ASSESSMENT OF THE QUALITY OF WILDLAND SOIL OF OLI FOREST KAINJI LAKE NATIONAL PARK BORGU SECTOR, NIGERIA

BY

Stephen Kayode OMOTUGBA BSc (1995), MSc (2008) (ABU)
PhD/SCIEN/02146/2009-2010

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DECLARATION

I declare that the work in this Dissertation entitled ASSESSMENT OF THE QUALITY OF WILDLAND SOIL OF OLI FOREST KAINJI LAKE NATIONAL PARK BORGU SECTOR, NIGERIA has been carried out by me in the department of Chemistry. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other Institution.

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OMOTUGBA STEPHEN KAYODE DATE

CERTIFICATION

This dissertation entitled ASSESSMENT OF THE QUALITY OF WILDLAND SOIL OF OLI FOREST KAINJI LAKE NATIONAL PARK BORGU SECTOR, NIGERIA BY STEPHEN KAYODE OMOTUGBA meets the regulations governing the award of Degree of Doctor of Philosophy of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

....
Prof. C. E. Gimba Date
Chairman, Supervisory Committee
Chemistry Department, A. B. U., Zaria

....
Prof. E. B. Agbaji Date
Member, Supervisory Committee
Chemistry Department, A. B. U., Zaria

....
Dr. K. I. Omoniyi Date
Member, Supervisory Committee
Chemistry Department, A. B. U., Zaria

....
Prof. V. O. Ajibola Date
Head of Department, Chemistry
A. B. U., Zaria

....
Prof. A. A. Joshua Date
Dean Postgraduate School
A. B. U., Zaria

DEDICATION

This Dissertation is dedicated to my wife Mrs. Josephine Omotugba, and the children, Grace, Michael, David and Rachael.

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ABSTRACT

Seasonal study of some potentially environmental toxic heavy metals Cd, Cr, Ni, Pb, Zn, and Cu in soil was carried out in five different vegetation zones of Oli Camp, Kainji Lake National Park at two different depths (0 – 15 cm and 15 – 30 cm) in the wet and dry seasons of 2011 and 2012. The vegetations are *Isoberlinia* woodland (S1), *Terminalia macroptera* woodland (S2), *Burkea African/Detarium microcarpum* woodland (S3), *Riparian* forest (S4) and *Diospyrus mespiliformis* (S5). The soil samples were analysed for physicochemical parameters and the mean heavy metal contents using atomic absorption Spectrophotometry. For the wet season of 2011 at 0 - 15 cm depth levels of metal in (mg/kg) were in the order S1: Cd (10.73 ± 2.00), Zn (14.63 ± 0.90), Pb (20.08 ± 3.40), Ni (29.14 ± 2.90), Cu (34.21 ± 0.00); and Cr (39.39 ± 2.30), and S2: Cd (11.56 ± 4.00), Ni (12.03 ± 3.45), Pb (18.97 ± 4.50), Cu (24.11 ± 2.78); Cr (47.34 ± 6.70), and Zn (85.07 ± 1.40). The values for S3: Cd (7.17 ± 2.45), Zn (12.51 ± 0.90), Pb (19.73 ± 1.00), Ni (24.67 ± 1.20), Cr (37.48 ± 2.22), and Cu (47.52 ± 2.10); S4: Cd (8.00 ± 1.30), Ni (10.93 ± 1.00), Zn (19.44 ± 2.30), Pb (19.74 ± 1.00), Cu (35.21 ± 0.00), and Cr (37.96 ± 3.00). In S5 the order: Cd (1.95 ± 0.00), Cu (7.92 ± 0.40), Ni (25.27 ± 1.80), Pb (10.74 ± 1.20), Cr (40.35 ± 2.60), and Zn (211.35±4.30) was obtained. Generally, the heavy metal level obtained for the sub soil (15 – 30 cm) was less than the to-soil counterpart in the wet season of 2011. The mean value of metals in the soils during the wet season of 2011 at 15 – 30 cm depth follow the order of Zn > Cu > Cr > Ni > Pb > Cd for the different vegetation zones studied. The levels of the metals during the dry season of 2011 were generally lower at the 0 - 15 cm and 15 – 30 cm depths compared to the wet season values. The lowest value for the dry season was Cd (0.74 ± 0.02 to 2.26 ± 0.01); and the highest was Zn (160.06 ± 0.56 to 323.08 ± 2.10) mg/kg. During the wet season of 2012, a similar trend in the level of

metals like in 2011 was obtained, with no significant difference ($P < 0.05$). The soil samples in the wet and dry seasons of 2011 had the physico - chemical parameters values: pH of 6.65 to 6.95 and 5.3 to 6.7; conductivity of 10.00 ± 2.50 to 101.50 ± 2.12 μScm^{-1}; organic matter, 1.79 ± 0.30 to 2.64 ± 0.51 in the different vegetation zones at the 0 - 15 cm and 15 – 30 cm depths respectively, the order was similar for the wet and dry season of 2012 at the two depths. The result of the sequential extraction of Oli Forest soil at the different vegetation zones shows that Cd, Cr, Ni, Pb, Zn and Cu existed in the fractions in order; residual > carbonate > Fe-MnO > Exchangeable > Organic > Water soluble fractions. High abundance of the metals in the residual fraction implies that the metals are of lithogenic origin and low mobility of the metals in the studied soil. The average potential mobility for the metals studied is in the order: Cr > Cu > Zn > Pb > Ni > Cd. The metals generally have low mobility factor (MF). An enrichment factor (EF) < 1.5 was obtained for the metals, indicating possible crustal materials or natural weathering processes as major source of the metals in the studied areas. In addition, geo - accumulation index < 1.0 was obtained for the metals indicating that the soils from the different vegetation zones of Oli Forest have background metal concentration. This study serves to create awareness on the pollution indices of heavy metals in Oli Forest of Kainji Lake National Park, and calls for the attention of stakeholders in the mitigation of metal pollutant as this is barely monitored.

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GLOSSARY AND ABBREVIATION

Glossary

Bioavailability = Metals available to the environment.

Total metal = Mean concentration of each metal studied.

Soil quality index = It is very useful and efficient method for assessing the overall soil quality.

Speciation = Chemical fractionation process of identifying and quantifying the concentration of forms by means of extraction and AAS analysis.

Abbreviations

AAS = Atomic Absorption Spectroscopy.

ANOVA = Analysis of variance.

CB = Carbonate bound

CEC = Cation exchange capacity.

DPR - EGASPIN = Department of Petroleum Resources – environmental Guidelines and Standards for the Petroleum Industry in Nigeria

DRB = Development Research Bureau.

EC = Electrical conductivity.

EX = Exchangeable

FMO = Iron-Manganese oxide.

GWRTAC = Ground Water Remediation Technologies

KLNP = Kainji Lake National Park.

mg/kg = Milligram per kilogram

NJDEP = New jersey Department of Environmental protection.

NRC = National Research Council.

OB = Organic bound

OM = Organic Matter

pH	=	Power of hydrogen
RES	=	Residual.
S1	=	*Isoberlinia* woodland
S2	=	*Terminialia macroptera* woodland
S3	=	*Burkea africana/Detarium microcarpum* woodland
S 4	=	*Riparian* foret
S5	=	*Diospyrus mespiliformis* woodland
SPLP	=	Synthetic Precipitation Leaching Procedure
TCLP	=	Toxicity Characteristic Leaching Procedure
UNEP	=	United Nation Environment Protection
USDHHS	=	United States Department of Health and Human Services
USEPA	=	United States Environmental Protection Agency
VCI	=	Van Commodities International

CHAPTER ONE

1.0 INTRODUCTION

If there is anything on earth that seems simple and ordinary, it is the soil beneath our feet. Other than farmers, people hardly think of it and when we do, we merely view it as little more than a place where grasses grow and earthworms crawl. Yet the soil is a complex, mixture of minerals and organic materials, built up over billions of years, and without it life on planet earth would be impossible (Soil, 2012).

However, background concentration of these organic materials, trace elements, phosphorus, series of anions and cations in soils are important due to recent interest in contamination potential and toxic effect of these elements on human, wildlife and the environment. High background concentration of trace elements, whether natural or anthropogenic, could result in mobilization and release into surface and subsurface water and subsequent incorporation into the food chain.

Soil factors such as organic matter, type and amount of clay, pH, and cations exchange capacity (CEC) influence the quantity of trace elements available for mobilization and release or sorption in a soil. It is believed that many savannah soils are prone to leaching and high risk of erosion under the prevailing tropical rain storms which may equally affect the mineral nutrients in soil. Kainji Lake National Park soil is not an exception. This is confirmed by the report of Milligan (1979) that nutrient levels of nitrogen and phosphorus are low, despite the relatively high organic carbon content reported by Pullan and de Leuw (1964). The nutrient values decreases regularly with depth as observed by Siderius (1974). This study assessed and evaluated the various fractions of some selected heavy metals

content, physical and chemical speciation in the soil of Oli forest at Kainji Lake National Park (KLNP), Borgu sector, Nigeria.

1.1 Game Reserves in Nigeria

1.1.1 The Place of Kainji Lake National Park

There are several National Parks in Nigeria that were established by Decree. The concept of evolution of National Parks in Nigeria was first introduced in 1979 through Decree No 46 of 1979 and later followed by Decree No 36 of 1991. A total of six National Parks were established: The nation's premier National Park (Kainji Lake National Park) was established in Kwara State by Decree No 36 of 1979. Others are Chad Basin in Borno Yobe State, (Decree No 36 of 1991) with landmass of 2, 258 km^2., Gashaka Gumti in Taraba State with a total land areas of 6,731 km^2 (Decree No 36 of 1991)., National Park in Cross River (Okavango section and Oban section) having a land mass of 4,000 km^2 (Decree NO 36 of 1991) and in 1992, Yakari Game Reserve was upgraded to the status of a National Park and thereafter handed over to the State Government of Bauchi State in 2006. Two additional Parks, Kamuku National Park, Kaduna State, and Okomu National Park were established by virtue of Decree 46 of 1999 (now, an Act).

One of the statutory responsibilities of the Nigeria National Park Service, amongst other functions is to preserve, enhance, protect and manage vegetation and wild animals in the National Parks. In order to achieve these goals enumerated above, detail understanding of the physical and the chemical properties of the soils that act as habitat to the wild animals and vegetations become very important.

Kainji Lake National Park was established in 1976. The Park is made up of two sectors namely the Zugurma sector and the Borgu sector. The total rangeland cover for Borgu

sector is approximately 3,970.83 km^2, while that of Zugurma sector is 1,370 km^2 (Aremu *et al.,* 2007). The entire Park lies between latitudes 9^o 40'N and 10^o 23'E and longitudes 3^o 30'N and 5^o 50'E (Amusa *et al.,* 2012). The vegetation of the Borgu sector is transitional between the Sudan and Northern Guinea Savannah types, while that of the Zugurma sector is typically Northern Guinea Savannah woodland (Child, 1974; DRB, 2004; Milligan, 1979).

The vegetation of Borgu sector is differentiated by hydrological, as well as soil factors into five different types viz: the *Isoberlinia* woodland, the *Terminalia macroptera* woodland, the *Burkea africana/Detarium microcarpum* woodland savannah, riparian (Child, 1974) and a distinct vegetation type of limited size, *Diospyros mespiliformis* dry forest. The ecosystem consist of a diverse fauna resources which include: lion (*Panthera leo L.*), Bush buck (*Tragelaphus scriptus pall*.), Gambia mongoose (*Mungos gambianus L.*), Western hartebeest (*Alcelaphus buselaphus pall.*) etc. Annual rangeland soil has the capacity to support high primary productivity and accumulate significantly below ground organic matter and sequester carbon, which supports climate regulation and functional nutrient cycles.

In addition, the Oli River flows from the Republic of Benin through the Borgu sector into the Niger River, which breaks into pools during dry season and serves as the only source of water for the wild animals. Long term average annual rainfall is between 900 and 1100 mm (Aremu *et al*., 2007) with a peak in July - August. Rain rarely falls between November and March. The annual evapo - transpiration in the study area ranges from 1400 to 1560 mm, with rainfall/evapotranspiration ratio ranging from 0.64 to 0.89. The mean annual relative humidity is 53%.

The study area is a region described by DRB (2004) as rural and agricultural and is the most important economic activity engaging more than 75% of the active labour force in the community. Beside crop production, the people of the area also engage in fishing and livestock production (Amusa *et al.,* 2007). Increasing population and unrestrained anthropogenic activities are impacting negatively on the rich bio - diversity of the study area. Illegal grazing, poaching, bush burning, farming, fishing and general encroachment into reserved areas are human activities threatening the protection of soil, flora and fauna in the area.

1.1.2 Soil Quality Index and Ecological Implications

Soil quality index is increasingly proposed as an integrative indicator of environmental quality (NRC, 1993), food security and economic viability (Lal, 1999). Therefore, it would appear to be an ideal indicator of sustainable land management. Soil quality index helps to assess changes in the dynamics of soil properties caused by external factors. It identifies problem areas and assesses differences between management systems and is valuable to measure the sustainability of land and soil management systems now and in the future (Doran, 1994). Soil quality index is used for assessing the overall soil condition and response to management, or resilience towards natural and anthropogenic forces. Soil quality index may be inferred from various soil indices derived from physical, chemical or biological attributes that reflect its condition and response. Soil quality is the capacity of a specific soil to function, within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and support human health and habitation (Karlen *et al.*, 1997).

Soil quality is a dynamic interaction between various physical, chemical and biological soil properties, which are influenced by many external factors such as land use, land management, the environment and socio-economic priorities. Therefore, soil quality is considered a key element of sustainable agriculture (Warkentin, 1997) because it is essential to support and sustain crops, range and woodland production and helps to maintain other natural resources, such as water, air and wildlife habitat. Therefore an integrated soil quality index based on the weighted contribution of individual soil property to maintain the soil quality may serve as a better indicator of soil quality for different land uses. Soil texture, drainage conditions and slope aspect are not well correlated with climatic parameters, but vary with land uses and control soil organic carbon (SOC) fate (Awasthi *et al.,* 2005; Tan *et al.,* 2004).However, it is related largely to vegetation and topographical features (Franz Meier *et al*., 1985).

1.2 Statement of Problem

Rangelands are valuable natural resources that provide forage for livestock as well as wildlife habitat and recreational opportunities. It regulates the quantity and quality of water for the surrounding watersheds. Rangeland soil contributes to water quality by immobilizing and transforming nutrients and contaminants, and acts as a groundwater filter. It has been identified by Malan and Van Niekerk (2005) that rangeland soil degradation can be caused by overgrazing, drought, improper recreational use, and other anthropogenic and natural stress. Information about the Kainji Lake National park (Oli Forest) soil is important for the protection of these natural resources.

Degradation of this reserved area can negatively impact the surrounding watersheds through soil erosion and desertification. Therefore, there is an urgent need for natural resource conservators of this park and others across the nation to periodically access the soil status of the rangeland. Development of data collection systems and ecological assessment methods are required to evaluate and monitor these resources (National Research Council, 1994).

Livestock overgrazing, climate change and certain types of land use could lead to a decline in rangeland condition. Arid and semi-arid ecosystems are especially prone to degradation due to climatic conditions. Anderson and Holte (1981) had observed that the time scales and vegetal dynamics associated with the recovery process is not fully understood for these ecosystems. Akinyemi (2007) had reported that this semi arid zone is prone to leaching and high risk of erosion under the prevailing tropical rain storms and agricultural practices. Depletion of soil organic matter (Kadeba, 1978 and Akinyemi, 2003) and low nutrient throughout the region due mainly to environmental conditions and cultural practices have been reported. Therefore, this study is carried out to assess the physical, selected heavy metals and the organic fractions of the soil in Oli Camp range land, at Kainji Lake National Park Borgu Sector in Nigeria.

1.3. Justification

In general, alteration in soil structure and nutrient levels affect the establishment, growth and survival of plant species and in turn lead to a change in woodland structure and composition. Akinyemi (2007) have reported the strong relationship between soil, plants, fauna composition and density in some ecosystem, thus the bio - diversity of the park is

highly dependent on the soil properties. Since plants which serve as producers greatly depend on the soil, thus assisting in maintain the food chain. As a result, this study becomes imperative as it will present an update on the seasonal variation in soil physical properties, total elemental composition, speciation study of some trace metals in the soils and the organic fractions.

1.4 Aim

The study aim at assessing the soil physicochemical and chemical speciation of selected metals status of Oli forest soils Kainji Lake National Park.

1.5 Objectives of the Study

The specific objectives towards achieving the aim are to:

I. Classify the soils of oli forest into different vegetation zones;
II. Determine the physical properties of the soils of the different vegetation zones as a function of season;
III. Determine levels of the selected metals present in soil of the various vegetation zones as function of season;
IV. Carry out speciation study of some trace metals in soil of the various vegetation zones.
V. Use soil enrichment factor and geo-accumulation index to assess the pollution level of the soils of Oli forest at the different vegetation zones.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1. Rangeland Soil Quality

Rangeland plays important roles in determining the socio-economic condition of rural people (HMGPN/NPC, 1993). The study area does not only support a large number of plant and animal species, it also provides a livelihood for Borgu people. Well managed rangelands have diversified grass species and higher carrying capacity (Hermans and Vereiujkan, 1995). Use of rangeland for enhancing animal production is viewed as a means of improving the quality of rural life (UNEP, 1979). Livestock overgrazing minimizes the availability of forage to wildlife leading to degradation of grazing land (Kunwar, 2003).

2.1.1. Soil aggregate stability

Soil forms the basis for all vegetation growth and plays a key role in the hydrological, carbon and nutrient cycles of ecosystems (Li *et al*., 2007). Soil organic matter (SOM) has been adapted as an indicator of soil fertility based on the rationale that it contributes significantly to soil physical, chemical and biological properties, that affect vital ecosystem processes of rangelands (Hopmans *et al.*, 2005).

Soil aggregate stability (SAS) is widely recognized as a key indicator of soil and rangeland health (Herrick *et al*., 2001). It is related to a number of ecosystem properties, processes, and functions, including the quantity and composition of the organic matter, soil biotic activity, infiltration capacity, and resistance to erosion. Soil aggregation has potential benefits on soil moisture status, nutrient dynamics, and erosion reduction (Sainju, 2006).

Soil aggregate stability is a good indicator of organic matter content (Li *et al*., 2007), biological activity and nutrient cycling in the soil (Amezketa, 1999). The amount of organic matter increases after the decomposition of litter and dead roots. Stable aggregates result from this process because soil biota produces material that binds particles together (Shrestha *et al*., 2007). Changes in aggregate stability may serve as early indicators of recovery or degradation of ecosystems (Amezketa, 1999).

