EFFECT OF LANDUSE TYPES ON GEOCHEMISTRY OF SOIL IN THE NORTHERN GUINEA SAVANNA OF NIGERIA

BY

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DECLARATION

I declared that this thesis entittled "Effect of land use types on the geochemistry of soils in the Northern Guinea Savanna of Nigeria" was carried by me in the Department of Soil Science under the supervision of Dr. Nafiu Abdu and Prof. (Mrs.) E.Y. Oyinlola. Information derived from literature have been duly acknowledged in the text and a list of references provided. No part of this work was previously presented for another degree or diploma at this or any other institution.

Sign …………………………. Date…………………………...
Fatima Abubakar
(Student)

The above declaration is confirmed

Sign .... Date ....
Dr. Nafiu Abdu
(Major supervisor)

CERTIFICATION

This thesis entitled "Effect of land use types on geochemistry of soils in the Northern Guinea Savanna of Nigeria" by Fatima Abubakar meet the regulations governing the award of the degree of Master of science in soil science of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

Sign…………………………………. Date……………………………...
Dr. Nafi'u Abdu
(Chairman Supervisory Committee)

Sign………………………………….. Date…………………………………
Professor (Mrs.) E.Y. Oyinlola
(Member Supervisory Committee)

Sign…………………………………. Date…………………………………
Professor A.A. Yusuf
(Head of Department, Soil Science)

Sign…………………………………. Date…………………………………
Professor Abubakar Z. Sadiq
(Dean School of Postgraduate Studies)

DEDICATION

Dedicated to ALLAH (S.W.A) for everything in this life and to my beloved kids Ummulthulthum, Maryam and Muhammad, may Allah (S.W.A) grant you ‘‘hassana’’ in this world and in the hereafter.

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ABSTRACT

Evaluating the distribution (species and concentration) of chemical elements in the biosphere (rock, soil, water, plants, and air) and the study of chemical processes and reactions that govern the composition of and chemical flux between various states is essential in determining the fate and transport characteristics of elements, as well serving as an important facet of understanding the urban environment. Forty samples from surface soils (0 - 20cm) and profile pit were collected to evaluate the anthropogenic (human activities) and pedological (parent material) factor that influenced the natural abundance, distribution and behavior of Cu, Fe, Mn, Pb, Zn and Ti under four different land use (Pasture field, fertilized cropland, vegetable garden treated with municipal waste and forest land) in Zaria and Afaka, Northern Guinea Savanna of Nigeria. Soil pHwas slightly acidic. Sabo vegetable garden soil had the highest pH which is similar to Afaka forest while fertilized IAR farm though similar to NAPRI pasture field had the least. Exchangeable Ca was highest at Sabo vegetable garden which was not different from NAPRI pasture and fertilized IAR farm while Afaka forest had the least Ca content. Trend for Mg concentration is NAPRI pasture field > fertilized IAR farm > Sabo vegetable garden > Afaka forest. CEC values were lowest for Afaka forest and highest for Sabo vegetable garden with relatively higher values for fertilized IAR farm and NAPRI pasture field. Afaka forest had the highest OC and fertilized IAR farm had the least while NAPRI pasture field and Sabo vegetable garden had similar values. X-ray florescence spectrometry of the trace elements revealed that the concentration of these elements were lower than their common range in soil (WHO/Lindsay 1979) Pb (0.0 – 4400mg/kg), Ti (1580 - 2590mg/kg),Cu (40 - 50mg/kg), Fe (6180 - 23050mg/kg), Mn (10 - 90mg/kg) and Zn (0.0 - 40mg/kg),Assessment of contamination using contamination factor (C_f) and geo accumulation index (I_{geo}) showed no evidence of contamination by the studied elements. Enrichment factor (EF) revealed that the elements

originated from natural source. Geochemical balance (%) indicated depletion of most of the elements across the locations while Cu, Mn, Fe and Pb accumulation in some locations indicated high concentration of these metals in the localized parent material. Correlation matrix for NAPRI soil showed significant relationship between all the trace elements and pH, OC, Fe_d,Al_d and Al_o while clay correlated with Fe, Zn correlated Ti and Fe_o. In fertilized IAR farm, OC correlated with all trace elements, pH with Pb, clay and Fe_d with Mn, Pb, Zn and Ti, Fe_o with all elements except Pb and Zn, Al_d with all element while Al_o with Mn and Ti. In Sabo vegetable garden, the elements correlated with each other and with clay, pH, Fe_d, Fe_o and Al_o, OC correlated with only Pb, Zn and Ti while Al_d correlated only with Zn. Afaka forest revealed significant inter-element correlation as well as correlation of the metals with free Fe and Al oxides, OC correlated with Cu, Mn and Ti, clay with Fe, Pb and Ti while pH with Fe and Pb. Zn did not correlate with any of the elements and soil properties. Factor analysis for the different land use showed that the studied elements though be influenced by different pedogenic processes are of similar origin. Clay mineralogy of the soils revealed that NAPRI pasture field was dominated by 2:1 non-expanding clay mineral with traces of 1:1 clays, fertilized IAR farm had a wide variation of minerals, Sabo vegetable garden had 2:1 clay mineral dominating the surface horizon while the subsurface horizon is dominated by hematite. The mineralogy of Afaka forest is dominated by hematite at the surface horizon while 1:1 clay dominated the subsurface horizon.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF PLATES

CHAPTER ONE

1.1. INTRODUCTION

Geochemistry is an evaluation of the distribution (species and concentration) of chemical elements in the biosphere (rock, soil, water, plants, and air) and includes the study of chemical processes and reactions that govern the composition of and chemical flux between various states (Kabata-Pendias and Pendias, 2001; Neuendorf *et al*., 2005). It is the science that uses the tools and principles of chemistry to explain the mechanisms behind major geological systems such as the earth's crust and its oceans.

Geochemistry is functional in characterization of soil types, determining soil processes, ecological evaluation, or issues related to soil quality and health, such as evaluating suitability of soils for urban or agricultural land use (Wilson *et al.*, 2008). Therefore, assessing soil physicochemical properties is paramount to understanding the potential status of elements in soils of different land uses (Allen and Pilbeam, 2007; Alexandra *et al.*, 2013).

Knowledge of geochemistry is regarded as one of the most important issues facing urban land use, and trace element distribution has been an important facet of understanding the urban environment (Cattle *et al.*, 2002; Chirenje *et al*., 2003; Murray *et al.*, 2004). Also, the knowledge of geochemical processes is essential to determining the fate and transport characteristics of harmful element from possible nuclear or waste materials.

Geological and pedological factors influence the natural abundance, distribution and behavior of elements in soils (Nael *et al.*, 2009; Chittamart *et al.*, 2010). The abundance of elements largely depends upon the nature of bedrocks, climatic conditions and mobility. According to Horsnail (2001), features of the landscape that can either significantly enhance or restrict geochemical mobility include topography, soil type, pH and Eh of ground water, presence or absence of decaying vegetation in soils as well as calcium carbonate precipitates in soils.

The soil differs from its parent material due to interactions between the lithosphere, hydrosphere, atmosphere and the biosphere (Chesworth, 2008). The rock in the vicinity of an agricultural field not only provides basic lithology (soil) but also contribute major and trace elements to the soil. Therefore, chemical composition of geologic systems (minerals, rocks, fluids, Earth reservoirs) may be described in terms of major and trace elements (Pietro and Placido, 2011).

The spatial distributions of elements are controlled primarily by natural geochemical processes, such as formation of soils from parent materials of varying composition, and by climate-driven processes that establish soil moisture regimes and levels of organic matter in soil. According to Dou and Li (2015), the manner in which elements are spatially distributed in a region were conditional by the regional environmental geological conditions and also influenced by human activities. Anthropogenic influences such as industrialization, urbanization, waste disposal, mining, and agriculture are regularly superimposed on these natural, or background, geochemical distributions.

Proper management of nutrients and micronutrients will enhance the productivity of the soil, thus far very little attention has been paid to evaluate the impact of local geology on the soils for better crop yield. This is of importance for determining background concentrations of elements from an environmental chemistry perspective particularly as many agricultural areas are now intimately mixed with industrial and urban areas.

Patterns of natural soil variability provide the starting point for understanding and measuring differences between natural concentrations of elements and anthropogenic effects.

The inherent characteristics of soil which are mainly the resultant of parent material and climate undergo subtle change due to different land management practices (Girma and Endalkachew, 2013). In addition, over exploitation (or degradation) of soils could diminish their ability to function in critical ecological and economical purposes (Rocheford, 2015).

Land use for agriculture causes great changes in the natural properties of soil. Particularly in the humid tropics, land-use changes have a great impact on soil geochemical properties (Townsend *et al*., 2002) since highly weathered soils with low inherent fertility, strong acidity and high proportion of iron (Fe) and aluminum (Al) oxides prevail (Nortcliff, 2010).

Land use refers to man's activities and the varied uses which are carried on over land (Keshava and Raghu, 2015). Land use impacts soil by altering the soil environment. In fact, the characteristics of soil can vary greatly across the entire urban landscape, including not only highly disturbed but also relatively undisturbed soils that are modified by management and urban environmental factors (Schleuß *et al.,* 1998; Pouyat *et al.,* 2003).

Depending on the land use, climate and vegetation, soil characteristics such as soil organic matter (SOM), aggregation and aggregate stability (Shrestha *et al*., 2007), bulk density, and water retention (Lal, 2003), pH and nutrient status (Benbi and Brar, 2009), and soil biota (Islam and Weil, 2000) tend to change. Any change in land use has important consequences for many biological, chemical, and physical processes in soils and so, indirectly, the environment (Goulding *et al.,* 1995; Luo *et al*., 2007). Therefore, due to changes in the land use pattern over the last few decades (Adriano, 2001), the knowledge of trace elements geochemistry for different land use types, which has scarcely been investigated, is of critical importance in assessing human impact on soil geochemistry.

1.1.2 STATEMENT OF PROBLEMS

The Nigerian Savanna region is currently witnessing increase in the intensity of agricultural land use to meet the demand of an ever increasing population. Also, urbanization is placing a greater demand on land in and around cities, and geochemistry of soils in these areas can mirror the shifting patterns of land use (Wilson *et al.*, 2008).

Currently there is limited information available to regulatory authorities with a mandate to manage metals in soils under different land use. Analysis of the effects of land use on metal concentrations in soils is, therefore, critical for the making of policies aimed at reducing metal inputs to soil and guaranteeing the maintenance or even improvement of soil functions.

Soil pollution (especially metal pollution) has become an important environmental issue in many countries, identification of geochemical processes is the key for understanding the behavior, association, and distribution of metals in the geological system.

1.1.3 JUSTIFICATION

Much of the current emphasis on geochemistry in soil science is related to the chemistry of trace elements controlling the movement, distribution, and fate in plants and soils of native pools and anthropogenic additions of elements (Abdu et al., 2011a,b; Roberts *et al.*, 2005) thus very little attention has been paid to evaluate the impact of land use on the soil geochemistry for better environmental management especially in soils of the Nigerian savanna.

There is international recognition of the importance of understanding the geochemistry of soils. The international geoscience community for many years focused on geochemistry of stream sediments related to mineral resource exploration (Wilson *et al*., 2008).In the last two decades, they have shifted emphasis to understanding the geochemical composition of the earth's surface in an effort of achieving sustainable worldwide development (Darnley *et al.*, 1995; Plant *et al.*, 2000). Therefore, there is also the need for sub-continental (regional) geochemical studies.

Land use activities can have significant impacts on the physical, biological and chemical processes that form soil (Rocheford, 2015). Yet the understanding of linkages between land use and geochemistry of soils is limited.

Soil quality/soil health decisions regarding land use and possible reclamation or restoration often require geochemistry.

Regolith or soil geochemistry also finds global significance in geochemical mapping, development of geochemical databases and in the determination of the background composition of the soils in a region before mining activity starts. Such baseline data on regolith composition although applicable to exploration, are vital to monitoring pollution when the ore extraction process starts (Melvin *et al.*, 2011).

1.1.3. OBJECTIVES OF THE STUDY

The main objective of this study was to determine the changes in the soil geochemical composition as influenced by the different land use types while the specific objectives are to determine the:

a) Anthropogenic and pedological factors influencing the natural abundance, distribution and behavior of selected trace elements in the soil.
b) Geochemical relationship between the selected trace elements (Cu, Fe, Mn, Pb, Zn and Ti) and the soil properties.
c) Mineral composition of the soils under the different land use pattern

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Soils of the Northern Nigerian Savanna

Soils of the northern Guinea Savanna of Nigerian which stretches from latitude 7^0-12^0N is characterized by the sub-humid climate covering over 50% of the land area (Olowookere, 2015). The Nigerian Savanna soils are largely classified as tropical ferruginous and specifically as Acrisol in the FAO system or Alfisols (Typic Haplustalf) in the USDA Soil Taxonomy System (Ogunwole *et al.,* 2001). The soils are form on Loess material overlying basement complex (Saleh, 2011). According to Vanlauwe *et al.* (2002), the soils are characterized by low activity kaolinite clays with the presence of Fe-oxyhydroxides which constitutes 80 -90%. Crystalline oxide fractions are predominant in savanna soils relative to the amorphous forms. The cationic nutrient and water holding capacity of these soils are usually low due to the nature of the dominant clay mineral. In many areas in the savanna, plinthite and iron pan occurs at shallow depth or at the surface. The soils are generally shallow, yellowish grey or yellowish brown in the layer and have red or reddish brown subsurface and lower horizon with high clay content. The soils are highly weathered with weak surface aggregation which is primarily induced by Fe and Al (Salako, 2003).This gives its coarse textured surface which when unprotected is prone to severe compaction and accelerated erosion (Odunze, 2006). The soils have supra optimal temperature and the soil reaction processes is associated with the nature of the surface activity of the dominant clay, therefore, the soil fraction are generally medium to slightly acidic. The agricultural value of the soils is usually rated poor to average in term of soil moisture deficiency and nutrient levels. Nutrient levels are often low with very low buffering capacity (Vanlauwe and Sanginga, 2004) due to low organic matter content of the soils. Oguntoyinbo *et al.* (2005)

reported that the soils of the tropics are known to have low organic matter contents (2.0-10g/kg).This may be due to the fact that most savanna soils are under continuous cultivation, poorly managed with the use of heavy implements which increases soil compaction and erosion, leaching of basic cations and high rates of acidification (Vanlauwe and Sanginga, 2004; Ogunwole, 2008). The organic matter content influences many properties of the soils and thus low nutrient supply for crops need. Jones and Wild (1975), Odunze (2003) and Abdu and Udofot (2015) also found that the soils are low in organic matter (< 2.0 - 10.0g/kg), phosphorus (< 3.0 - 7.0ppm), cation exchange capacity CEC (< 6.0 - 10.0cmolkg), total nitrogen (< 0.5 - 1.5g/kg), indicating that the soils have low productivity potentials. They also found that the native soil N is so low that all cereals respond mainly to N fertilizer amendments. The underlying geology and the soil forming processes as well as high preponderance of Fe and Al oxides caused the low phosphate (PO_4^{3-}) contents of the savanna soils of Nigeria (Jones and Wild, 1975; Esu, 1989; Nafiu, 2009), therefore the available P status of savanna soils is a function of P content of the parent material which is low for most soils of the Nigerian savanna. The low available P content of the savanna soils is also attributed to the low soil pH and also due to the fact that these soils are typically high in Fe and Al oxides. The soils are reported to be acidic to neutral in reaction (pH 5.0 - 7.0) while the exchangeable potassium (K) are often high (0.2 - 0.3cmol/kg) compared with other elements, although K content varies widely with parent materials. Calcium and magnesium are the dominant exchangeable cations in virtually all savanna soils and few deficiencies have been reported. The main fertility constraints of the soils of the Nigerian savanna is more chemical than physical. Information on soil micronutrient status of northern Nigeria savanna soils is scanty (Oyinlola and Chude, 2010). Studies in the northern Guinea savanna dealing extensively on macronutrients and information on trace elements geochemistry in the area is needed.

2.2 Land use Pattern in Northern Nigerian Savanna

The land use pattern of a region is the outcome of the natural and socioeconomic factors and their utilization by man in time and space (Oluwabunmi and Ayoade, 2014).The soils of the tropical savannas, along with the distinctive wet/dry climate, are a major determinant of vegetation in the region, and of potential land uses. Land use patterns have impact on the local and global environmental conditions as well as economic and social welfare. Land use and land cover change may be an important driver of global environmental change, the extent and nature of global land use practices are still poorly characterized. Although land use data are needed in the analysis of environmental processes and problems that must be understood if living conditions and standards are to be improved or maintained at current levels especially at this population exploding era (Ikusemoran,, 2009). Yet data on land use patterns in northern Nigerian savanna are scanty and fragmentary. However, the dominant land use in this area is agriculture. Even though there have been several studies on different land use, most studies conducted on agricultural land use not only in the northern Nigerian savanna (Buba, 2015) but also in some other parts of the world (Luo *et al.,* 2007; Kiakojouri and Gorgi, 2014) do not clearly classify the type of agricultural land use to any predefined class. This means that there is no any predefined classification on agricultural land use since land use practices vary considerably across the world (both within and between nations)**.** There are many sources of agricultural inventory data at the national and sub national levels (e.g. total area in croplands for a particular country), these do not provide sufficiently detailed geographic descriptions of land use practices. In addition, a number of detailed global land cover maps now exist, but only a few of them explicitly consider land that is under human management. Even when this has been done, as in the case of the Matthews (1983) data set, the nature and spatial extent of land use within a region is not specified explicitly. In the northern Guinea savanna of Nigeria, specifically in Kaduna state, the major types of land use in the area include farming, firewood, forestry and timber exploitation, livestock farming as well as industrial and urban development. Arable farming consists of subsistence farming characterized by intensive and continuous cultivation of mostly cereals and vegetable crops. The dry season (November to April) experiences soil cultivation using irrigated agriculture to produce sugar cane, maize, tomato, onion, pepper, and vegetables (Maniyunda *et al*., 2007; Bennett *et al*., 1979). Therefore, it can be clearly deduced that the major land use pattern in this area is cropland, pastureland/rangeland and forestland.

