were determined directly by an atomic absorption spectrometer (Buck Scientific Model 210 VGR). Dissolved Cu^{2+} was determined from a 20 mL leachate filtered through 0.45 µm membrane immediately after leachate collection and preserved by adding 3 mL HNO_3 (1+1)/L

3.6 Particle size determination

The hydrometer method as described by Bouyoucos (1963) was used for this analysis. A 51 g soil sample was weighed into a „milkshake" mix cup. To this, 50.0 mL of 5 % sodium hexametaphosphate along with 100 mL distilled water were added. The mixture was shaken for 15 minutes after which the suspension was transferred from the cup into a 1000 mL measuring cylinder and distilled water was added to reach the 1000 mL mark. The mixture was inverted several times until all soil particles were in suspension. The cylinder was placed on a flat surface and the time noted. The first hydrometer and temperature readings were taken at 40 seconds. After the first readings the suspension was allowed to stand for 3 hours and the second hydrometer and temperature readings taken. The first reading indicates the percentage of sand and the second reading percentage clay.

Calculations:

% Sand = 100 – [H_1 + 0.2 (T_1 – 20) – 2.0] x 2

% Clay = [H_2 + 0.2 (T_2 – 20) – 2.0] x 2

% Silt = 100 – (% sand + clay)
where:

H_1 = Hydrometer reading at 40 seconds

T_1 = Temperature at 40 seconds

H_2 = Hydrometer reading at 3 hours

T_2 = Temperature at 3 hours

0.2 (T – 20) = Temperature correction to be added to hydrometer reading

- 2.0 = Salt correction to be added to hydrometer reading.

3.7 Cation exchange capacity

The cation exchange capacity (CEC) of the soils was determined using the protocols provided in FAO (2008). Five grams of soil was weighed into a 500 mL centrifuge tube. This was followed by the addition of 25 mL of 1.0 M sodium acetate solution to the tube. The content was shaken in a reciprocating shaker for 5 minutes and centrifuged at 2000 rpm for 5 minutes to obtain a clear supernatant liquid. This was followed by a complete decantation of the supernatant. The process was repeated with ethanol until the electrical conductivity (EC) of the decant read less than 40 ms/cm. The adsorbed Na was displaced using ammonium acetate. The decant was collected in 100 mL volumetric flask fitted with a funnel and filter paper. The content was then made to volume with ammonium acetate solution. The sodium concentration was determined by flame photometry, after preparing a series of Na standard solutions in the range 0-10 m.e/L Na.

Calculations

The ammonium acetate extractable Na (i.e. extractable Na) in m.e/100 g soil was estimated as follows:

$$\frac{\text{Sodium Conc.of extract in meq/litre(y)x100}}{\text{Weight of soil in g (5)}} \times \frac{\text{Volume of extract in mL (100)}}{1000} = \frac{Yx10}{5} = 2Y$$

The displaced Na was actually a measure of the CEC of the soil. Therefore, the meq. Na per 100 g soil is actually me exchangeable cations (Ca, Mg, Na, and K)/100g soil.

3.8 Soil pH (1:1)

A 10.0 g of soil sample was weighed into a 50-mL beaker, followed by the addition of 10 mL $CaCl_2$ solution. The soil was allowed to absorb the $CaCl_2$ solution without stirring, and was then stirred thoroughly for 10 seconds using a glass rod. The suspension was then stirred continuously for 30 minutes, and the pH was recorded on the pH calibrated meter (FAO, 2008).

3.9 Organic carbon/ organic matter

Percent organic carbon was determined by adopting the FAO (2008) standard using the Walkley and Black, (1934) procedure: One gram (1.0 g) of the soil sample was weighed into a 500 mL conical flask and a 10 mL of 0.1667 M $K_2Cr_2O_7$ solution was added followed by 20 mL concentrated H_2SO_4 containing Ag_2SO_4. This was mixed thoroughly and allowed to stand on asbestos sheet for 30 minutes. A 10 mL of NaF solution and 2 mL of diphenylamine indicator were added to the solution. This was titrated with standard 0.5

M Fe_2SO_4 solution to a bright green colour. The blank was ran without sample simultaneously.

The percentage of organic C was calculated by:

$$\frac{10\,(S-T)x\,0.003}{S} \times \frac{100}{Wt\ of\ soil} \qquad\qquad (3.6)$$

As 1.0 g of soil was used, this equation was simplified to:

$$\frac{3\,(S-T)}{S} \qquad\qquad (3.6.1)$$

Where:

S = millilitres of FeSO4 solution required for blank

T = millilitres of FeSO4 solution used for the sample titration

0.003= weight of C (1000 mL 0.1667 M $K_2Cr_2O_7$= 3.0 g C)

Thus, 1.0 mL 0.1667 M $K_2Cr_2O_7$= 0.003g C

Organic C recovery of this method is estimated to be about 77 percent. Therefore, the actual amount of C (Y) will be:

Percent value of organic carbon obtained x 100/77

OR

Organic carbon obtained (C) x 1.3 $\qquad\qquad$ (3.6.2)

Therefore OM = Y x 1.724 $\qquad\qquad$ (3.6.3)

(Organic matter contains 58 percent organic C, hence 100/58= 1.724, i.e. van Bemmelen factor.

3.10 Determination of the saturated hydraulic conductivity

The saturated hydraulic conductivity (K_s) measurements were determined using the falling head permeameter method similar to that described by Bonsu and Laryea (1989). In the measurement, core samples were obtained from the 0-30 cm depths. The cores were immersed and saturated in water from below. A large empty can with perforated bottom was filled with fine gravel. The core was placed on the gravel supported by a plastic sieve. The whole system was placed over a sink in the laboratory and water was gently added to give hydraulic head in the extended cylinder. The fall of the hydraulic head H_t at the soil surface was measured as a function of time t using a water manometer with a meter scale. Saturated hydraulic conductivity was calculated by the standard falling head equation as:

$$K_s = \left(\frac{aL}{At}\right).\ln\left(\frac{H_o}{H_t}\right);\qquad\qquad\qquad(3.7)$$

Where, a is the surface area of the soil, A is the surface area of the water, H_o is the initial hydraulic head and L is the length of the soil sample. By rewriting equation (1), a regression of $\ln\left(\frac{H_o}{H_t}\right)$ on t with slope $b = K_s\left(\frac{A}{La}\right)$ was obtained. Since $a = A$ in this particular case, K_s was simply calculated as:

$$K_s = bL \qquad\qquad\qquad(3.7.1)$$

3.11 Determination of available water capacity

The sample retainer rings were placed on the porous plate. (Figure 3.1) The whole sample was then transferred into the ring. Distilled water was added to the porous plate until it reached halfway up the outside of the rings. The plate was covered and allowed to stand overnight. More water was added to maintain the water level. After saturation, the plate was transferred to the pressure chamber and the outlet tubes were connected. A tube was

then connected from the pressure chamber to the bottom of a 500 mL burette. The appropriate pressures of -0.033 Mpa and -1.5 Mpa were applied. At equilibrium, the burette tap was closed and the pressure in the chamber was released. The soil was then transferred from the ring into a weighing can and the moisture contents determined. The available water capacity was then calculated as follows:

$$AWC = FC - PWP \tag{3.8}$$

where:

FC = Field capacity (Water content at -0.033 MPa)