The stability of aggregates is affected by soil texture, the predominant type of clay, extractable iron and extractable cations (Li *et al*., 2007), the amount and types of organic matter present, and type and size of the microbial population (Caravaca *et al*., 2002). Calcium ions associated with clay generally promote aggregation, whereas sodium promotes dispersion. Soils that have a high content of organic matter have greater aggregate stability, primarily after decomposition begins and microorganisms have produced chemical breakdown products (Shrestha *et al*., 2007). Any practice that leads to a decrease in soil organic matter tends to decrease the water stability of aggregates (Lu *et al*., 1998). Disturbance of the soil surface by grazing animals has beneficial and detrimental effects on aggregate stability. It incorporates litter and standing dead vegetation into the soil, increasing the content of organic matter. It also breaks the soil apart, exposing the organic matter glues to degradation and loss by erosion (Caravaca *et al*., 2002). Over-grazing that significantly reduces plant production disrupts the formation of aggregates by reducing the inputs of organic matter. Grazing is more likely to increase aggregate stability in areas where an unusually large amount of standing dead material is on the soil surface, and the risk of erosion is not increased by removal of plant material and disturbance of the soil surface (Shrestha *et al*., 2007).

2.2 Factors Affecting Metal Mobility in Soils

Soil is the main source of trace elements for plants, both as micronutrients and pollutants. Some exceptions are in situations of heavy atmospheric deposition of pollutants or from flooding by contaminated waters (Kabata-Pendias, 2004). Soil conditions play a crucial role in trace element behaviour. Several factors control the processes of mobility and availability of elements in the soil. These include: pH, electrical conductivity, and soil texture.

2.2.1 Effect of pH on metal mobility in soils

pH is generally acknowledged to be the principal factor governing concentration of soluble and plant available metals (Brallier *et al*., 1996). Several studies have shown that mobility of heavy metals is pH dependent (Iwegbue *et al*., 2006; Gonzalez-Fernandez *et al*., 1982). Metal solubility tends to increase at lower pH (Tills and Alloway, 1983; Garcia-Miragaya, 1984; Ram and Verloo, 1985; Sanchez-Camazano *et al*., 1994; Chuan *et al*., 1996; Thornton, 1996). Spent lubricating oil in soils as stated by Vwioko *et al*., (2006) and Achuba *et al*., (2008) depress pH. According to Iwegbue *et al*.,(2006) soil pH serves as a useful index of availability of nutrients, the potency of toxic substances present in the soil and the physical properities of the soil. In the study of heavy metals in soil profiles of automobile mechanics waste dumps in Nigeria, (Iwegbue *et al*., 2006) recorded a pH range of 4.80-7.06, the stated values in the study sites indicated a generally high tendency for high availability of these metals hence, this is a natural mechanism for increasing the risk of, metal uptake by plants.

The importance of pH in the solubility of metals has been demonstrated in numerous

laboratory studies. For example, Tyler (1987) predicted from leaching experiment that, at a pH of 4.2, 70 - 200 years would elapse before 10% of the Pb in an organic horizon A would have leached out of the soil, compared to 17 - 20 years at pH 2.8. The corresponding figures for Cd were reported as 6 - 20 years and 1.3 - 1.7 years respectively. Xiong and Lu (1993) observed that the solubility of Zn in soil decreased 100-fold for each unit increase in pH.

An important aspect of the effect of pH on metal mobility is the buffering capacity of soils for acidity. (Helios – Rybicka *et al*., 1994) reported that a high carbonate content of smelter – impacted soils enhanced the soils buffering capacity and that, as a consequence of constant and elevated pH, the high concentrations of metals in soils would not be rapidly leached. (Young *et al*., 1993) found that the ability of clay soils to retain metals as pH decreases was directly dependent on the initial soil pH and on the soil's buffering capacities.

(Rieuwerts *et al*., 1998) asserted that absorption of metals may become significant at approximately pH 3-5 for Pb and Cu and around pH 5-6.5 for Zn and Cd. However, absorption of Cd has been observed at pH values of 3.7 and 4. Precipitation of insoluble solids appears to become important at approximately pH 6-7 for Pb, Zn, Cd and Cu. In theory, at pH values around 6 or 7, very little metal is likely to be found in solution.

Salinity and especially alkalinity can cause major impacts on plant production. Extreme values of soil pH, which affect the solubility of most of the elements necessary for plant growth, is an insidious problem in some regions. Soil pH affects the solubility of nutrients and uptake by plants (Rezaei and Gilkes 2005). Soil pH often affects plant community composition because plants differ in nutrient requirements and soil acidity or basicity

tolerance. Soil pH is influenced by elevation because soil parent materials of higher pH occur at the lower elevation (Laughlin and Abella, 2007).

2.2.2 Electrical conductivity and soil metal ions content

Electrical conductivity (EC) is influenced by salinity, water content, bulk density and texture, and these are important properties related to the quality of soils (Corwin *et al.*, 2003). It has been reported that Salinity and alkalinity are of major influence on plant production, including the yield of rangelands (Rezaei and Gilkes, 2005). Soil electrical conductivity is influenced among other factors by salinity, water content, clay content and organic matter. The predominant mechanism causing the accumulation of salt is loss of water through evapour - transpiration, leaving the ever-increasing concentrations of salts in the remaining water (Corwin and Lesch, 2005).

Salinity is a dynamic soil property, and varies temporally and spatially with depth and across landscape. Salinity varies primarily due to the process of leaching, with topographic effects contributing to this variation (Corwin *et al*,. 2003). Surface topography plays a significant role in influencing spatial EC variation. The difference in cation exchange capacity of soils is influenced by organic carbon and clay content. The cation exchange capacity values indicate the capacity of soil to retain nutrient cations against leaching (Ludwig *et al*., 2001).

2.2.3. Soil Texture and Soil Metal ion Solubility

The influence of soil texture on the solubility of metal in soils is best expressed by assessing the division of soils into clay, silt and sand fractions. These terms are in turn

defined by particle size fractions of the soil with respective classifications of < 2 µm, 2-50 µm and > 50 µm (Qian *et al*., 1996).

The strong affinity of Pb and other metals to clay fraction is demonstrated by the ranking, in terms of absorption, clay > silt > sand (Anderson, 1979). Eriksson (1989) found that for a given total Cd concentration, Cd was more soluble and plant available in sandy soil than in clay soil. In another study the extractability of Pb, Zn, Cd and Cu by ammonium acetate was always lower in loamy soils than in sand soils (Scokart *et al*., 1983).

Qian *et al*., (1996) studied soil texture in relation to extractable (0.1M HCl and DTPA) concentrations of Pb and Cu stating that metals were generally enriched in the clay fraction, whilst relatively large amounts of available Cu and Pb were recorded in the fine sand fraction, available Pb were also high in the clay fraction. Accumulation of metal in the clay fraction was attributed to the high surface area for adsorption and to the presence of clay minerals, organic matter, Fe-Mn oxides and sulphides.

Metals are probably adsorbed on clay minerals or are occluded in the clay lattice (Qian *et al*., 1996). The susceptibility of Pb to extraction from the clay fraction was attributed to a high proportion of the metal in adsorbed form, which is easily extracted compared to that present in the crystal lattice. A high degree of extractability was also observed in sand fractions of the soil, this was attributed to the low binding strength of these fractions.

Soil texture is also a fundamental property which largely determines the water balance and the potential biomass carbon production, and in turn carbon input and stabilization. Soil moisture content is determined by soil texture, which may influence the composition of the plant community (Laughlin and Abella, 2007). Soil texture also has a predominant effect on biomass production and soil organic carbon in rangeland soils (Scholes and Archer, 1997).

There is a positive relation between texture and soil organic carbon. This could be attributed to the stabilization of organic compounds by clay particles and the influence of texture on the water availability for biological activities (Noellemeyer *et al*., 2006). Standing biomass is lower in soils dominated by sand and not significantly different for silt and clay dominated soils (Laughlin and Abella, 2007).

Plant cover change and off-site removal of biomass could decrease organic matter in soil, deteriorating important soil physical parameters and consequently increasing soil erosion (Li *et al*., 2007). The soils that are dominated by sand class are highly limited in nutrient and water retention. Soil productivity is reduced also by the large proportion of gravel and stones in the soil due to the limited root growth (Salako *et al*., 2006).

2.3. Soil Nutrient Dynamics

2.3.1. Organic matter content and soil metal mobility

Soil organic matter is comprised of humic substances or humus, and non-humic substances. The humus comprises of humic, fulvic acids and humins These are the fraction of soil organic matter which has been extensively decomposed and is resistant to further alteration (Foth, 1978). Organic matter accumulates at the soil surface, mainly as a result of decomposing plant materials. Though the organic matter content of soils is often small compared to that of clay, organic fraction has a significant influence on metal binding (Zimdahl and Skogerboe, 1977).

The mechanisms involved in the retention of metals by organic matter appear to include both complexation and adsorption. That is, inner sphere reactions may take place as well as

ion exchanges (Evans, 1989). This is reflected in reports describing the interactions between metals and organic matter in terms of ion exchange (Singh and Sekhon, 1977; Elliott *et al.,* 1986), in terms of complexation (Zimdahl and Skogerboe, 1977; Jones and Jarvis, 1981; Elliot *et al*., 1986).

Several studies have investigated the influence of soil organic matter on plant uptake of metals. Inferring that organic matter content showed no correlation with Pb uptake (John, 1972), showed positive association with Zn uptake (MacLean, 1976; Martin *et al*., 1982) and negative association with Cd uptake (Maclean, 1976; Street *et al*., 1977). Miller and Friedland (1994) reported an association between the movement of Pb down the soil profile and the organic matter content of forest soils. Some of the solid phase organic matter of the soils appeared to be mobile and a significant quantity of Pb appears to be transported through soils along with the organic matter.

Most petroleum components are generally non - ionic and therefore, associate more readily with the organic than with the mineral particles in the soil (Testa and Winegardner, 1991). According to Piezynski *et al*., (2000), soil organic matter may sorb toxins, thereby, reducing their bioavailability. This was concluded from the study on the effects of oil spill and cleans-up on dominant US Gulf coast marsh marophtes.

There is a positive relationship between soil organic carbon and the capacity of the soil to supply essential plant nutrients including nitrogen, phosphorus and potassium (Rezaei and Gilkes, 2005). Soil nitrogen content follows soil carbon content in grassland soils (Conant and Paustial, 1998). The relationship between organic carbon and landscape attributes, to

positive relationship between organic carbon and nutrient elements. Existence of organic carbon serves as a reliable and sensitive indicator for rangeland health (Rezaei and Gilkes, 2005).

Soil under rangeland management do contain high level of organic all (Lu *et al.,* 1998). In addition, Li *et al.,* (2007) reported that soil organic carbon plays an important role in improving soil physical, chemical, and biological properties for sustained plant growth. The soil carbon balance is maintained by plant litter inputs, which enter the soil as particulate organic carbon.

Rangeland sustainability is related to soil carbon and nutrient balance and the capability to maintain adequate soil conditions for water availability and root development (Noellemeyer *et al*., 2006). The soil under shade such as tree coverage community accumulates more soil organic carbon due to the influence of tree canopy on the soil temperature regime. The different carbon dynamics are as a result of a high proportion of woody debris under shade, and different removal rates of aboveground biomass by grazing in the open communities (Simion *et al*., 2003).

Changes in soil carbon can occur in response to a wide range of management and environmental factors (Schuman *et al.,* 2002). Grazing management provides enough time between occupation periods and in turn stimulates growth of herbaceous species and improves nutrient cycling in grassland ecosystems (Schuman *et al.,* 2002). Disturbance of rangelands has a negative impact on soil structural properties and water holding capacity, these are related to losses of soil organic carbon pools (Li *et al*., 2007). Deterioration in soil

structural properties decreases soil infiltration and water retention and accelerates soil erosion.

2.3.2 The role of phosphorus in soil nutrient dynamics

Phosphorus is an essential macronutrient because of the relatively large amounts of it required by plants and it is also essential to living organism. Phosphorus is one of the three nutrients generally added to soils in fertilizers. One of the main roles of Phosphorus in living organisms is in the transfer of energy. Organic compounds that contain Phosphorus are used to transfer energy from one reaction to drive another within cells. Adequate availability for plants stimulates early plant growth and hastens maturity. Although Phosphorus is essential for plant growth, mismanagement of soil Phosphorus can pose a threat to water quality. The concentration of Phosphorus is usually sufficiently low in fresh water so that algae growth is limited. When lakes and rivers are polluted with Phosphorus excessive growth of algae often results. High levels of algae reduce water clarity and could lead to decrease in dissolved oxygen as the algae decays, and such condition can be very detrimental to game fish populations.

Phosphorus does not occur by itself in nature, it is always combined with other elements to form many different phosphates, some of which are very complex. Phosphorus is receiving more attention as a non-renewable resource (Cordell *et-al.,* 2009; Gilbert, 2009). One unique characteristic of P is its low availability due to slow diffusion and high fixation in soils. All of this implies that it can be a major limiting factor for plant growth.

In soils, P may exist in many different forms. In practical terms, however, P in soils is thought to exist in three pools: solution P, active P and fixed P

The solution P pool is very small and will usually contain only a fraction of a kilogramme per acre. The phosphorous in solution will usually be in the orthophosphate form, but small amounts of organic P may exist as well. Plants will only take up P in the orthophosphate form. The solution P pool is important because it is the pool from which plants take up P, and is the only pool that has any measurable mobility. Most of the P taken up by a crop during a growing season will probably have moved only an inch or less through the soil to the roots. A growing crop would quickly deplete the P in the soluble P pool, if the pool was not being continuously replenished.

The active P pool is P in the solid phase which is relatively easily released to the soil solution, the water surrounding soil particles. As plants take up phosphate, the concentration of phosphate in solution is decreased and some phosphate from the active P pool is released. Because the solution P pool is very small, the active P pool is the main source of available P for crops. The ability of the active P pool to replenish the soil solution P pool in a soil is what makes a soil fertile with respect to phosphate. An acre of land may contain several kilogramme to a few hundred kilogramme of P in the active P pool. The active P pool will contain inorganic phosphate that is adsorbed to small particles in the soil and thereafter reacts with elements such as calcium or aluminium to form somewhat soluble solids, and organic phosphate that is easily mineralized.

Adsorbed phosphate ions are held on active sites on the surfaces of soil particles. The amount of phosphate adsorbed by soil increases as the amount of phosphate in solution increases and vice versa. Soil particles can act either as a source or a reservior of phosphate to the surrounding water depending on the conditions. Soil particles with low levels of

adsorbed P that are eroded into a body of water with relatively high levels of dissolved phosphate may adsorb phosphate from the water, and vice versa.

The fixed P pool of phosphate will contain inorganic phosphate compounds that are very insoluble and organic compounds that are resistant to mineralization by microorganisms in the soil. Phosphate in this pool may remain in soils for years without being made available to plants and may have very little impact on the fertility of the soil.

The inorganic phosphate compounds in this fixed P pool are more crystalline in their structure and less soluble than those compounds considered to be in the active P pool. Some slow conversion between the fixed P pool and the active P pool does occur in soils (Gilbert, 2009).

2.4. Soil Chemistry in Relation to the Potential Risks of Heavy Metals

Many heavy metals act as biological poisons even at parts per billion (ppb) levels. The toxic elements accumulated in organic matter in soils are taken up by growing plants (Dara, 1993). Metals are not toxic in the condensed free elements but are dangerous in the form of cations and when bonded to short chains of carbon atoms (Bairds, 1995). Many metals with important commercial uses are toxic and hence undesirable for indiscriminate release into the environment (Bunce, 1990).

The uncontrolled input of heavy metals in soils is undesirable, because once accumulated in the soil, the metals are generally very difficult to remove (Smith *et al*., 1996). Subsequent problems may be toxicity to the plant growing on the contaminated soils and uptake by the plants resulting in high metal levels in plant tissues. Generally, at the biochemical levels, the toxic effects caused by excess concentrations of heavy metals in living tissues include

competition for sites with essential metabolites, replacement of essential ions, reactions with –SH groups, damage to cell membrances and reactions with the phosphate groups (Alloway and Ayres, 1997). Kabata-Pendias (2004) concluded that the excess of these metals in soils is a stronger stress to plants than their deficiency.

Toxic effects of metals such as cadmium, lead, mercury and so on to man and wild life are well known. This category of metals is not required by man even in small amounts (Tyler, 1981 and Borgmann, 1983). However, metals such as copper and zinc are classified as essential to life due to their involvement in certain physiological processes. Elevated levels of these metals have however been found to be toxic (Spear, 1981). The presence of toxic heavy metals in the environment continues to generate a lot of concern to environmental scientists, government agencies and health practitioners. This is due to the health implications of their presence since they are non - essential metals that are not required for any function either by plants or animals (Greenland and Hayes, 1981), hence they are usually monitored for health purposes.

The most common heavy metal found at contaminated sites, in order of abundance are Pb, Cr, As, Zn, Cd, Cu, and Hg (USEPA, 1996). These metals are important since they are capable of decreasing crop production due to the risk of bio - accumulation and biomagnification in the food chain. There is also the risk of superficial and groundwater contamination. Knowledge of the basic chemistry, environmental and associated health effects of these heavy metals is necessary in understanding their speciation, bio - availability and remedial options.

The fate and transport of a heavy metal in soil depends significantly on the chemical form

and speciation of the metal. Once in the soil, heavy metals are adsorbed by initial fast reactions (minutes, hours), followed by slow adsorption reactions (days, years) and are, therefore, redistributed into different chemical forms with varying bio - availability, mobility, and toxicity (Shiowatana *et al.,* 2001 and Buekers, 2007). This distribution is believed to be controlled by reactions of heavy metals in soils such as: (i) mineral precipitation and dissolution, (ii) ion exchange, adsorption and desorption (iii) aqueous complexation, (iv) biological immobilization and mobilization, and (v) plant uptake (Levy et al., 1992).

2.5. Some Heavy Metals of Environmental Concern

2.5.1. Lead

Lead is a metal belonging to Group XIV and period 6 of the Periodic Table with atomic number 82, atomic mass 207.2, density 11.4 g cm^{-3}, melting point 327.4°C and boiling point 1725°C. It is a naturally occurring, bluish-grey metal usually found as a mineral combined with other elements, such as sulphur as in (PbS, $PbSO_4$) or oxygen as in ($PbCO_3$) and ranges from 10 to 30 mg kg^{-1} in the earth's crust (USDHHS, 1999). Typical mean Pb concentration for surface soils worldwide averages 32 mg kg^{-1} and ranges from 10 to 67 mg kg^{-1} (Kabata and Pendias, 2001).

Lead ranks fifth behind Fe, Cu, Al and Zn in industrial production of metals. About half of the Pb used in the U.S. applied to the manufacture of Pb storage batteries. Other uses include solders, bearings, cable covers, ammunition, plumbing, pigments and caulking. Metals commonly alloyed with Pb are Antimony (in storage batteries); Calcium and Tin (in

maintenance-free storage batteries); Silver (for solder and anodes); Strontium and Tin (as anodes in electro winning processes); Tellurium (pipe and sheet in chemical installations and nuclear shielding); Tin (solders), and Antimony and Tin (sleeve bearings, printing, and high-detail castings., (Manahan, 2003).