2.2.1 Effect of Land use Patterns on the Soil

Over the course of history, humans have modified drastically Earth's environment through our land use practices. Population increase also poses a burden on the natural ecosystem encouraging abuse and misuse of soils, increased land value and land use conflicts. Land-use activities whether converting natural landscapes for human use or changing management practices on human-dominated lands have transformed a large proportion of the planet's land surface. By clearing tropical forests, practicing subsistence agriculture, intensifying farmland production, or expanding urban centers, human actions are changing the world's landscapes in pervasive ways (DeFries *et al.*, 2004) Although land-use practices vary greatly across the world, their ultimate outcome is generally the same: the acquisition of natural resources for immediate human needs, often at the expense of degrading environmental conditions. Several decades of research have revealed the environmental impacts of land use throughout the globe, ranging from changes in atmospheric composition to the extensive modification of Earth's ecosystems. For example, land-use practices have played a role in changing the global carbon cycle and, possibly, the global climate: Since 1850, roughly 35% of anthropogenic CO_2 emissions resulted directly from land use (Houghton and Hackler, 2001). Anthropogenic nutrient inputs to the biosphere from fertilizers and atmospheric pollutants now exceed natural sources and have widespread effects on soil, plant and water quality as well. Land use has also caused declines in biodiversity through the loss, modification, and fragmentation of habitats; degradation of soil and water; and over exploitation of native species. Land-use activities, primarily for agricultural expansion and timber extraction, have caused a net loss of 7 to 11million km^2 of forest in the past 300 years (FAO, 2004). Highly managed forests, such as timber plantations in North America and oil-palm plantations in Southeast Asia, have also replaced many natural forests and now cover 1.9 million km^2 worldwide (Williams, 1990). Many land-use practices (e.g., fuel-wood collection, forest grazing, and road expansion) can degrade forest ecosystem conditions in terms of productivity, biomass, stand structure, and species composition even without changing forest area (Foley et al., 2005). Land use can also degrade forest conditions indirectly by introducing pests and pathogens, changing fire-fuel loads, changing patterns and frequency of ignition sources, and changing local meteorological conditions. In agro ecosystems, frequent soil disturbance accelerates turn- over rates of macro aggregates and limits the physical stabilization of labile soil organic matter compounds (Houghton and Hackler, 2001). Different types of land use, which include trampling, arable cultivation, grazing and mowing affected the floristic structure of plant community and soil physicochemical properties in different ways (Buba, 2015). Girma and Endalkachew (2013) analyzed soil properties and soil organic carbon stock under different land use and concluded that the types of land use, intensity of cultivation and fertilizer sources are major factors responsible for soil properties transformation. Also, Habtamu *et al.*(2014)

concluded that land use has significant impacts on soil physical and chemical properties. Investigation of the effects of different land uses on soil organic carbon and total nitrogen (Abera and Belachew, 2011) shows that land use systems influences soil organic carbon and total nitrogen in soils. Most studies showed that land use affect soil organic matter, total nitrogen, pH, exchangeable bases (Kosmas *et al.*, 2000; Pulleman *et al.*, 2000; Solomon *et al.*, 2000; Wang *et al.*, 2001; Leifeld and Kogel-Knabner, 2005; Pouyat *et al.*, 2007; Nweke, 2014). Contrastingly, Moges *et al.* (2013) found that no significant variation in bulk density, pH, total nitrogen and exchangeable bases with respect to land use types. However, similar studies showed that land use affect soil bulk density (Don *et al.*, 2010), total and available phosphorus (Wang *et al.*, 2001; Duguma *et al.*, 2010), cation exchange capacity (Kosmas *et al.*, 2000), organic carbon and total nitrogen (Yimer *et al.*, 2007). Majority of studies conducted on land use examined the effect of land use on water (Jeffrey and Wilcock, 2000; Tong and Cheng, 2002; Zhang and Wang, 2012). Although there are many studies that examined the effect of land use on the soil but most of these studies were conducted in other regions of the world and majority of these studies assessed the effect of land use change.

2.3 Geochemistry of Savanna Soil

Geochemistry of savanna soil addresses the complex interaction and inter-relationship between chemical elements and their compounds in the savanna soil, the influence of past and present anthropogenic (agricultural and non-agricultural) activities on these and the impact or effect of geochemical parameters on the soil. Geochemistry lies at the heart of environmental science and environmental concerns. The geochemistry involved in many environmental issues has become an increasing important aspect of scientific debate. Problems such as acid rain, the ozone hole, the greenhouse effect and global warming, water and soil pollution are geochemical problems.

Addressing these problems requires knowledge of geochemistry. Similarly, most of our non-renewable resources, such as metal ores and petroleum, form through geochemical processes. Locating new sources of these resources increasingly requires geochemical approaches. The biogeochemical functioning of Earth surface environments is increasingly affected by human activity. The geochemistry and mineralogy of soils are controlled by three principal factors (1) composition of parent materials, conventionally defined as the mineral or organic material in which soils form, (2) changes in parent materials produced by natural chemical, biological, and physical soil-forming processes acting over time and space, and (3) anthropogenic soil disturbances (Jenny 1941). The environmental changes due to mankind occur at the local, regional and global scale. An important task of geochemical research is to characterize these changes and to predict the responses of natural systems to anthropogenic perturbations. Thus geochemistry reveals that the Earth's surface and deep interior are intimately connected and the entire planet operates as an integrated system (Williams, 2015). The spatial distribution of soils derived from different parent materials generally governs the levels of elements abundance in the natural environment, although these may be affected to some extent by local modifying factors. Despite the fact that there are numerous geochemical studies conducted at regional levels, most of these looked at the geochemical composition of rocks (Al-Hafdh and El Shaafi, 2015; Siddiquie and Shaif, 2015), groundwater (Mahlknecht *et al.*, 2008; Abdu and Abubakar, 2013; Bhutiani et al., 2016) or sediments (Ludington *et al.*, 2006; Lapworth *et al.*, 2012), with very few studies on geochemistry of soils though most of the sites discussed are not located within northern guinea savanna of Nigeria. (Islam et al., 2015). There are quite a number of studies that assessed the anthropogenic contribution to the chemical composition of soils of this region but the focused was not on geochemistry. One of the most important geochemical properties of soils is their content of trace elements (Adriano, 2001). Soil minerals containing trace elements serve as reservoirs for the elements, releasing them slowly into the soil solution as weathering continues. Accumulation of trace elements, whether essential or not, has the potential to restrict the soil biological functions, cause toxicity to plants and contaminate the food chain (Loska *et al.*, 2004). Background concentrations of trace elements in soils are, therefore, important due to the recent interest in contamination potential and toxic effects of these elements on humans and the environment. The Nigerian savanna with a north to south lateral extent of more than 1,000 km presents spatially varied climatic conditions of semi-arid at the extreme northern border to sub-humid conditions close to the forest region in the south and varied geology; present conditions that could favor differential accumulation of trace elements. Trace elements enter an agro-ecosystem from both natural and anthropogenic sources (Raji *et al.*, 2015). Trace elements are, therefore, either inherited from the soil parent material or are inputs from human activities. The nature of the parent material, expressed as soil properties and processes, and the environmental factors shaping such processes as climate, vegetation, atmospheric input, etc. are the major factors determining the distribution and amounts of the trace elements in the soils (Frear, 1951; He *et al.*, 2005). More work is needed on those trace elements that are essential to human health but have harmful effect unless critical, narrow range is maintained.

2.4. Forest Soils

Vegetation plays an important role in soil formation and development as it accelerates local weathering (Phillips *et al.*, 2008). Vegetation cover influences the soil in a number of ways principally through accumulation of organic matter thus the effect of trees on the soil chemical properties is a function of series of factors such as nutrient uptake, leachates from tree bark, foliage, roots and organic acids from decomposing litters (Samndi, 2012). Forest ecosystem contributes a lot of organic matter to the soil. Forest trees alters their surroundings as they grow. Ground vegetation and micronutrient also change as a result of nutrient uptake, shading, blanketing by leaf litters, organic matter decay and subsequent leaching of nutrients (Samndi, 2006). Fresh litter is composed of a large number of complex organic compounds. The cation exchange capacity of acids forest soils is largely composed of pH dependent charges particularly forest soils whose colloidal fraction is composed of organic material and 1:1 clay mineral. Calcium (Ca) is a member of the alkaline earth elements and the most needed member by plants. Ohta (1990) also stated that Ca, magnesium (Mg) and potassium (K) are intensively utilized by trees and soil fauna, these elements are then gradually released into the soil as the trees mature, thus increasing these exchangeable cations in the soil. David and Grigal (1995) studied the effect of pine plantation and adjacent deciduous forest on soil Ca and reported that the deciduous stands had greater mass of Ca in the 0- 4cm mineral layer. Okoro et al., (1999) reported that Ca content varied with plantation species and soil depth. The nutrient concentration also varied with plantation age as observed by Braise *et al.* (1995). who stated that exchangeable Ca and Mg concentration decrease linearly with plantation age. Potassium is derived from feldspars and micas existing in soil in inorganic compounds. Humic and fulvic acids from decomposing litters have been reported to react with most elements are capable of attacking primary minerals liberating elements from the mineral structure. Apart from the effect of organic acids on mineral, plants uptake has also been reported by Tice *et al.* (1996) to remove K from the interlayer of biotite, thus returning it to the soil surface through fall and decomposition of litter. Fisher (1995) investigated the ameliorative effect of plantation trees species on degraded rainforest soil and stated that some of the species significantly increased the K content of the soil beneath them. Tice *et al.* (1996) reported that oak foliage contains twice as much K as pine foliage thus returning more K to the soil surfaces through litter fall and decomposition. The higher content of exchangeable K under some tree species was attributed to their deep-rooted nature which enable them to extract nutrient from a deeper and larger volume of soil (Samndi, 2006) thus concentrating in a small volume on the surfaces. The chemical composition of forest floor has significant effect on the rate of litter decomposition and on the soil population and tree growth. Homann *et al.* (1995) evaluated soil organic carbon content of 499 pedons in largely forested soil and found that the organic carbon of mineral soils ranged from 0.9 to 24g/kg. (mean 6.5) for 0 to 20cm depth and 23 to 88g/kg (mean 15.8) for 0 to 100cm depth. The total amount of organic carbon in the litter layer of soil differ between ages (Alrikson and Olsson,1995). Organic carbon contained in soil varies with vegetation or tree types as reported by Davies (1995), who compared organic carbon under pine with grassland and stated that organic matter level was 15 to 19% lower under pine. Okoro et al., (1999) also reported lower organic carbon under teak plantation than natural vegetation, which they attributed to slower rate of mineralization of litter fall under teak. Nitrogen is accumulated in soils in the form of plant and animal residues. the amount of nitrogen in soil at any given time depend on the presences of organic matter and its rate of decomposition/mineralization, total N in forest soil is found largely in the humus layer of the forest floor and in the A horizon (Samndi, 2006). Nitrogen content and mineralization are highest in the uppermost centimeter of the soils. This high N level in the surfaces horizon was also reported by (Raji, 2008; Maniyunda, 2012 and Ningi, 2015) who attributed it to the contribution of organic matter in the upper horizon. Stith and Yowhanson (1992) studied differences in soil and leaf litterfall N- dynamic for five forest plantations and reported that vegetation influences N cycling in forest soils with average seasonal soil NO_3^- and NH_4^+ content (mg/kg) of 3.9 and 3.4 for red oak and 7.7 and 5.8 for European larch. According to Fisher

(1995), species with higher nutrient concentration and recycling property accumulated more nutrient beneath them thus increasing soil nutrient content. He also hypothesized that those low molecular weight organic acids in the rhizosphere chelate Fe and Al and releases P into the soil solution. Aluko (2001) also stated that under Pinus caribea, mycorrhizal association promoted a more efficient P uptake from P deficient soil thereby increasing P content beneath it. Katyal and Sharma (1991) and Sharma *et al.* (2000) reported strong correlation between organic matter and DTPA-extractable Zn, Cu, Mn and Fe, thus confirming the roles of organic matter in the availability of these elements. Samndi (2006) evaluated soil properties and development under teak plantation and indicated the dominance of magnetite in soil under young plantation, mixed mineralogy was obtained as the trees grows older while for the oldest plantation, kaolinite was the dominate clay mineral with traces of hematite and goethite suggesting increased level of pedogenesis as plantation ages.

2.5 Effect of Long-term Fertilization on Geochemistry of soil

Fertilizer use is a key factor for increasing agricultural production and its utilization has increased rapidly in the last few decades, mainly due to adoption of high yielding and nutrient responsive crop cultivars in large parts of the country. There are concerns about whether continuous use of such fertilizers over a long period of time will cause an accumulation of metals to high levels, thereby increasing risk to environmental and human health (Huang *et al.*, 2004; Abdu *et al.*, 2011b). Fertilization can affect soil physical, chemical and biological characteristics (Xie and Zhou, 2008). Adoption of chemical fertilizers has largely replaced traditional practices of using manure and other organic amendments. In agricultural systems, soil conservation and management decisions affect the soil chemical properties. The main objective of applying fertilizer to any crop is to improve the overall yield of the crop, hence emphasis has been placed on inorganic fertilizers. However, management of mineral fertilizers has become increasingly critical in crop production from both economic and environmental standpoints (Adeniyan and Ojeniyi, 2005). The use of mineral fertilizers is limited because of high cost and scarcity i.e. insufficiency in supply and distribution which has not been of advantage of the local farmers. Besides this, there is also a lot of soil problems associated with the use of chemical or mineral fertilizers. Since salt content is one of the most critical characteristics of chemical fertilizers; they are expected to be harmful to agriculture in the long run as salts are harmful to plants as well as soil (Gsplantfoods7, 2013). Continuous use of these chemical fertilizers depletes essential soil nutrients and minerals that are naturally found in fertile soil. The use of chemical fertilizers does not help replenish all soil nutrients and its fertility contrary to the popular belief; but, replenish only nitrogen, potassium and phosphorous (Gsplantfoods7, 2013). Phosphorous does not dissolve in water and its overuse may cause hardening of soil. Soil fertility and vegetation growth depend much on the balanced supply of essential nutrients and minerals. As such, overuse of specific nutrient(s) may cause imbalance in the supply of soil nutrients further resulting in soil degradation and the loss of equilibrium of a stable soil. Application of ammonia (NH_3) containing fertilizers produces an immediate alkaline effect due to hydrolysis. However, oxidation and subsequent nitrification of such fertilizers produces long term acidity effect (Forth and Royd, 1998; Brady and Weil, 2002). It is also accepted that the historical routine use of agrochemicals (such as pesticides and fertilizers) may have resulted in undesirable concentrations of trace elements in the environment (Luo *et al.*, 2007). More so, application of mineral fertilizer continuously on the soils of the savanna were found to reduce soil pH, microbial population and activities, organic matter content, buffering capacity and cation exchange capacity of the soils (Rayar, 2000; Chu *et al.*, 2007; Liu *et al.*, 2010; Xie and Zhou, 2008). Inorganic fertilizers contain trace quantities of metals like Cd, Pb, As, and other trace elements of environmental relevance (Ajayi *et al.*, 2012; Nicholson *et al.*, 2003). Also, Sharma and Subehia (2003) reported that continuous application of nitrogenous fertilizers alone aggravates the problem of soil acidity by lowering soil pH from 5.8 to 4.7 and increasing exchangeable aluminum. On the contrary, Bi *et al.*(2014) conduced a long-term experiment to investigate the effect of chemical fertilizer on rice yield, yield trend, soil properties and agronomic efficiency and found that all fertilizer treatments had no significant effect on soil pH and soil organic carbon but generally increased nutrient content when corresponding elements were applied. Increased awareness of the cheap source, availability and the fact that organic manure supplements as well as ameliorates pollution and soil deteriorative problems associated with long term continuous used of inorganic fertilizer, researchers on fertilizers have shifted attention to assessing the combined effect of both the inorganic and organic fertilizer source on crop yield and yield parameters mainly with few evaluating the chemical contribution of these to the soil. Continuous application of fertilizers has increased heavy metal concentrations in soil, root and other organs of products. Carbonell *et al.* (2011) conducted a research to investigate the effects of municipal waste composts and mineral fertilizers on soil properties. The results showed NPK fertilizers increased the amount of Cd and Ni concentrations on one hand and decreased mercury concentration on the other hand in soil. Xie and Zhou (2008) evaluated cypermethrin persistence and soil properties as affected by long term fertilizer management and found that soil physicochemical properties varied significantly after applying different fertilizers over a long period of time. Yargholi and Azarneshan (2014) studied the long-term effects of pesticides and chemical fertilizers usage on soil properties and heavy metals accumulation. Their results showed that soil physical characteristics such as bulk density were changed in long-term.

They also found that heavy metals accumulation in soil were highly affected. Czarnecki and During (2015) tested the effects of different mineral fertilizer variations on soil properties (pH, OC, CEC and pseudo-total and mobile metal (Cd, Cu, Mn, Pb, Zn) contents of soils after 14 years of fertilizer application and also determine residual effects of the fertilization 8 years after cessation of fertilizer treatment. They found a significant decrease in soil pH and an evident increase in soil carbon content and CEC with fertilization. Moreover, pseudo- and mobile metal (Cd, Cu, Mn, Pb, Zn) contents in the soils increased. Eight years after termination of the fertilization in the soil samples taken from soil profiles of the fertilized plots (NPK) for monitoring the residual effects of the fertilizer application, a decrease of 82.6, 54.2, 48.5, 74.4, and 56.9% in pseudo-total Cd, Cu, Mn, Pb, and Zn contents, respectively, was observed. As the enrichment of metals in soils occurs over long time periods, monitoring of the long-term impact of fertilization is necessary to assess metal accumulation in agricultural soils.