PWP = Permanent wilting point (Water content at -1.5 MPa)
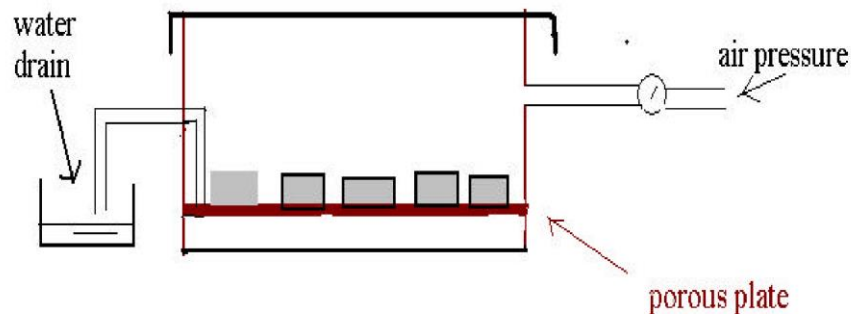
Figure 3.1: A typical set up of the pressure plate apparatus

3.12 Bulk density (ρ_b)

The dry bulk density was determined from soil cores collected on the field (two days after rains) with core samplers (Klute, 1986). The core sampler with a diameter of 10.16 cm and a height of 30 cm was driven into the soil vertically with the aid of wooden plank and a mallet to fill the sampler. The cylinders were covered and sent to the laboratory and oven dried at 105ºC for 48 hours to a constant mass. The oven dried soils were weighed and

the dried bulk densities were calculated by dividing the oven dried mass (M_s) by the total volume of the soil (V_t). Thus, the dry bulk density was calculated from the formula:

$$\rho_b = \left(\frac{M_s}{V_t}\right)$$ (3.9)

3.13 Prediction of the annual movement of copper

Equation (4.0) was used to predict the center of mass of the copper metal.

$$X = \frac{Q/W}{1+\rho_b K_d/\theta V}$$

(4.0)

Where;

X = Chemical displacement [L]

Q = Annual precipitation [L]

W = Available water content [L^3]

ρ_b = Bulk density [ML^3]

K_d = Partition coefficient, K_d value for copper from literature is 2.7 g/L. (Allison *et al.*, 2005) [ML^3]

θ_v = Volumetric moisture content at field capacity [L^3]

Sample calculations are presented in Appendix 2.0

3.14 Statistical analysis

The data collected on the various parameters were subjected to analysis of variance using GenStat statistical package (12th Edition). The design used for both sites was Randomised complete Block Design (RCBD). Means were separated using least

significant difference (Lsd) at 5 % probability level. Each treatment was replicated four times. A 200 mg Nordox application was used for the sorption studies. The regression among the parameters were also determined. Standard Error of difference was also used to compare the difference if any between the two sites.

CHAPTER FOUR

4.0 RESULTS

4.1 Physical properties of the soils

The mean values of the physical properties of the experimental soils are presented in Tables 4.1. The texture of both Nta and Temang series were all sandy loam at all depths except at the 0-10 cm depth of the latter, which was loamy sand. The saturated hydraulic conductivity and available water content were higher in Nta series than in Temang series. The permanent wilting point was higher at Temang series than Nta series. The soil bulk density and water content at field capacity of both soil series were similar.

Table 4.1: Physical and hydraulic properties of the experimental sites

PARAMETERS	NTA SERIES			TEMANG SERIES		
	Depth (cm)					
	0-10	10-20	20-30	0-10	10-20	20-30
% Sand	74.48	71.38	75.28	75.28	69.78	72.28
% Silt	21.8	19.4	11.50	20.75	20.00	19.25
% Clay	3.72	9.22	13.22	3.97	10.22	8.47
Texture	S L	S L	S L	L S	S L	S L
	0-30 cm					
K_s (cm/h)*	3.78			3.24		
ρ_b (g/cm³)*	1.570			1.560		
θ_v FC (cm³/cm³)*	0.308			0.307		
θ_v PWP (cm³/cm³)*	0.123			0.138		
AWC (cm³/cm³)*	0.185			0.169		

*Parameters were measured within 0-30 cm depth of soil; S L = Sandy Loam; L S = Loamy Sand.

4.2 Some chemical properties of the experimental soils

The selected chemical properties of the experimental soils are presented in Table 4.2. The mean values of organic carbon were higher in Nta than Temang series at all depths, although the values were low. As expected, the soil organic carbon contents at the 0-10 cm depth in both soil series was significantly higher than those of the other depths. The values recorded for the Nta series ranged from 0.290 to 0.898 % for the 20-30 cm and 010 cm depths respectively with a mean of 0.523 %. The corresponding values for the Temang soil were in the range of 0.060 to 0.411 % with a mean value of 0.199 %. The pH values of the Temang series, ranging from 4.67 to 5.03 were in the strongly acidic range. On the other hand, the pH of the Nta series was neutral, slightly acid and moderately acid for the 0-10cm, 10-20 and 20-30 cm depths.

The CEC of both Nta and Temang series were low with values of Nta ranging from 1.42 to 1.96 cmol/kg at the 20-30 cm and 0-10 cm depths respectively whereas it ranged from 1.350-2.420 cmol/kg for 0-10 cm and 20-30 cm respectively with a mean value of 1.885 cmol/kg. However, there were no significant difference ($p < 0.05$) among them at each site. The CEC at 0-10 cm was 3.06 % and 27.6 % higher than 10-20 and 20-30 cm depths respectively. Between the latter two depths, the former was 25.3 % higher in CEC. While the CEC decreased with depth in the Nta series, it increased in the Temang series with the values of the latter ranging between 1.35 and 2.42 mg/kg at the 0-10 cm and 20-30 cm respectively. The CEC of the 20-30 cm depth was 44.2 % and 7.0 % greater than that of the 0-10 cm and 10-20 cm depths respectively. There was no significant difference observed in the initial Cu content recorded in Nta soil series at the various soil depths

whereas in Temang soil series significant differences were observed. The amount of Cu recorded at the 0-10 cm depth was significantly higher than that of the 10-20 cm and 20-30 cm depths in both soil series. The available copper content recorded under the Nta series was generally higher than that under the Temang series.

Table 4.2: Chemical properties of the experimental soils

Depth (cm)	Nta series				Temang series			
	CEC cmol/kg	pH (1:2.5)	O.C. (%)	Cu mg/kg	CEC cmol/kg	pH (1:1)	O.C. (%)	Cu mg/kg
0-10	1.96	6.72	0.90	0.19	1.35	5.03	0.41	0.17
10-20	1.90	6.56	0.38	0.15	2.25	4.65	0.13	0.05
20-30	1.42	6.23	0.29	0.13	2.42	4.67	0.06	0.06
Lsd (5 %)	0.72	0.53	0.27	0.08	0.72	0.19	0.09	0.06

4.3 The impact of different application rates and soil depth on copper sorption The influence of copper loads and soil depth on copper sorption are presented in Tables 4.3, 4.4 and 4.5.

4.3.1 The impact of copper load on sorption

The different application rates significantly ($p < 0.05$) affected copper sorption in the Nta and Temang series. At all the rates of copper applied, considerable differences in copper sorption were recorded in the Nta series but not in the Temang series. The different rates of copper applied significantly increased copper sorption in relation to the control in the Temang series but among the different application rates, no significant difference was recorded.