Ionic lead, Pb(II), lead oxides and hydroxides, and lead-metal oxyanion complexes are the general forms of Pb that are released into the soil, groundwater, and surface waters. The most stable forms of lead are Pb(II) and lead-hydroxy complexes. Lead(II) is the most common and reactive form of Pb, forming mononuclear and polynuclear oxides and hydroxides (GWRTAC, 1997). The predominant insoluble Pb compounds are lead phosphates, lead carbonates (formed when the pH is above 6) and lead hydroxides (Raskin and Ensley, 2000). Lead sulphide (PbS) is the most stable solid form within the soil matrix and forms under reducing conditions, when increased concentrations of sulphide are present. Under anaerobic conditions a volatile organolead (tetramethyl lead) can be formed due to microbial alkylation (GWRTAC, 1997).

Lead(II) compounds are predominantly ionic whereas Pb(IV) compounds tend to be covalent (for example tetraethyl lead, $Pb(C_2H_5)_4$). Some Pb(IV) compounds, such as PbO_2, are strong oxidants. Lead forms several basic salts, such as $Pb(OH)_2{\cdot}2PbCO_3$, which was once the most widely used white paint pigment and the source of considerable chronic lead poisoning to children who eat peelings from white paint. Many compounds of Pb(II) and a few Pb(IV) compounds are useful. The two most common of these are lead(IV) oxide and lead sulphate, which are participants in the reversible reaction that occurs during the charge and discharge of lead storage battery.

In addition to the inorganic compounds of lead, there are a number of organolead compounds such as tetraethyl lead. The toxicities and environmental effects of organolead compounds are particularly noteworthy because of the former widespread use and distribution of tetraethyllead as a gasoline additive. Although, more than 1000 organolead compounds have been synthesized, those of commercial and toxicological importance are largely limited to the alkyl (methyl and ethyl) lead compounds and their salts (for example dimethyldiethyllead, trimethyllead chloride and diethyllead dichloride).

Inhalation and ingestion are the two routes of exposure of toxic metals and the effects from both are the same. Pb accumulates in the body organs such as brain, this may lead to poisoning (plumbism) or even death. The gastrointestinal tract, kidneys and central nervous system are also affected by the presence of lead. Children exposed to lead are at risk for impaired development, lower IQ, shortened attention span, hyperactivity and mental deterioration, with children under the age of six being at a more substantial risk. Adults usually experience decreased reaction time, loss of memory, nausea, insomnia, anorexia and weakness of the joints when exposed to lead (NSC, 2009).

Lead is not an essential element. It is well known to be toxic and its effects have been more extensively reviewed than the effects of other trace metals. Lead can cause serious injury to the brain, nervous system, red blood cells and kidneys (Baldwin and Marshall, 1999). Exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing young and infants being more sensitive than adults. Lead poisoning, which is so severe to cause evident illness, is now very rare. Lead performs no known essential

function in the human body, it can merely do harm after uptake from food, air, or water. Lead is a particularly dangerous element, as it can accumulate in individual organisms, but also in entire food chains.

The most serious source of exposure to soil lead is through direct ingestion (eating) of contaminated soil or dust. In general, plants do not absorb or accumulate lead, however, soil test indicates high level of lead in soil. Studies have shown that lead does not readily accumulate in the fruiting parts of vegetable and fruit crops (for example corn, beans, squash, tomatoes, strawberries and apples). Higher concentrations are more likely to be found in leafy vegetables (e.g. lettuce) and on the surface of root crops (e.g. carrots). Since plants do not take up large quantities of soil lead, the lead levels in soil considered safe for plants will be much higher than soil lead levels where eating of soil is a concern (pica). Generally, it has been considered safe to use garden produce grown in soils with total lead levels less than 300 mg/kg. The risk of lead poisoning through the food chain increases as the soil lead level rises above this concentration. Even at soil levels above 300 mg/kg, most of the risk is from lead contaminated soil or dust deposits on the plants rather than from uptake of lead by the plant (Rosen, 2002).

2.5.2. Chromium

Chromium is a first-row transition metal of Group VI in the Periodic Table, with the following properties: atomic number 24, atomic mass 52, density 7.19 g cm^{-3}, melting point 1875 °C, and boiling point 2665 °C. It is one of the less common elements and does not occur naturally in elemental form, but only in compounds. Chromium is mined as a primary ore product in the form of the mineral chromite, $FeCr_2O_4$. Major sources of Cr-

contamination include release from electroplating processes and the disposal of Cr containing wastes (Smith *et al*., 1995). Chromium(VI) is the form of Cr commonly found at contaminated sites. Chromium can also occur in the +3 oxidation state, depending on pH and redox conditions. Chromium(VI) is the dominant form of Cr in shallow aquifers where aerobic conditions exist. Chromium(VI) can be reduced to Cr(III) by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions often encountered in deeper groundwater.

Major Cr(VI) species include chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) which precipitate readily in the presence of metal cations (especially Ba^{2+}, Pb^{2+}, and Ag^{+}). Chromate and dichromate also adsorb on soil surfaces, especially iron and aluminum oxides. Chromium (III) is the dominant form of Cr at low pH (< 4). Cr^{3+} forms solution complexes with NH_3, OH^-, Cl^-, F^-, CN^-, SO_4^{2-} and soluble organic ligands. Chromium (VI) is the more toxic form of chromium and is also more mobile. Mobility of Chromium (III) is decreased by adsorption to clays and oxide minerals below pH 5 and low solubility above pH 5, due to the formation of $Cr(OH)_3$ (Chrostowski *et al.*, 1991). Chromium mobility depends on sorption characteristics of the soil, clay content, iron oxide content and the amount of organic matter present. Chromium can be transported by surface runoff to surface waters in its soluble or precipitated form. Soluble and un-adsorbed chromium complexes can leach from soil into groundwater. The leachability of Cr (VI) increases as soil pH increases. Most Cr released into natural waters is particle associated, however, and is ultimately deposited into the sediment (Smith *et al.*, 1995). Chromium is associated with allergic dermatitis in humans (Scragg, 2006).

2.5.3. Arsenic

Arsenic is a metalloid in Group XV and period 4 of the Periodic Table. It occurs in a wide variety of minerals, mainly as As_2O_3 and can be recovered from processing of ores containing mostly Cu, Pb, Zn, Ag and Au. It is also present in ashes from coal combustion. Arsenic has the following properties: atomic number 33, atomic mass 75, density 5.72 g cm^{-3}, melting point 817°C, and boiling point 613°C, and exhibits fairly complex chemistry. It is present in several oxidation states −III, 0, III, V., (Smith *et al*., 1995). In aerobic environments, As(V) is dominant, usually in the form of arsenate (AsO_4^{3-}) in various protonation states: H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}.

Arsenate and other anionic forms of arsenic behave as chelates and can precipitate when metal cations are present (Bodek *et al*., 1988). Metal arsenate complexes are stable only under certain conditions. Arsenic(V) can also co-precipitate with or adsorb onto iron oxyhydroxides under acidic and moderately reducing conditions. Co-precipitates are immobile under these conditions, but arsenic mobility increases as pH increases (Smith *et al.*, 1995). Under reducing conditions, As(III) dominates, existing as arsenate (AsO_3^{3-}), and its protonated forms H_3AsO_3, $H_2AsO_3^-$ and $HAsO_3^{2-}$.

Arsenate can absorb or co-precipitate with metal sulphide and has a high affinity for other sulphur compounds. Elemental arsenic and arsine, AsH_3, may be present under extreme reducing conditions. Biotransformation (via methylation) of arsenic creates methylated derivatives of arsine, such as dimethyl arsine $HAs(CH_3)_2$ and trimethylarsine $As(CH_3)_3$ which are highly volatile. Since arsenic is often present in anionic form, it does not form complexes with simple anions such as Cl^- and SO_4^{2-}. Arsenic speciation also includes organometallic forms such as methylarsinic acid $(CH_3)AsO_2H_2$ and dimethylarsinic acid

$(CH_3)_2AsO_2H$. Many As compounds adsorb strongly to soils and are therefore transported only over short distances in groundwater and surface water. Arsenic is associated with skin damage, increased risk of cancer, and problems with circulatory system (Scragg, 2006).

2.5.4. Zinc

Zinc is a transition metal with the following characteristics: it is a member of Period 4, Group II with an atomic number 30, atomic mass 65.4, density 7.14 g cm^{-3}, melting point 419.5°C and boiling point 906°C. Zinc occurs naturally in soil, about 70 mg kg^{-1} in crustal rocks (Davis and Jones, 1988), but Zn concentrations rises unnaturally, due to anthropogenic additions. Most Zn added to soil occur during industrial activities, such as mining, coal, and waste combustion and steel processing. Many foodstuffs contain certain concentrations of Zn. Drinking water also contains certain amounts of Zn, which may be higher when it is stored in metal tanks. Industrial sources or toxic waste sites may cause the concentrations of Zn in drinking water to reach levels that can cause health problems. Zinc is a trace element that is essential for human health its shortage can cause birth defects.

The world's Zn production is still on the rise which means that more and more Zn ends up in the environment. Pollution of water bodies with Zn, result from presence of large quantities of Zn in wastewater of industrial plants. The consequence is that Zn-polluted sludge is continually being deposited by river banks. Zinc may also increase the acidity of waters. Some fish can accumulate Zn in their bodies, when they live in Zn-contaminated waterways. When Zn enters the bodies of these fish, they are able to biomagnify Zn up in the food chain. Plants often have a Zn uptake that their systems cannot handle, due to the accumulation of Zn in soils. Finally, Zn can interrupt the activity in soils, as it negatively

influences the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter (Greany, 2005).

2.5.5. Cadmium

Cadmium is located at the end of the second row of the transition elements with atomic number 48, atomic weight 112.4, density 8.65 g cm^{-3}, melting point 320.9°C and boiling point 765°C. Together with Hg and Pb, Cd is one of the big three heavy metal poisons and is not known for any essential biological function. In its compounds, Cd occurs as the divalent ion. Cadmium is directly below Zn in the periodic table and has a chemical similarity to that of Zn, an essential micronutrient for plants and animals. This may account in part for cadmium's toxicity, because Zn is an essential trace element, its substitution by Cd may cause the malfunctioning of metabolic processes (Campbell, 2006).

The most significant use of Cd is in Ni/Cd batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance, and high tolerance to physical and electrical stress. Cadmium coatings provide good corrosion resistance coating to vessels and other vehicles, particularly in high-stress environments such as marine and aerospace. Other uses of cadmium are, pigments, stabilizers for polyvinyl chloride (PVC), in alloys and electronic compounds. Cadmium is also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products. In addition, acid rain and the resulting acidification of soils and surface waters have increased the geochemical mobility of Cd, and as a result its surface-water concentrations tend to increase as lake water pH decreases (Campbell, 2006). Cadmium is produced as an

inevitable by-product of Zn and occasionally lead refining. The application of agricultural inputs such as fertilizers, pesticides and biosolids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants increase the total concentration of Cd in soils. The bioavailability of Cd determines whether plant Cd uptake occurs to a significant degree (Weggler *et al.*, 2004). Cadmium is very bio-persistent but has few toxicological properties and, once absorbed by an organism, remains resident for many years.

Since 1970s, there has been sustained interest in possible exposure of humans to Cd through their food chain, for example, through the consumption of certain species of shellfish or vegetables. Concerns regarding this latter route (agricultural crops) led to research on the possible consequences of applying sewage sludge (Cd-rich bio-solids) to soils used for crops meant for human consumption, or of using cadmium-enriched phosphate fertilizer (Campbell, 2006). This study led to the stipulation of the highest permissible concentrations for a number of food crops (Mclaughlin *et al.*, 2000).

Cadmium in the body is known to affect several enzymes. It is believed that the renal damage that results in proteinuria is the result of Cd adversely affecting enzymes responsible for reabsorption of proteins in kidney tubules. Cadmium also reduces the activity of delta-aminolevulinic acid synthetase, arylsulphatase, alcohol dehydrogenase, and lipoamide dehydrogenase, whereas it enhances the activity of delta-aminolevulinic acid dehydratase, pyruvate dehydrogenase, and pyruvate decarboxylase (Manahan, 2003). The most spectacular and publicized occurrence of cadmium poisoning resulted from dietary intake of cadmium by people in the Jintsu River Valley, near Fuchu, Japan. The victims were afflicted by *itai itai* disease, which means *ouch, ouch* in Japanese. The symptoms are the result of painful osteomalacia (bone disease) combined with kidney malfunction.

Cadmium poisoning in the Jintsu River Valley was attributed to irrigated rice contaminated from an upstream mine producing Pb, Zn, and Cd. The major threat to human health is chronic accumulation in the kidneys leading to kidney dysfunction. Food intake and tobacco smoking are the main routes by which Cd enters the body (Manahan, 2003). Cadmium is one of the most toxic elements with reported carcinogenic effects in human (Goering *et al*., 1994). It accumulates mainly in the kidney and liver and high concentration has been found to lead to chronic kidney dysfunction (Awofolu, 2005 and Okoronkwo *et al*., 2005). Cadmium induces cell injury and death by interfering with calcium regulation in biological systems. It has also been implicated as an endocrine disrupter. Apart from the health problems it poses, the metal, together with other elements form a toxic 'soup' that often acts synergistically. That is, the effect of single elements is often multiplied by the presence of other elements. Cadmium is chemically very similar to zinc and are found in the +2 oxidation state. It is believed that much of the physiological action of cadmium arises from its chemical similarity to zinc. Specifically, Cd may replace Zn in some enzymes thereby altering the stereochemistry of the enzyme and impairing its catalytic activity. Disease symptoms ultimately results. Cadmium can also cause painful osteomalacia (bone disease) and destruction of red blood cells (Okoronkwo *et al*., 2005).

2.5.6. Copper

Copper is a transition metal which belongs to period 4 and group I of the Periodic Table with atomic number 29, atomic weight 63.5, density 8.96 g cm^{-3}, melting point 1083°C and boiling point 2595°C. The metal's average density and concentrations in crustal rocks are 8.1×10^3 kg m^{-3} and 55 mg kg^{-1} respectively (Davis and Jones, 1988).

Copper is the third most used metal in the world (VCI, 2011). Copper is an essential micronutrient required in the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. In plants, Cu is especially important in seed production, disease resistance, and regulation of water. Copper is indeed essential, but in high doses, it can cause anaemia, liver and kidney damage and stomach and intestinal irritation.

Copper normally occurs in drinking water from Cu pipes, as well as from additives designed to control algal growth. Though copper's interaction with the environment is complex, research shows that most Cu introduced into the environment is, or rapidly becomes, stable and results in a form which does not pose a risk to the environment. In fact, unlike some man-made materials, Cu is not magnified in the body or bio - accumulated in the food chain.

In the soil, Cu strongly complexes to organic matter implying that only a small fraction of copper will be found in solution as ionic copper in the form of Cu(II). The solubility of Cu is drastically increased at pH 5.5 (Martinez and Motto, 2000), which is rather close to the ideal farmland pH of 6.0 – 6.5 (Eriksson *et al*., 1997).

Copper and Zn are two important essential elements for plants, microorganisms, animals, and humans. The connection between soil and water contamination and metal uptake by plants is determined by many chemical and physical soil factors as well as the physiological properties of the crops. Soils contaminated with trace metals may pose both direct and indirect threats. Direct, through negative effects of metals on crop growth and yield, and indirect, by entering the human food chain with a potentially negative impact on human health. Even a reduction of crop yield by a few percent could lead to a significant long-term loss in production and income. Some food importers are now specifying acceptable

maximum contents of metals in food, which might limit the possibility for the farmers to export their contaminated crops (Bjuhr, 2007).

2.5.7. Mercury

Mercury belongs to same group of the Periodic able with Zn and Cd. It is the only liquid metal at standard temperature and pressure. It has atomic number 80, atomic weight 200.6, density 13.6 g cm^{-3}, melting point −13.6°C, and boiling point 357°C, and is usually recovered as a by-product of ore processing (Smith *et al.*, 1995). Release of Hg from coal combustion is a major source of Hg contamination. Releases from manometers at pressure-measuring stations along gas/oil pipelines also contribute to Hg contamination. After being released to the environment, Hg usually exists in mercuric (Hg^{2+}), mercurous (Hg_2^{2+}), elemental (Hg^o), or in the alkylated form (methyl/ethyl mercury). The redox potential and pH of the system determine the stable forms of Hg that would be present. Mercurous and mercuric mercury are more stable under oxidizing conditions. When mildly reducing conditions exist, organic or inorganic Hg may be reduced to elemental Hg, which may then be converted to alkylated forms by biotic or abiotic processes. Mercury is the most toxic in its alkylated forms which are soluble in water and volatile in air (Smith *et al*., 1995).

Mercury (II) forms strong complexes with a variety of both inorganic and organic ligands, making it very soluble in oxidized aquatic systems (Bodek *et al.,* 1988). Sorption to soils, sediments and humic materials is an important mechanism for the removal of Hg from solution. Sorption is pH dependent and increases as pH increases. Mercury may also be removed from solution by co-precipitation with sulphides. Under anaerobic conditions, both organic and inorganic forms of Hg may be converted to alkylated forms by microbial

activity, such as by sulfur-reducing bacteria. Elemental mercury may also be formed under anaerobic conditions by demethylation of methyl mercury, or by reduction of Hg(II). Acidic conditions (pH < 4) also favor the formation of methyl mercury, whereas higher pH values favor precipitation of HgS (Smith *et al*., 1995).

2.5.8. Nickel

Nickel is a transition element with atomic number 28 and atomic weight 58.69. In low pH regions, the metal exists in the form of the nickelous ion, Ni(II). In neutral to slightly alkaline solutions, it precipitates as nickelous hydroxide, $Ni(OH)_2$, which is a stable compound. This precipitate readily dissolves in acid solutions forming Ni(III) and in very alkaline conditions; it forms nickelite ion, $HNiO_2$, that is soluble in water. In very oxidizing and alkaline conditions, nickel exists in form of the stable nickelo-nickelic oxide, Ni_3O_4, that is soluble in acid solutions. Other nickel oxides such as nickelic oxide, Ni_2O_3, and nickel peroxide, NiO_2, are unstable in alkaline solutions and decompose by giving off oxygen. In acidic regions, however, these solids dissolve producing Ni^{2+} (Pourbaix, 1974).

Nickel is an element that occurs in the environment only at very low levels and is essential in small doses, but can be dangerous when present in amount above the maximum tolerable. This can cause various kinds of cancer on different sites within the bodies of animals, mainly in those that live near refineries. The most common application of Ni is as an ingredient of steel and other metal products.

The major sources of nickel contamination in soils are metal plating industries, combustion of fossil fuels, and nickel mining and electroplating (Khodadoust *et al.,* 2004). Nickel is released into the air by power plants and trash incinerators and settles to the ground after undergoing precipitation reactions. It usually takes a long time for nickel to be removed from air. Nickel can also end up in surface water when it is a part of wastewater streams. The larger part of all Ni compounds that are released to the environment will adsorb to sediment or soil particles and become immobile as a result. In acidic soils, however, Ni becomes more mobile and often leaches down to the adjacent groundwater. Micro - organisms can also suffer from growth decline due to the presence of Ni, but they usually develop resistance to Ni after a while. Nickel is not known to accumulate in plants or animals and as a result Ni has not been found to biomagnify up the food chain. For animals Ni is an essential foodstuff in small amounts. (Khodadoust *et al.,* 2004).