2.6 Effect of Pasture Cultivation on Geochemistry of Soil

Pasture vegetation has important and beneficial impacts on soil quality (Betteridge *et al.*, 1994; Teague *et al.*, 2011), and its effective management is therefore important. By carefully managing the health of the plant community in pastures, soil quality can be substantially increased. Also, good pasture management practices foster effective use and recycling of nutrients. Pasture is an important factor in the genesis of soils. Jenny (1941), in his discussion on organisms as a soil forming factor, treated pasture/vegetation as an independent as well as a dependent variable. Pasture influences the soil supporting it by the deposition of dead plants material. The accumulation of these organic materials exerts a decisive influence on the morphological, physical, chemical and mineralogical properties of the underlying mineral soil (Reyhan *et al.*, 2006). Pastures are believed to cause improvement in the nutrient availability in impoverished soils. However, evidence of this ameliorative capacity has generally been attributed to the soil properties. Dezzeo *et al.* (2004) stated that soil properties most directly influenced are organic carbon and nitrogen. It seems that pasture species composition may also affect soil properties (Franzluebbers *et al.*, 2000a). Ghosh *et al.* (2006) assessed long term effect of pasture on soil quality in acid soil and concluded that soil organic carbon is increased by 30%. Franzluebbers *et al*. (2000b) also concluded that in the long-term, managed grass systems have nearly equivalent potential to store soil organic carbon as forest land. Studies on pasture across the world concentrated on the effects of grazing on pasture soils (Kariuki *et al.*, 2010; Zarekia *et al.*, 2012; Niu *et al.*, 2009). Since the 1960s the demand for milk and meat has doubled and tripled, respectively, in the developing countries (FAO, 2009). Therefore, to successfully manage pasture fields for increased productivity, there is the need for proper understanding of the soil geochemical processes as influenced by long term pasture cultivation.

2.7 Effect of Municipal Waste on Soil Geochemical Properties

Human activities in urban centers have resulted in the generation of a large quantity of waste known as municipal solid waste. Solid waste varies in composition, which may be influenced by factors such as location and culture affluence (Adefemi and Awokunmi, 2009). Municipal wastes as organic manure consists of garbage from households, markets and small scale industries, and simply dumped, rarely incinerated or burnt in the open (Ezeaku *et al.*, 2003). For long, soil has been recognized to be an important medium for organic waste disposal. Deporte *et al.* (1995) have explained that composted urban wastes in many areas are being added to agricultural land for both waste disposal and to improve soil fertility. Such compost serves as nutrient source for plant due to its organic matter content. However, it may increase the level of potentially harmful trace metals and various persistent organic toxins (Nriagu, 1998). Long term application of urban waste on cultivated fields can undoubtedly improve soil fertility and provide crop nutrient needs of farmers, but it can likely lead to negative and potentially harmful changes in soil physical and chemical characteristics due to increasing toxicity (Ezeaku *et al.*, 2003). Yakubu (2006) evaluated the chemical and heavy metals content of municipal waste used in fertility maintenance in Zaria and concluded that waste are nutrients rich and very high in fertility but with possibility of adding to soil sodicity and heavy metals contamination. Even though composition of municipal waste varies from place to place but could have the same elemental constituents which only varies in quality (Brady and Weil, 1999). However, composting has been reported to be a feasible way of converting available organic waste into inorganic fertilizer for the cultivation of numerous crops with better yield (Sridhar *et al.*, 1985; 1992; Adeoye *et al.*, 1993; John, 1994). It is assumed that addition of fresh municipal wastes to the soil provide nutrients, which will freely undergo mineralization, thus activating the cycles of these nutrients in soils (Ayuso *et al.*, 1996). Many works done on municipal wastes have reported that waste contains significant amounts of total N and OC. These wastes also contain toxic heavy metals like Zn, Cu, Pb, Cd (Chikelu, 1998; Anikwe, 2000; Anikwe and Nwobodo, 2002). Many studies have shown that soil fertility is increased after land application of organic wastes (Hart and Speir, 1992; Agbim and Adeoye 1994; Yakubu, 2006). In every ton of municipal wastes added to soils, 16.5kg N, 21.4 kg P, 17.3kg K and 120. 6kg Ca were supplied (Adediran *et al.*, 1999). Anikwe and Nwobodo (2002) found that municipal wastes application to soil affect soil productivity by provision of essential and non-essential mineral elements for plants growth. Increased in pH after the addition of municipal wastes may be due to high organic matter content which tend to buffer the soil by preventing excessive pH changes due to the release of exchangeable cations during mineralization of the organic matter (Woomer *et al.*, 1994). Organic wastes can produce significant increase in soil N (Mbagwu and Piccolo,1990). Organic wastes are often valuable source of P, and hence can be used to increase soil P status. Per unit mass, the organic fraction is the most chemically active portion of the soil. It is a reservoir for various essential elements, a source of cation exchange capacity and soil buffering, and is a large geochemical reservoir of carbon (Bohn *et al.*, 2001). Previous research on geochemistry of trace/ heavy metals in soil treated with municipal wastes as supplement to inorganic fertilizer source in Nigeria are limited as they focused on the accumulation of these metals in soils and crops (Amakhian *et al.*, 2003; Ezeaku, 2003; Ibitoye and Ipinmoroti, 2004; Ayuba *et al.*, 2005; Eddy *et al.*, 2005; Okoronkwo *et al.*, 2005; Pasquini, 2006). Others concentrated on complementing the organic and inorganic fertilizer sources on yield and the metal concentration in crops (Ipinmoroti *et al.*, 2004; Adenawoola and Adejoro, 2005; Adeniyan and Ojeniyi, 2005; Yakubu, 2006). Therefore, studies are required that will comprehensively look at the influence of municipal wastes on the distribution, behavior and mobility of the metals.

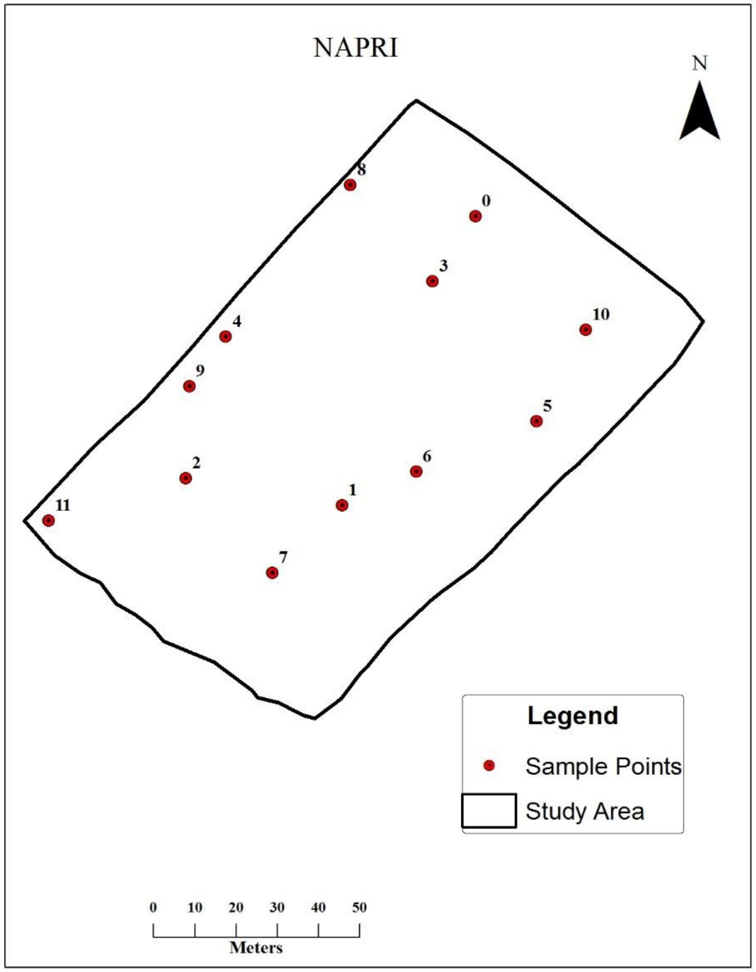
CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Site description

The soil samples for the study were collected from four different land use patterns; A 56yrs forest reserve dominated by Eucalyptus camaldulensis, E. tereticornis with smaller areas of Pinus caribaea, P. oocarpa, a garden where cabbage, carrot and lettuce were planted and municipal waste was used as fertilizer source, pasture field where gamba grass was cultivated for over 40yrs and soil under long-term fertilizer treatment (NPK and Urea). The forest soil was collected from Afaka forest, Kaduna, soil under pasture was collected from National Animal Production Research Institute (NAPRI), Zaria, vegetable garden soil was collected from Sabon Gari, Zaria while the soil under long-term fertilizer treatment was collected from the Institute for Agricultural Research farm (IAR), Zaria.

The Afaka Forest Reserve Kaduna lies between latitude 10^{0} $33^{'}$ and 10^{0} $40^{'}$N and longitude 07^{0} $15^{'}$E while Zaria is located between latitude 11^{0} $00^{'}$ and 11^{0} $30^{'}$N and longitude 07^{0} $30^{'}$ and 08^{0} 00 E both in the Northern Guinea Savanna ecological zone of Nigeria. The climate of Zaria is characterized by an average rainy season of about six months, lasting from May to October with its peak in August and a dry/harmattan season of also about six months, lasting from November through April as well as a highest day temperature of about 38^{0}C during April/May. The mean annual rainfall of Zaria is approximately 1,000mm while the Afaka forest has a long term mean annual rainfall of 1270mm, lasting from mid-April to October, dry harmattanfrom November to March and highest day temperature of 29^0C during April.



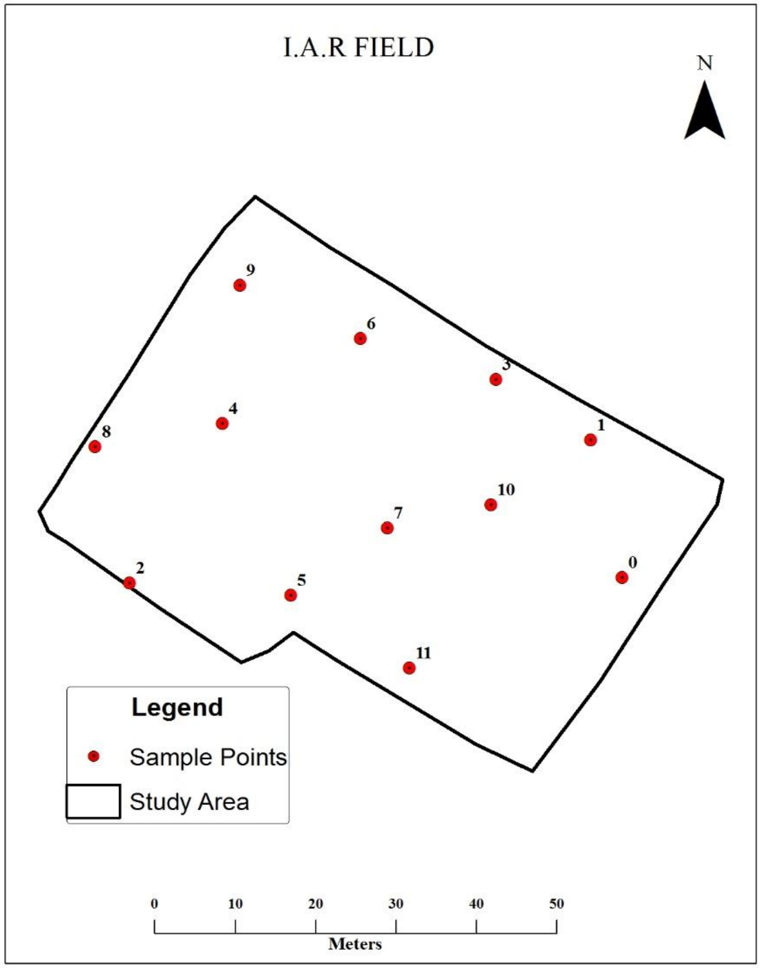
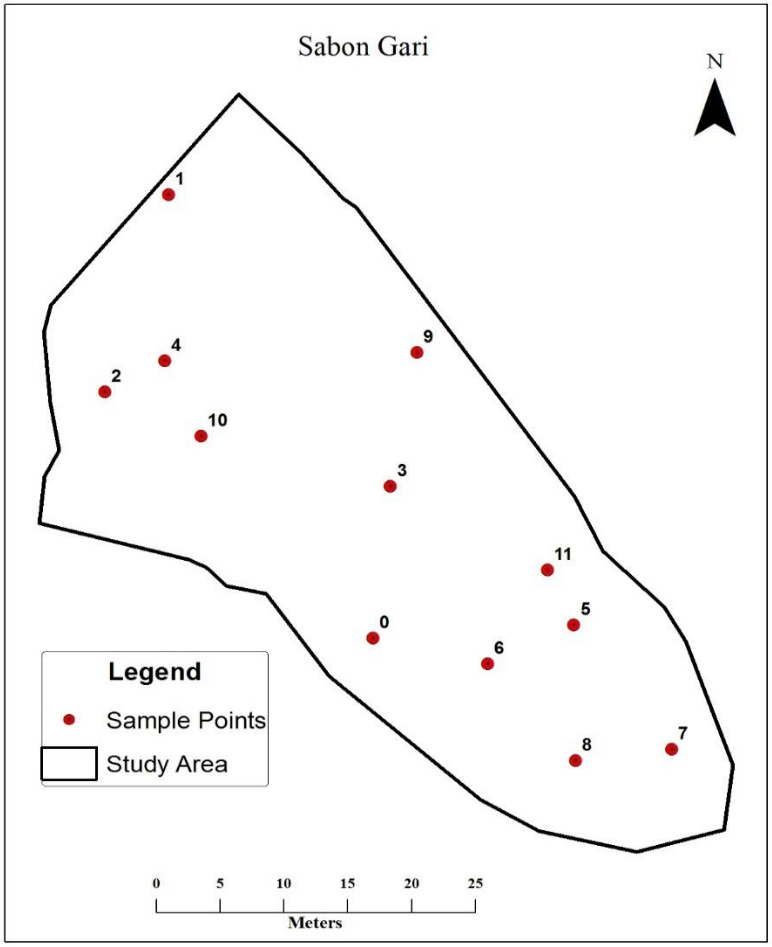


Fig 1. Ecological map showing the sampling site at NAPRI

Fig 2. Ecological map showing sampling site at I.A.R field



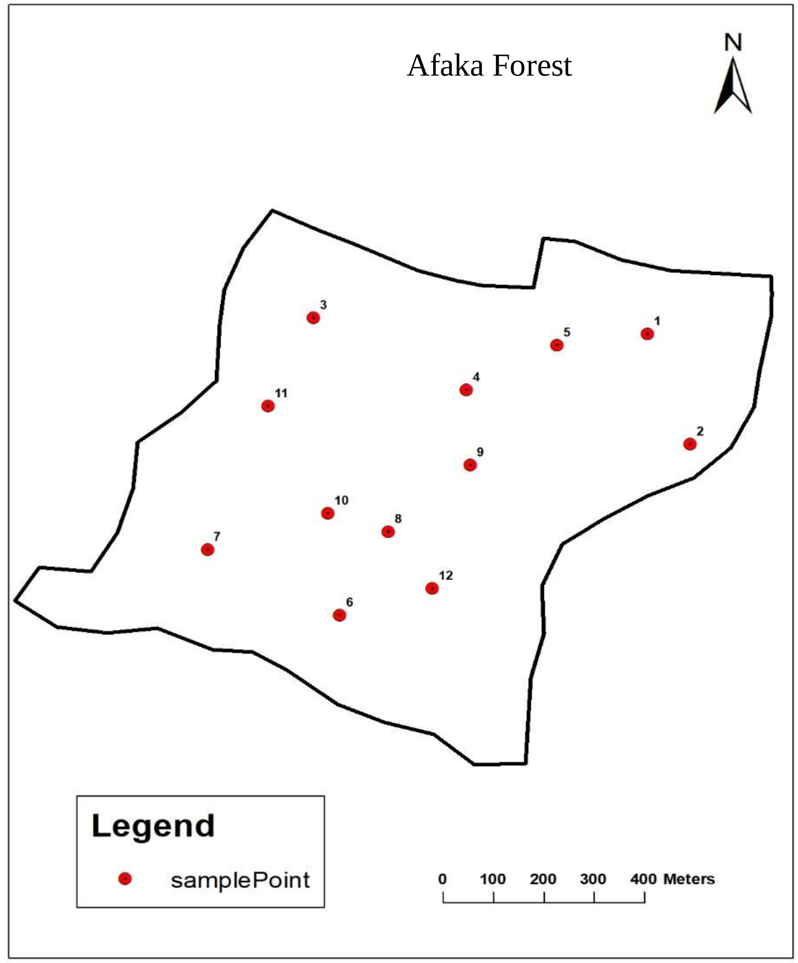


Fig 3. Ecological Map of the Sampling area at Sabon gari

Fig 4. Ecological Map of the Sampling area at Afaka forest

3.1.1. Geology of Zaria

Zaria geology is underlain by basement complex rock such as granites, quartzites, schist and gneisses (Iloeje, 2004). Shobayo *et al.* (2013) classified the soil base on the criteria and nomenclature of USDA Soil Taxonomy (Soil Survey Staff, 1999) as mostly plinthustalf or Euric Luxisols according to World Reference Base for Soil Resources (WRB) (FAO-ISRIC-ISSS, 1998). As the soils were classified Luxisols, they had argic horizons which was overlain by loamy sand to coarser texture. The soil of the Afaka forest is Alfisol, plinthustalfs, sandy loam (Lawal, 2013) while the parent material included gneisses, magmatite and granite. Schist, phyllite, quartzite and pegmatite are also common.

3.2 Soil Profile Sampling

Purposive soil sampling was conducted and for each land use, a profile pit of approximately 1m by 2m wide was excavated to a depth of beyond 1.5 m except where there is a restriction (water table and plinthite) and described by a pedologist. Different genetic horizons were delineated and 28 subsamples were collected in duplicate from each identified horizon, bulk to form 14 composite samples. A total of 48 surface samples were also collected randomly and bulk to foam 12 composite samples. For bulk-density determination, additional undisturbed core samples were collected. Soil sampling was done during dry season (December-January).

Plate 1. Profile pit at pasture field

Plate 2. Profile pit at fertilized field

Plate 3.Profile pit at Sabon gari

Plate 4. Profile pit at Afaka forest

3.3 Soil Preparation and Analyses

3.3.1 Preparation of Soil Samples

The soil samples were air-dried, crushed and then passed through a 2-mm diameter mesh after which standard laboratory techniques were used to determine some physical and chemical properties of the soil. All the analyses were carried out in the laboratory of the Department of Soil Science, Faculty of Agriculture, Ahmadu Bello University, Zaria.**3.3.2 Soil Reaction (pH)**

3.3.2 Soil Reaction (pH)

The soil pH was determined in both water and 0.01M $CaCl_2$ solution in the soil to water ratio 1:2.5. Ten (10) grams of the soil samples were weighed and twenty (25) ml of distilled water was added and stirred. The pH of the suspension was read using a pH meter after 30 minutes. The same procedure was repeated using 0.01M $CaCl_2$.