A particular trend was observed in Temang soil series where the amount of copper ion sorbed to the soil at 100 mg was higher than both the 150 and 200 mg application rates but the differences observed between 100 and 200 mg application rates was not significant. Conversely, application of Cu at 200 mg in the Nta series recorded higher Cu sorption in comparison to the 100 and 150 mg application rates. Also, a significant difference in Cu sorption was observed between the 100 and 150 mg application rates. The increasing order of copper sorption was 0 < 150 < 100 < 200 and 0 < 150 < 200 < 100 for Nta and Temang soil series respectively. Also across the sites at the various copper load significant difference was observed in only the 0 mg application rate.

Table 4.3 Effect of copper load on sorption

Rates (mg)	Nta series	Temang series	SED
		mg/kg	
0	0.153	0.085	0.020
100	0.962	0.914	0.458
150	0.582	0.656	0.281
200	1.113	0.739	0.414
Lsd (5 %)	0.190	0.262	-

SED= Standard Error of Difference

4.3.2 Cu distribution with soil depth

The vertical distribution of copper along the soil columns differed significantly ($p < 0.05$) as soil depth increased (Table 4.4). Generally, the amount of copper sorbed decreased with increasing soil depth in both soil series. Significantly, higher Cu sorption was recorded at the 0-10 cm soil depth than at the 10-20 and 20-30 cm depths in soils under both series. The Cu sorbed at the 20-30 cm soil depth in Nta series was significantly higher than that

of Temang series. In relation to the Cu sorbed at the 0-10 and 10-20 cm soil depths, no statistical differences were recorded between the two sites.

Table 4.4 Impact of soil depth on Cu sorption

Depth (cm)	Nta series	Temang series	SED
	mg/kg		
10	1.639	1.458	0.363
20	0.275	0.246	0.072
30	0.193	0.091	0.019
Lsd (5 %)	0.164	0.23	-

4.3.3 Interaction effect of of soil depth and application rates

The interaction effect of different copper rates at varying depths are presented in Table 4.5. Significant difference (p<0.05) between the interaction effect of different copper rates and soil depths were observed. Generally, as the depths of soil increased (i.e. at constant application rates), the Cu sorbed reduced. Substantial amount of Cu was sorbed at the 0-10 cm depth than the 10-20 and 20-30 cm depth at all the rates of copper applied in soils of both series. For the Nta series, the copper sorbed at the application rate of 200 mg at soil depth of 0-10 cm was the highest whereas the lowest (exclusive of the control) was recorded at the application rate of 200 mg at soil depth of 20-30 cm. The amount of Cu sorbed in the Temang series was highest at the application rate of 100 mg at soil depth of 0-10 cm and lowest (exclusive of the control) at the application rate of 100 mg at soil depth of 20-30 cm. Also, a peculiar trend observed in both soil series is the sorption of more Cu at 100 mg application rate than 150 mg application rate in both soil series.

Table 4.5 Interaction effect of soil depth and application rates on Cu sorption

Depth	Nta series				Temang series			
(cm)			Rates (mg/kg)					
	0	100	150	200	0	100	150	200
10	0.173	2.387	1.277	2.718	0.155	2.405	1.666	1.608
20	0.135	0.234	0.270	0.462	0.040	0.283	0.182	0.479
30	0.150	0.263	0.199	0.158	0.059	0.055	0.119	0.132
Lsd (5 %)	0.329				0.453			

4.6 Prediction of the annual movement of copper at both sites

The chemical displacement of copper in both soil series varied, with Temang soil series recording the higher chemical displacement as compared to Nta soil series. Annual movement of copper at both sites were 4.17 and 4.58 cm for Nta and Temang soil series, respectively. The average time required for Cu to reach the groundwater aquifer in Nta series was 40.72 years whereas that required for Temang soil series was 75.55 years. As shown in appendix 2.0