2.6 Soil Concentration Ranges and Regulatory Guidelines for some Heavy Metals

The specific type of metal contamination found in a contaminated soil is directly related to the operation that occurred at the site. The range of contaminant concentrations and the physical and chemical forms of contaminants will also depend on activities and disposal patterns for contaminated wastes on the site. Other factors that may influence the form, concentration, and distribution of metal contaminants include soil and ground-water chemistry and local transport mechanisms (GWRTAC, 1997).

Soils may contain metals in the solid, gaseous or liquid phases and this may complicate analysis and interpretation of reported results. For example, the most common method for determining the concentration of metals contaminants in soil is via total elemental analysis (USEPA Method 3050). The level of metal contamination determined by this method is

expressed as mg metal kg^{-1} soil. This analysis does not specify requirements for the moisture content of the soil and may therefore include soil water. This measurement may also be reported on a dry soil basis.

The level of contamination may also be reported as leachable metals as determined by leach tests, such as the toxicity characteristic leaching procedure (TCLP USEPA Method 1311) or the synthetic precipitation-leaching procedure, or SPLP test (USEPA Method 1312). These procedures measure the concentration of metals in leachate from soil contacted with an acetic acid solution (TCLP., DPR-EGASPIN, 2002) or a dilute solution of sulphuric and nitric acid (SPLP). In this case, metal contamination is expressed in mgL^{-1} of the leachable metal.

Other types of leaching tests have been proposed including sequential extraction procedures (Finzgar, 2007; Ure *et al.*, 1979 and extraction of acid volatile sulphide (DiToro *et al.*, 1992). Sequential procedures contact the solid with a series of extracting solutions that are designed to dissolve different fractions of the associated metal. These tests may provide insight into the different forms of metal contamination present. Contaminant concentrations can be measured directly in metals-contaminated water. These concentrations are most commonly expressed as total dissolved metals in mass concentrations (mg L^{-1} or gL^{-1}) or in molar concentrations (mol L^{-1}).

In dilute solutions, a mg L^{-1} is equivalent to one part per million (ppm), and μgL^{-1} is equivalent to one part per billion (ppb). Riley *et al.*, (1992) and NJDEP (1996) have reported soil concentration ranges and regulatory guidelines for some heavy metals. In

Nigeria, in the interim period, whilst suitable parameters are being developed, the Department of Petroleum Resources (DPR-EGASPIN, 2002) has recommended guidelines on remediation of contaminated land based on two parameters intervention values and target values.

CHAPTER THREE

MATERIALS AND METHOD

3.0 MATERIALS AND METHODS

3.1 Materials

3.1.1 List of Apparatus and Equipment

1. Fume cupboard
2. pH meter/conductivity meter (HANNA)
3. Analytical balances
4. Atomic Absorption Spectrophotometer ().
5. Centrifuge.
6. Hydrometer
7. Oven

3.1.2 Preparation of Solutions

3.1.2.1 List of Reagents

1. Concentrated trioxonitrate (V) acid
2. Hydrofluoric acid
3. Concentrated hydrochloric acid
4. Perchloric acid (60%)
5. Tetraoxosulphate (VI) acid
6. Hydrogen peroxide
7. Lead nitrate

8. Cadmium nitrate
9. Nickel nitrate
10. Copper metal
11. Zinc oxide
12. Potassium nitrate
13. Potassium dichromate
14. Ammonium acetate
15. Hydroxylamine hydrochloride
16. Magnesium nitrate
17. Disodium ethylenediamine tetraacetic acid
18. Potassium chloride
19. Barium chloride
20. Iron sulphate
21. Sodium hydrogen carbonate
25. Calcium chloride

3.1.2.2 *Stock solutions*

Cadmium(II) solution: This was prepared by dissolving 2.7435 g of $Cd(NO_3)_{2.}$. $4H_2O$ in a 100 cm^3 beaker in a minimum amount of distilled, deionized water. The dissolved solution was then transferred into a 1000 cm^3 standard flask and diluted to mark with distilled deionzed water to give 1000 pmm Cadmium stock solution.

Chromium(II) solution: This was prepared by dissolving 5.6577 g $K_2Cr_2O_7$ in a 100 cm^3 beaker in a minimum amount of distilled deionized water. The dissolved solution was

transferred into a 1000cm^3 standard flask and diluted to mark with distilled deionized water to give 1000 pmm chromium(II) solution.

Copper(II) Solution: This was prepared by dissolving 1.0000 g Cu metal in a 100 cm^3 beaker in minimum amount of 1:1 HNO_3. The dissolved solution was then transferred into a 1000cm^3 standard flask and diluted to mark with distilled deionized water to give 1000 pmm copper(II) solution.

Iron(II) solution: This was prepared by dissolving 4.9643 g $Fe(SO_4)_2$.7H2O in a 100 cm^3 beaker in a minimum amount of 1:1 HNO_3. The dissolved solution was then transferred into 1000 cm^3 standard flask and diluted to mark with distilled deionized water to give 1000 pmm Iron(II) solution.

Nickel(II) solution: This was prepared by dissolving 4.9523 g of Ni $(NO_3)_2.6H_2O$ in a 100 cm^3 beaker in a minimum amount of distilled deionized water. The dissolved solution was transferred into a 1000 cm^3 standard flask and diluted to mark with distilled deionized water to give 1000pmm nickel(II) solution.

Lead(II) Solution: This was prepared by dissolving 1.5985 g Pb $(NO_3)_2$ in a 100 cm^3 beaker in a minimum amount of distilled deionzied water. The dissolved solution was then transferred into 1000 cm^3 standard flask and diluted to mark with distilled deionized water to give 1000 pmm Lead(II) solution.

Zinc(II) Solution: This was prepared by dissolving 1.2444 g ZnO in a 100 cm^3 beaker in a

minimum amount of 1:1 HNO_3. The dissolved solution was then transferred into 1000 cm^3 standard flask and diluted to mark with distilled deionzied water to give 1000 pmm Zinc(II) solution.

Potassium Solution: This was prepared by dissolving 2.5897 g KNO_3 in a 100cm^3 beaker in minimum amount of distilled deionized water. The dissolved solution was then transferred into 1000 cm^3 standard flask and diluted to mark with distilled deionized water to give 1000 pmm potassium solution.

Magnesium(II) solution: This was prepared by dissolving 10.6670 g $Mg(NO_3)_2.6H_2O$ in a 100 cm^3 beaker in a minimum amount of distilled water. The dissolved solution was then transferred into a 1000 cm^3 standard flask and diluted to mark with distilled deionized water to give 1000 pmm magnesium solution.

Calcium(II) solution: This was prepared by dissolving 2.7750 g $CaCl_2$ in a 100 cm^3 beaker in minimum amount of distilled deionized water. The dissolved solution was then transferred into 1000 cm^3 standard flask and diluted to mark with distilled deionized water to give 1000 pmm calcium solution.

3.1.2.3 *Standard Working Solutions*

These were obtained by serial dilution.

3.1.2.4 *Preparation of other solutions*

Preparation of 1.0 mol dm^{-3} Magnesium nitrate

A 1.0 moL^{-1} Mg $(NO_3)_2$ was prepared by dissolving 148.0 g $Mg(NO_3)_2$ in a 500 cm^3 beaker

in a minimum amount of distilled deionized water. The dissolved solution was then transferred to a 1000 cm^3 standard flask and diluted to the mark with distilled deionized water.

Preparation of 8.8 mol dm^{-3} hydrogen peroxide, H_2O_2

This was prepared by measuring 874.85 cm^3 of 30% H_2O_2 and transferred into a 1000 cm^3 standard flask and then diluted to the mark with distilled deionized water.

Preparation of 0.02 mol dm^{-3}trioxonitrate (v) acid HNO_3

This was prepared by measuring 1.37 cm^3 of concentrated HNO_3 and transferred it into a 1000 cm^3 standard flask then diluted to the mark with distilled deionized water.

Preparation of 3.5 mol dm^{-3} mmonium acetate, CH_3COONH_4

This was prepared by dissolving 269.5 g CH_3COONH_4 in a 500 cm^3 beaker in a minimum amount of distilled deionized water. The dissolved solution was then transferred to a 1000cm^3 standard flask and diluted to the mark with distilled deionized water.

Preparation of 0.05 mol dm^{-3} disodium Ethylenediamine tetraacetic acid, Na_2EDTA

This was prepared by dissolving 18.61 g of Na_2EDTA in a 100 cm^3 beaker in a minimum amount of distilled deionized water. The dissolved solution was then transferred it into a 1000 cm^3 standard flask and diluted to the mark with distilled deonized water.

Preparation of 0.1 mol dm^{-3} hydroxylamine hydrochloride, $NH_2OH.HCI$

The solution was prepared by dissolving 6.949% $NH_2OH.HCI$ in a 100 cm^3 beaker in a

minimum amount of distilled deionized water. The dissolved solution was then transferred to a 1000cm^3 standard flask and diluted to the mark with distilled deionized water.

Preparation of Ferroin indicator:

This was prepared by dissolving 7.425 g of O-phenanthroline and 3.475 g $FeSO_4$. $7H_2O$ in a separate 100 $cm,^3$ beaker in a minimum amount of distilled water. The dissolved solutions were then transferred quantitatively into 500 cm^3 standard flask mixed thoroughly and diluted to the mark with distilled water.

Preparation of 50% w/v Calgon (sodium hexametaphosphate)

This was prepared by dissolving 500 g calgon in a 500 cm^3 beaker using a minimum amount of distilled water. $NaHCO_3$ was then added to bring the pH of the dissolved solution to 9.0. The dissolved solution was then transferred quantitatively into 1000 cm^3 standard flask and diluted to the mark with distilled water.

Preparation of 0.02 mol L^{-1} Potassium dichromate solution

This was prepared by dissolving 49.04 g $K_2Cr_2O_7$ previously dried at 103^oC to constant weight in a 100 cm^3 beaker in minimum amount of distilled water. The dissolved solution was then transferred quantitatively into a 1000 cm^3 standard flask and diluted to the mark with distilled water.

Preparation of 0.25 mol dm^{-3} ammonium ferrous sulphate ($(NH_4)_2SO_4.FeSO_4.6H_2O$)

This was prepared by dissolving 196 g of ammonium ferrous sulphate in a 200 cm^3 beaker using minimum amount of distilled water and then 10 cm^3 of concentrated H_2SO_4 was

added. The resulting solution was stirred thoroughly with a glass rod to have a homogenous mixture, it was then transferred into a 1000 cm^3 standard flask and diluted to the mark with distilled water.

3.1.3 Description of Study Area

The study area is Kainji Lake National Park (KLNP) Borgu sector. KLNP is the premier park in Nigeria covering a total area of 5340.82 km^2 and composed of two non-contiguous sectors, the Borgu and Zugurma sectors (Amusa *et al.,* 2010). The Borgu sector cover an area of 3,970.02 km^2 while Zugurma sectors, covers an area of 1,370 km^2. The two sectors are separated by the Kainji Lake, a lake impounded on the Niger River for hydroelectric power generation. The entire park lies between latitude $9^o40'$N and $10^o23'$E and longitudes $3^o30'$N and $5^o50'$E (Tuna Wildlife Consultant NARDES, 1983). The vegetation of the Borgu sector is differentiable by hydrological as well as soil factors into five major types viz: the *isoberlinia* woodland, *terminalia macroptera* woodland, *Burkea africana/Detarium microcarpum* woodland, *riparian forest* and the *Diospyrus mespiliformis* dry forest (Child, 1974; Afolayan, 1978).

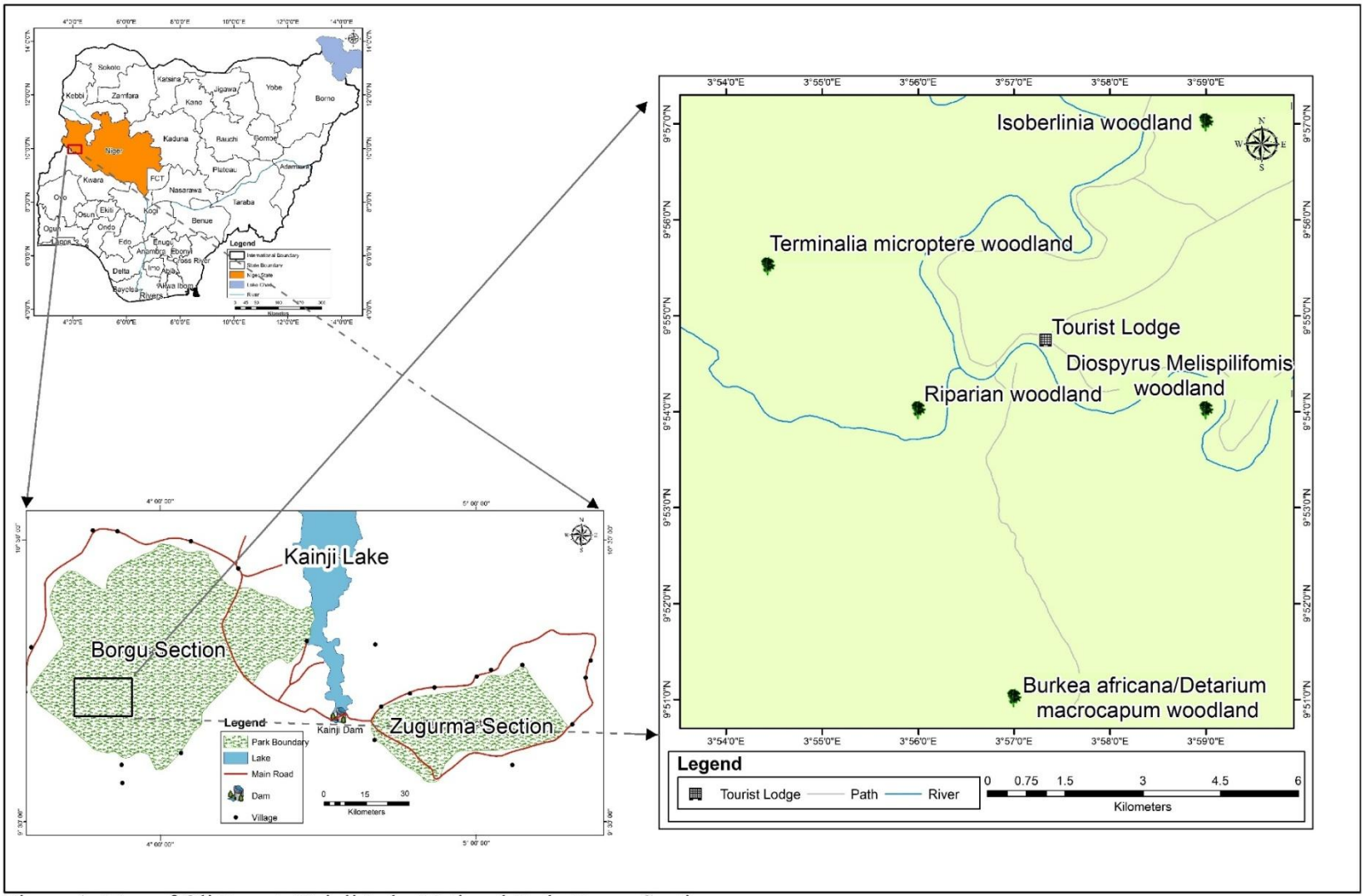


Figure 1: Map of Oli Forest, Kainji Lake National Park, Borgu Section
Source: Adapted and modified from the administrative map of Nigeria and Google Earth, 2013

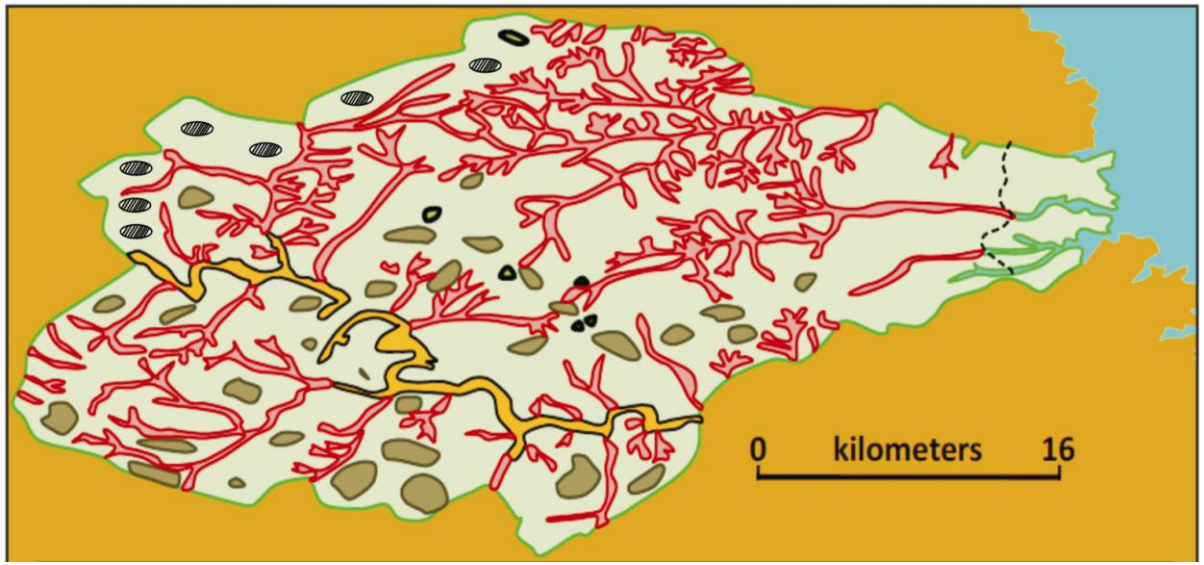


Figure 3.2: A generalised vegetation map of the Borgu sector, Kainji Lake National Park Nigeria

***Deteriamum microcapum* woodland** **Riparian woodland forests**

***Isoberlinia* woodland** ***Termilania macroptera* woodland**

Diospyrosmespiliformis* Dry woodland** ***Oli river complex

3.1.4 Sampling sites description

The entire sample sites are reserved region of the park. Random sampling was used toselect the sample sites. This was done based on the vegetation pattern: *Isoberlinia woodland, Termilania macroptera woodland, Burkea anafricana woodland, Riparian forest woodland and Diospyrus melispiformis dry forest* as shown in Fig 3.2. The sampling sites Fig3.1 were selected at different vegetation zones of Oli camp, Borgu sector of Kainji Lake National Park.