3.3.3 Exchangeable Bases

Exchangeable bases which include Calcium (Ca), Potassium (K), Sodium (Na) and Magnesium (Mg) were extracted using 1.0 N ammonium acetate (NH_4OAC) at pH 7.0. Potassium and Na contents of the extract were determined by reading with 410 Sherwood flame photometry, while Ca and Mg were determined using atomic absorption spectrophotometer (AAS) (AA 500 PG Instrument, UK).

3.3.4 Cation Exchange Capacity (CEC)

The CEC of the soil was determined by leaching the soil with 1N $NH_{4.}AOC$ (Rhoades, 1982). The soil was soaked overnight in 1N NH_4OAC and subsequently leached with 1N NH_4Cl and washed with ethanol. After washing with 1N NaCl, the leachate was distilled and titrated with 0.1N HCl with boric acids for trapping NH_4^+ions.

3.3.5 Total Nitrogen (TN)

Total N was determined by Kjeldahl steam distillation method (Bremmer and Mulvaney, 1982). One gram of the soil was digested with 10ml of concentrated sulphuric acid, the digest was diluted with 100ml of distilled water. 10ml of the aliquot was distilled with sodium hydroxides. The distillate was titrated with 0.01N H_2SO_4 to pink end point.

3.3.6 Available Phosphorous (Av.P)

Available phosphorus was determined using Bray 1 extraction method. The available P was extracted from 10g of the soil using ammonium fluoride in hydrochloric acid and the P in the solution was measured colorimetrically (Bray and Kurtz, 1945).

3.3.7 Organic Carbon (OC)

Organic carbon was determined by dichromate wet oxidation method of Walkley-Black as described by Nelson and Sommers (1986). One gram of the soil was digested with potassium dichromate using concentrated tetraoxosulphate (VI) acid for 30 minutes after which 100mL of water was added. This was back titrated with ferrous ammonium sulphate using barium diphenylamine sulphate as indicator.

3.3.8 Particle-size distribution

Particle size distribution was determined by the Bouycous hydrometer method according to Gee and Bauder (1986). Fifty gram of the soil was shaken with 100ml of 5% calgon (sodium hexametaphosphate) for 30 minutes for complete dispersion. The suspension was transferred into 1000ml measuring cylinder and made to mark with water. Hydrometer readings were taken at 40seconds and 2 hours. A blank containing no soil was carried through the same procedures to correct the readings taken in the soil suspension.

3.3.9 Bulk Density (BD)

The bulk density was determined using the procedures described by Blake and Hartge (1986). The mass of the soil after drying in an oven for 24hours at 105^0C was calculated and divided by volume of soil (volume of the cylindrical core sampler). Note that the volume included both solids and soil pores. The soil volume was obtained by using the formula for the volume of a cylinder ($\pi r^2 h$).

3.3.10 Free Iron and Aluminum oxides

Free iron and Aluminum oxides were extracted according to the methods of Mehra and Jackson (1960) using citrate bicarbonate dithionite (CBD) and the ammonium oxalate (NH_4OAC) method as described by Juo *et a*l. (1974). The Fe in the extract was determined by AAS while the Al was determined colorimetrically after the destruction of organic matter as describe by Jackson (1958).

3.4 Separation of Clay Fraction from Silt and Sand Using the Siphon Method (Pretreatment for X-ray Diffraction and X-ray Florescence)

Fifty grams each of the soil samples was weighed into a 100ml measuring cylinder and made to mark with distilled water. The suspension was sieved through 50µm sieve and the filtrate was collected inside a plastic bowel. The filtrate in the bowel containing the silt and clay were transferred into a 4-litre transparent plastic gallons with the aid of a wide necked funnel. The suspension was allowed to stand for 24hours and the supernatant was siphoned into a receiving plastic bowl. The gallons were filled with water and allowed to stand for another 24hours for siphoning and sedimentation. To concentrate the clay fraction, 50g of MgOAC salt was added to each clay suspension and allowed to flocculate overnight. The supernatant solution was decanted and the concentrated clay suspension from the plastic bowls were transferred into a 50ml centrifuge tubes, centrifuged and the supernatant solution was decanted. The clay was scoop out using a spatula into a weighed crucible and dried overnight in an oven at 105^{0}C. Note that the procedure above was carried out after the removal of organic matter, exchangeable cations and sesquioxides from the soil samples following the method described by Kunze and Dixon (1986).

3.4.1 X-ray Diffraction of the Clay Fractions

The x-ray diffraction of the clay fraction was determined at the National Steel and Raw Materials Exploration Agency, Malali, Kaduna. The mineralogy of the clay fraction was determined after saturating the powdered clay with few drops of a dispersant solution (ethanol) and spread evenly onto a glass slide. It was then air dried and scanned by XRD. A diffraction pattern was obtained using CuKα radiation and a Shimadzu X-ray diffractometer (XRD-6000). The samples were step scanned between 2 and 45^0 2θ using scanning speed of 4^0/min at sampling pitch of 0.020^0 and a preset time of 0.30 seconds.

3.4.2 X-ray Florescence Analyses

The powdered clay was moistened with four drops of 10% polyvinyl chloride (PVC) in toluene, mixed thoroughly to form a homogenous sample, the sample was then allowed to dry. Pellets was then prepared by pressing the powder filled in a cup using a set of dies and automatic hydraulic press (40 Ton). Some selected trace elements (Pb, Co, Fe, Ti, Mn, Zn and Cu) were determined from the pellet using radioisotope excited X-ray fluorescence spectrometry at the Research and Development unit (R and D) of the Defence Industry Cooperation of Nigeria (DICON), Kakuri, Kaduna.

3.5 Geochemical Evaluation

3.5.1 Geochemical Balance Evaluation

Mass balances calculation was used to evaluate soil metal pools as they combine mobility, distribution, flows, and soil retention characteristics. They are also useful to evaluate gains and losses of elements as a result of management or land use patterns (Shotbolt *et al.*, 2008) and of weathering processes (Ndjigui *et al.*, 2008). Several methods have been applied to study element balances in soils and geologic material. Gains and losses as a result of soil management using the immobile element approach (Agbenin, 2001; Ndjigui *et al.*, 2008; Abdu *et al.*, 2011c) were evaluated and the percentage gain or loss in the concentration of each element in the different land use was compared with the concentration in an uncultivated reference soil using the following equation of Ndjigui *et al.* (2008):

$$\%\ \text{change} = \left[\frac{Xa/Ia}{Xu/Iu} - 1\right] \times 100$$

where *X*a is the element concentration of the soil sample of the different land use, *X*u is the element concentration of the reference soil sample, *I*a is the concentration of the immobile element in the soil sample from the soil under different land use and *I*u is the concentration of the immobile element in the uncultivated reference soil sample. Titanium (Ti) was used as a reference element because of its insignificant anthropogenic origin and the fact that it has a consistent concentration throughout the profiles of similar soils in the Nigerian savannah (Abdu et al., 2011c). It has a naturally uniform concentration (Daskalakis and O'Connor, 1995) and is mainly derived from weathering of crustal rock minerals (Schutz and Rahn, 1982). Furthermore, this element is associated with many rock-forming minerals such as anatase and rutile (TiO_2), ilmenite ($FeTiO_2$), sphene ($CaTiSiO_5$), and zirconolite ($CaZrTi_2O_7$).

3.5.2 Enrichment Factor (EF)

Since trace metals occur naturally in the earth's crust, it cannot be assumed that an environment is automatically anthropogenically contaminated when trace metals are found in its soil. The metal EF method (widely used normalizing measure) was utilized to distinguish between natural and anthropogenic metal sources (Selvaraj *et al.*, 2007). The enrichment factor (EF) for each metal (Abraham and Parker, 2008) was calculated by normalizing its concentration against that of the immobile reference element Ti. Thus, enrichment factor (EF) is defined as

$$\text{EF} = \frac{Mc}{Tic} \Big/ \frac{Mref}{Tiref}$$

where Mc and Tic are the concentrations of the element and the reference element in the contaminated soil, M_{ref} and Ti_{ref} and are the concentrations of the element and the reference element in the reference soil. Enrichment factor values close to unity indicate that the metal is of crusted origin, values < 1 indicate mobilization or depletion of the metal, and values > 1 suggest anthropogenic enrichment (Abdu *et al.*, 2011c).

3.5.3 Contamination factor

To measure the intensity of contamination of a given element in the soil sample, the metal contamination factor (CF) was used. The value for the contamination factor (CF) was described by calculating the ratio between the metal content in a given soil sample and the normal concentration levels. The intensity of contamination according to Abdu *et al.* (2011c) is reflected on a scale with 0 indicating no contamination, 1 none to medium, 2 moderate, 3 moderate to strong, 4 strong, 5 strong to very strong, and 6 high contamination. The level of soil contamination by a metal is often expressed in terms of a CF:

$$C_f = \frac{Metal\ content\ in\ soil}{Background\ value\ of\ metal}$$

While calculating the CF of the soil, the world crustal average contamination of the trace metals under consideration was taken.

3.5.4 Geo - accumulation Index

The index of geo-accumulation provides a simple and quick method to assess metal contamination by comparing the level of metal obtained to the background levels. Thus, the geo-accumulation index (*I*geo) allows the assessment of metal contamination through a comparison of the metal concentration in the contaminated soil with its concentration prior to contamination (Loska *et al.*, 1997), but it does not give further information to the mobilization and bioavailability of the trace element (Forstner *et al.*, 1990). The I*geo* value reflects the degree of contamination of the sediments by a metal (Taylor and McLennan, 1995). The value of the geo-accumulation index is described by the following equation:

$$\text{Igeo} = \frac{log\,2\ Cm}{1.5\ Bm}$$

where *Cm* is the concentration of the metal *m* in the polluted (contaminated) soil and *Bm* is the geochemical background concentration of the metal *m* (Muller, 1979). The factor 1.5 was introduced as a correction factor to normalize the background metal concentration for lithospheric and anthropogenic effects (Loska *et al.*, 1997). According to (Taylor and McLennan, 1995) the interpretation of the obtained results is as follows in which:

I*geo* ≤ 0 is practically uncontaminated,

0 < I*geo* < 1 is uncontaminated to moderately contaminated,

1 < I*geo* < 2 moderately contaminated,

2 < I*geo* < 3 moderately to heavily contaminated,

3 < I*geo* < 4 heavily contaminated,

$4 < Igeo < 5$ heavily to very heavily contaminated, and

$Igeo \geq 5$ very heavily contaminated.

3.6 Statistical Analysis

All the data were subjected to analysis of variance (ANOVA) and the means were ranked using least significant difference (LSD). Pearson correlation coefficient was used to determine the geochemical relationship between the metals and soil properties while factor analyses was used to determined elements of similar geochemical behavior and grouped based on geochemical affinity (Bellehumeur *et al.*, 1994). All statistical analyses were performed using SAS 9.1 software (SAS, 2011).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Effect of land use pattern on chemical properties of soils.

Results of soil analyses for profile and surface soils are presented in Tables 1 and 2 respectively. Results obtained for soil pH (H_2O) were higher than pH in $CaCl_2$ for both tables. For the profile soils, the highest pH was observed in the garden (6.8) and forest (6.6) while fertilized field recorded the least (6.28), although it is statistically not different from NAPRI pasture field (6.30). High pH values observed garden may be due to high organic matter content of municipal waste which buffer the soil and prevent excessive pH change while for lower pH observed for the fertilized IAR farm may be due to the fact that long-term application of chemical fertilizer reduced the soil pH (Chu *et al*., 2007; Liu *et al*., 2010; Xie and Zhou, 2008). The values are within the pH level of 4.8 - 6.9 reported by Raji *et al.* (2015) in some soils of the Nigerian savanna.

Exchangeable $Ca^{2+}$and Mg^{2+} showed significant variation with land use (Table 4.1). Higher exchangeable bases (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) were recorded in the surface soils (Table 4.2) than the horizon soils. Higher Ca, Mg and Na observed for the garden is associated to the fact that municipal waste (garbage from households, markets and industries) used as organic manure releases exchangeable cations during mineralization while the high K in the pasture field is associated to the dominant mineral (muscovite, phlogopite and chrysotile) in the land use as K is derived from the interlayer of feldspars and micas.

The garden soil although similar to fertilized field (2.70) and pasture field (2.51) but significantly different from forest soil (1.73) recorded the highest CEC values (2.71) reflecting the high exchangeable bases observed for this location. Compared to horizon soils, higher CEC values

	Depth	Sand	Silt	Clay	TXL	BD	pH		OC	TN	Av.P	Ca	Mg	K	Na	CEC
		⟵ g/kg ⟶				Mg/m^3	H_2O	$CaCl_2$	⟵ g/kg ⟶		mg/kg	⟵		Cmol/kg ⟵		
Pasture field	0-27	661	200	139	SL	1.21	6.4	5.9	1.33	2.80	1.29	1.73	0.35	0.03	0.03	2.24
	27-69	581	200	219	SCL	1.43	6.3	5.8	1.21	2.10	1.23	1.97	0.41	0.21	0.04	2.82
	69-120	641	240	119	SL	1.61	6.2	5.7	1.28	0.00	1.23	1.46	0.43	0.17	0.10	2.46
		627.7	**213**	**159**		**1.42**	**6.30**	**5.8**	**1.27**	**1.63**	**1.25**	**1.72**	**0.40**	**0.14**	**0.06**	**2.51**
Fertilized field	0-20	561	200	239	SCL	1.64	6.4	5.2	1.38	2.10	4.73	0.95	0.32	0.03	0.04	2.13
	20-44	541	240	219	SCL	1.33	6.0	5.9	1.19	0.70	1.23	1.97	0.40	0.03	0.04	2.94
	44-110	441	280	279	CL	1.73	6.1	5.9	1.19	0.70	1.23	1.90	0.42	0.03	0.07	2.93
	110-182	521	240	239	SCL	1.44	6.6	6.0	1.22	2.80	1.4	1.65	0.43	0.04	0.08	2.80
		516	**235**	**244**		**1.54**	**6.28**	**5.8**	**1.24**	**1.60**	**2.15**	**1.62**	**0.39**	**0.03**	**0.06**	**2.70**
Garden	0-10	721	160	119	SL	1.82	6.3	5.4	1.27	6.30	9.63	1.85	0.32	0.02	0.06	2.55
	10-30	681	180	139	SL	1.61	6.7	5.6	1.21	0.70	1.93	2.04	0.35	0.03	0.08	2.81
	30-47	621	120	159	SCL	1.4	6.7	5.4	1.19	2.10	2.28	2.00	0.38	0.04	0.13	2.95
	47-70	601	200	199	SCL	1.78	7.0	5.7	1.27	0.00	2.45	1.80	0.38	0.05	0.07	2.51
		656	**165**	**179**		**1.65**	**6.80**	**58**	**1.24**	**3.03**	**4.07**	**1.92**	**0.36**	**0.04**	**0.09**	**2.71**
Forest	0-17	140	140	139	SL	1.47	6.5	5.9	1.42	0.70	2.98	1.16	0.33	0.02	0.06	1.77
	17-69	140	140	219	SCL	1.14	6.6	5.3	1.46	0.00	1.58	0.45	0.18	0.30	0.05	1.60
	69-97	180	180	279	SCL	1.47	6.7	5.5	1.41	0.70	1.75	0.33	0.18	0.07	0.05	1.83
		634.3	**153**	**212**		**1.36**	**6.60**	**5.6**	**1.43**	**0.47**	**2.10**	**0.65**	**0.23**	**0.13**	**0.05**	**1.73**
LSD		22.53^{NS}	17.79^{NS}	7.96^{NS}		0.29^{NS}	0.31^{*}	0.42^{NS}	0.07^{**}	2.42^{NS}	2.23^{*}	0.58^{**}	0.09^{**}	0.10^{NS}	0.04^{NS}	0.35^{**}

Table 4.1: Mean values of selected physical and chemical properties of the profile soils under the different land use types

Numbers in bold are means, TN = Total nitrogen, Av-P = Available Phosphorus and TXL = Soil Textural Class.

Table 2: Mean values of selected physicochemical properties of the surface soils under the different land us types

	Depth	Sand	Silt	Clay	TXL	BD	pH		OC	TN	Av.P	Ca	Mg	K	Na	CEC
	Cm	← g/kg →				Mg/m^3	H_2O	$CaCl_2$	← g/kg →		mg/kg	← Cmol/kg →				
Pasture field	0-20	701	193	106	SL	1.4	6.0	5.4	1.0	2.8	4.8	3.6	1.4	0.04	0.003	5.2
Fertilized field	0-20	661	233	106	SL	1.5	5.8	5.3	0.5	1.9	10.2	3.1	0.7	0.02	0.010	4.1
Garden	0-20	702	207	86	SL	1.3	6.7	6.3	1.6	6.7	4.6	7.9	5.6	0.05	0.140	13.9
Forest	0-20	741	193	66	SL	1.2	6.3	5.9	1.4	3.7	5.4	3.6	2.0	0.04	0.010	5.8
LSD		4.35^{*}	4.48^{NS}	2.23^{*}		1.2^{*}	0.07^{NS}	0.42^{**}	0.7^{*}	3.23^{NS}	3.4^{*}	2.95^{*}	1.75^{**}	0.03^{NS}	0.05^{**}	4.6^{*}

TXL = Soil Textural Class, BD = bulk density, TN = Total nitrogen and Av-P = Available Phosphorus were recorded for the surface soils, this may be attributed to the high organic matter content at the surface compared to the lower horizons.

The forest soil has the highest OC content of 1.43 g/kg the garden soil and fertilized field recorded the least with a value of 1.24g/kg which is significantly not different from what was obtained for the pasture field (1.27 g/kg) (Table 4.1). The high OC in the forest may be attributed to high organic matter content. For the surface soil (Table 4.2), the garden soil (1.6) although similar to the forest (1.4) had the highest OC values which is not different from the pasture field (1.0) while fertilized field (0.5) had the least. However, the pasture field and fertilized field are significantly not different.