4.7 Relationship of organic carbon, soil pH, clay and cec with sorbed copper. Copper

sorption was correlated with organic carbon, soil pH, clay and CEC for both soil series and the results are presented in Figures 4.1a, 4.1b, 4.1c and 4.1d. From the results, The R^2 values for Nta soil series were 0.999, 0.6682, 0.8988 and 0.4487 whereas that for Temang soil series were 0.9964, 0.9714, 0.85156 and 0.9992 for Organic carbon, Soil pH, Clay and CEC respectively in both sites. There was negative correlation between Clay and copper sorption in both soil series. Also, CEC had a negative relationship with copper sorption at Temang series whereas that for Nta series was positive.
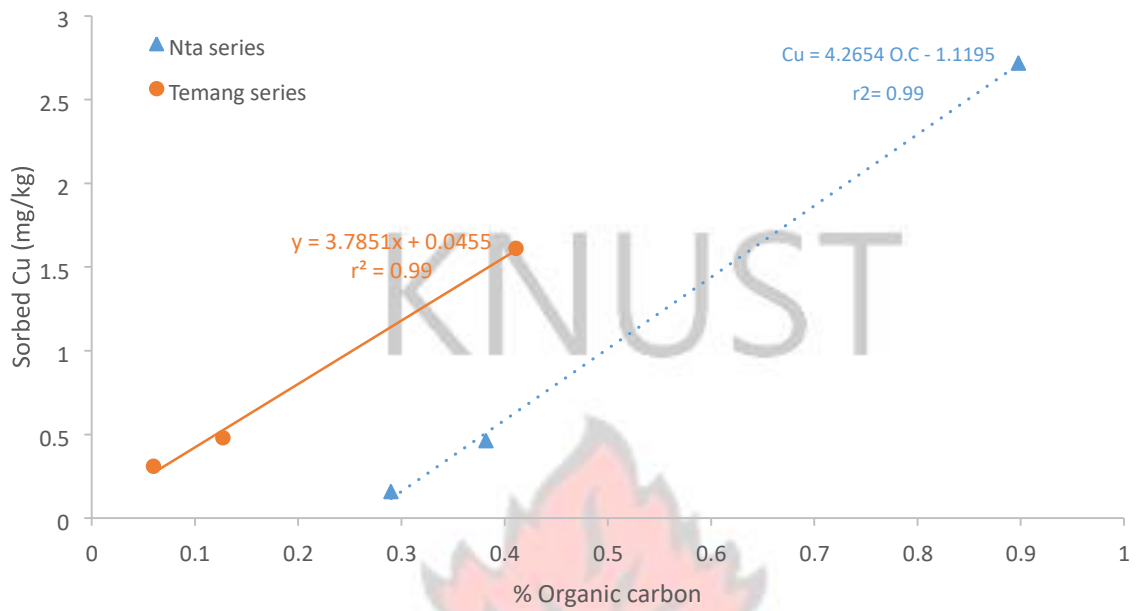
Figure 4.1a: Relationship between copper sorption and organic carbon
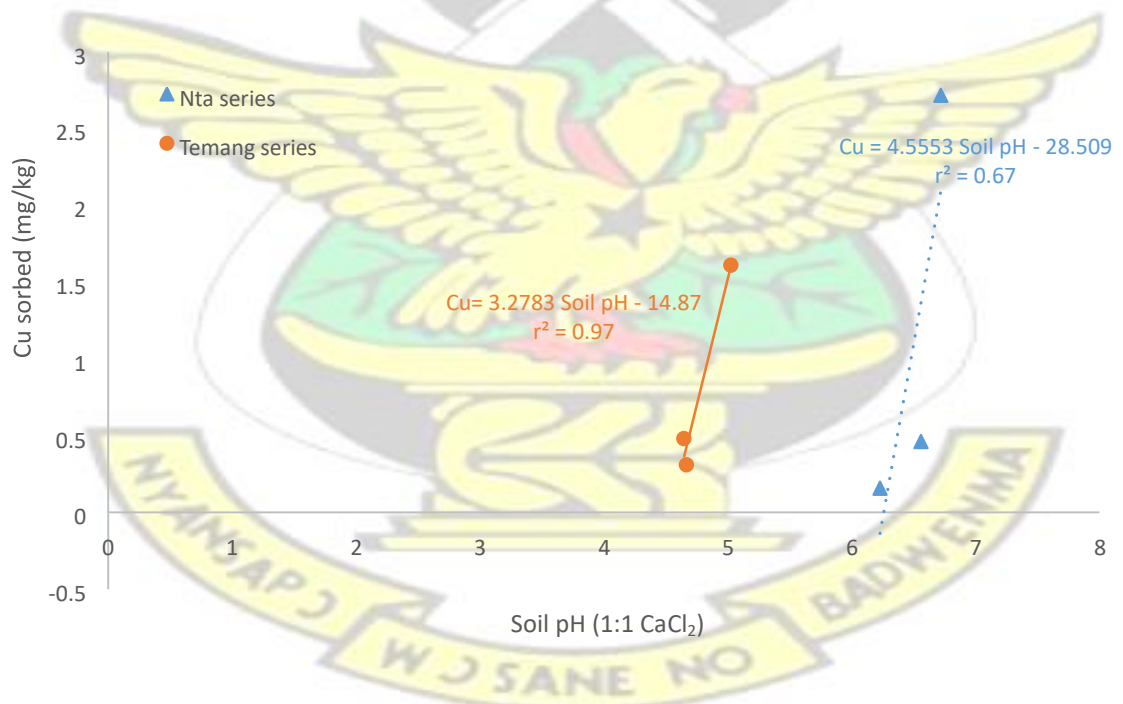
Figure 4.1b: Relationship between copper sorption and soil pH
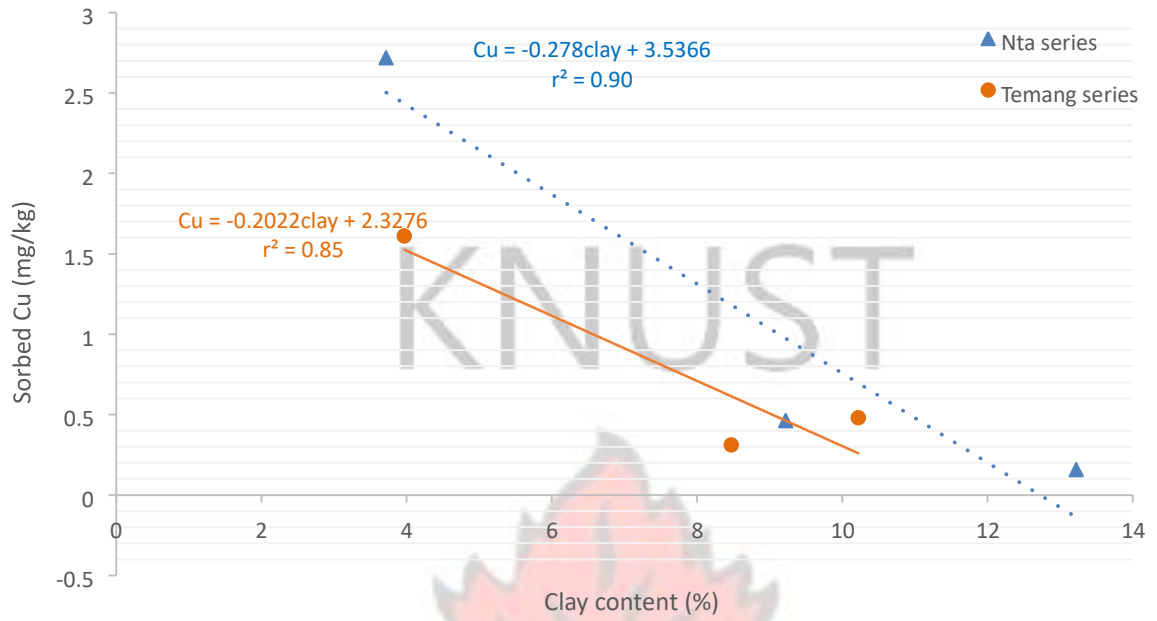
Figure 4.1 c: Relationship between copper sorption and clay
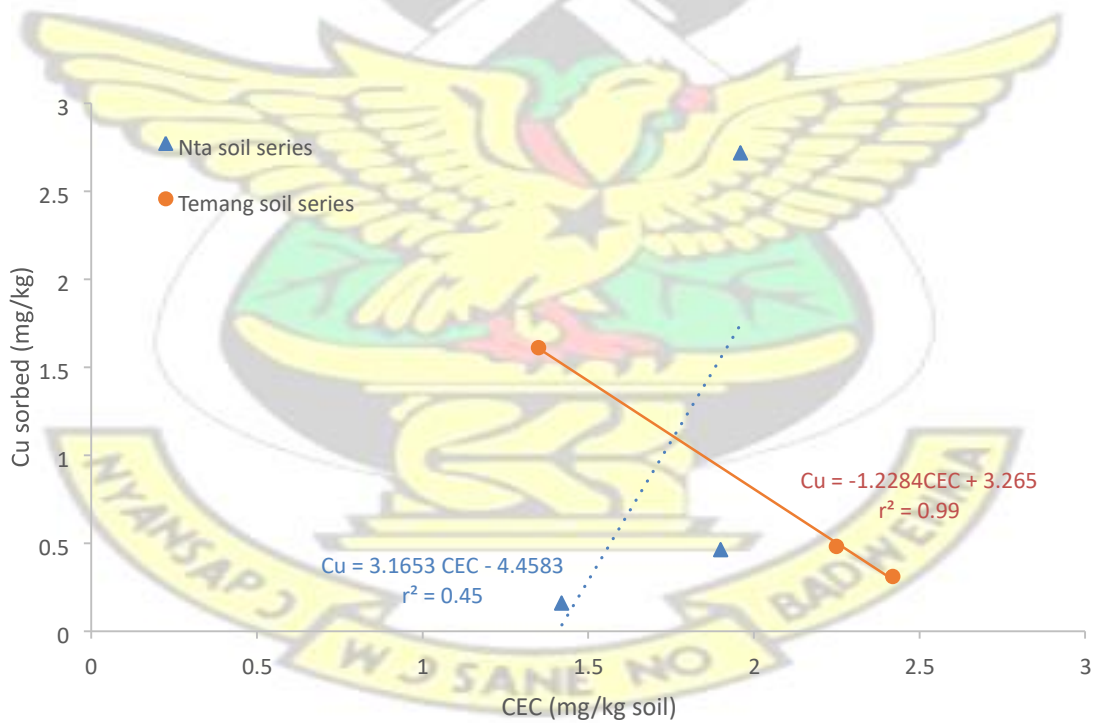
Figure 4.1d: Relationship between copper sorption and cec.