Isoberlinia woodland is located at longitude 9^{o} 54.49 N and 3^{o} 56.79 E with bearing 186^{o}, *Terminalia microptera woodland* is located at longitude 9^{o}55.30 N and 3^{o}54.267 E, with bearing of 184^{o}, *Burkea africana/detarium macrocarpum woodland* has a bearing of 185^{o}, and longitude 9^{o}54.086 N and 3^{o}59.294 E, *Diospyrus mespiliformis dry forest* is limited in size has a bearing of 182^{o} with longitude 9^{o}51.593 N and 3^{o}57.781 E, while *Riparian forest and woodland* is located at longitude 9^{o}54.496 N and 3^{o}56.790 E respectively.

The average rainy season (May to October) for the five vegetation zones in Oli forest varies from 1, 100 mm in the eastern part to 1,150 mm in the western part of the park. The lowest temperature of the vegetation zones is about 12^{o}C between December and January, and the mean maximum temperature obtained during the months of February, March and April is 35^{o}C (Aremu, 2007). Some of the animals common to the different vegetation zones studied include: Roan antelope (*Hippotragus equinus*), Western hartebeest (*Alcelaphus baselaphus*), Oribi (*Ourebia ourebi*), Grey duiker (*Sylvicapra grimmia*), Patas monkey (*Erythrocebus patas*), Kob (*Adenota kob*) , Lion (*Panthera pardus*) and Hippopotamous (*Hippotragus amphibus*) which is commonly found in *Riparian forest*.

3.1.5 Sample collection

Five plots were identified for the study in each of the five vegetation zones in Oli forest. Each plot was separated by a fire trace of 5 m to prevent fire occurrence. Soil samples were collected from each site during rainy and dry seasons of 2011 and 2012 at two depths (0 - 15 cm and 15 - 30 cm) using a metal auger from the randomised observation points. A total number of thirty (30) soil samples were collected at the 0 – 15 cm and 15 – 30 cm depths in the dry and wet seasons of each year of 2011 and 2012 into transparent polyethylene bags. These were labelled and the taken to the laboratory for treatment and analyse. Analyse of each of the soils sample were carried out in triplicate. The total number of samples analysis were three hundred and sixty samples (180 samples per year).

3.1.6 Sample pre-treatment

Each set of the soil samples was homogenised and air - dried, it was then sieved via 2 mm mesh and another portion through 0.5mm mesh (Akinyemi, 2007) to remove rock fragments, surface plant litre and coarse root materials.

3.2 Methods

3.2.1 Determination of physicochemical parameters of soils

3.2.1.1 *Particle size distribution*

The method described by Bouyoucos (1951) was used to determine particle size distribution. A 50 g amount of 2mm sieved soil of five vegetation zones (0 - 15 cm) was weighed into a 250 cm^3 plastic beaker. After which 100 cm^3 of 50% calgon was added and then stirred with a glass rod and then 100 cm^3 distilled water was added and stirred. The

beaker was then left to settle for about 30 min with occasional stirring, and then transferred into a 250 cm^3 plastic container and shaken on an end to end shaker for ten minutes.

The mixture was then transferred into a 1000 cm^3 measuring cylinder and made to the mark with distilled water. The suspension in the cylinder was mixed vigorously using a long handle plunger, making sure that the sediment at the bottom was thoroughly disturbed before the hydrometer reading was taken. Readings of the hydrometer at 40 s and 2 h were taken respectively.

A blank cylinder was prepared by making 100 cm^3 of the 50% calgon solution up to the 1000 cm^3 mark with distilled water. The blank hydrometer reading was then taken at the respective time interval. The temperature of the suspension and blank were also taken.

The corrected hydrometer readings C (g/I) were obtained by subtracting the blank reading R_L (g/I) from the hydrometer readings in the soil suspensions R (g/I) and adding 0.36 g/I for every degree above 20 ^{O}C

$C = R - R_L + (0.36T)$

Where T = Room temperature at $20^{O}C$.

$$\% \, Clay = \frac{(Corrected \;\; 2\, h - Blank)}{Weight \, of \;\; soil \;\; taken} \, X \; 100$$

$$\% \, silt = \frac{(Corrected \;\; 40\, s - Blank)}{Weight \, of \;\; soil \;\; taken} \, X \; 100$$

$$\% \, Sand = 100 - (\% \, clay + \% \, silt \, \%)$$

The procedure 3.2.1.4 was then repeated for the soil collected at 15 - 30 cm depth for each of the five vegetation zone in triplicate. For the entire determination n = 360 samples.

3.2.1.2 *Determination of pH*

A 10.0 g amount of the air-dried soil sample of each sampling site was weighed into a 50 cm^3 beaker and 20 cm^3 distilled deionized water added. The mixture was then allowed to stand for 30 min with occasional stirring with glass rod, after which the electrodes of a pre-calibrated HANNA pH meter (model 111991000) were inserted into the partly settled suspension of each soil sample and the pH of the soil taken (Hendershot *et al;* 1993).

3.2.1.3 *Determination of electrical conductivity (***Herdershot, et al.,** *1993)*

The electrical conductivities of each of the soil samples was measured according to the method of Hendershot *et al*., (1993) as follows. A 10 g amount of the 2 mm air-dried soil samples of each collection was weighed into a plastic container and 20 cm^3 deionized water added; so that soil to water ratio was 1:2, the mixture was then stirred several times for about 30 min. Then the soil suspensions of each soil by vegetation zone and depth was allowed to stand for 30 min undisturbed. The electrodes of the conductivity meter was then inserted into the settled suspension and the electrical conductivity of the soil recorded in μScm^{-1}. The electrical conductivity meter was calibrated using 0.1M KCl before use and the conductivity read as (Bamgbose *et al*., 2005).

3.2.1.4 *Determination of organic matter (***Walkey and Black,** *1934)*

The method of Walkey and Black (1934) was employed for the determination of organic matter. In this method, organic carbon is oxidized by $K_2Cr_2O_7$ in the presence of H_2SO_4

leading to the formation of CO_2 according to the operation given below:

$2K_2Cr_2O_7 + 6H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 3O_2$

$3C + 3O_2 \rightarrow 3CO_2$

A 1.0 g amount of each of the soil samples colleted from each of the five vegetation zone in Oli forest at 0 - 15 cm depth was weighed in triplicates into 250 cm^3 conical flask. Thereafter, 10 cm^3 of 0.02 mol/dm^3 $K_2Cr_2O_7$ was pipetted into each flask and swirled gently to disperse the soil, followed by addition of 20 cm^3 concentrated H_2SO_4. The flask was then swirled gently until soil and reagents were thoroughly mixed.

The mixture was then allowed to settle for 30 min on a glass plate. Then 100 cm^3 distilled water was added with 4 drops of ferroin indicator. This was titrated with 0.25 mol dm^{-3} ammonium ferrous sulphate. Blank titration was similarly carried out. The same procedure was carried out for the soil samples collected at 15 - 30 cm depth at each of the five vegetation zones in triplicate (360) for all. The percentage organic carbon is given by the equation.

$$\%\ Organic\ carbon = \frac{(Blank\ Titre - \ Actual\ Tire\ X\ 0.3\ X\ \ f)}{Weight\ of\ \ air - dried\ \ soil\ \ taken}$$

Where f = correction factor = 1.33

m = Concentration of ferrous sulphate

Then % organic matter in soil = % organic carbon X 1.729

3.2.1.5 *Exchangeable cations determination* (Henderson, *et al.*,1993)

The exchangeable cations were determined by the method described by Hendershot *et al* (1993). The cation exchange capacity (CEC) was determined by the sum of exchangeable cations (Shrivastava and Benerjee, 2004). A 2 g amount of each soil sample was collected from Oli forest into 30 cm^3 centrifuge tube. After which 20 cm^3 of 0.1 mol dm^{-3} $BaCI_2.2H_2O$ was added and shaken for 2 h. The tubes were then removed from the shaker and placed in a centrifuge and centrifuged at about 10000 rpm for 30 min. The supernatant was then carefully decanted and filtered into plastic bottles each sample was then taken for analysis of exchangeable cations using a flame photometer. Each determination was carried out in triplicate and the mean calculated ± standard deviation.

3.2.1.6 Determination of Available Phosphorous (Agbenin, 1995)

15 cm^3 of 1000 mol/dm^3 NH_4F and 25 cm^3 of 0.5 mol/dm^3 KCl were mixed with 460 cm^3 of distilled water and the mixture stored in a glass bottle giving the extraction solution. Then 0.2197 g of KH_2PO_4 was oven dried at 105^oC for 1 h and dissolved in distilled water and diluted to 1000cm^3 in volumentric flask (1 cm^3 = 0.05 ppm of P). Working standards were prepared. Absorbances were read with colorimeter at 670 nm. 35 cm^3 of the extracted solution was added and then agitated for 1 min and filtered into dry beaker. Filtration was repeated until filtrate was clear. 10 cm^3 of the filtrate was taken and 0.4 cm^3 of ammonium molybdate reagent (Denige's reagent) and 2 drops of stannous chloride were added. Absorbance was measure after 11 min for all samples at 690nm and concentrations recorded from the curve.

$$mgPO_4^{-3}\ kg^{-1} = \frac{conc.(from\ curve)\ X\ extracting\ volume}{aliquot\ of\ volume\ X\ sample\ weight}$$

3.2.2 Digestion of soil samples

A 5.0 g amount of the soil samples was collected from the five vegetation zones at Oli forest (0 - 15 cm) depth was weighed into a 250 cm^3 conical flask and moistened with few drops of water to prevent sputtering. Thereafter 3 cm^3 of 30%, H_2O_2 was added and left to settle for 60 min, until the vigorous reaction ceased. Then 75 cm^3 of 0.5 mol dm^{-3} solution of HCI was added following which the content was heated gently on the hot plate for 2 h, deionized water was added to avoid drying of the mixture. The digestion was allowed to cool, and then filtered into a 50 cm^3 standard flask. The content was then diluted to 50 cm^3 mark in a volumetric flask with the same acid solution. Triplicate digestions of each sample together with blank were carried out. The levels of Cd, Cr, Cu, Ni, Pb and Zn in the digest were determined using atomic absorption spectroscopy (Fast Sequential AAS Variance 240) in wet and dry season of year 2011. Soil samples collected at 15 - 30 cm depth for each of the vegetation zones were also subjected to the same procedure above in triplicate, n = 360. The analysis was done for the dry and wet season of year 2012. The same procedure was repeated for control soil sample collected from Zugurma sector in Kainji Lake National Park.

3.2.3 Sequential extraction (chemical fractionation) of soil samples

Sequential extraction was carried out on the principle of selective extraction, proposed by Tessier *et al* (1979) and Shrivastava and Benerjee (2004) with the following modifications:

$Mg(NO_3)_2$ was used instead of $MgCl_2$ to extract exchangeable fractions because the chloride ion can complex metals (Shrivastava and Benerjee, 2004) and increase the solubility of several heavy metals within the soil.

To carry the sequential extraction of the soils of Oli forest, the following steps were undertaken:

Fraction I (Water Soluble) – The method of Ma and Rao (1997) was used. Air dried soil sample 1.0 g from each vegetation zone was poured into a beaker and 15 cm^3 of deionized water added with continuous agitation for 2 h. It was centrifuged and the supernatant liquid decanted, and then made up to the 50 cm^3 mark with deionized water in a volumetric flask. The supernatant was then taken for analysis.

Fraction II (Exchangeable Fraction). The residual from the water soluble extraction (FI) was shaken at room temperature with 16 cm^3 of 1.0 mol dm^{-3} $Mg(NO_3)_2$ at pH 7.0 for 1 h. This was centrifuged and the supernatant liquid decanted and then made up to 40 cm^3 with double distilled water prior to analysis (Tessier *et - al.,* 2004).

Fraction III (Acid extractable – Carbonate Bound Fraction). To the residue obtained from the exchangeable fraction above, 10 cm^3 of 1 mol dm^{-3} NaOAc was added and pH 5 adjusted with HOAc) with continuous agitation for 5 h. This was centrifuged and the supernatant liquid decanted and then made up to 50 cm^3 with deionized water after which it was taken for analysis. NaOAc solublises carbonates (calcites, dolomite) and releases entrapped metals (Shrivastava and Benerjee, 2004).

Fraction IV (Reducible – Fe – Mn Oxides and Hydrogen Fractions) The residue from FIII was leached with 20 cm^3 of 0.1 $moldm^{-3}$ $NH_2OH.HCl$ (Adjusted to pH 5 with 25% v/v HOAc) at 96^oC for 6 h with occasional agitation. This was then centrifuged and the supernatant liquid decanted and made up to 50 cm^3 with deionized water and then taken for analysis. $NH_2OH.HCl$ reduces Fe and Mn oxides to soluble forms (Shrivastava and Benerjee, 2004).

Fraction V (Oxidizable – Organic Matter Bound Fraction). To the residue from fraction IV (reducible – Fe – Mn oxides and hydroxide fraction), 10 cm^3 H_2O_2 (8.8 mol dm^{-3}) was added then 3 cm^3 0.02 mol dm^{-3} HNO3 and agitation for 5 h at 98^oC. Amount of 10 cm^3 CH_3COONH_4 (3.5 mol dm^{-3}) was added as an extracting agent.This mixture was centrifuged and the supernatant liquid was made up to 40 cm^3 with deionized water and taken for analysis. HNO_3 and H_2O_2 oxidise organic matter and solubilise sulphides. Oxidised organic matter releases complexed, adsorbed and chelate metals (Shrivastava and Benerjee, 2004).

Fraction VI -- Residual fraction (bound to silicates and detrital materials)

According to (Shrivastava and Benerjee (2004) residue from Fraction V was digested using HCl-HNO_3/HF (0.35:12 w/v) Soil/solution ratio) in acid digestion Teflon cups. This was dried to ash for 2 h and evaporated to dryness. The residue was diluted to 40 cm^3 with distilled water prior to analysis. After each of the successive extraction, the samples were centrifuged at 4500 rpm for 15 min (Shrivastava and Benerjee, 2004). The supernatants liquid were removed with pipette and filtered with Whatman No. 42 filter paper. The

residues were washed with deionized water followed by vigorous hand shaking and 15 min centrifugation before the next extraction. The volume of water used for rinsing was kept to a minimum to avoid excessive solubilization of the solid materials. The process was carried out in triplicate for a particular sample from each of the vegetation zones for the wet and dry season of 2011 (n = 180 samples) and also for the wet and dry season of 2012 (n = 180 samples). The control soil samples were equally prepared and analysed for each extraction type. All extracts were analysed for the metals (Cd, Cr, Ni, Pb, Zn and Cu) using Atomic Absorption Spectrophotometer (model AA240FS fast sequential AAS).

3.2.4 Enrichment Index

Enrichment index (EI) for each element was calculated to evaluate anthropogenic influences on the studied metals in different vegetation surface soils using the following formula (*Idris, et al*.,2006).

$$EI = \sum \frac{C_m / C_p}{N}$$

Where Cm = concentration value for the metals

Cp = permissive level of the metals in the soil

N = numbers of metal selected

Generally, an EI value of about 1.0 suggests that the source of a given metal may be entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002). Also EI values > than 1.5 suggests that a significant portion of a given metal is delivered to the

soil from non-crustal materials or non-natural weathering processes, and then anthropogenic sources become an important contribution (Feng *et al*., 2004).

3.2.5 Geo-accumulation Index (I_{geo})

This index was equally used to assess metal pollution level in the soils of Oli forest, beside enrichment index. Igeo is defined using the equation:

$$I_{g_{eo}} = \log_2 \left(C_n \Big/ 1.5B_n \right)$$

Where,

Cn = measured concentration of heavy metals in the soil,

Bn = Geochemical background value,

1.5 is the background matrix correction in factor due to lithogenic effects.

And the values for various metals at different vegetation zones are presented in Table

3.2.6 Quality Assurance

Quality control test was performed on the soil samples in order to validate the experimental procedures. This was carried out by spiking the pre - digested soil samples with multielement metal standard solution (0.5 mgL^{-1} of Cd and Cr and $5mgL^{-1}$ for Cu, Fe, Ni, Pb and Zn), according to Awofolu (2005). Glasswares, sample containers and crucibles were washed with liquid soap, rinsed in distilled water and soaked in 10% HNO_3 for 24 h to remove any contamination by heavy metals, they were then washed thoroughly with distilled deionized water (Momani *et al;* 2002) and dried to ensure that no contamination was introduced.

3.2.6.1 Spiking Experiment

Representative soil samples from the five vegetation zoneswere digested in triplicates together with the blanks and run on the Atomic Absorption Spectrophotometer. The amount of metal concentrations present in the samples was determined from calibration curve. These gave the amount of metalin the unspike samples and provided the basis for the spiking experiment.

3.2.7 Statistical analysis

The results of the metal compositions in the soils of the five vegetation zones of Oli camp were subjected to statistical analysis, using SPSS version 17.0. The Pearson correlation coefficient statistical function was carried out to compare relationship between the metals The standard deviation for the concentration of metal ions in the soils of the five vegetation zones of Oli forest. Student's t-test was used to express the significant difference between each metal as a function of the variation in vegetation zone. The metals were examined for dependence upon some soil factors through the use of correlation analysis.

CHAPTER FOUR

4.0 RESULTS

4.1 Physical Properties

4.1.1 Particle size Distribution

The physical characteristics of the soils of the five vegetation zones of Oli camp, for both the wet and dry season of 2011 are presented in Table 4. 2 and Table 4.3 respectively. The soil was essentially sand - loam at depth (0 - 15 cm) and loamy - sand at depth (15 - 30 cm) for *Terminalia macrocarpum* wood land and *Isoberlinia* wood land, *Detarium microptera* wood land, *Riparian* wood land, and *Diospyros mespiliformis* dry forest respectively. The result of the different soils analysed as revealed in Table 4.2 - 4.5 showed that sand is the most variable among the soil depth both in the wet and dry season, and silt the least. Sand proportions decreased while those of silt increased with soil depth. The clay content is low but more variable than silt and it increases with soil depth. Generally, average percentage of sand at 0 - 15 cm and 15 - 30 cm soil depths were 68.70 ±3.06% and 78.50 ±0.85% respectively.

4.1.2 Soil pH

The soil pH in water was between 6.8 (*Burkea africana/Microptera* w*oodland*) and 7.5 (*Diospyrus mespiliformis*) during dry season of both year 2011 and 2012, while the wet season values for the year 2011 and 2012 were between 6.6 (*Isoberlinia* woodland) to7.5 (*Terminalia macroptera* woodland). However, these values are almost of the same magnitude.

4.1.3 Electrical Conductivity

Considering 0 - 15 cm depth, the highest value (101.50 ± 2.12) was recorded at *Terminalia macroptera* woodland and the least (10.00 ± 2.50 µS cm^{-1}) at *Diospyrus mespiliformis forest* during wet season of 2011. In the dry season the values; 0.09 ± 0.01 (*Isoberlinia* woodland); 0.08 ± 0.01 (Terminalia *macroptera* woodland); 0.09 ± 0.0 (*Burkea africana/*Detarium *microcarpum*); 0.02 ± 0.00 (*Riparian*) and 0.12 ± 0.04 (*Diospyrus mespiliformisforest*) were recorded at the surface soil. The same trend was recorded at 15 – 30 cm depth in 2011 and for both 0 - 15 cm and 15 – 30 cm during wet and dry season of 2012.