The total nitrogen (TN) expressed in g/kg showed no variation with land use and its mean value ranged from 0.47 for forest soil to 3.03 for garden soil (Table 4.1), while for the surface soil (Table 4.2), garden soil (mean 6.5) is higher than the forest soil (mean 3.7). Pasture field (mean 2.8) is statistically similar to forest soil while fertilized field had the least (mean 1.9). The least TN observed for fertilized field might be attributed to N loss through either plant uptake, leaching and or volatilization while highest TN content recorded for garden soil may be as a result of the fact that organic wastes contain high concentration of total N (Mbagwu and Piccolo, 1990). It was also reported by Adediran *et al*., (1999) that in every ton of municipal wastes added to soils, 16.5kg N, 21.4 kg P, 17.3kg K and 120.6kg Ca were supplied.

The garden soil recorded the highest available P (mean 4.07) although fertilized field with a (mean 2.15) and the forest soil (mean of 2.10) (Table 4.1). Pasture field which recorded the least (mean 1.25) is statistically not different from fertilized IAR farm. However, the different land use did not affect the Av-P content of the soil. Surface soils (Table 4.2), recorded higher values, fertilized field had the highest P concentration of 10.15 mg/kg while the garden soil had the least P concentration of 4.61 mg/kg. Pasture field with P concentration of 4.79 mg/kg and the forest soil with concentration of 5.43 mg/kg were significantly not different from values obtained for the garden soil. The Av-P was observed to decreased with depth, although Iris *et al.* (2009) had reported that mineral P fertilization resulted in the building up of plant available P in the top soil compared to non-fertilized plots and decreased with increasing soil depth.

4.2 Effect of Land use on Soil Texture and Bulk Density

The data for particle size distribution of the various horizons and surface soils is presented in Tables 4.1 and 4.2 respectively and showed no variation with land use. Silt and sand recorded higher values for the surface soils [(193.33 - 233.33 g/kg), (661 – 741 g/kg) respectively] compared to the profile soils with values of 153 – 235 g/kg and 516 – 656 g/kg respectively. The reverse is the case for the horizon clay content with a value of 159 - 244 g/kg and surface soils with a clay content of 65.67 - 105.67g/kg, indicating possible clay movement (eluviation) from the top layer to the layer below. These findings were in line with others (Habtamu e*t al*., 2014 and Moges *et al*., 2013) who showed increased clay fraction with increasing depth. The soil texture is sandy loam at the surface and sandy clay loam at the lower horizons except in the case of fertilized field. This is an indication of the homogeneity of soil forming processes and similarity of parent materials (Forth, 1998). However, over a very long period of time, pedogenesis processes such as erosion, deposition, eluviation, and weathering can change the soil texture (Brady and Weil, 2002).

The bulk density values (Mg/m^3) are presented in Tables 4.1 and 4.2 for horizon and surface soils respectively. The bulk density for horizon soils ranges from (mean 1.36) for the forest soil to (mean1.65) for the garden soil, while for surface soils, fertilized field recorded the highest value (mean 1.51) which is statistically similar to the pasture field (mean 1.44). The values observed for

Table 4.3: Mean Concentration of Extractable Iron and Aluminium oxides (ppm) of the Profile soil samples

Location	Depth (cm)	Fe_d	Fe_{ox}	Al_d	Al_{ox}
Pasture Field	0-27	33.44	4.47	18.60	0.93
	27-69	32.77	3.79	39.00	4.96
	69-120	28.73	5.82	33.54	3.95
Fertilized Field	0-20	30.75	4.47	11.85	2.37
	20-44	33.44	3.79	51.35	2.37
	44-110	30.08	3.12	31.67	4.67

	110-182	30.08	4.47	39.00	0.22
Garden	0-10	34.12	3.79	15.59	0.36
	10-30	32.10	4.47	33.54	0.50
	30-47	29.40	3.79	36.99	5.82
	47-70	30.75	4.47	0.72	3.23
Forest	0-17	38.84	5.14	0.65	3.81
	17-69	40.86	3.79	0.07	4.53
	69-97	40.00	4.47	1.65	4.53
LSD		2.48^{**}	1.09^{NS}	7.54^{**}	2.62^{NS}

Table 4.4: Mean extractable Iron and Aluminium oxides (ppm) of the Surface Soils under the Different Land use types

Depth (cm)	**Fe_d**	**Fe_{ox}**	**Al_d**	**Al_{ox}**

Pasture field	0-20	17.27	6.06	6.07	0.62
Fertilized field	0-20	23.04	8.77	5.93	0.68
Garden	0-20	56.66	15.22	5.59	0.63
Forest	0-20	20.66	9.11	4.37	0.53
LSD		7.74**	4.06**	1.22*	0.06**

the garden soil (1.27) although similar to that obtained for the pasture field was not statistically different from that of the forest (1.18) which is the least. The highest bulk density observed for Sabo vegetable garden soil despite its high content of organic matter and fertilized field might be attributed to the fact that more intensive cropping (year-round cultivation) gave rise to higher bulk density as frequent tilling increases compaction.

4.3 Pedogenic forms of Iron and Aluminum oxide

The data on pedogenic forms of iron and aluminum oxides content of the profile and surface soils are presented in Table 4.3 and 4.4 respectively. The citrate bicarbonate dithionite extractable iron oxide (Fe_d) values (mg/l) varied significantly with land use. Forest soil had the highest (mean 39.9) which is significantly different from the other land use. Higher Fe_d observed for the forest might be attributed to the presence of plinthite at the shallower depth. The oxalate extractable iron oxide (Fe_{ox}) for profile soils showed no different among the land use and ranged from 3.96 - 4.69 mg/l while for the surface soils, both Fe_d and Fe_o recorded lower values except for the garden soil where the highest mean values are 56.66 and 15.22 respectively. This might be due to possibly high concentration of Fe in the municipal waste. Dithionite extractable Al_d (mg/l) varied significantly with land use and is presented in Table 4.3 and 4.4 for profile and surface soils respectively. Fertilized field soil (mean 33.47) recorded the highest Al_d values for profile soils although not different from the pasture field (mean 30.47) and the garden soil (mean 21.71) while the forest soil recorded the least value of 0.79. Lower Al_d values were observed for surface soil ranging between 4.37 - 6.07mg/l. The oxalate extractable Al_o (mg/l) showed no variation with land use and ranged from 2.41 - 4.29 for profile soils while for the surface soil, fertilized field has the highest mean Al_o value of 0.68 although not different from the pasture field that has 0.62 and the garden soil having 0.63 but significantly not similar to that of the forest soil having a value of 0.53. However, forest recorded the least Al_o content. The higher values observed for Fe_d and Al_d confirmed the dominance of crystalline forms of the oxides over the amorphous form as earlier observed by Kparmwang (1993), Maniyunda (1999), Raji *et al*. (2000) and Samndi (2012).

4.4 Trace elements content of the soils

The selected trace elements determined by XRF included copper (Cu), iron (Fe), manganese (Mn), lead (Pb), zinc (Zn) and titanium (Ti) and data obtained (mg/kg) are presented in Table 5. Among all trace elements determined, only iron (Fe) varied significantly with land use.

4.4.1 Copper (Cu)

Concentration of copper (Cu) ranges from 40 - 50 mg/kg (Table 4.5), it is rated, according to Esu (1991) micronutrient fertility rating, as generally high (> 2mg/kg) lower than the common range of 2-250mg/kg Cu in soil (WHO, 1998).Although the distribution of this element in the soil profiles was fairly uniform reflecting that the element is relatively immobile. The values obtained in this study were higher than the range of values earlier reported by others (Oyinlola and Chude, 2010; Kparmwang *et al*., 1998) in soils of the region and soils elsewhere (Mulima *et al*., 2015; Biwe, 2012; Mustapha and Singh, 2003). The high values obtained might be attributed to management practice and/or parent material in the region. Even though Maniyunda (2012) had earlier observed high Cu content in the soil of the region, it could be predicted that in the nearest future, there is tendency of Cu toxicity to occur in these soils.

4.4.2 Iron (Fe)

The garden soil has mean Fe concentration of 12680 mg/kg which is the least value for the element followed by the fertilized field with a mean value of 13430mg/kg. Although forest soil has the highest mean values of 19720mg/kg, it is not different statistically from the values observed for the pasture field having a mean value of 18290mg/kg. However, Fe was the most abundant of all the metals observed in this study. Contrary to the Fe distribution pattern observed by Abdu *et al*.(2011a) in urban soils under long term irrigation and Zaccone *et al.*(2007) in peat bog, the concentration of Fe in this study was observed to increase with depth indicating that Fe is of lithogenic or pedogenic origin. According Lindsay (1979), the values observed in this study is lower than common range in soil 7,000 – 550,000mg/kg. The values observed were higher than values reported by Abdu *et al*. (2011a); Mulima *et al*. (2015); Oyinlola and Chude (2010); Mustapha and Singh (2003) and Kparmwang *et al*. (2000). Generally, available Fe is high in the tropical soils (Oyinlola and Chude, 2010), but the high Fe values recorded for the forest soils and pasture field soils might be attributed to the plinthite observed at a shallower depth in this locations.

4.4.3 Manganese (Mn)

The extractable Mn content of the soils did not show any variation with land use as there was no significant difference between the values observed in all the land use patterns. The distribution pattern of Mn in this study followed similar trend observed by Oyinlola and Chude (2010). According to WHO permissible limits, the soils' Mn concentration was lower than its range in the soil (50 - 350mg/kg). Mn content observed in this studies were higher than values reported earlier in northern Nigeria savanna soils (Kparmwang *et al.*,1995; Mustapha et al, 2003; Oyinlola and Chude, 2010; Mulima *et al*., 2015). However, Maniyunda, (2012) had earlier reported high Mn concentration in the soil of the region.

Location	**Depth (cm)**	**Cu**	**Fe**	**Mn**	**Pb**	**Zn**	**Ti**
Pasture field	0-27	40	13090	90	3300	0.0	2400

	27-69	50	21290	20	0.000	10	1890
	60-120	60	20480	20	0.000	20	2080
Fertilized field	0-20	20	6180	60	0.000	0.0	1920
	20-44	40	15220	70	2900	20	1970
	44-110	40	15970	10	0.000	0.0	1910
	110-182	40	16330	60	0.000	10	1980
Garden	0-10	60	13350	80	4400	40	2590
	10-30	40	12260	60	0.000	10	1760
	30-47	40	12800	10	0.000	0.0	1580
	47-70	30	12320	20	0.000	10	1770
Forest	0-17	40	13360	80	3100	0.0	1920
	17-69	50	23050	30	0.000	0.0	1830
	69-97	40	22750	70	0.000	0.0	1890
LSD		**18^{NS}**	**4042.6****	**43^{NS}**	**2177^{NS}**	**21.7^{NS}**	**350.4^{NS}**

Table 4 5: Mean Values (XRF) Concentration of Trace Elements (mg/kg) in the Soils under the Different Land Use Types

4.4.4 Lead (Pb)

In all the land use, Pb was only observed at the surface horizon except in the case of the fertilized field where it was recorded at the subsurface horizon. Pb has been considered as the most widespread contaminant of the metals studied (Oliver, 1997), it concentration in this study are higher than the range of values reported by Agbenin, 2002 and Abdu *et al*. (2011a and b). The pattern of Pb distribution in the soil profile reflect that it is relatively immobile. This is consistent with the findings of Agbenin (2002) and Abdu *et al*. (2011a and b) who observed limited Pb movement in soils of the northern Nigerian Savanna. Although lead is primarily of pedogenic origin but elevated concentrations may reflect anthropogenic pollution (Abdu *et al*., 2011a). Naturally, Pb is inherited from soil parent material such as galena which slowly oxidizes during weathering (Kabata-Pendias, 2001). The trend for high concentration of Pb in the upper depths may be as a result of anthropogenic enrichment through human activities. It could also reflect the metals affinity for organic matter (Agbenin, 2002). Lead fixation by organic matter has been shown to be more important than fixation by hydrous oxides (Li and Shuman, 1996), and the surface horizons of most soils contain higher organic matter relative to the successive lower horizons.

4.4.5 Zinc (Zn)

The extractable Zn content was not recorded in forest soil. The highest mean values (20mg/kg) of Zn although lower than the common range in soil (10 - 300mg/kg; WHO, 2001) was observed at the surface soil of the garden. Pasture field and the fertilized field have similar values of 10mg/kg of Zn in the subsurface horizons. The values recorded for these soils fall above the 1.2 – 4. 0 mg/kg obtained by Kparmwang and Malgwi (1997), 1.5-2.1mg/kg reported by Oyinlola and Chude (2010) and 0.48 to 0.78mg/kg reported by Mustapha *et al.* (2010) for the soils in the same region. Zinc had been reported to be generally of low mobility in soils (Chesworth, 1991) and has a tendency of being adsorbed on clay size particles (Sims and Johnson, 1991; Alloway, 2008).

4.4.6 Titanium (Ti)

The soils from the pasture field recorded the highest values for Ti, followed by soils of the fertilized field. However, values obtained for fertilized field were not significantly different from values recorded for the garden soil as well as the forest. The total Ti concentration observed in this study did not show variation with land types. The distribution of this element in the profile is fairly uniform reflecting that its relatively immobile. A similar distribution pattern was also observed by Abdu *et al*. (2011a) who reported that the fairly uniform distribution of this element in the profile suggests that this element is most likely derived from anatase and rutile minerals. Titanium has very low mobility under almost all environmental conditions, mainly due to the high stability of the insoluble oxide TiO_2 under all, but the most acid conditions, *i.e.* below pH 2 (Brookins, 1988). The global average for Ti in soil has been estimated as 0.33% Ti, although it is lower for podzols and Histosols (Kabata-Pendias, 2001). The values observed in this study were slightly lower than the range of 2200mg/kg- 17900mg/kg reported by Raji *et al*. (2015) and 4,620mg/kg - 14,300mg/kg reported by Abdu *et al*. (2011a) for urban soils under long term waste water irrigation in Kano, Nigeria.

4.5 Geochemical Evaluation

Mass balance calculation (Table 4.6) for the trace elements was negative for almost all the metals reflecting metal depletion compared to the natural background concentration of these elements. However, Sabo vegetable garden soil showed gain in Cu concentration (11.2% and 19.62%) for surface and subsurface horizon respectively, Mn (118.35%) at subsurface and Pb (5.23%) at the surface. This might be attributed to the fact that municipal waste contains toxic heavy metals like Zn, Cu, Pb, Cd as earlier reported by several researchers (Chikelu, 1998; Anikwe, 2000; Anikwe and Nwobodo, 2002). Copper accumulation (36%) observed at the subsurface horizon of NAPRI pasture field might be due to high Cu content of the parent material as well as Cu additives added to animal feed which enriches the pasture field through droppings. Manganese (122%) accumulation observed at the subsurface horizon of IAR fertilized farm possibly result from long term fertilization. This is in line with the findings of Czarnecki and Düring (2015) who observed an increased in Cd, Cu, Mn, Pb and Zn concentration after 14 years of mineral fertilization. The gains in Fe (0.01%, 0.03%) and Mn (2.86%) concentration showed at Afaka subsurface horizon and Pb (0.01%) at surface horizon might be attributed to high content of these metals in the localized parent material.

The contamination factor values for all the trace elements in virtually all the locations was below 2 indicating no to medium contamination (Table 4.7) except Mn that showed moderate contamination at the subsurface horizons of fertilized IAR farm (C_f 2.33) and Sabo vegetable garden soil with C_f value of 2.0.

Geo accumulation (Table 4.8) values for all the trace elements in all the locations were far below 1 revealing the unpolluted nature of the study areas. Several researchers had earlier reported the non-polluted nature of the Nigerian Savanna soils (Raji *et al.*, 2015; Abdu *et al.*, 2011b; Agbenin and Felix-Henningsen, 2001).

Enrichment factor values (Table 4.8) for most of the elements across the locations were below 1and for a very few slightly above 1. This indicated that the trace elements originated from the parent materials of the study areas. The fact that accumulation of Cu, Mn, Fe and Pb occur in some locations does not mean the soils were anthropogenically contaminated since their C_f and I_{geo} values revealed no contamination but might be due to high concentration of these metals in the localized parent material above the world average.