4.9 Relationship between copper application rate and copper sorption

The relationship of copper sorption and copper application rate is presented in Figure 4.2 and Table 4.6 for both soil series. Both soil series had a positive correlation with R^2 of 0.67 and 0.55 for Nta and Temang series respectively.
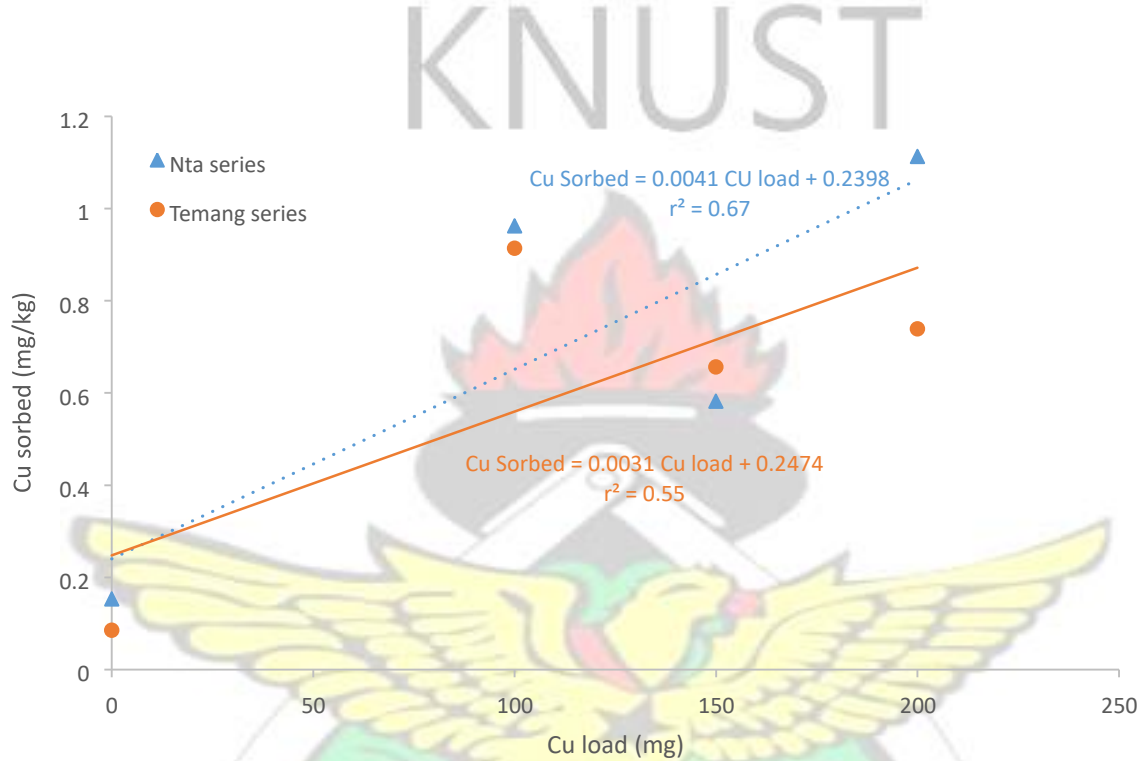
Figure 4.2: Relationship between copper application rates and copper sorption

4.10 Relationship between soil depth and copper sorption.

The relationship between soil depth and copper sorption (at the various depths) in both soils is presented in Figure 4.3. The regression equations produced R^2 value of 0.792 and 0.834 for Nta and Temang series respectively. From the regression equations a unit increase in soil depth will reduce Cu sorption by 0.723 and 0.684 mg/kg in the Nta and Temang soil series respectively.
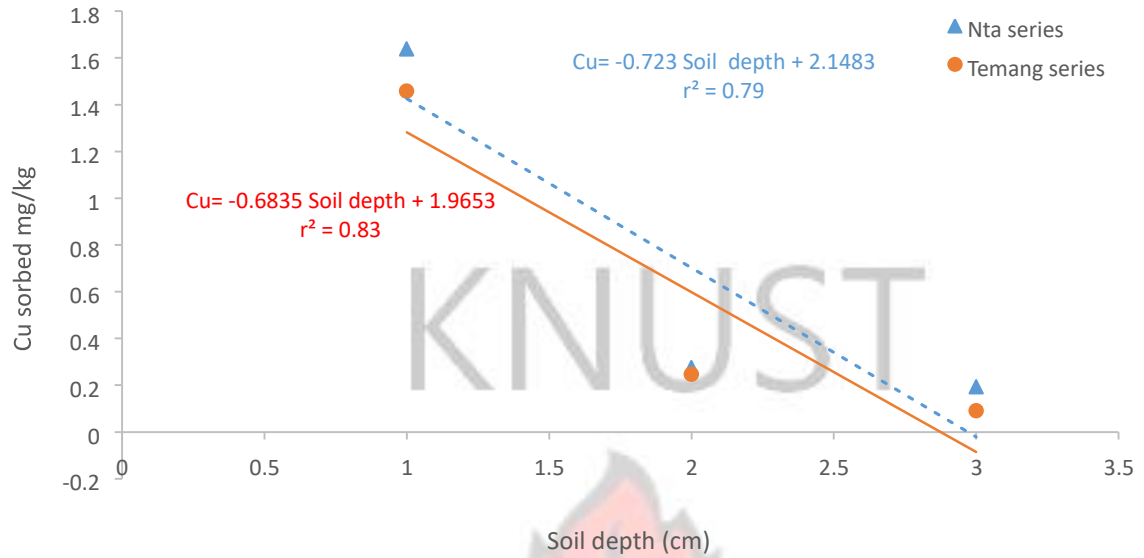
Figure 4.3: Relationship between soil depth with copper sorption

Table 4.6: Relationship table between Cu sorption and the selected soil characteristics

Explanatory variable	Nta series		Temang series	
	Equations	r^2 (r)	Equations	r^2 (r)
O.C	Cu = 4.265O.C. - 1.120	0.999 (0.999)	Cu = 3.785O.C. + 0.05	0.996 (0.998)
pH	Cu = 4.555pH - 28.509	0.668 (0.817)	Cu = 3.278pH - 14.87	0.971 (0.985)
Clay	Cu = -0.278C + 3.537	0.899 (0.948)	Cu = -0.202C + 2.328	0.852 (0.923)
CEC	Cu = 3.165CEC - 4.458	0.449 (0.670)	Cu = -1.228CEC + 3.265	0.999 (0.999)
Cu app. Rate	Cu = 0.004CuL + 0.240	0.67 (0.819)	Cu = 0.003CuL + 0.247	0.552 (0.743)
Soil depth	Cu = -0.723D + 2.148	0.792 (0.890)	Cu = -0.684D + 1.965	0.834 (0.913)

O.C. = Organic Carbon; D = Soil depth; C = Clay content; CuL = Cu load; r= correlation coefficient.

CHAPTER FIVE

5.0 DISCUSSION

Physico-chemical properties of the soils

The physical properties of the soils did not differ much as did the chemical properties especially the SOC and the pH. This may be due to the different vegetation types of the two soils and also the different topo-sites.

5.1 Impact of soil characteristics on copper sorption

Several soil characteristics may affect the kind of interaction Cu may have with a soil matrix. The results of the impact of some soil properties on copper sorption are discussed below.

5.1.1 The impact of soil organic carbon on copper sorption

Organic carbon is a major component of the soil which accounts for the magnitude of copper sorption in the soil (del Castilho *et al.*, 1993; Sauve *et al.*, 1997). By its characteristics negative charges, soil organic carbon (SOC) is capable of bonding and forming stable complexes with copper and thereby increase its sorption. Increasing amount of SOC is, therefore, expected to increase the sorption of copper, the total of which ranges from 2 to 100 mg kg^{-1} in soil (Landon, 1991). This is amply demonstrated by the results of this study Tables 4.2 and 4.5. The highest SOC within the 30 cm soil depth, which was at the 0-10 cm depth, recorded the highest sorbed Cu in both the Nta and Temang soil series. As the SOC decreased with depth, so also did Cu sorption, this is further supported by the positive correlation of Cu with SOC, the regression equations of

which recorded R^2 of 0.999 and 0.996 under the Nta and Temang soil series respectively (Figure 4.1a). The regression equations showed that a unit increase in the amount of SOC increased Cu sorption by 4.27 and 3.79 mg kg^{-1} in the Nta and Temang soil series respectively. The former soil, therefore, sorbed more Cu than the latter, being 11.24 % per unit increase in SOC.