4.1.4 Organic Matter

The organic matter is low, the seasonal range is between 1.35% and 5.48% at (0 - 15 cm) depth; 1.36% and 2.99% at (15 - 30 cm) depth in wet season of 2011 Table 4.2. During dry season of 2011, organic matter range was between 1.79% and 3.06% at (0 - 15 cm) depth; 1.32% and 2.11% at (15 - 30 cm) depth, (Table 4.3). In 2012, the values of organic matter recorded at Oli forest for the five different vegetation zones in dry and wet season were slightly lower than those recorded for 2011 (Tables 4.4 and 4.5). The range is between 1.59% and 2.96% at (0 - 15 cm) depth; 1.12% and 1.85% at (15 - 30 cm) depth in dry season, while the range are between 1.8% and 5.80% at (0 - 15 cm) depth; 1.60% and (3.75% at 15 - 30 cm) depth during wet season.

4.1.5 Cation Exchangeable capacity

The cation exchange capacity (CEC) is low in the various vegetation soils analysed with the highest value (17.40) cmol/kg during wet season of 2011 being at *Diospyrus mespiliformis*

zone and the least value (3.75) cmol/kg at *Terminalia macroptera* woodland. The highest value recorded in dry season of 2012, was (6.50) cmol/kg being at Burkea *africana/Detarium microcarpum* and the least value (3.55) cmol/kg was recorded for *Terminalia macroptera* woodland. During wet season of 2012, the highest value 16.95 cmol/kg was recorded at *Diospyrus mespiliformis* zone and the least 3.75 cmol/kg at *Isoberlinia* woodland. The result equally revealed that the cation exchangeable capacity decreased with depth as it shown in Table 4.1 - 4.4. In wet season of 2011, control values are in the order: CEC $(0.88 \pm 0.09)_{0-15\ cm}$ and $(0.86 \pm 0.01)_{15-30\ cm}$; OM $(0.64 \pm 0.0.01)_{0-15\ cm}$ and $(0.95 \pm 0.02)_{15-30\ cm}$; EC $(6.50 \pm 2.71)_{0-15\ cm}$ and $(5.00 \pm 1.80)_{15-30cm}$; pH $(7.15 \pm 0.11)_{0-15\ cm}$ and $(7.15 \pm 1.05)_{15-30\ cm}$; Silt $(22.00 \pm 0.40)_{0-15\ cm}$ and (26.00 ± 0.00)15 – 30cm; Sand $(72.00 \pm 0.00)_{0-15\ cm}$ and $(26.00 \pm 0.00)_{15-30\ cm}$; Clay $(6.00 \pm 0.00)_{0-15\ cm}$ and $(5.00 \pm 0.01)_{15-30\ cm}$ and AP $(6.25 \pm 1.00)_{0-15\ cm}$ and $(4.01 \pm 1.00)_{15-30cm}$. During dry season of 2011 the control values are presented in Table 4.2 and the trend in order: CEC $(4.50 \pm 0.14)_{0-15\ cm}$ and $(4.30 \pm 0.00)_{15-30\ cm}$; OM $(2.39 \pm 0.01)_{0-15\ cm}$ and $(1.86 \pm 0.21)_{15-30\ cm}$; EC $(0.10 \pm 0.0)_{0-15\ cm}$ and $(0.08 \pm 0.001)_{15-30cm}$; pH $(7.15 \pm 0.11)_{0-15\ cm}$ and $(7.15 \pm 1.05)_{15-30\ cm}$; Silt $(11.00 \pm 1.41)_{0-15\ cm}$ and (9.00 ± 1.41)15 – 30 cm; Sand $(79.00 \pm 1.41)_{0-15\ cm}$ and $(80.00 \pm 0.00)_{15-30\ cm}$; Clay $(10.00 \pm 0.00)_{0-15\ cm}$ and $(11.00 \pm 1.41)_{15-30\ cm}$ and AP $(10.75 \pm 0.35)_{0-15\ cm}$ and $(14.25 \pm 0.5)_{15-30cm}$.

Table 4.1: Physicochemical parameters of the soils of Oli forest different vegetation zones in wet season of 2011

	(%)								
Sample Location	**Clay**	**Silt**	**Sand**	**pH_{H2O}**	**pH_{CaCl2}**	**EC(µS cm^{-1})**	**OM(%)**	**CEC(cmol/kg)**	**AP(ppm)**
***Isoberlinia* Woodland**									
0 – 15 cm	7.50±0.71	11.00±1.41	81.50±2.12	6.65±0.21	6.35±0.07	61.50±2.12	1.35±0.00	6.65±0.07	66.50±5.50
15 – 30 cm	8.00±0.00	10.00±0.00	82.00±0.00	7.15±0.07	6.50±0.14	82.00±2.83	1.36±0.01	4.45±0.07	12.25±2.50
***Terminalia macroptera* Woodlland**									
0 – 15 cm	10.00±0.00	10.00±0.00	45.00±9.50	6.95±0.07	6.35±0.07	60.50±0.71	2.92±0.00	5.30±0.14	36.75±1.20
15 – 30 cm	9.00±1.41	7.00±1.41	84.00±0.00	7.80±0.00	6.50±0.14	101.50±2.12	1.50±0.01	4.60±0.14	31.50±3.80
Burkea africana/Detarium microcarpum woodland									
0 – 15 cm	8.00±0.00	21.00±1.41	71.00±1.41	6.95±0.07	5.15±0.07	60.50±0.71	1.64±0.00	8.80±0.14	15.75±2.40
15 – 30 cm	11.00±1.41	20.00±0.00	69.00±1.41	6.90±0.00	6.15±0.07	51.00±1.41	1.95±0.00	8.60±0.00	17.75±2.50
Riparian Forest									
0 – 15 cm	10.00±0.00	14.00±0.00	76.00±0.00	6.85±0.07	6.25±0.07	50.00±0.00	2.54±0.00	11.40±0.14	15.75±1.00
15 – 30 cm	8.00±0.00	13.00±1.41	79.00±1.41	7.00±0.14	6.45±0.07	51.00±1.41	1.38±0.04	9.55±0.07	21.00±0.00
Diospyrus mespiliformis Forest									
0 – 15 cm	14±0.00	16±0.00	70±2.00	6.8±1.20	6.4±0.09	29±0.00	5.48±1.00	17.4±3.00	8.75±1.00
15 – 30 cm	20±0.00	16±1.00	64±1.41	6.7±0.45	6.1±1.00	10±2.50	2.99±0.05	11.2±0.80	12.25±2.00
Control									
0 – 15 cm	6.00±0.00	22.00±0.40	72.00±1.41	7.50±0.70	7.15±0.11	6.50±2.71	0.64±2.66	0.88±0.98	1.57±2.00
15 – 30 cm	5.00±0.01	26.00±0.00	69.00±0.01	7.90±1.50	7.15±1.05	5.00±1.81	0.95±2.00	0.86±0.10	1.77±0.00

S1: *Isoberlinia* woodland; S2: *Terminalia macroptera* woodland; S3: *Burkea africana/Microcarpum* woodland; S4: *Reparian* Forest; ss
S5: *Diospyrus mespiliformis*
EC : Electrical conductivity
OM: Organic matter
CEC: Cation exchange capacity
AP: Available phosporus

Table 4.2: Physicochemical parameters of the soils of Oli forest at different vegetation zone in dry season of 2011

	(%)								
Sample Location	**Clay)**	**Silt**	**Sand**	**pH_{H2O}**	**pH_{CaCl2}**	**EC(µScm^{-1})**	**OM(%)**	**CEC(cmol/kg)**	**AP(ppm)**
***Isoberlinia* Woodland**									
0 – 15 cm	10.00±0.00	11.00±1.40	79.00±1.40	7.30±0.10	6.70±0.50	0.09±0.01	2.29±0.30	4.75±0.35	15.00±1.41
15 – 30 cm	10.00±0.00	11.00±1.40	79.00±1.40	7.40±0.20	5.90±0.20	0.08±0.01	1.32±0.25	4.35±0.21	85.88±0.18
***Terminalia macroptera* Woodlland**									
0 – 15 cm	9.00±1.40	19.00±1.40	72.00±0.00	7.20±0.50	6.50±0.70	0.08±0.01	2.50±0.71	5.20±0.42	18.20±0.99
15 – 30 cm	8.00±0.00	11.00±1.40	81.00±1.40	7.50±0.70	6.4±0.80	0.09±0.02	2.04±0.66	3.75±0.21	15.44±0.79
***Burkea Africana/Detarium microcarpum* woodland**									
0 – 15 cm	12.00±0.00	20.00±0.00	68.00±0.00	6.80±0.30	5.80±0.30	0.09±0.01	3.06±0.20	6.75±0.35	12.63±0.53
15 – 30 cm	15.00±1.40	19.00±1.40	66.00±0.00	7.40±0.90	5.30±0.80	0.06±0.03	1.72±0.40	6.40±0.42	8.09±0.30
Riparian Forest									
0 – 15 cm	10.00±0.00	9.00±1.40	81.00±1.40	7.50±0.70	6.30±0.60	0.02±0.00	1.79±0.30	5.05±0.64	10.75±0.35
15 – 30 cm	10.00±0.00	8.00±0.00	82.00±0.00	7.50±0.70	6.30±0.80	0.04±0.02	1.75±0.35	5.60±0.57	6.57±0.62
Diospyrus mespiliformis Forest									
0 – 15 cm	9.00±1.40	11.00±1.40	80.00±0.00	7.50±0.50	6.70±0.50	0.12±0.04	2.64±0.51	4.75±0.35	11.25±1.06
15 – 30 cm	10.00±0.00	10.00±0.00	80.00±0.00	8.10±1.30	7.10±1.30	0.09±0.01	2.11±0.56	4.40±0.14	15.00±1.41
Control									
0 – 15 cm	10.00±1.30	20.00±0.51	70.00±1.50	7.80±0.30	7.80±1.30	0.00±0.01	1.00±0.00	2.05±1.05	6.25±0.50
15 – 30 cm	8.00±1.40	19.00±1.40	73.00±1.32	8.40±0.90	7.30±0.09	0.01±0.00	1.50±0.40	1.40±0.12	4.01±1.00

S1: *Isoberlinia* woodland; S2: *Terminalia macroptera* woodland; S3: *Burkea africana/Microcarpum* woodland; S4: *Reparian* Forest;
S5: *Diospyrus mespiliform*

EC : Electrical conductivity
OM: Organic matter
CEC: Cation exchange capacity
AP: Available phosporus

Table 4.3: Physicochemical parameters of the soils of Oli Forest at different vegetation zones in Dry season of 2012

Sample Location	(%)			pH_{H2O}	pH_{CaCl2}	$EC_{(uS\ cm^{-1})}$	OM (%)	$CEC_{(cmol\ kg^{-1})}$	AP (ppm)
	Clay	Silt	Sand						
Isoberlinia Woodland									
0 – 15 cm	9.50±0.71	10.50±2.12	80.00±2.83	7.25±0.21	6.30±0.00	0.08±0.00	2.04±0.05	4.50±0.00	14.00±0.00
15 – 30 cm	10.00±0.00	10.00±0.00	80.00±0.00	7.20±0.00	5.80±0.14	0.07±0.01	1.12±0.03	4.20±0.00	84.38±1.94
Terminalia macroptera Woodlland									
0 – 15 cm	8.00±0.00	20.00±0.00	72.00±0.00	7.55±0.07	6.25±0.35	0.07±0.01	2.25±0.35	4.95±0.07	16.75±1.06
15 – 30 cm	9.00±1.41	10.00±0.00	81.00±1.41	7.90±0.14	5.90±0.14	0.07±0.00	1.54±0.05	3.55±0.07	14.44±0.62
Burkea Africana/Detarium microcarpum woodland									
0 – 15 cm	11.00±1.41	20.00±0.00	69.00±1.41	6.55±0.07	5.70±0.14	0.08±0.01	2.96±0.06	6.50±0.00	12.13±0.18
15 – 30 cm	16.00±0.00	19.00±1.41	65.00±1.41	6.70±0.00	4.85±0.21	0.04±0.00	1.52±0.12	6.15±0.07	7.69±0.27
Riparian Forest									
0 – 15 cm	10.00±0.00	10.00±0.00	80.00±0.00	8.10±0.14	5.90±0.14	0.01±0.00	1.59±0.02	4.50±0.14	10.25±0.35
15 – 30 cm	10.00±0.00	8.00±0.00	82.00±0.00	7.75±0.35	5.85±0.21	0.03±0.00	1.50±0.00	5.35±0.21	6.32±0.26
Diospyrus mespiliformis Forest									
0 – 15 cm	10.00±0.00	11.00±1.41	79.00±1.41	7.45±0.49	6.25±0.07	0.10±0.01	2.39±0.16	4.35±0.21	10.75±0.35
15 – 30 cm	11.00±1.41	9.00±1.41	80.00±0.00	8.10±1.27	6.10±0.14	0.08±0.01	1.86±0.21	4.30±0.00	14.25±0.35

S1: *Isoberlinia* woodland; S2: *Terminalia macroptera* woodland; S3: *Burkea africana/Microcarpum* woodland; S4: *Reparian* Forest;
S5: *Diospyrus mespiliform*

EC : Electrical conductivity
OM: Organic matter
CEC: Cation exchange capacity
AP: Available phosporus

Table 4.4: Physicochemical parameters the soils ofOli Forest at different vegetation zones in wet season of 2012

	(%)								
Sample Location	**Clay**	**Silt**	**Sand**	**pH_{H2O}**	**pH_{CaCl2}**	**EC(µS cm^{-1})**	**OM(%)**	**CEC(cmol kg^{-1})**	**AP(pmm)**
Isoberlinia Woodland									
0 – 15 cm	8.50±2.12	11.00±1.41	80.50±3.54	6.50±0.00	6.00±0.00	0.05±0.00	2.00±0.00	6.30±0.42	42.50±3.54
15 – 30 cm	10.00±2.83	9.00±1.41	81.00±1.41	6.70±0.14	6.50±0.14	0.07±0.00	1.90±0.14	3.70±0.99	15.00±0.00
Terminalia macroptera Woodlland									
0 – 15 cm	10.00±0.00	10.00±0.00	45.00±2.50	6.80±0.00	6.00±0.14	0.06±0.00	3.00±0.00	4.60±0.85	36.38±0.53
15 – 30 cm	10.00±0.00	6.00±0.00	84.00±0.00	7.65±0.21	6.30±0.14	0.12±0.01	1.60±0.14	4.25±0.35	30.75±1.06
Burkea Africana/Detarium microcarpum woodland									
0 – 15 cm	10.00±0.00	20.00±0.00	72.00±0.00	6.55±0.07	5.15±0.07	0.07±0.00	1.85±0.07	8.35±0.49	15.38±0.53
15 – 30 cm	12.00±0.00	20.00±0.00	68.00±0.00	6.80±0.14	6.00±0.71	0.05±0.00	2.15±0.21	8.80±0.28	16.75±1.06
Riparian Forest									
0 – 15 cm	11.00±1.41	15.00±1.41	76.00±0.00	6.65±0.07	6.35±0.21	0.06±0.00	3.05±0.07	11.15±0.21	15.38±0.53
15 – 30 cm	10.00±0.00	12.00±0.00	78.00±0.00	6.70±0.00	5.90±0.14	0.05±0.00	1.65±0.07	9.25±0.35	21.00±0.00
Diospyrus mespiliformis Forest									
0 – 15 cm	13.00±1.41	14.00±2.83	73.00±4.24	6.70±0.14	5.90±0.14	0.04±0.00	5.80±0.28	16.95±0.64	9.75±1.06
15 – 30 cm	20.00±0.00	16.00±0.00	64.00±0.00	6.60±0.14	6.05±0.07	0.02±0.00	3.75±0.35	11.10±0.14	13.00±0.00

S1: *Isoberlinia* woodland; S2: *Terminalia macroptera* woodland; S3: *Burkea africana/Microcarpum* woodland; S4: *Reparian* Forest;
S5: *Diospyrus mespiliform*

EC : Electrical conductivity
OM: Organic matter
CEC: Cation exchange capacity
AP: Available phosporus

4.1.6 Availabe Phosphorous

Available phosphorus concentrations in the surface (8.75±1.00 to 66.50 ±5.50) and subsurface soil (12.25 ±2.00 to 31.50 ±3.80) examined in wet season of 2011 and in dry season 10.75 ±0.35 to 18.20 ±0.99 and 6.57 ±0.62 to 85.88 ±0.18 were recorded for surface and subsurface soil respectively. During dry season of 2012, available phosphorus at surface and subsurface soil are 10.25 ±0.35 to 16.75 ±1.06; 6.32 ±0.26 to 84.38 ±84.38 ±1.94 respectively. In wet season of 2012 9.75 ±1.06 to 42.50 ±3.54 was recorded at surface soil and 13.00 ±0.01 to 30.75 at subsurface. These values are generally low but higher than the soil outside the park. There was variation in phosphorus concentrations with soil depths (0 – 15 cm and 15 – 30 cm) and also between the sites Tables 4.2 to 4.5.

4.2 Statistical Analysis of the Physico - chemical Parameter of the soils of Oli Forest

The physico - chemical parameter data were subjected to statistical analysis using SPSS version 17.0 and multivariate correlation between some various soil physicochemical parameters across the seasons as shown in Tables 4.6 – 4.13. Some of the parameters were found statistically correlated with each other.

In wet season of 2011 (Table 4.6) the trend of positive correlation at 0 - 15 cm depth between the physicohemical parameters is in the order:

CEC versus clay, silt and organic;

OM versus clay, silt and pH;

EC versus sand and pH.

There was no significant difference between this parameter at this depth ($P \geq 0.05$)

In wet season of 2011 at 15 – 30 cm depth the correlation obtained Table 4.7 is in the order:

CEC versus clay, silt and OM

OM versus clay and silt

EC versus sand and pH. In the dry season of 2011 at 0 – 15 cm depth positive correlation as shown Table 4.8 is in the order:

CEC versus clay, silt, EC and OM

OM versus clay, silt and EC

EC versus Silt and pH

AP versus sand and EC and

Negative correlation occurred among:

EC versus clay and sand

CEC versus sand and pH

OM versus sand and pH

In the dry season of 2011 correlation between physico - chemical parameter, Table 4.9 at 15 – 30 cm follows the order:

CEC versus clay and silt

OM versus sand, pH and EC

EC versus sand and pH

Silt versus clay.

The same physicochemical parameter were considered in the wet and dry season of 2012 (Tables 4. 10 – 4. 13). There was positive correlation between the soil parameter at 0 – 15 cm and 15 - 30 cm in the order:

For 0 – 15 cm in wet season of 2012,

CEC Vs. Clay, silt sand and OM

OM Vs. Clay, silt and pH

EC Vs. Sand and pH

Silt Vs. Clay

pH Vs. Clay and Sand

AP Vs. Sand, pH and EC.