Table 4.6: Geochemical Balance of the Trace Elements in the Soils of the Different Land Use Types

	Depth (cm)	Cu	Fe	Mn	Zn	Pb	Ti
Pasture field	00-27	-20.0	-21.62	-7.00	-100	-14.83	0.00
	27-69	-99.03	-10.56	-35.45	-100	-100.00	0.00
	69-120	36.0	-18.18	-74.04	-100	-100.00	0.00
Fertilized field	0-20	-50.0	-53.75	-20.00	-100	-100.00	0.00
	20-44	-25.69	-38.66	122.94	-100	-100.00	0.00
	44-110	-1.05	-30.52	-85.86	-100	-100.00	0.00
	110-182	-4.55	-31.46	-19.55	-100	-100.00	0.00
Garden	0-10	11.2	-25.93	-24.02	-100	5.23	0.00
	10-30	-16.82	-44.69	118.35	-100	-100.00	0.00
	30-47	19.62	-32.68	-82.91	-100	-100.00	0.00
	47-70	-19.92	-42.16	-69.49	-100	-100.00	0.00
Forest	0-17	-100.0	-44.75	-6.25	-100	0.01	0.00
	17-69	-100.0	0.01	10.00	-100	-100.00	0.00
	69-97	-100.0	0.03	2.86	-100	-100.00	0.00

Table 4.7: Contamination Factor of Trace Elements in the Soils of the Different Land Use Types

	Depth (cm)	Cu	Fe	Mn	Pb	Zn	Ti
Pasture field	0-27	1.00	0.98	1.23	1.06	0.00	1.25
	27-69	1.00	0.92	0.66	0.00	0.00	1.03
	69-120	1.50	0.90	0.29	0.00	0.00	1.10
Fertilized field	0-20	0.50	0.46	0.75	0.00	0.00	1.00
	20-44	0.80	0.66	2.33	0.00	0.00	1.08
	44-110	1.00	0.70	0.14	0.00	0.00	1.01
	110-182	1.00	0.72	0.86	0.00	0.00	1.05
Garden	0-10	1.50	1.00	1.00	1.42	0.00	1.35
	1-30	0.80	0.53	2.00	0.00	0.00	0.96
	30-47	1.00	0.56	0.14	0.00	0.00	0.84
	47-70	0.75	0.54	0.29	0.00	0.00	0.94
Forest	0-17	1.00	1.00	1.00	1.00	0.00	1.00
	17-69	1.00	1.00	1.00	0.00	0.00	1.00
	69-97	1.00	1.00	1.00	0.00	0.00	1.00

Table 4.8: Geo-accumulation Index of the Trace Element in the Soils under the Different Land Use

	Depth	Cu	Fe	Mn	Pb	Zn	Ti
Pasture field	0-127	0.05	0.00	0.00	0.38	0.00	0.00
	27-69	0.06	0.00	0.00	0.00	0.00	0.00
	69-120	0.07	0.00	0.00	0.00	0.01	0.00
Fertilized field	0-20	0.03	0.00	0.00	0.00	0.00	0.00
	20-44	0.05	0.00	0.00	0.37	0.01	0.00
	44-110	0.05	0.00	0.00	0.00	0.00	0.00
	110-182	0.05	0.00	0.00	0.00	0.00	0.00
Garden	0-10	0.07	0.00	0.00	0.40	0.02	0.00
	10 – 30	0.05	0.00	0.00	0.00	0.00	0.00
	30-47	0.05	0.00	0.00	0.00	0.00	0.00
	47-70	0.04	0.00	0.00	0.37	0.00	0.00
Forest	0-17	0.05	0.00	0.00	0.00	0.00	0.00
	17-69	0.06	0.00	0.00	0.00	0.00	0.00
	69-97	0.05	0.00	0.00	0.00	0.00	0.00

Depth (cm) Cu Fe Mn Pb Zn Ti

Table 4.9: Enrichment Factor of Trace Elements in the Soils of the Different Land use Types

Pasture field	0-27	0.80	0.78	0.93	0.85	0.00	0.00
	27-69	0.97	0.89	0.65	0.00	0.00	0.00
	69-120	1.36	0.82	0.26	0.00	0.00	0.00
Fertilized field	0-20	0.50	0.46	0.80	0.00	0.00	0.00
	20-44	0.74	0.61	2.23	0.00	0.00	0.00
	44-110	0.99	0.69	0.14	0.00	0.00	0.00
	110-182	0.95	0.69	0.80	0.00	0.00	0.00
Garden	0-10	1.11	0.74	0.76	1.05	0.00	0.00
	10-30	0.83	0.55	2.18	0.00	0.00	0.00
	30-47	1.20	0.67	0.17	0.00	0.00	0.00
	47-70	0.80	0.58	0.31	0.00	0.00	0.00
Forest	0-17	0.00	0.55	0.94	1.00	0.00	0.00
	17-69	0.00	1.00	1.10	0.00	0.00	0.00
	69-97	0.00	1.00	1.03	0.00	0.00	0.00

4.6 Mineralogy of the Clay Fraction

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material. It identifies and characterize the nature of clay mineral as well as provide information which cannot be determine by any other method. Identification of the minerals contained in the clay fraction was done based on the basal spacing values expressed in Armstrong (Ǻ) and the 2 thetha values.

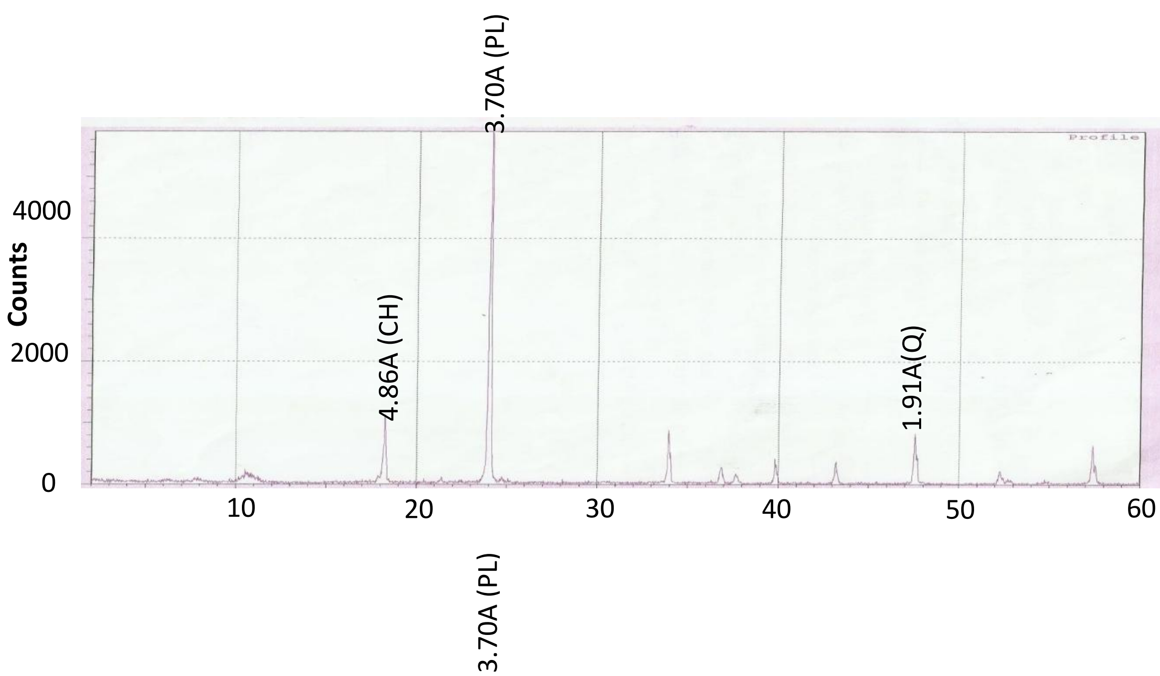
4.6.1 Mineralogical Characteristic of NAPRI Pasture Field Soil

Results of XRD for NAPRI pasture field (Table 4.10) present nine (9) strongest peak with phlogopite (3.70Ǻ) dominating both the surface and subsurface horizons (Bt1 and Bt2) followed by chrysotile (4.90Ǻ). Other minerals detected are quartz (1.91Ǻ) in the surface horizon and muscovite (1.60Ǻ) in the subsurface horizons. The occurrence of phlogopite and muscovite indicate the dominance of non-expanding minerals and further explains the reasons for the high K content of this study area. The major sources of non-exchangeable K in soils are K-rich 2:1 clay minerals (Raheb and Heidari, 2012). Ghosh and Singh (2001) reported that soils with high content of 2:1 clay minerals (micas, vermiculite and high-layer-charge smectite) contain larger amounts of non-exchangeable K than those with kaolinite and other siliceous minerals.

Depth	2thetha	d(A)	I/I1	Chemical formula	Mineral name
0-27	24.0203	3.70185	100	$KMg_3(Si_3Al)O_{10}(OH)_2$	Phlogopite
	18.2497	4.85729	17	$Mg_3(Si_2\text{-}xO_5)(OH)_4\text{-}4x$	Chrysotile
	47.535	1.91129	16	SiO_2	Quartz
27 – 69	24.0131	3.70295	100	$KMg_3(Si_3Al)O_{10}(OH)_2$	Phlogopite
	18.2606	3.70295	34	$Mg_3(Si_2\text{-}xO_5)(OH)_4\text{-}4x$	Chrysotile
	57.4164	1.60363	14	$KAl_2(Si_3Al)O_{10}(OH,F)_2$	Muscovite

Table 4.10: Mineralogical Characteristic of Soils of the NAPRI Pasture Field Indicating the Strongest Peaks

69 – 120	23.8625	3.72597	100	$KMg_3(Si_3Al)O_{10}(OH)_2$	Phlogopite
	18.0625	4.90721	11	$Mg_3(Si_2 -xO_5)(OH)_4 -4x$	Chrysotile
	57.2848	1.60701	7	$(KH_{30})Al_2Si_3AlO_{10}(OH)_2$	Muscovite



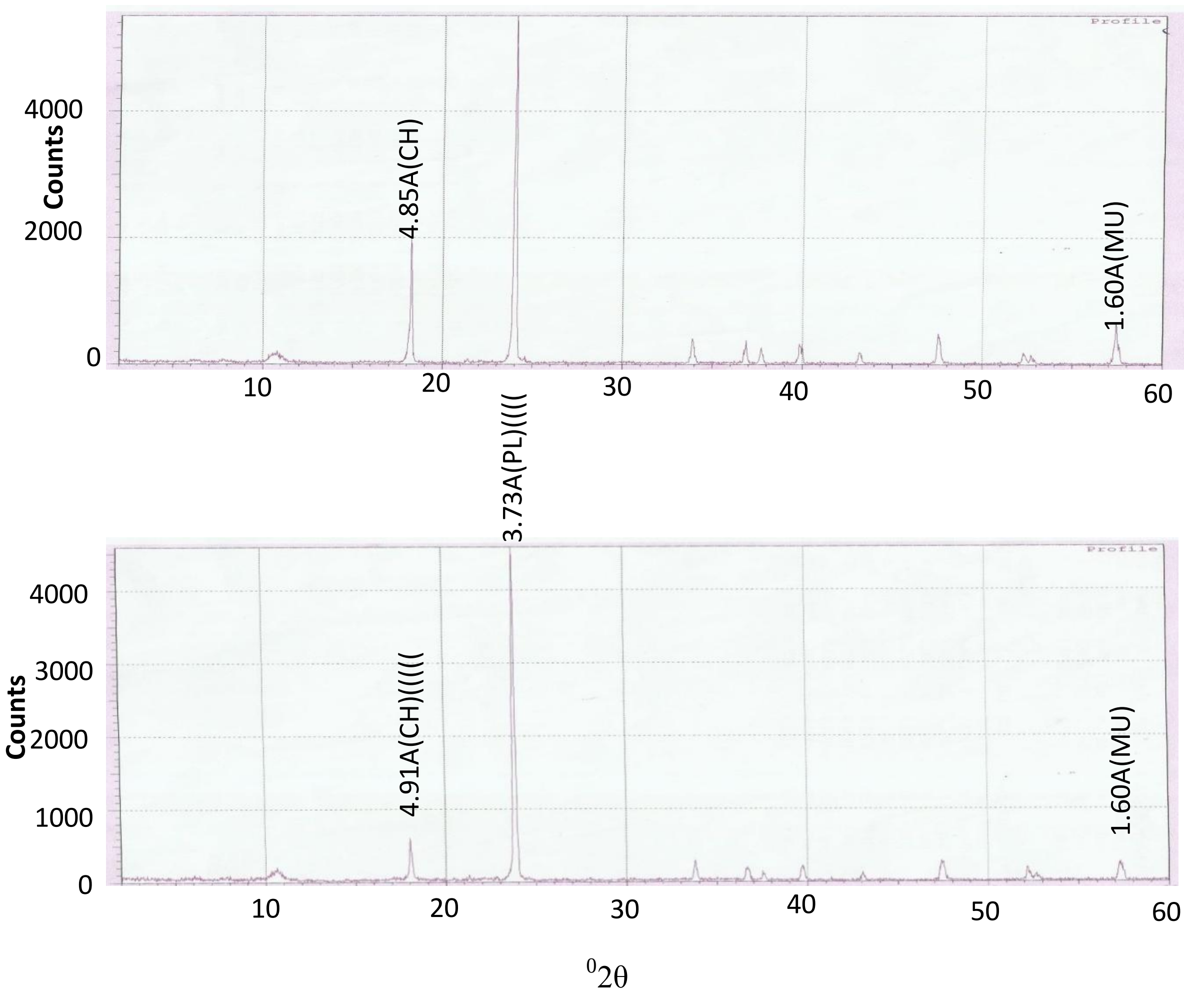


Fig 5. X-ray diffractograms of clay particles of NAPRI pasture showing Ap, Bt1 and Btc horizons. CH= Chrysotile, Q = Quartz, PL = Phlogopite, MU = Muscovite

4.6.2 Mineralogical Characteristics of Fertilized IAR Farm Soil

IAR fertilized farm (Table 11) was dominated by beddeyelite (3.69Ǻ) followed by saponite (3.62Ǻ) and Quartz (1.91A) in the surface horizon (AP). Montmorillonite (3.69Ǻ), kaolinite (3.57Ǻ) and cristobalite (3.58Ǻ) dominated the subsurface horizon reflecting an increased level of weathering. Samndi (2012) reported that the dominance of montmorillonite, kaolinite and magnetite are indication of increased level of weathering. The wide variation in mineral composition of the soil influenced their mineralogical classification to be mixed mineralogical class (Soil Survey Staff, 2010).

Table 4.11: Mineralogical Characteristics of Soils of the Fertilized IAR Farm Indicating the Strongest Peaks

Depth	2thetha	d(A)	I/II	Chemical formula	Mineral name
0 – 20	24.1121	3.68797	100	ZrO_2	Baddeyelite
	24.5983	3.61616	19	$Mg_x(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2.4H_2O$	Saponite
	47.6491	1.9070	15	SiO_2	Quartz
20 – 44	24.0699	3.69434	100	$KMg_3(Si_3Al)O_{10}(OH)_2$	Montmorillonite
44 – 110	24.9111	3.57146	100	$Al_2Si_2O_5(OH)_4$	Kaolinite
110 – 182	24.8749	3.57657	100	SiO_2	Cristobalite

3.67A (BD)

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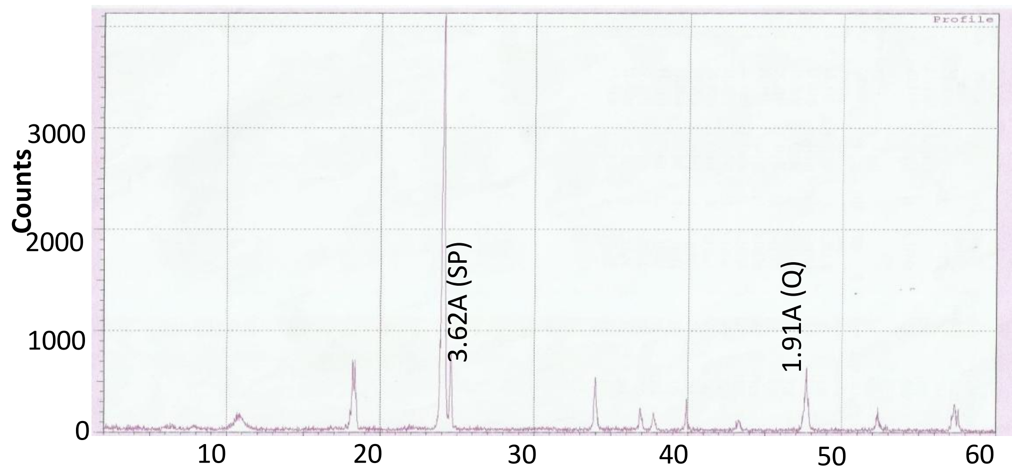


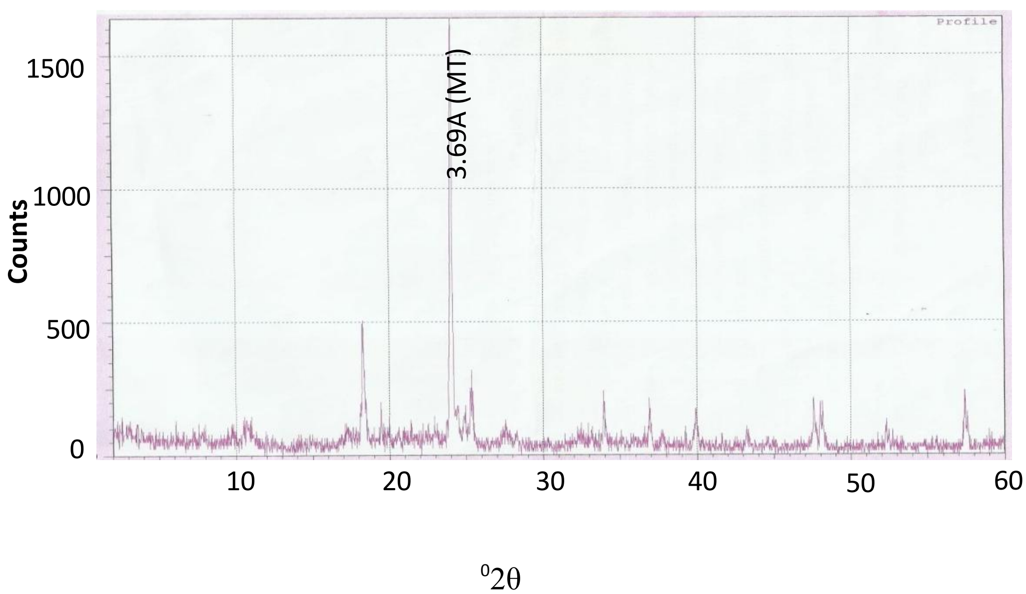


Fig 6. X-ray diffractograms of clay particles of IARfield showing Ap, Bt1 horizons. BD = Baddeyelite, SP = Saponite, Q = Quartz, MT = Montmorillonite

3.57A (KN)