The implication of these observations are that, increased Cu sorption has the potential to influence the concentration of Cu in the soil solution as indicated by Landon (1991). This, in turn, can affect the bioavailability of Cu to plants (del Castilho., 1993) since Cu availability is governed mainly by its total amount in the soil. On the other hand, increased SOC through organic matter addition can reduce Cu toxicity (>100 mg kg^{-1}), especially in areas where agricultural soils are subject to continuous application of copper-based fungicides or at mining areas.

Intuitively, by sorbing Cu, increasing the SOC of agricultural soils, particularly at the surface 10 cm layer, can reduce the transport of Cu through overland flow into surface water bodies and leaching into groundwater. This is a desirable effect in managing Cu pollution of rivers, streams and aquifers. The practical way of achieving SOC increases in agricultural landscapes is through retaining as much vegetative residues on the soil as possible, application of manure, non-burning of crop residues, prevention of bush fires and controlling water and wind erosion.

5.1.2 The effect of soil pH on copper sorption

All micronutrients, including Cu, become more available with increasing acidity.

According to Landon (1991), the availability of Cu decreases slowly with increasing pH, but the nature of the interaction is not completely understood. A plausible mechanism could be sought from the impact of pH on Cu sorption. The results of the study showed Cu sorption to increase with increasing pH (Figure 4.1b). This could potentially constrain Cu availability as generally observed. As reported by Garbisu and Alkorta (2001) and Gisbert *et al.* (2003), increasing soil pH to 6.5 or higher can result in copper immobilization in the soil making it less available to plants. This is because Cu is more soluble at lower pH levels. In this study (Table 4.2), a pH change from 6.23 to 6.72 (a 7 % increase), increased Cu sorption from 0.193 to 1.639 cmol/kg soil (an increase of 88 %) in the Nta series. For the Temang series, an increase of pH from 4.67 to 5.03 (an increase of 7.2 %), increased Cu sorption from 0.091 to 1.458 cmol/kg (an increase of 94 %). Small increases in soil pH can, therefore, cause tremendous increases in Cu sorption and thereby potentially restrict the availability of Cu to plants. The relationship of soil pH and Cu sorption revealed a positive correlation with r being 0.985 and 0.817 for the Nta and Temang soil series respectively. The regression equations showed a unit increase in soil pH to increase Cu sorption by 3.28 and 4.56 mg kg^{-1} in the Temang and Nta soil series. It is noteworthy to point out these impacts of the dependent variables have been presented in the context of their magnitude in the different soil depths (0-10 cm, 10-20 cm and 20-30 cm) which did not have the same contact time of the spiked Cu solution due to the lag in the transport rate of the solution with depth. Thus, the contact time of the surface layers was more than the sub-layers with a potential for increased sorption. This is a characteristic of the column leaching method used in this study which is a closer simulation of fungicide transport under field conditions. It will be instructive to study

what the relationship of Cu sorption would be if a given soil with different levels of the dependent variables (e.g SOC, Clay, pH, CEC) was spiked with Cu solutions under similar contact time. It is envisaged that the relationship of the variables with Cu sorption could be different.

5.1.3 The effect of clay on copper retention

Apart from SOC, clay minerals also adsorbed Cu. Although there are reported cases of a positive correlation existing between copper sorption and clay (silicate minerals), oxides and hydroxides (Pampura *et al*., 1993), the results obtained from this study showed a negative correlation (Figure 4.1c). For instance, in Nta soil series, at 0-10 cm soil depth, the clay content of 3.72 % sorbed 2.718 mg/kg of Cu. By the positive correlation (as reported in literature), Cu sorption, which was expected to increase in the layers below because of higher clay contents of 9.22 and 13.22 % at depth of 10-20 cm and 20-30 cm, respectively rather decreased. This behaviour was similar to those observed in the Temang soil series where copper sorption was greatest in the upper layer (0-10 cm) containing the least amount of clay. This deviation may be due partly to the method employed in this study. In most cases, the sorption of pesticides is measured with soil suspensions through the batch method (Chaplain *et al*., 2011). The intensive shaking of the soil-pesticide solution using the method can lead to the pulverization and dispersion of soil structure, which increase the sorption sites for Cu sorption. This is in contrast to the leaching method used in this study which involves transport of Cu through undisturbed soil columns and therefore simulates what happens in the field. Therefore, the batch method can lead to an overestimation of sorption. The decreased sorption of

Cu with increasing clay content with respect to soil depth could be due to the longer contact time of the leaching solute with the top 0-10 cm depth with lower clay than the 10-20 and 20-30 cm depths which had higher clay content.

5.1.4 The effect of CEC on copper sorption

The mean Cu sorption for the 30 cm depth was 0.702 and 0.598 mg kg^{-1} in the Nta and Temang series, respectively, being 15 % higher in the former soil. The assessment of the impact of CEC on Cu sorption was done through a regression analysis, which gave two contrasting results, whilst the correlation between CEC and Cu sorption was positive in the Nta series, it was negative in the Temang series. The implication is that Cu sorption increased with increasing CEC in the Nta series and decreased with increasing CEC in the Temang series. According to Landon (1991), measured CEC values often depend critically on soil pH, as well as SOC and the amount and type of clay minerals. The complex interaction of these influencing factors and their interrelationships in different soils may account for the observed results. Nevertheless, an attempt was made to explain the underlying causes of these observations by examining the relationship between CEC and the influencing factors of SOC, clay and pH. It is presumed that the relative dominance of these factors on the magnitude of CEC and their impact on cationic adsorption may effect similar trends in the relationship of CEC with Cu sorption. In the Nta series, CEC correlated positively with SOC (r = 0.69; R^2 = 0.48) and pH (r = 0.97; R^2 = 0.95); and negatively with clay (r = -0.87; R^2 = 0.76). The CEC was positively correlated with Cu sorption (r= 0.67; R^2= 0.45) as did SOC (r= 0.99; R^2=0.99), (Graphs are shown in the appendix). It was therefore presumed that, the dominant determinant of CEC in the Nta series was SOC. In the case of the Temang series, the correlation of CEC was positive

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with clay (r = 0.91; R^2 = 0.83); and negative with SOC (r = -0.999; R^2 = 0.999) and pH (r = -0.98; R^2 = 0.96). In this circumstance, clay was presumed to be the major determinant of the magnitude of CEC, since both correlated negatively with Cu sorption with r and R^2 being -0.999 and 0.999 for CEC; and -0.92 and 0.85 for clay. These observations amply indicate that undisturbed field soil columns could cause variable and complex responses to Cu sorption in different soils and under variable influencing factors, the underlying reasons of which defy simple one factor explanations.