Similar trend of relationship occurred in wet season of 2012 at depth 15 - 30 cm with positive correlation (Table 4.11) in the order:

CEC versus clay, silt, sand and OM

OM versus clay and silt

EC versus pH and sand

Silt versus clay

pH versus sand

AP versus pH and EC

Negative correlation was recorded at both 0 – 15 cm and 15 – 30 cm during wet season of 2012 in the orded: For 0 – 15 cm;

CEC versus Sand pH and EC

OM versus sSand, pH and EC

EC versus Clay and Silt

pH versus Clay and Silt

Sand versus Clay and Silt

AP versus Clay, silt, OM and CEC

For 15 – 30 cm; the order is:

CEC versus pH, and EC

OM versus sand, pH and EC.

EC versus Clay and Silt

Sand versus Clay and Silt

AP versus clay, Silt, Sand, OM and CEC.

In the dry season of 2012, positive correlation at 0 - 15 cm depth follows the trend as shown in Table 4.12.

CEC versus clay, silt, EC and OM

OM versus clay, silt, EC and OM

EC versus clay, silt and pH

pH versus sand. Not significant at $P \geq 0.01$.

In the dry season of 2012 at 15 – 30 cm, there was positive correlation (Table 4.13) between:

OM versus clay, pH and EC

EC versus sand, pH

CEC versus clay, silt, sand and OM

Negative correlation was also observed at depth 0 – 15 cm during dry season of 2012 in order: CEC, OM and EC versus Sand and pH

pH versus Clay and Silt

Silt versus Clay

Sand versus Clay and Silt

AP versus Clay, Sand and pH

Negative correlation also occurred at 15 – 30 cm depth in dry season of 2012 in the order:

EC versus clay and silt

OM versus sand and

CEC versus clay ($P \leq 0.05$) and silt content ($P \leq 0.01$).

Table 4.5 Correlation matrix among soil physicochemical parameters (0 – 15 cm) in wet season of 2011

Parameter	Clay	Silt	Sand	pH_{H2O}	pH_{CaCl2}	EC	OM	CEC
Clay	1.000							
Silt	-0.211	1.000						
Sand	-0.632	0.200	1.000					
pH_{H2O}	0.500	0.105	-0.949	1.000				
pH_{CaCl2}	-0.056	-0.949	0.105	-0.389	1.000			
EC	-0.833	-0.316	0.316	-0.333	0.500	1.000		
OM	0.949	-0.400	-0.800	0.632	0.105	-0.632	1.000	
CEC	0.105	0.800	0.400	-0.211	-0.738	-0.632	-0.200	1.000

**. Correlation is significant at the 0.05 level (2-tailed).*
***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

Table 4.6: Correlation matrix among soil physicochemical parameters (15 – 30 cm) in wet season 2011

Parameter	Clay	Silt	Sand	pH_{H2O}	pH_{CaCl2}	EC	OM	CEC
Clay	1.000							
Silt	0.316	1.000						
Sand	-0.316	-1.000**	1.000					
pH_{H2O}	-0.316	-1.000**	1.000**	1.000				
pH_{CaCl2}	-0.500	-0.949	0.949	0.949	1.000			
EC	-0.056	-0.949	0.949	0.949	0.889	1.000		
OM	0.949	0.400	-0.400	-0.400	-0.632	-0.211	1.000	
CEC	0.105	0.600	-0.600	-0.600	-0.738	-0.738	0.400	1.000

**. Correlation is significant at the 0.05 level (2-tailed).*
***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

Table 4.7: Correlation matrix among soil physicochemical parameters (0 - 15 cm) in dry season 2011

Parameter	Clay	Silt	Sand	pH_{H2O}	pH_{CaCl2}	EC	OM	CEC	AP
Clay	1.000								
Silt	0.400	1.000							
Sand	-0.573	-0.980**	1.000						
pH_{H2O}	-0.779	-0.868	0.944*	1.000					
pH_{CaCl2}	-0.873	-0.577	0.703	0.765	1.000				
EC	-0.111	0.280	-0.227	-0.213	0.273	1.000			
OM	0.429	0.748	-0.761	-0.749	-0.409	0.754	1.000		
CEC	0.869	0.750	-0.857	-0.911*	-0.950*	0.016	0.660	1.000	
AP	-0.279	0.547	-0.430	-0.289	0.227	0.180	0.148	-0.062	1.000

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter

EC - Electrical conductivity

CEC - Cations exchangeable capacity

AP - Available phosphorus

Table 4.8: Correlation matrix among soil physicochemical parameters (15 - 30 cm) in dry season 2011

Parameter	Clay	Silt	Sand	pH_{H2O}	pH_{CaCl2}	EC	OM	CEC	AP
Clay	1.000								
Silt	0.857	1.000							
Sand	-0.944*	-0.979**	1.000						
pH_{H2O}	-0.241	-0.347	0.317	1.000					
pH_{CaCl2}	-0.708	-0.752	0.762	0.843	1.000				
EC	-0.425	-0.049	0.200	0.438	0.435	1.000			
OM	-0.258	-0.143	0.194	0.668	0.647	0.317	1.000		
CEC	0.875	0.575	-0.714	-0.312	-0.630	-0.800	-0.239	1.000	
AP	-0.197	-0.132	0.163	-0.274	-0.177	0.318	-0.767	-0.386	1.000

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

Table 4.9: Correlation matrix among soil physicochemical parameters (0 – 15 cm) in wet season 2012

Parameter	Clay	Silt	Sand	pH_{H2O}	pH_{CaCl2}	EC	OM	CEC	AP
Clay	1.000								
Silt	0.297	1.000							
Sand	-0.748*	-0.829**	1.000						
pH_{H2O}	-0.100	-0.651*	0.475	1.000					
pH_{CaCl2}	0.172	-0.655*	0.426	0.329	1.000				
EC	-0.708*	-0.605	0.841**	0.653*	0.146	1.000			
OM	0.542	0.257	-0.467	-0.069	0.184	-0.543	1.000		
CEC	0.495	0.602	-0.662*	-0.309	-0.089	-0.637*	0.803**	1.000	*
AP	-0.559	-0.543	0.635*	0.207	0.110	0.419	-0.407	-0.657*	1.000

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

Table 4.10: Correlation matrix among soil physicochemical parameters (15 – 30 cm) in wet season 2012

Parameter	Clay	Silt	Sand	pH_{H2O}	pH_{CaCl2}	EC	OM	CEC	AP
Clay	1.000								
Silt	0.393	1.000							
Sand	-0.156	-0.021	1.000						
pH_{H2O}	-0.133	-0.440	0.081	1.000					
pH_{CaCl2}	-0.073	-0.344	0.184	0.382	1.000				
EC	-0.546	-0.492	0.178	0.819**	0.258	1.000			
OM	0.498	0.094	-0.172	-0.360	-0.175	-0.582	1.000		
CEC	0.484	0.418	0.193	-0.370	-0.331	-0.620	0.787**	1.000	
AP	-0.483	-0.551	-0.259	0.227	0.034	0.279	-0.422	-0.590	1.000

**. Correlation is significant at the 0.05 level (2-tailed).*
***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

Table 4.11: Correlation matrix among soil physicochemical parameters (0 – 15 cm) in dry season 2012

Parameter	Clay	Silt	Sand	pH_{H2O}	pH_{CaCl2}	EC	OM	CEC	AP
Clay	1.000								
Silt	-0.166	1.000							
Sand	-0.044	-0.978**	1.000						
pH_{H2O}	-0.450	-0.564	0.667	1.000					
pH_{CaCl2}	-0.712	-0.328	0.484	0.332	1.000				
EC	0.013	0.249	-0.256	-0.661	0.393	1.000			
OM	0.369	0.691	-0.779	-0.914*	-0.325	0.712	1.000		
CEC	0.459	0.779	-0.887*	-0.799	-0.749	0.165	0.790	1.000	
AP	-0.791	0.575	-0.415	-0.152	0.460	0.266	0.126	0.085	1.000

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

Table 4.12: Correlation matrix among soil physicochemical parameters (15 – 30 cm) in dry season 2012

Parameter	Clay	Silt	Sand	pH_{H2O}	pH_{CaCl2}	EC	OM	CEC	AP
Clay	1.000								
Silt	0.930*	1.000							
Sand	-0.973**	-0.990**	1.000						
pH_{H2O}	-0.753	-0.835	0.817	1.000					
pH_{CaCl2}	-0.903*	-0.963**	0.956*	0.901*	1.000				
EC	-0.407	-0.333	0.367	0.440	0.555	1.000			
OM	0.135	-0.049	-0.022	0.548	0.189	0.153	1.000		
CEC	0.820	0.660	-0.734	-0.656	-0.781	-0.815	0.026	1.000	
AP	-0.289	-0.187	0.230	-0.255	0.176	0.412	-0.781	-0.369	1.000

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

4.3 Total metal concentrations in soils of different vegetation zones in Oli forest in 2011

The total metal concentration values in various soils investigated for both wet and dry seasons at two depths (0 - 15 cm and 15 - 30 cm) are presented in Tables 4.14 and 4.15. The total metal concentrations were found to vary greatly in *Terminalia macrocarpum* woodland, with the maximum value of metal concentration being recorded for Zinc at the two depths in dry season. While the least value was recorded for Cadmium (1.4 mg/kg) at depths (0 - 15 and 15 - 30 cm). The mean concentration values of Cd, Cu and Ni have little or no variation in *Terminalia macrocarpum* woodland soil but for Cr, Pb and Zn concentration values varied widely as shown in Table 4.13.

The metal concentrations in the soil of *Burkea africana/Detarium microcarpum* woodland followed the same trend as found in *Terminalia macrocarpum* woodland. Although the mean Zn concentration (323.08 mg/kg) and (416.35 mg/kg) in *Burkea africana/Microcarpum* woodland at 0 - 15 cm and 15 - 30 cm depth respectively were the highest among the other metal concentrations, and also among the vegetation zones studied.

Cadmium has the least mean level recorded in *Burkea africana* woodland soil and equally had the least values among the vegetation zones studied (0.81 mg/kg)$_{0\ -\ 15\ cm}$ and (0.74 mg/kg)$_{15\ -\ 30\ cm.}$ Little variation in metal concentration was noticed among Cr, Ni and Pb in the dry season (Table 4.15), but there was wide variation in the metal concentrations when compared to the levels of Cu (6.72 mg/kg)$_{0\ -\ 1\ 5cm}$ and (4.18 mg/kg)$_{15\ -\ 30\ cm}$. Concentration values (302.54 mg/kg)$_{0\ -\ 15\ cm}$ and (160.06 mg/kg)$_{15\ -\ 30\ cm}$ remained the highest recorded in the soil samples investigated at *Riparain forest* in dry season of 2011for Zinc. The mean

levels of Ni, Cr, and Pb recorded fall within the same range. (8.43 mg/kg to 27.76 mg/kg). The least values recorded for Cd and Cu 1.73 mg/kg and 2.02 mg/kg respectively at *Riparain forest* (Table 4.15). The highest concentration of Zinc was found consistent.

In wet season at *Isoberlinia* woodland, the levels of metals in the surface soil (0 - 15 cm) followed the order: Cd (10.73 ± 2.00); Cr (39.39 ± 2.30); Ni (29.14 ± 2.90); Pb (20.08 ± 3.40); Zn (14.63 ± 0.90) and Cu (34.21 ± 0.09) mg/kg, (Table 4.13). Cu had the highest concentration while the lowest value was recorded for cadmium. During the same wet season of 2011 at sub surface (15 – 30 cm), the order of level of metal was; Cd (10.68 ± 3.90); Cr (34.53 ± 4.50); Ni (27.93 ± 1.00); Pb (19.22 ± 3.40); Zn (19.21 ± 1.00) and Cu (40.75 ± 1.20) mg/kg, Table 4.13. During dry season at *Isoberlinia* woodland at 0 – 15 cm depth, the values followed order Cd (1.95 ± 0.50); Cr (32.33 ± 1.20); Ni (18.55 ± 4.90); Pb (13.41 ± 2.00); Zn (307.34 ± 17.20) and Cu (2.26 ± 0.30) mg/kg. Zn hd the highest value and the least was recorded for cadmium. The trend at 15 – 30 cm depth followed order: Cd (1.16 ± 0.20); Cr (33.58 ± 1.20); Ni (16.77 ± 4.90); Pb (14.12 ± 1.20); Zn (187.45 ± 3.20) and Cu (3.23 ± 1.20) mg/kg, (Table 4.14).

In *Diospyrus mespiliformis forest,* the trend of levels of metals during wet and dry seasons follows the order: Cd (1.95 ± 0.00); Cr (40.35 ± 1.20); Ni (25.27 ± 4.90); Pb (10.74 ± 1.20); Zn (211.35 ± 17.20) and Cu (7.92 ± 0.40) mg/kg and Cd (1.72 ± 0.59); Cr (36.66 ± 3.20); Ni (18.29 ± 1.56); Pb (13.74 ± 05); Zn (199.53 ± 17.20) and Cu (5.76 ± 1.00) mg/kg respectively. The control values at 0 - 15 cm and 15 – 30 cm depths is in orded (0.34 ± 0.20) and (0.48 ± 0.01) mg/kg respectively in wet and (0.20 ± 0.01) and (0.41± 0.01) mg/kg in dry season. Zn had the highest values at both depths while Cd has the least values also at 0 - 15 cm and 15 - 30 cm depths.

Table 4.13: Total metal concentration in the soils of Oli forest at different vegetation zones in wet season 2011

Sample Location	Metal (mg/kg)					
	Cd	**Cr**	**Ni**	**Pb**	**Zn**	**Cu**
***Isoberlinia* Woodland**						
0 – 15 cm	10.73±2.00	39.39±2.30	29.14±2.90	20.08±3.40	14.63±0.90	34.21±0.00
15 – 30 cm	10.68±3.90	34.53±4.50	27.93±1.00	19.22±3.40	19.21±1.00	40.75±1.20
***Terminalia macroptera* Woodlland**						
0 – 15 cm	11.56±4.00	47.34±6.70	12.03±3.45	18.97±4.50	85.07±1.40	24.11±2.78
15 – 30 cm	10.11±1.20	31.02±2.00	204.37±10.89	18.63±2.90	17.01±1.00	23.27±10.87
***Burkea Africana/Detarium microcarpum* woodland**						
0 – 15 cm	7.17±2.45	37.48±5.70	24.67±1.20	19.73±1.00	12.51±0.90	47.52±2.10
15 – 30 cm	9.22±1.90	35.93±1.20	29.99±3.00	18.48±0.00	10.68±1.50	37.21±1.40
Riparian Forest						
0 – 15 cm	8.00±1.30	37.96±3.00	10.93±1.00	19.74±1.00	19.44±2.30	35.21±0.00
15 – 30 cm	6.94±0.89	29.35±1.00	26.02±2.50	19.75±2.54	12.56±1.20	50.92±1.00
***Diospyrus mespiliformis* Forest**						
0 – 15 cm	1.95±0.00	40.35±7.60	25.27±1.80	10.74±1.20	211.35±4.30	7.92±0.40
15 – 30 cm	1.72±0.59	36.66±3.20	18.29±1.56	13.79±0.50	199.53±10.15	5.76±1.00
Control						
0 – 15 cm	0.34±0.20	3.00±0.98	0.61±0.20	1.00±0.00	0.11±0.01	0.65±0.00
15 – 30 cm	0.48±0.10	1.57±1.00	1.52±0.07	1.56±0.30	0.50±0.00	1.47±0.90

S1: *Isoberlinia* woodland
S2: *Terminalia macroptera* woodland
S3: *Burkea africana/Microcarpum* woodland
S4: *Reparian* Forest
S5: *Diospyrus mespiliformis*

Table 4. 14: Total metal concentration in the soils of Oli forest at different vegetations zones in dry season 2011

Sample Location	Metal (mg/kg)					
	Cd	**Cr**	**Ni**	**Pb**	**Zn**	**Cu**
***Isoberlinia* Woodland**						
0 – 15 cm	1.95±0.50	32.33±1.20	18.55±4.90	13.41±2.00	307.34±17.20	2.26±0.30
15 – 30 cm	1.16±0.20	33.58±1.00	16.77±2.00	14.12±1.20	187.45±3.20	3.23±1.20
***Terminalia macroptera* Woodlland**						
0 – 15 cm	1.42±0.30	33.04±2.30	19.47±1.00	9.18±3.40	193.62±2.40	2.79±0.20
15 – 30 cm	1.42±0.90	23.55±2.00	14.03±0.50	18.48±1.45	264.75±5.89	2.85±1.20
***Burkea Africana/Detarium microcarpum* woodland**						
0 – 15 cm	0.81±0.05	47.25±1.00	24.48±2.30	14.55±1.80	323.08±20.10	6.72±3.00
15 – 30 cm	0.74±0.02	44.20±0.00	27.60±3.65	16.95±0.56	416.35±2.50	4.18±1.00
Riparian Forest						
0 – 15 cm	1.73±0.67	27.76±3.00	15.86±2.00	8.43±1.00	302.54±4.50	2.24±0.56
15 – 30 cm	1.16±0.98	24.18±8.50	17.33±1.53	15.02±1.56	160.06±7.89	2.02±1.20
Diospyrus mespiliformis Forest						
0 – 15 cm	1.00±0.50	38.04±4.90	15.85±0.78	11.56±1.20	195.55±3.50	2.13±0.69
15 – 30 cm	2.26±0.89	51.94±2.70	34.69±1.00	11.08±1.89	203.63±6.70	5.50±0.92
Control						
0 – 15 cm	0.20±0.01	1.21±1.00	0.90±0.00	0.50±0.00	0.61±0.10	0.10±0.10
15 – 30 cm	0.41±0.01	0.71±0.02	1.30±0.20	1.10±0.05	1.28±0.23	0.23±0.00

S1: *Isoberlinia* woodland
S2: *Terminalia macroptera* woodland
S3: *Burkea africana/Microcarpum* woodland
S4: *Reparian* Forest
S5: *Diospyrus mespiliformis*

4.4 Total metal concentration in soil of Oli forest at different zones in 2012

The result for the total metal concentration in soils of the different vegetation zones in Oli forest in the second year, 2012 is presented in Tables 4.15 and 4.16 respectively. In *Isoberlinia* wood land, the concentration of metals investigated during wet season is in the order: Cu > Cr > Ni > Pb > Zn > Cd as shown in Table 4.15 (wet season).

In *Terminalia macroptera* woodland soil Zinc has the highest concentrations (85.07 $mg/kg)_{0\ -\ 15\ cm}$ and $(17.01\ mg/kg)_{15\ -\ 30\ cm}$ and least value is for cadmium (9.67 ± 3.27) mg/kg at surface soil and (8.68 ± 2.88) mg/kg at sub surface soil. The levels of metals at depth 0 - 15 cm is in the order: Cd (9.67± 3.27); Cr (39.91± 11.32); Ni (10.24 ± 0.23); Pb (14.39 ± 7.00) Zn (80.93 ± 4.17) and Cu (21.28 ± 4.60) mg/kg in wet season of year 2012. The values at sub surface (15 – 30 cm) were in the order: Cd (8.68± 2.88); Cr (24.38 ± 9.87); Ni (155.67 ± 69.67); Pb (14.08 ± 7.00) Zn (12.91 ± 6.43) and Cu (21.28 ± 4.60) mg/kg.