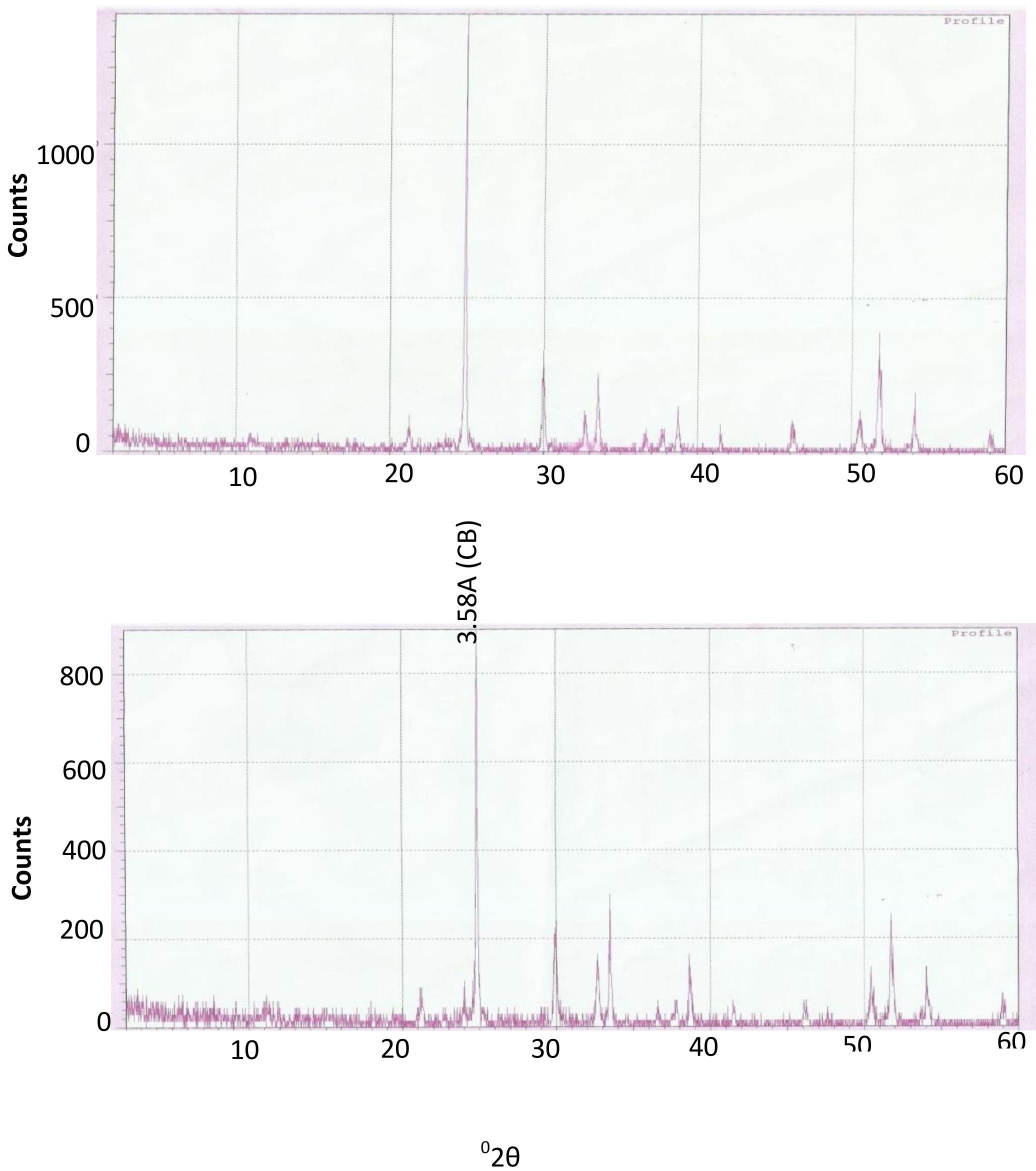


Fig 7. X-ray diffractograms of clay particles of IARfield showing Bt2 and Btc horizons. KN = Kaolinite, CB = Cristobalite.

4.6.3 Mineralogical Characteristics of Sabo Vegetable Garden Soil

In Sabo vegetable garden (Table 4.12), montmorillonite (3.70Ǻ) dominated the surface horizon followed by phlogopite (4.86Ǻ) and anthophyllite (1.91Ǻ) while hematite (3.58Ǻ) dominated the subsurface horizons. The dominance of montmorillonite is an indication of the poor drained condition of the soil of the area. Similarly, Ojanuga (1979) attributed montmorillonite to poor drainage and kaolinite to well-drained soil condition. The dominance of hematite in the subsurface horizon might be due to the presence of Fe bearing mineral in the soil of the area. More hematite is found under well drained soils than in soils with limited drainage.

Table 4.12: Mineralogical Characteristics of Sabo Vegetable Garden Soil Indicating the Strongest Peak

Depth	2thetha	d(A)	I/II	Chemical formula	Mineral name
0 -10	24.00058	3.70406	100	$KMg_2Al_3(Si_{10}Al_2)O_{30}$	Montmorillonite
	18.2315	4.8621	25	$KMg_3(Si_3Al)O_{10}(OH)_2$	Phlogopite
	47.5021	1.91254	13	$Mg_7Si_8O_{22}(OH)_2$	Anthophylli
10-30	24.8799	3.57587	100	Fe_2O_2	Hematite
30 – 47	24.6639	3.5753	100	Fe_2O_3	Hematite
47 - 70	24.0443	3.69821	100	Fe_2O_3	Hematite

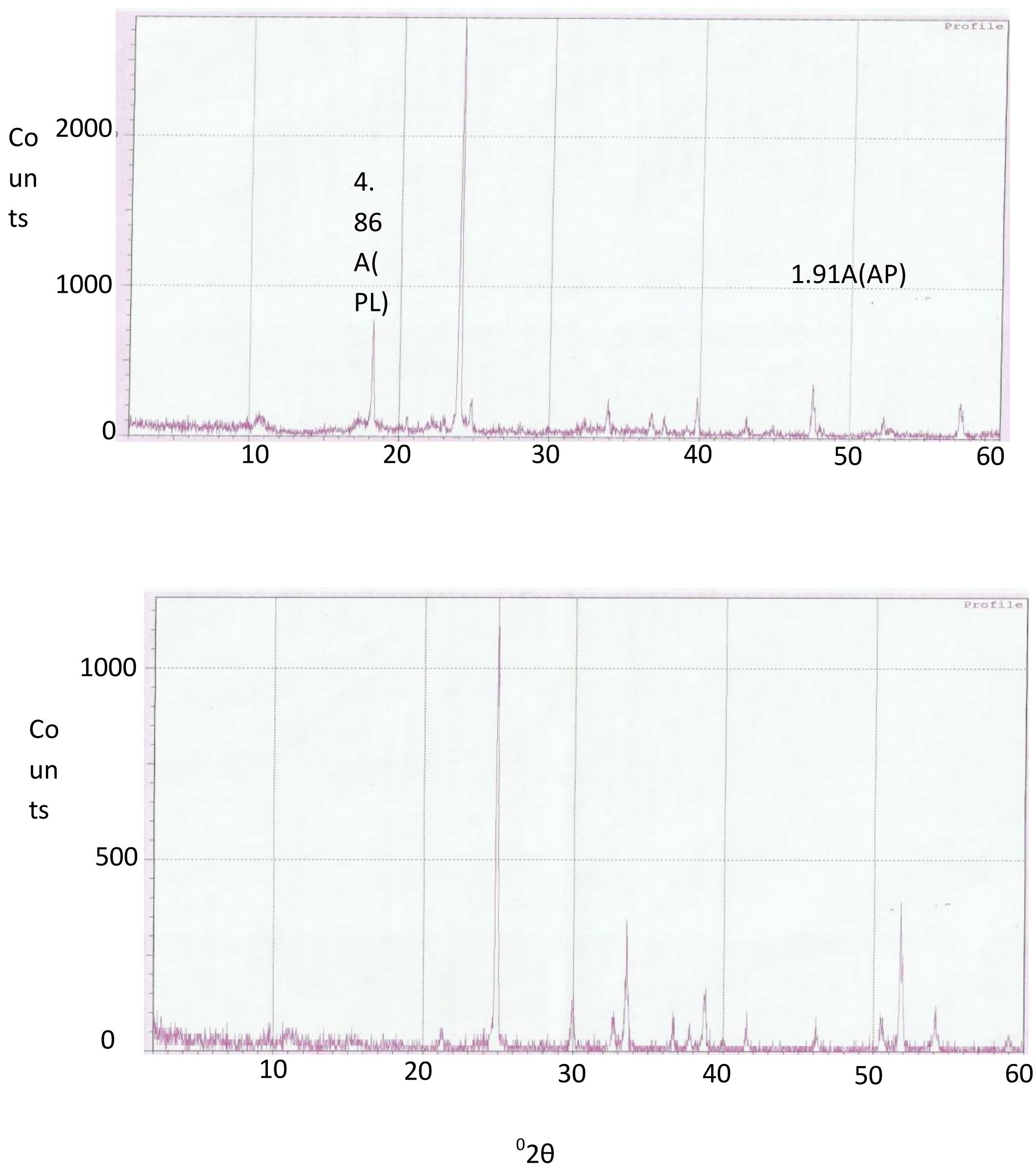
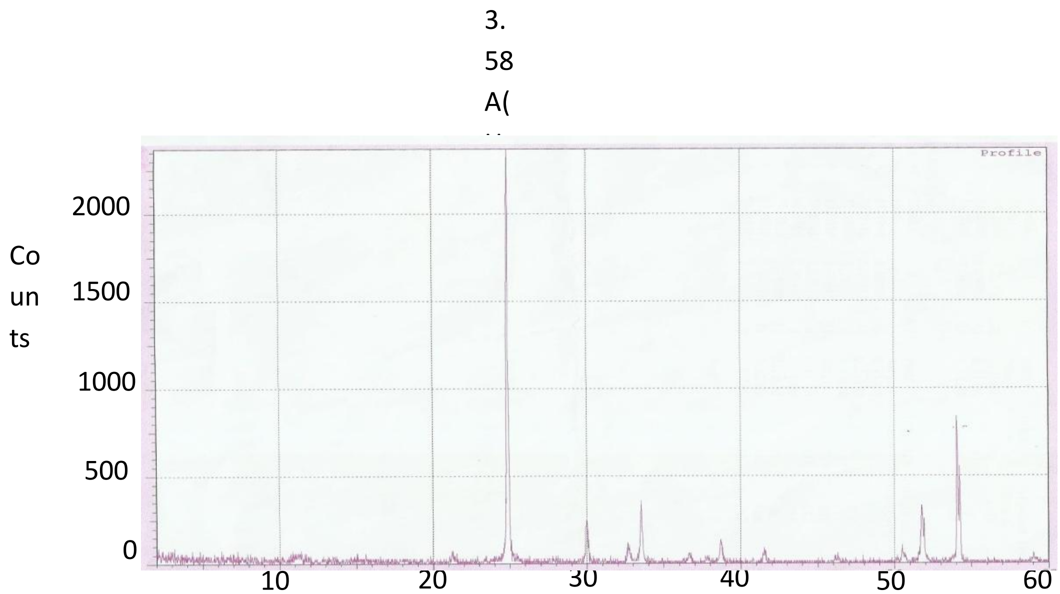


Fig 8. X-ray diffractograms of clay particles of the vegetable garden showing Ap and Bt1 horizons. MT = Montmorillonite, AP = Anthophyllite, PL = Phlogopite, HM = Hematite



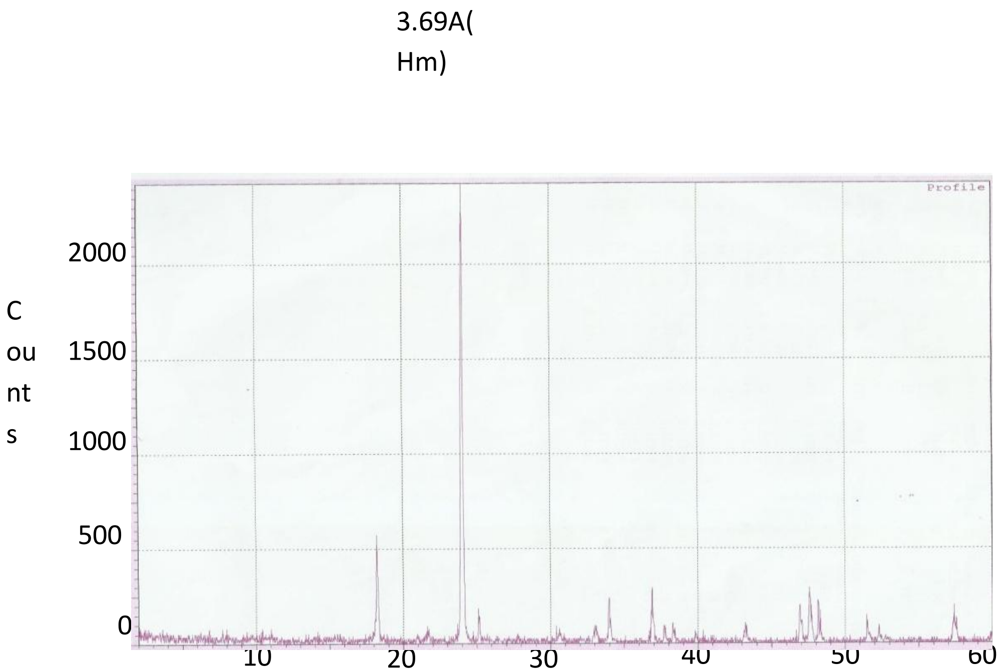


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Fig 9. X-ray diffractograms of clay particles of the vegetable garden showing Bt2 and Btc horizons. Hm = Hematite

4.6.4 Mineralogical Characteristics of Afaka Forest Soil

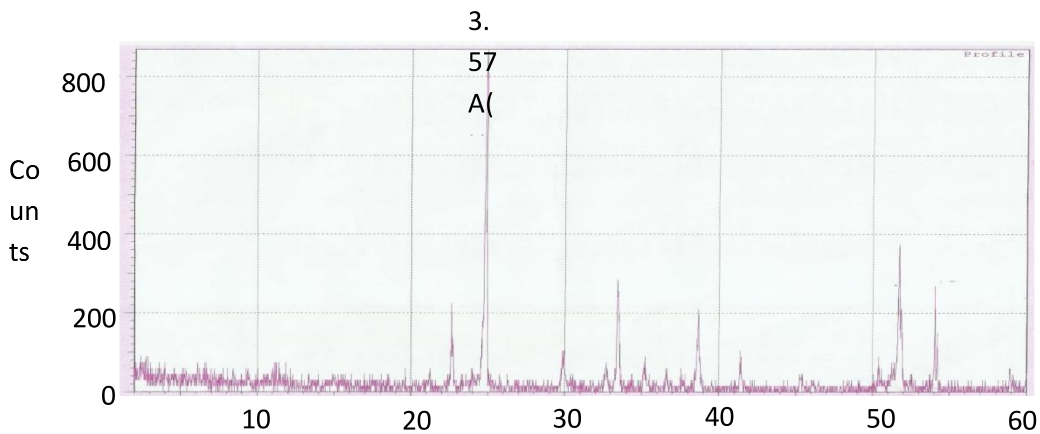
Soils of Afaka forest was dominated by hematite (3.58Ǻ, 3.71Ǻ) in the surface (Ap) and subsurface (Bt_1) horizons while phlogopite (3.71Ǻ) dominated the subsurface (Bt_2) horizon. Chrysotile (4.86Ǻ) and nacrite (1.91Ǻ) were also found in trace amount in the subsurface horizons (Table 4.13). The dominance of hematite in this soil might be attributed to high plinthite in the soil of the area. According to Yaro (2005), plinthite has the highest Fe content which occur as hematite (αFe_2O_3) and the formation of hematite is favored by warm dry condition with small amount of organic matter which is a typical condition in the tropical savanna.

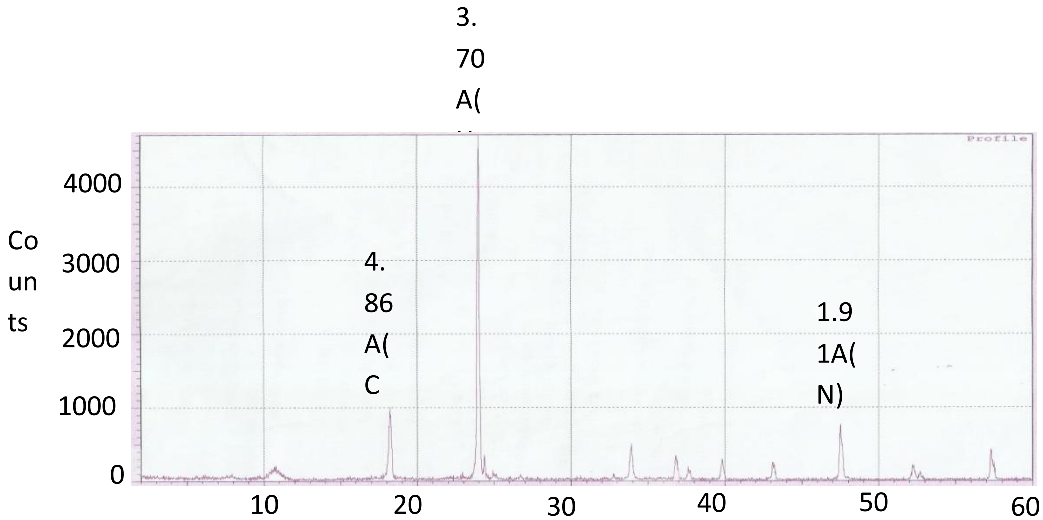
Table 4.13: Mineralogical Characteristics of Soils of Afaka Forest Indicating the Strongest

Depth	2thetha	d(A)	I/I1	Chemical formula	Mineral name
0-17	24.8654	3.57792	100	Fe_2O_2	Hematite
17 – 67	23.9802	3.70795	100	Fe_20_3	Hematite
	18.2341	4.86141	20	$Mg_3(Si_2\text{-}XO_5)(OH)_4\text{-}4X$	Chrysotile

Peaks

	47.5141	1.91208	18	$Al_2Si_3O_5(OH)_4$	Nacrite
67 – 92	23.9987	3.70514	100	$KMg_3(Si_3Al)O_{10}(OH)_2$	Phlogopite
	18.3604	4.8594	12	$Mg_3(Si_2\ \text{-}xO_5)(OH)_4\text{-}4X$	Chrysotile





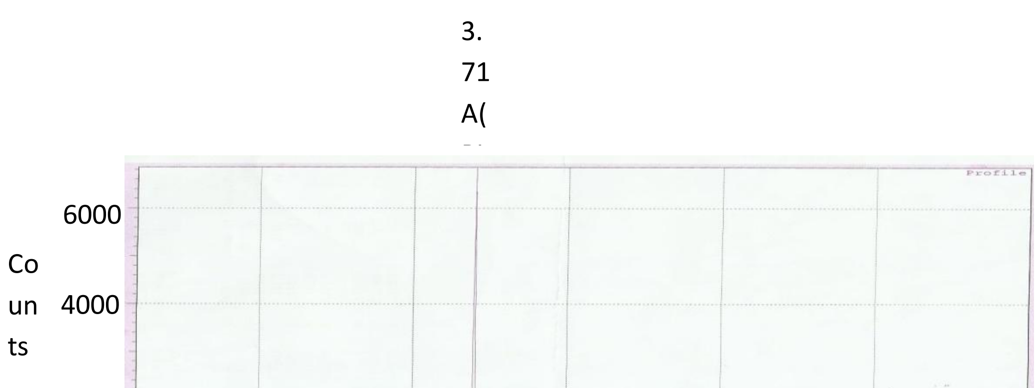


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Fig 10. X-ray diffractograms of clay particles of the Afaka forest showing Ap, Bt1 and Btc horizons, CH = Chrysotile, PL = Phogopite, N HM = Hematite

4.7 Correlation Coefficient Matrix Between the Trace Elements and Soil Properties

Pearson correlation coefficient of the pasture field (Table 4.14) indicated highly significant inter element correlation ($p \leq 0.01$). Fe and Zn correlated with each other positively (r = 0.63**) and with Cu (r = 0.97**, r = 0.80**) respectively, Fe correlated negatively with Mn (r = - 0.99**), Pb (r = - 0.99**) and Ti (r = -0.96**). Zn correlated negatively with Mn (r = - 0.69**), Pb (r = - 0.69**) and Ti (r = - 0.38*). Cu correlated negatively with Mn (r = - 0.99**), Pb (r = - 0.99**) and Ti (r = - 0.86). Ti correlated positively with Mn and Pb (r = 0.93**) while Pb and Mn observed a positive correlation (0.99**). Contrary to the findings of Abdu *et al*.(2011b) and Raji *et al*., (2015) who observed a strong positive inter element correlation, this study indicated strong but 60% negative correlation among the trace elements. This might probably result from the fact that availability of these elements is controlled by different pedogenic factors. Result of the correlation of the trace elements with pH showed the influence of pH on the origin and availability of all the trace elements probably through chemical weathering. The significant correlation between OC and Mn, Pb and Ti (r = 0.79**, r = 0.79**, r = 0.96** respectively) signifies the important role of OM in the availability of these elements probably through formation of stable organo-metal complex. Only Zn and Fe correlated with clay indicating the high affinity of these elements for clays.