5.2 The relative Cu sorption capacity of Nta and Temang series

The capacity of a soil to adsorb Cu is an important factor in managing high levels of Cu and toxicity in the soil. A soil with a low content of inherent Cu is expected to have a high potential to take more of applied Cu because of free cation adsorption sites. Such a potential was implicit in the two experimental soils due to their low inherent Cu content compared with the common total Cu of 2 to 100 mg kg^{-1} found in soils. In this context, the Nta series adsorbed more Cu than the Temang series at all levels of Cu application. The increased sorption could be due to the relatively higher SOC content and pH of the Nta than Temang series which, for the 30 cm depth, averaged 0.52 % and 6.5 respectively for the Nta and 0.21 % and 4.78 for the Temang. The SOC of the former soil series was 60.23 % higher than the latter series with their corresponding slightly acidic and strongly acidic conditions. As indicated earlier, Cu sorption is positively correlated with SOC and pH, implying that a soil with relatively higher SOC content and pH, as in the Nta than the Temang series, will adsorb more copper as shown by the result of the study. Apart from the chemical properties of the soil such as SOC, pH and CEC, the physical properties,

such as texture, water content, bulk density and hydraulic conductivity, play a major role in the movement of Cu within the soil to the groundwater. The results showed the annual Cu movement in the soil to be 4.17 and 4.58 cm y^{-1} for the Nta and Temang series respectively. If the depth to groundwater was the same, Cu movement into groundwater would be faster in the Temang series (Loamy sand at the 0-10 cm and Sandy loam at both 10-20 and 20-30 cm) than the Nta series (Sandy loam for the 0-30 cm depth). However, because of the variable topo-site of the two soils, the distance to the groundwater will differ being 1.70 m and 3.46 m for the Nta and Temang series respectively (appendix 2). Accordingly, the travel time to the groundwater will also differ. The calculated average time to reach the groundwater aquifer was 40.72 and 75.55 years under the Nta and Temang series respectively. Such information is relevant in decisions concerning the disposal and management of municipal liquid waste or industrial effluents containing Cu.

5.3 The effect of copper application rates on copper sorption

Areas subjected to continuous application of Cu-based agrochemicals (fungicides, pesticides) such as Nordox in cocoa farms may accumulate high levels of Cu in the soil. Such a situation can arise with increasing rates of copper application. This, in turn, can provide more Cu in the soil to be available for various depletion and immobilization processes, such as, plant uptake, leaching, erosion and adsorption by SOC and Clay minerals. Because these processes occur simultaneously and interactively at any given time, it is difficult to isolate and establish consistent trends in the sole impact of increasing Cu application rates on any of the processes, particularly, sorption which is the subject matter of this study. Thus, the results of the main effect of the different rates of Cu

application did not show any consistent decreasing or increasing Cu sorption trends. However, in both soils, Cu was significantly less (p<0.05) under the control than any of the increased rates. In the Nta series, the 100 and 200 application rates did not effect significant differences in the magnitude of Cu sorption, but recorded significantly (p<0.05) higher sorption than the 150. Sorption under the 200 application rate was, however, 13.6 % higher than that of the 100.

Copper sorption in the Temang series did not differ significantly under the application rates of 100, 150 and 200. However, sorption under 100 was 28 % and 19 % higher than 150 and 200 respectively. In order to establish the relationship between Cu sorption and increasing rates of Cu application, the data was subjected to regression analysis. In both soils, the correlation was positive, being 0.82 and 0.74 for the Nta and Temang series. The respective coefficients of determination were 0.67 and 0.55. The regression equations showed that a unit increase in copper application rate, increases Cu sorption by 0.003 and 0.004 mg kg^{-1} in the Temang and Nta series respectively.

5.4 The effect of soil depth on copper sorption

The amount of Cu sorbed was also influenced by soil depth. For a 30 cm soil depth at 10 cm increments from the surface, Cu sorption decreased with depth, being highest and lowest at the 0-10 cm and 20-30 cm depths respectively. The pH, SOC, CEC and clay at the different depths and their relationship with Cu adsorption are implicated in this observation. In both the Nta and Temang series, pH and SOC decreased with depth, whilst clay increased. The relationship of these three parameters with Cu sorption showed pH and SOC to be positively correlated with Cu sorption whilst that with clay is negative.

The implication is that decreasing pH and SOC and reducing clay result in reduced Cu sorption. It is therefore not surprising that Cu sorption decreased with soil depth.

5.5 Association of organic carbon, soil pH, clay and cec with sorbed copper From the various relationships established, known quantities of soil organic carbon/ soil pH/ clay or CEC could be used to predict the amount of Cu that will be sorbed. For an instance, in the case of Nta soil series with regression equation for organic carbon and Cu; Cu = 4.265 O.C. - 1.120 meant that an increased in soil organic carbon value by one unit will cause sorption to increase by 4.256, and an R^2 of 0.999 meant that 99 % of the variations in copper sorption could be explained by changes in soil organic carbon with the remainder being residuals.

The relationships established could also be a useful predictive tool in terms of estimating the amount of copper that would be sorbed within the magnitude of the measured parameters. It must therefore be pointed out that since the equations are empirical, they are, in the main, valid for the conditions and methodology (column leaching) under which this study was conducted.

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS

From the overall research, the conclusions and recommendations made are as below: Investigation and quantification of the factors influencing copper transport and sorption through experiments such as laboratory column leaching are easy to perform and do not require costly equipment. Column leaching experiments provide valuable information for making predictions as to the future state of our soil systems.

The amount of Cu sorbed in both soil series was influenced by soil depth. Cu sorption decreased with depth being highest and lowest at the 0-10 cm and 20-30 cm depths respectively. The soil pH, SOC, CEC and clay content at the different depths and their relationship with Cu adsorption are implicated in this observation.

It is established that SOC is a major component of soil which accounts for the magnitude of Cu sorption in soil. By its characteristic negative charges, it is capable of bonding and forming stable complexes with Cu and thereby increasing its sorption as was amply demonstrated in this study. As SOC decreased with depth, so did Cu sorption, this was further supported by the positive correlation of SOC with Cu, the regression equations also showed Nta series to sorb more Cu than Temang as a result of higher SOC in the former. The implications of these observation are that, increased Cu sorption has the potential to influence the concentration of Cu in the soil solution. This, in turn, affects the bioavailability of Cu to plants. On the other hand, increased SOC through organic matter additions can reduce Cu toxicity, especially in areas where agricultural soils are subjected to continuous application of copper-based fungicides or at mining areas. Intuitively, by sorbing Cu, increasing the SOC of agricultural soils, particularly at the surface 10 cm layer, can reduce the transport of Cu through overland flow into surface water bodies and leaching into groundwater. This is a desirable effect in managing Cu pollution of rivers, streams and aquifers. The practical way of achieving SOC increases in agricultural landscape is through retaining as much vegetative residues on the soil as possible. It is also recommended that industries processing heavy metals like Cu set up a large column leaching apparatus with the cartridge made of organic rich material like biological charcoal to continuously clean (recycle) their effluents before disposing them into the environment.

The result of this study also showed Cu sorption to increase with increasing soil pH, thus copper is soluble at lower soil pH levels. This could potentially constrain Cu availability. The regression equations showed a unit increased in soil pH caused Nta series to sorb more Cu than Temang series. Therefore, in copper contaminated soils, the addition of lime to bring the pH up is desirable in order to get most of the copper from the liquid phase thereby limiting its availability and transport to underlying mineral horizons and subsequently into water bodies.

Whilst the correlation between CEC and Cu sorption was positive in Nta series, it was negative in the Temang series. It is observed that as SOC influenced CEC in the Nta series, the clay content influenced CEC in Temang series. These observations amply indicate that undisturbed field soil columns could cause variable responses to Cu sorption in different soils and under variable influential factors, the underlying reasons of which defy a simply one factor explanation.

The result obtained in this study showed a negative correlation between clay and Cu. This deviation may be due to the method employed in this study, because most of the time, sorption is measured with a batch method.

The capacity of a soil to sorb Cu is an important factor in managing high levels of Cu and toxicity in soil. Apart from the soil chemical properties, the physical properties play a major role in Cu movement within the soil to the groundwater. The result showed annual movement of copper in the soil to be 4.17 and 4.58 cm/year for the Nta and Temang series, respectively. Therefore, if the depth to groundwater is the same, Cu movement into groundwater would be faster in the Temang series than the Nta series. However, because

of the variable topo-site of the two soils, the distance to the groundwater also differed, therefore, the calculated average time to reach the groundwater aquifer was 40.72 and 70.55 years under Nta and Temang series respectively. This information is relevant in decisions concerning the disposal and management of municipal liquid waste or industrial effluents containing Cu.

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APPENDIX 1

Appendix 1a: a graph showing the plot of mean $\ln(Ho/Ht)$ against time for the

determination of saturated hydraulic conductivity at Nta soil series.
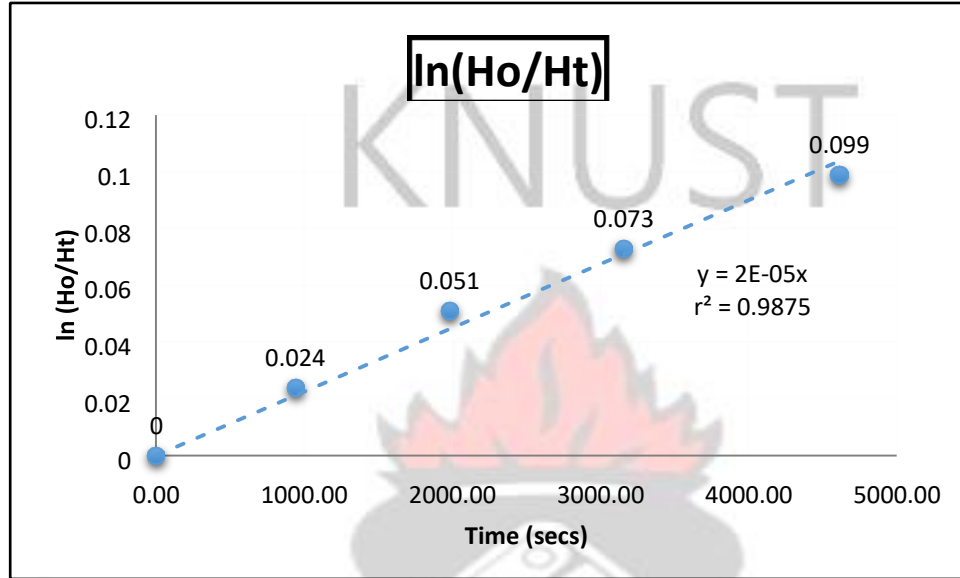
Appendix 1b: a graph showing the plot of mean $\ln(Ho/Ht)$ against time for the

determination of saturated hydraulic conductivity at Temang soil series.
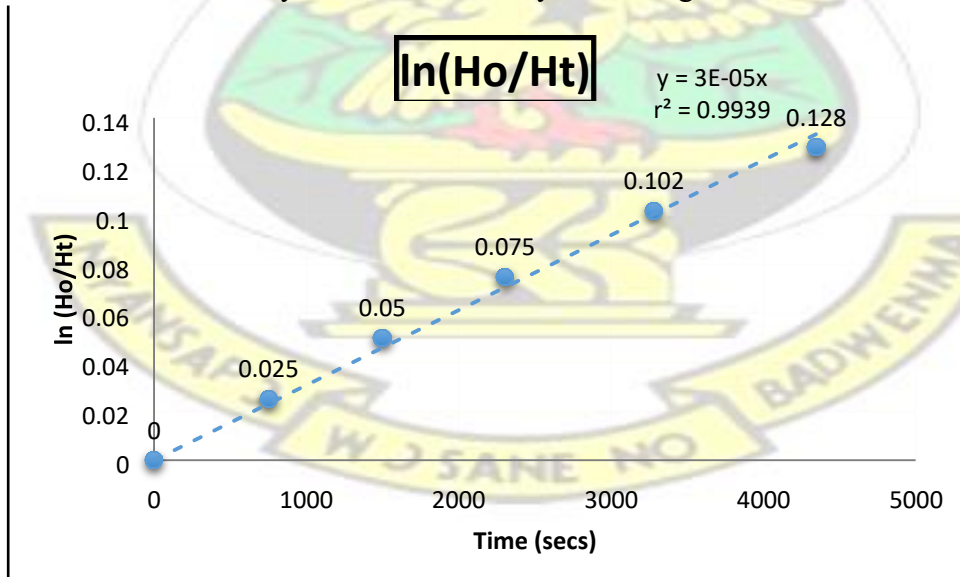
Appendix 2.0: Prediction of the annual movement of copper at both sites.

$$X = \frac{Q/W}{1+\ell bKd/\theta V}$$

Where;

X = Chemical displacement

Q = Annual precipitation

W = Available water content

ρ_b = Bulk density

K_d = Partition coefficient, K_d value for copper from literature is 2.7 g/L. (Allison *et al.*, 2005)

θ_v = Volumetric moisture content at field capacity

Annual copper movement at Nta soil series

X = cm?

Q = 11.40 cm (Volume of influent/ Area of column)

$\theta_v = 0.308$ cm³/cm³

$\rho_b = 1.57$ g/cm³

W = FC-PWP = 0.185 cm³/cm³

Which implies $X = \dfrac{11.40/0.185}{1+1.57*2.7/0.308}$

$= 4.17$ cm/ year.

Cu^{2+} will therefore move 4.17 cm every year.

The average time required for this copper to reach the groundwater aquifer is

$T = \dfrac{100H}{X} = \dfrac{100*1.698}{4.17} = 40.72$ years

1.698 m= the vertical distance from the point of soil sampling to the groundwater.

Annual copper movement in Temang series

X = cm?

Q = 11.40 cm (Volume of influent/ Area of column)

$\theta_v = 0.307$ cm^3/cm^3

$\rho_b = 1.56$ g/cm^3

$W = FC\text{-}PWP = 0.169$ cm^3/cm^3

Which implies $X = \dfrac{11.40/0.169}{1+1.56*2.7/0.307}$

$= 4.58$ cm/ year.

Cu^{2+} will therefore travel by 4.58 cm every year.

The average time required for this copper to reach the groundwater aquifer is

$T = \dfrac{100H}{X} = \dfrac{100*3.46}{4.58} = 75.55$ years

3.46 m= the vertical distance from the point of soil sampling to the groundwater.

Appendix 3: calculation of the amount of 'artificial rain' for the columns.

From the OECD 312 guidelines for the testing of chemicals, the amount required to leach a column with an internal diameter (i.d) of 4 cm in an area experiencing an annual precipitation of 1000 mm is 251 mL per column. Hence, by proportion 924.433 mL of „artificial rain" was applied for a column with an i.d of 10.16 cm in an area with an annual precipitation of 1450 mm.

Appendix 4: Relationships between CEC and SOC, pH and Clay.

CEC = -3.0841 O.C + 2.6214
r² = 0.999

CEC = 0.6261 O.C + 1.4323
r² = 0.4806

CEC = -2.6539 pH + 14.693
r² = 0.9614

CEC = 1.1502 pH - 5.7193
r² = 0.9511