In fertilized IAR farm (Table 4.15), Cu correlate with Fe ($r = 0.98^{**}$) and Mn ($r = -0.48^{*}$) indicating that Cu have similar properties, such as ionic radius, as it falls in the same group with Mn and Fe in the periodic table. Mn and Pb correlated with each other (0.49^{*}) and with Zn ($r = 0.60^{**}$, $r = 0.92^{**}$) and Ti ($r = 0.65^{**}$, $r = 0.47^{*}$) respectively. Ti correlate with Fe ($r = 0.47^{*}$) and Zn ($r = 0.78^{**}$). The strong negative correlation between the trace elements and the soil OC and clays signifies that the concentration of these elements decrease with increase OC and clay.

The correlation matrix of Sabo vegetable garden soil (Table 4.16) revealed a highly significant positive inter-elements correlation ($p \leq 0.01$). This is an indication that these elements originate from similar sources as earlier reported by Abdu *et al*. (2011b) and Raji *et al*. (2015). OC was found to correlate with Pb ($r = 0.49^{*}$), Zn ($r = 0.64^{**}$) and Ti ($r = 0.61^{**}$). Tisdale *et al.* (2003) had reported that micronutrients formed stable complexes with soil organic matter. Contradicting the results obtained by Manta *et al*. (2002) and Bhuiyan *et al*. (2010), this study showed negative correlation between the trace elements and the soil pH and clay. This implies that these elements are more soluble under acidic condition and hence more available.

Correlation matrix for Afaka forest soil (Table 4.17) showed a highly significant correlation among the trace elements except for Zn that showed no correlation with all the elements and soil properties. As the case of NAPRI pasture field soil, the inter- element relationship shown is 60% negative. Organic carbon correlate with Cu ($r = 0.94^{**}$), Mn ($r = -0.95^{**}$) and Ti ($r = -0.83^{**}$). Clay correlated with Fe ($r = 0.89$), Pb ($r = -0.90$) and Ti ($r = -0.40$) while pH correlate with Fe ($r = 0.85$) and Pb ($r = -0.87$). The correlation of the trace elements with OC, pH and clays reflect the influence of these properties on the availability of these elements.

Correlation between the free Fe and Al oxides with trace elements and soil properties is an indication of the widespread occurrence of these oxides in the soils of the region and their role in providing binding sites for the trace elements. Raji *et al*. (2015) earlier reported similar result and confirmed that free iron oxides are widely spread in the strongly weathered tropical environment and also provide adsorption sites for plant nutrients. Soils containing high amounts of clay minerals, oxides and organic matter tend to accumulate higher metal concentrations because these compounds have pronounced metal binding properties (Palumbo *et al*., 2001; Castillo-Carrión *et al*., 2007).

Table 4.14: Pearson Correlation Matrix of Trace Elements and Selected Soil Properties of NAPRI Pasture field

Parameter	Cu	Fe	Mn	Pb	Zn	Ti	OC	Clay	PH	Fed	Feo	Ald	Alo
Cu	1												
Fe	0.97**	1											
Mn	-0.99**	-0.99**	1										
Pb	-0.99**	-0.99**	0.99	1									
Zn	0.80**	0.63**	-0.69**	-0.69**	1								
Ti	-0.86**	-0.96**	0.93**	0.93**	-0.38*	1							
OC	-0.68**	-0.84**	0.79**	0.79**	-0.10	0.96**	1						
Clay	0.17	0.41*	-0.33	0.33	-0.45*	-0.65**	-0.84**	1					
pH	-0.94**	-0.82**	0.87**	0.87*	-0.96**	0.62**	0.38*	0.19	1				
Fe_d	-0.73**	-0.54**	0.61**	0.61**	-0.99**	0.27	-0.01	0.55*	0.92**	1			
Fe_o	0.35	0.09	-0.19	-0.19	0.84**	0.19	0.46*	-0.87**	-0.65**	-0.89**	1		
Al_d	0.91**	0.99**	-0.97**	-0.97**	0.48*	-0.99**	-0.92**	0.56**	-0.71**	-0.38*	-0.07	1	
Al_o	0.92**	0.99**	-0.97**	-0.97**	0.50**	-0.99**	-0.91**	0.54**	-0.72**	-0.40*	0.05	0.99**	1

* significant at $p < 0.05$, ** significant at $p < 0.01$

Table 4.15: Pearson Correlation Matrix of Trace Elements and Selected Soil Properties of IAR Fertilized Farm

Parameter	Cu	Fe	Mn	Pb	Zn	Ti	OC	Clay	PH	Fed	Feo	Ald	Alo
Cu	1												
Fe	0.98**	1											
Mn	-0.48*	-0.34	1										
Pb	0.08	0.25	0.49*	1									
Zn	0.26	0.43	0.60**	0.92**	1								
Ti	0.35	0.47*	0.65**	0.47*	0.78**	1							
OC	-0.93**	-0.97**	0.34	-0.42*	-0.51**	-0.39*	1						
Clay	0.34	0.18	-0.98**	-0.67**	-0.76**	-0.72**	-0.15	1					
pH	-0.17	-0.22	0.24	-0.67**	-0.37	0.26	0.46*	-0.07	1				
Fe_d	-0.12	0.05	0.58**	0.98**	0.86**	0.40*	-0.23	-0.72**	-0.64**	1			
Fe_o	-0.53**	-0.49*	0.76**	-0.18	0.03	0.44*	0.63**	-0.62**	0.79**	-0.08	1		
Al_d	0.72**	0.83**	0.15	0.72**	0.86**	0.71**	-0.88**	-0.34	-0.40*	0.57**	-0.30	1	
Al_o	0.05	-0.02	-0.73**	-0.01	-0.35	-0.81**	-0.15	0.66**	0.73**	-0.02	-0.86**	-0.18	1

* significant at $p < 0.05$, ** significant at $p < 0.01$

Table 4.16: Pearson Correlation Matrix of Trace Elements and Selected Soil Properties of the Sabo Vegetable Garden

Parameter	Cu	Fe	Mn	Pb	Zn	Ti	OC	Clay	PH	Fed	Feo	Ald	Alo
Cu	1												
Fe	0.90**	1											
Mn	0.77**	0.42*	1										
Pb	0.98**	0.88**	0.74**	1									
Zn	0.94**	0.79**	0.76**	0.98**	1								
Ti	0.95**	0.77**	0.81**	0.98**	0.99**	1							
OC	0.33	0.15	0.35	0.49*	0.64**	0.61**	1						
Clay	-0.62**	-0.22	-0.96**	-0.63**	-0.70**	-0.75**	-0.52**	1					
pH	-0.95**	-0.86**	-0.76**	-0.87**	-0.78**	-0.80**	-0.02	0.55**	1				
Fe_d	0.82**	0.47*	0.97**	0.84**	0.88**	0.91**	0.56**	-0.95**	-0.73**	1			
Fe_o	-0.64**	-0.90**	-0.08	-0.58**	-0.43*	-0.41*	0.25	-0.18	0.70**	-0.1	1		
Al_d	-0.04	0.03	0.01	-0.22	-0.38*	-0.33	-0.93**	0.2	-0.29	-0.23	-0.33	1	
Al_o	-0.62**	-0.22	-0.96**	-0.63**	-0.70**	-0.74**	-0.51**	0.99**	0.56**	-0.95**	-0.18	0.19	1

* significant at $p < 0.05$, ** significant at $p < 0.01$

Parameter	Cu	Fe	Mn	Pb	Zn	Ti	OC	Clay	PH	Fed	Feo	Ald	Alo
Cu	1												
Fe	0.61**	1											
Mn	-0.99**	-0.58**	1										
Pb	-0.59**	-0.99**	0.55**	1									
Zn	0.00	0.00	0.00	0.00	1								
Ti	-0.97**	-0.77**	0.96**	0.76**	0.00	1							
OC	0.94**	0.29	-0.95**	-0.27	0.00	- 0.83**	1						
Clay	0.18	0.89**	-0.15	-0.90**	0.00	-0.40*	- 0.17	1					
pH	0.10	0.85**	-0.06	-0.87**	0.00	-0.33	-0.25	0.97*	1				
Fe_d	0.87**	0.92**	-0.86**	-0.91**	0.00	-0.96**	0.65**	0.64**	0.57**	1			
Fe_o	-0.91**	-0.88**	0.90**	0.86**	0.00	0.98**	- 0.72**	-0.57**	-0.50**	-0.99**	1		
Al_d	0.71**	-0.13	-0.74**	0.16	0.00	-0.53*	0.91**	-0.56**	- 0.63**	0.28	-0.36	1	
Al_o	0.59**	0.99**	-0.55*	-1.00	0.00	-0.76**	0.27	0.90**	0.87**	-0.91**	-0.86**	-0.16	1

Table 4.17: Pearson Correlation Matrix of Trace Elements and Selected Soil Properties of the Afaka Forest

* significant at $p < 0.05$, ** significant at $p < 0.01$

4.8 Factor Analysis

To further examine the relationship between the trace elements and the soil properties, factor analysis was performed on the correlated trace elements. Factor analysis for the NAPRI pasture field revealed two factors (Table 4.18) with eigenvalues < 1 that explained 26% variation. Factor 1 (17%) positively covaries with CEC, Cu, Fe and Zn and negatively covaries with OC, pH, Mn, Pb and Ti. This association reflect the distinct pedogenic processes of formation. This further support the result of the correlation analysis. Factor 2 only describe an additional 9% of the variation with OC, CEC, clay, Zn and Ti having higher loadings. Clay having the highest factor loading reflect the affinity of Zn and Ti to clay.

IAR fertilized farm (Table 4.19) showed three factors with eigenvalues > 6 explaining more than 100% variation. Factor 1 (66%) positively covaries with the trace elements and negatively with OC. Higher loading factors (0.43 - 0.99) indicated that the trace elements from similar pedogenic source but their availability is strongly influenced by OC as they might be fixed through complexation with OM. Factor 2 accounts for more than 22% of the variation and is dominated by OC, pH, Mn, Pb, Zn and Ti. Organic carbon having higher loading further confirmed its role in the availability of the elements. 63% variation within the dataset was shown by factor 3 which is dominated by OC, pH, Mn and Zn.

Sabo vegetable garden soil showed three factors (Table 4.20 with eigenvalues > 3 that explained more than 100% of the variance. Factor 1 account for more than 79% variation and is dominated by all the trace elements and soil properties. The highest loading factor observed with pH is a reflection of the strong influence of pH on the availability of these metals. Abdu *et al*. (2011c) reported that the Nigerian savanna soil release of trace elements through pedogenesis is a pH dependent process. Factor 2 described 39% of the variance and is dominated by Fe, pH, CEC and

OC. It can be deduced that the release of Fe is strongly influenced by organic matter. Factor 3 (> 33%) reflect the strong inverse relationship existing between Mn and clays.

Afaka forest soil showed two factors (Table 4.21) with eigenvalues > 8 that explained more than 100% variation. Factor 1 account for 75% variation and positively covaries with CEC, Mn, Pb and Ti and negatively covaries with OC, pH, Cu and Fe. Factor 2 which account for 87% variance positively covaries with OC and Cu and negatively with CEC, pH, clay and Mn. It can be concluded that the availability of these elements is governed by different pedogenic processes

Table 4.18: Rotated Component Matrix of the Trace Elements and Selected Soil Properties of the Soil Samples of Pasture Field (NAPRI), loading Factors > 0.3 are Shown in Bold

Parameter	Factor 1	Factor 2
OC	**-0.653**	**0.757**
CEC	**0.653**	**-0.757**
Clay	0.136	**-0.991**
pH	**-0.947**	**-0.321**
Cu	**0.999**	-0.031
Fe	**0.959**	-0.283
Mn	**-0.981**	0.196
Pb	**-0.981**	0.196
Zn	**0.821**	**0.571**
Ti	**-0.839**	**0.544**
Eigenvalue	17.072	8.928
% of variance	81.44	89.29
Cumulative %	65.66	100

Table 4.19: Rotated Component Matrix of the Trace Elements and Selected Soil Properties of the Fertilized Field of IAR, loading Factors > 0.3 are Shown in Bold

Parameter	Factor 1	Factor 2	Factor 3
OC	**-0.989**	**0.862**	**-0.505**
CEC	**0.989**	0.041	-0.145
Clay	0.043	-0.041	0.145
pH	**-0.355**	**0.422**	**0.834**
Cu	**0.933**	**0.358**	0.018
Fe	**0.980**	0.19	0.052
Mn	-0.225	**-0.776**	**0.589**
Pb	**0.432**	**-0.887**	-0.165
Zn	**0.581**	**-0.789**	0.202
Ti	**0.518**	**-0.421**	**0.744**
Eigenvalue	13.15	6.54	6.31
% of variance	66.08	22.57	63.14
Cumulative %	50.57	75.72	100

Table 4.20: Rotated Component Matrix of the Trace Elements and Selected Soil Properties of Sabo Vegetable Garden, loading Factors > 0.3 are Shown in Bold

Parameter	Factor 1	Factor 2	Factor 3
OC	**0.558**	**-0.771**	0.306
CEC	**-0.558**	**0.771**	-0.306
Clay	**-0.781**	0.322	**0.536**
pH	**-0.838**	**-0.531**	0.127
Cu	**0.956**	0.285	0.061
Fe	**0.762**	**0.573**	0.395
Mn	**0.852**	-0.041	**-0.522**
Pb	**0.977**	0.136	0.162
Zn	**0.986**	-0.053	0.168
Ti	**0.996**	-0.04	0.082
Eigenvalue	15.278	7.33	3.392

% of variance	79.478	39.382	33.919
Cumulative %	58.76	86.95	100

Table 21: Rotated Component Matrix of the Trace Elements and Selected Soil Properties of the Soil Samples of Afaka Forest, loading Factors > 0.3 are Shown in Bold

Parameter	Factor 1	Factor 2
OC	**-0.596**	**0.803**
CEC	**0.596**	**-0.803**
Clay	**-0.689**	**-0.724**
pH	**-0.628**	**-0.779**
Cu	**-0.838**	**0.545**
Fe	**-0.942**	**-0.335**
Mn	**0.817**	**-0.576**
Pb	**0.933**	**0.361**
Zn	0.000	0.000
Ti	**0.941**	**-0.338**
Eigenvalue	16.265	8.735
% of variance	75.290	87.355
Cumulative %	65.06	100

CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS.

Soil samples were collected from Zaria and Afaka forest to assess the influence of four contrasting land use on the distribution, origin, behavior and association of Cu, Fe, Mn, Pb, Zn and Ti. Soil properties such as pH, Ca, Mg, Na, CEC, OC, Available P, clay, sand and bulk density significantly varies ($p < 0.05$) across the land uses for surface soils while only pH (H_2O), Ca, Mg, CEC and OC showed variation for pedon soils ($p < 0.01$). Among the studied trace elements, only Fe significantly varies with land use type. The high Cu, Fe and Pb concentration in the soils inferred the abundance of these elements in the soil parent material. This means that deficiency symptoms of these plant nutrients on crops grown on these soils is unlikely. Mn and Zn deficiency in the soils inferred the low content of this elements in the soil parent material. Adequate Ti concentration reflect that it has a consistent concentration throughout the profile of similar soils in the Nigerian Savanna. The significant inter-element correlation reflect that these elements originate from similar source while correlation between trace elements and soil properties (clay, OC, pH and Fe and Al oxides) point the importance of these properties in the availability of these elements. Geo accumulation index and contamination factor revealed no contamination, enrichment factor reflect no anthropogenic enrichment while mass balance evaluation showed depletion of the elements either through leaching, plant uptake or lost through weathering. Factor analysis further support the result of the correlation analysis and showed that these trace elements originated from similar pedogenic source probably, the parent material. Clay mineralogy of the soils revealed that NAPRI pasture field is dominated by 2:1 non-expanding clay mineral with traces of 1:1 clays, fertilized IAR farm had a wide variation of minerals, Sabo vegetable garden soil had 2:1 clay mineral dominating the surface horizon while the subsurface horizon is dominated by hematite. The mineralogy of Afaka forest is dominated by hematite at the surface horizon while 1:1 clay mineral dominated the subsurface horizon. Further research can be conducted to assess the influence of other land uses on the geochemistry of these elements.

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