At the *Burkea africana/Detarium microcarpum* soil, total metal concentrations for each of the metal studied are in the order: Cu (36.08 ± 0.17 mg/kg) > Cr (30.61 ± 0.11 mg/kg) > Ni (18.69 ± 0.93 mg/kg) > Pb (14.86 ± 0.73 mg/kg) > Zn (9.53 ± 0.50 mg/kg) > Cd (5.51 ±2.69 mg/kg) at depth 0 - 15 cm. and Cu (27.55± 13.43) > Cr (27.01 ± 2.90) > Ni (26.79 ± 5.17) > Pb (15.90 ± 3.75) > Zn (9.19 ± 2.63) > Cd (8.31 ± 1.95) mg/kg.

The trend in order of mangnitude obtained in *Isoberlinia* woodland was the same for *Burkea africana/Detarium microcarpum* woodland soil.

In Riparian forest soil, little variance was observed in the concentration of metals which follows order: Cu > Cr >Pb >Zn > Ni > Cd; For *Diospyrous mespiliformis* wood land soil, the concentration of the metals followed the ranking order; Zn > Cr > Ni > Pb > Cu > Cd, Zinc has the highest values at both depths, (211.35 mg/kg)$_{0 - 15 cm}$ and (199.53 mg/kg)$_{15 – 30 cm}$ and the least level was for Cd (2.42 ±0.64 mg/kg)$_{0 - 15 cm}$ and (1.96 ±0.32 mg/kg)$_{15 - 30 cm.}$

Among the vegetation studied during wet season, cadmium recorded the highest value in *Terminalia macroptera woodland* soil (9.67 ±2.27 mg/kg) and the least value of 2012, in *Diospyrous woodland* soil with (range 1.72 - 11.55 mg/kg). The highest mean value (39.91 ±1.32 mg/kg) of Cr concentration was in *Terminalia macrocarpum* soil while the least value (23.08 ±1.18 mg/kg) was in *Riparain forest* soil. The concentration values for Ni during wet season of 2012 were higher than those obtained in dry season of 2012 (10.24 - 155.67 mg/kg)$_{wet}$ and (13.78 - 34.44 mg/kg)$_{dry}$. The highest level of concentration (155.67 mg/kg)$_{15 – 30 cm}$ of Ni was in *Termilinia macroptera* woodland. While the least concentration levels for Ni in 2012 was found in *Riparain vegetation* soil (7.99 mg/kg)$_{0 – 15 cm}$ and (20.15 mg/Kg)$_{15-30 cm}$.

Pb had the least levels of concentration in *Diospyrous melispiformis forest* in wet season and dry seasons (12.37 mg/kg)$_{0 – 15 cm}$ and (8.26 mg/kg$_{15 – 30 cm}$ respectively, as shown in Table 4.15 and 4.16. The highest value of lead (16.79 mg/kg)$_{0 – 15 cm}$ and 16.45 mg/kg)$_{15 – 30 cm}$ in soil of Oli forest at different vegetation zones in wet season of 2012 was in *Isoberlinia* wood land soil and the least value (12.37 ± 2.31 mg/kg)$_{0 – 15 cm}$ a*t Diospyrus mespiliformis* forest. *Diospyrous mespiliformis* soil had the highest levels of concentration of zinc (213.93 and 202.29 mg/kg) at 0 – 15 cm and 15 – 30 cm respectively, while the least values

were (9.53 and 9.19 mg/kg) in *Burkea africana/Detarium microcarpum woodland* soil at depths 0 - 15 cm and 15 – 30 cm respectively. For *Burkea africana/Detarium microcarpum* vegetation soil, the result obtained in dry season varied slightly, with the highest level of Zn being $(321.55 \pm 4.88 \text{ mg/kg})_{0-15 \text{ cm}}$ and $412.99 \pm 6.81 \text{ mg/kg})_{15-30 \text{ cm}}$ and the least values were $191.21 \pm 5.43 \text{ mg/kg})_{0-15 \text{ cm}}$ and $(159.02 \pm 3.23 \text{ mg/kg})_{15-30 \text{ cm}}$.

The level of Cu obtained in both the wet and dry season of 2012 range from (8.80 – 36.08 mg/kg) at 0 - 15 cm depth in the wet season against (1.97 – 6.66 mg/kg) at the 0 – 15 cm depth in the dry season and (6.67 – 38.82 mg/kg) at the 15 -30 cm depth against (2.79 - 5.44 mg/kg) at the 15 - 30 cm depth in dry season. Among the soils of the five different vegetation zones of Oli forest being studied in the wet season of 2012, the highest concentration values was obtained for copper (38.82 mg/kg), in *Riparain forest* soil and the least concentration in *Diospyrous mespiliformis* dry wood land soil for Cu (6.66 mg/kg). The level of concentration for Cu during dry season was low and follows order: *Burkea africana/Detarium microcarpum* > *Terminalia macroptera* woodland > *Isoberlinia* > *Riparain forest* > *Diospyrous mespiliformis.* The control value for each metal at diferrent vegetation zones is also presented in Table 4.14 for the year, 2012 respectively. The trend in wet season is in order: Cd (0.55 ± 0.18); Cr (3.14 ± 0.68); Ni (0.80 ± 0.14); Pb (1.55 ± 0.16); Zn (0.83 ± 0.16); Cu (1.13 ± 0.09) mg/kg at 0 – 15 cm and Cd (0.65 ± 0.22); Cr (2.31 ± 0.55); Ni (2.4 ± 0.52); Pb (1.65 ± 0.24) Zn (0.94 ± 0.22); Cu (3.88 ± 1.1) at 15 – 30 cm depth.

During dry season trend is in order: (0.44 ± 0.09); Cr (2.76 ± 0.40); Ni (1.58 ± 0.02); Pb (0.83 ± 0.08); Zn (19.92 ± 5.20); Cu (0.22 ± 0.03) mg/kg at 0 – 15 cm and Cd (0.18 ± 0.03); Cr (2.39 ± 0.31); Ni (17.15 ± 1.81); Pb (1.48 ± 0.19) Zn (15.90 ± 0.22); Cu (0.40 ± 0.07) at 15 – 30 cm. .

Table 4.15: Total metal concentration in the soils of Oli forest at different vegetation zones in wet season of 2012.

Sample Location	Metal (mg/kg)					
	Cd	**Cr**	**Ni**	**Pb**	**Zn**	**Cu**
***Isoberlinia* Woodland**						
0 – 15 cm	8.10±3.89	29.64±14.34	26.36±4.80	16.79±5.05	11.97±4.05	30.25±5.78
15 – 30 cm	9.15±2.39	30.23±7.03	25.81±3.31	15.38±5.73	17.46±3.19	36.45±7.25
***Terminalia macroptera* Woodlland**						
0 – 15 cm	9.67±3.27	39.91±11.32	10.24±3.44	14.39±7.09	80.93±4.17	21.28±4.60
15– 30 cm	8.68±2.88	24.38±9.87	155.67±69.67	14.08±7.00	12.91±6.43	17.72±8.56
***Burkea Africana/Detarium microcarpum* woodland**						
0 – 15 cm	5.51±2.69	30.61±10.84	18.69±9.33	14.86±7.25	9.53±5.04	36.08±17.00
15 – 30 cm	8.31±1.95	27.01±12.90	26.79±5.17	15.90±3.75	9.19±2.63	27.55±13.43
Riparian Forest						
0 – 15 cm	5.54±3.81	31.43±9.79	7.99±4.92	15.62±6.57	14.65±6.97	32.25±4.85
15 – 30 cm	6.54±1.28	23.08±10.06	23.99±3.39	16.45±5.47	9.36±5.09	38.82±18.30
***Diospyrus mespiliformis* Forest**						
0 – 15 cm	2.42±0.64	41.68±1.87	27.14±2.64	12.37±2.31	213.93±3.64	8.80±1.22
15 – 30 cm	1.96±0.32	38.34±2.35	20.15±2.62	15.40±2.27	202.29±3.84	6.67±1.29
Control						
0 – 15 cm	0.55±0.18	3.14±0.68	0.80±0.14	1.55±0.16	0.83±0.16	1.13±0.09
15 – 30 cm	0.65±0.22	2.31±0.55	2.40±0.52	1.65±0.24	0.94±0.22	3.88±1.16

S1: *Isoberlinia* woodland
S2: *Terminalia macroptera* woodland
S3: *Burkea africana/Microcarpum* woodland
S4: *Reparian* Forest
S5: *Diospyrus mespiliformis*

Table 4.16: Total metal concentration in the soils of Oli forest at different vegetation zones in dry season of 2012

Sample Location	Metal (mg/kg)					
	Cd	**Cr**	**Ni**	**Pb**	**Zn**	**Cu**
***Isoberlinia* Woodland**						
0 – 15 cm	1.90±0.04	32.24±0.66	18.50±0.93	13.25±0.64	302.79±12.04	2.24±0.30
15 – 30 cm	1.12±0.04	33.46±1.19	16.64±1.22	13.86±1.03	187.04±3.49	3.11±0.55
***Terminalia macroptera* Woodlland**						
0 – 15 cm	1.40±0.11	33.01±1.26	18.90±2.06	9.03±0.88	191.21±5.43	2.70±0.72
15 – 30 cm	1.39±0.25	23.44±0.78	13.78±1.12	18.40±2.10	261.87±5.08	2.79±0.44
***Burkea Africana/Detarium microcarpum* woodland**						
0 – 15 cm	0.77±0.14	46.69±2.08	24.38±1.02	13.81±1.82	321.55±4.88	6.66±0.88
15 – 30 cm	0.69±0.11	43.14±2.49	27.40±1.34	16.59±1.22	412.99±6.81	4.15±0.38
Riparian Forest						
0 – 15 cm	1.70±0.45	27.56±1.20	15.75±1.06	8.26±1.14	300.90±4.38	2.22±0.38
15 – 30 cm	1.15±0.05	23.88±2.36	17.15±0.82	14.80±1.39	159.02±3.23	3.00±1.84
***Diospyrus mespiliformis* Forest**						
0 – 15 cm	0.97±0.14	37.75±2.62	15.68±1.44	11.44±0.59	194.85±3.47	1.97±0.58
15 – 30 cm	2.22±0.14	51.75±2.60	34.44±1.36	10.94±0.47	202.80±3.11	5.44±0.69
Control						
0 – 15 cm	0.44±0.09	2.76±0.40	1.58±0.20	0.83±0.08	19.92±5.20	0.22±0.03
15 – 30 cm	0.18±0.03	2.39±0.31	17.15±1.81	1.48±0.19	15.90±2.14	0.40±0.07

S1: *Isoberlinia* woodland
S2: *Terminalia macroptera* woodland
S3: *Burkea africana/Microcarpum* woodland
S4: *Reparian* Forest
S5: *Diospyrus mespiliformis*

Correlation matrix between metals in the soils of Oli forest at the different vegetation zones and physico - chemical parameter were carried out for wet and dry season of 2011 and 2012. (Table 4.17 to 4.25).

In wet season of 2011 at 0 – 15 cm Cd, Cr, and Zn were negatively related to silt ($r = 1.000$, $P \leq 0.01$) and CEC ($r = 0.800$, $P \leq 0.05$); and positively related to pH ($r = 0.949$, $P \leq 0.05$), EC ($r= 0.316$, $P \leq 0.01$), and OM ($r = 0.400$, $P \leq 0.01$) as shown in Table 4.17. Ni did not correlated with silt but had correlation with Sand, pH and EC. The same trends were obtained during wet and dry season of 2012 at both 0 - 15 cm and 15 – 30 cm depths. Cu at sub subsurface correlated negatively with almost all the physico – chemical parameter except for CEC and silt where it had positive correlation and $r = 0.400$ (Table 4.18). Pb had negative correlation with Clay ($r = 0.949$), Silt ($r = 0.200$), EC ($r = 0.105$), OM ($r = 0.800$) and positive correlation with Sand ($r = 0.200$), pH ($r = 0.316$) and CEC ($r = 0.200$) respectively.

Inter-elemental association was also evaluated by spearman's rank correlations coefficient, P and the results are shown in Table 4.26 to Table 4.31. The result in the dry season of 2011 revealed that some element pairs, for example Zn had a strong negative correlation with Cd and Pb ($P < 0.05$) Table 4.26. Cu has significant positive correlation with Pb ($P < 0.05$, $r =0.857$) and negative correlation with Zn ($P < 0.05$, $r = 0.935$). Ni did not correlate significantly with any of the metals studied as shown in Table 4.26. The same trend of relationship between metals was obtained at 15 – 30 cm depth in dry season of 2011 (Table 4.27). Correlation matrix of the metals in wet and dry seasons of 2012 at 0 – 15 cm and 15 – 30 cm was not different from trend obtained in 2011 (Table 4.28 – 4.31).

Table 4.17: Correlation matrix between metals in the soil of Oli Camp and the physicochemical parameters (0 – 15 cm) in wet season of 2011

Parameter	**Clay**	**Silt**	**Sand**	**pH_{H2O}**	**pH_{CaCl2}**	**EC**	**OM**	**CEC**
Cd	0.211	-1.000**	-0.200	-0.105	0.949	0.316	0.400	-0.800
Cr	0.211	-1.000**	-0.200	-0.105	0.949	0.316	0.400	-0.800
Ni	-0.949	0.000	0.400	-0.316	0.211	0.949	-0.800	-0.400
Pb	-0.833	0.316	0.949	-0.833	0.000	0.500	-0.949	0.316
Zn	0.738	-0.800	-0.400	0.105	0.632	-0.316	0.800	-0.400
Cu	-0.211	1.000**	0.200	0.105	-0.949	-0.316	-0.400	0.800

**. Correlation is significant at the 0.05 level (2-tailed).*
***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

Table 4.18: Correlation matrix between metals in the soil of Oli forest and the physicochemical parameters (15 – 30 cm) wet season of 2011

Parameter	**Clay**	**Silt**	**Sand**	**pH_{H2O}**	**pH_{CaCl2}**	**EC**	**OM**	**CEC**
Cd	-0.105	-0.600	0.600	0.600	0.738	0.738	-0.400	-1.000**
Cr	0.632	0.400	-0.400	-0.400	-0.316	-0.105	0.400	-0.400
Ni	0.738	-0.400	0.400	0.400	0.211	0.632	0.600	-0.400
Pb	-0.949	-0.200	0.200	0.200	0.316	-0.105	-0.800	0.200
Zn	-0.632	-0.800	0.800	0.800	0.949	0.738	-0.800	-0.800
Cu	-0.738	0.400	-0.400	-0.400	-0.211	-0.632	-0.600	0.400

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

Table 4.19: Correlation matrix between metals in the soil of Oli forest and the physicochemical parameters (0 - 15 cm) dry season of 2011

Parameter	Clay	Silt	Sand	pH_{H2O}	pH_{CaCl2}	EC	OM	CEC	AP
Cd	0.045	0.295	-0.273	-0.269	-0.025	-0.401	-0.270	0.021	0.757
Cr	-0.652	0.400	-0.218	0.063	0.397	0.179	0.044	-0.281	0.826
Ni	0.295	-0.057	-0.012	-0.231	0.131	0.729	0.511	0.069	-0.145
Pb	0.498	0.271	-0.349	-0.455	-0.446	-0.607	-0.235	0.362	0.362
Zn	-0.649	-0.158	0.281	0.459	0.523	0.603	0.218	-0.420	-0.134
Cu	0.870	0.342	-0.493	-0.680	-0.768	-0.450	0.076	0.700	-0.007

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

Table 4.20: Correlation matrix between metals in the soil of Oli forest and the physicochemical parameters (15 – 30 cm) dry season of 2011

Parameter	Clay	Silt	Sand	pH_{H2O}	pH_{CaCl2}	EC	OM	CEC	AP
Cd	0.070	0.330	-0.239	-0.940*	-0.747	-0.108	-0.609	0.021	0.420
Cr	0.517	0.538	-0.549	0.414	-0.067	0.451	-0.024	0.106	0.211
Ni	-0.530	-0.075	0.258	-0.205	0.116	0.438	0.412	-0.571	-0.166
Pb	0.049	0.072	-0.065	-0.951*	-0.675	-0.561	-0.623	0.258	0.218
Zn	-0.158	-0.258	0.228	0.985**	0.770	0.491	0.563	-0.296	-0.154
Cu	0.245	0.044	-0.125	-0.822	-0.663	-0.809	-0.721	0.524	0.189

**. Correlation is significant at the 0.05 level (2-tailed).*
***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

Table 4.21 Correlation matrix between metals in the soil of Oli forest soil and the physicochemical parameters (0 – 15 cm) wet season of 2012

Parameter	Clay	Silt	Sand	pH_{H2O}	pH_{CaCl2}	EC	OM	CEC	AP
Cd	-0.813	-0.558	-0.537	0.089	0.155	0.400	-0.667	-0.958*	0.889*
Cr	0.674	-0.374	-0.600	0.847	0.160	-0.505	0.810	0.382	-0.197
Ni	0.079	0.001	0.506	-0.479	-0.316	-0.638	0.282	0.362	0.017
Pb	-0.873	-0.122	0.316	-0.624	0.167	0.394	-0.850	-0.668	0.617
Zn	0.812	-0.208	-0.187	0.558	0.099	-0.744	0.952*	0.695	-0.390
Cu	-0.705	0.424	0.275	-0.619	-0.250	0.797	-0.917*	-0.567	0.196

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

Table 4.22: Correlation matrix between metals in the soil of Oli forest and the physicochemical parameters (15 – 30 cm) wet season of 2012

Parameter	Clay	Silt	Sand	pH_{H2O}	pH_{CaCl2}	EC	OM	CEC	AP
Cd	-0.918*	-0.397	0.719	0.453	0.494	0.724	-0.885*	-0.802	0.453
Cr	0.891*	0.345	-0.672	-0.491	0.098	-0.616	0.936*	0.388	-0.711
Ni	-0.344	-0.664	0.602	0.992**	0.353	0.893*	-0.416	-0.565	0.914*
Pb	0.033	0.608	-0.409	-0.822	-0.630	-0.733	0.062	0.599	-0.586
Zn	0.975**	0.319	-0.697	-0.374	-0.191	-0.622	0.967**	0.601	-0.504
Cu	-0.790	-0.151	0.496	-0.228	0.069	0.123	-0.741	-0.333	0.000

**. Correlation is significant at the 0.05 level (2-tailed).*
***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

Table 4.23: Correlation matrix between metals in the soil of Oli forest and the physicochemical parameters (0 – 15 cm) dry season of 2012

Parameter	Clay	Silt	Sand	pH_{H2O}	pH_{CaCl2}	EC	OM	CEC	AP
Cd	-0.459	-0.539	0.644	0.602	0.438	-0.502	-0.850	-0.634	0.224
Cr	0.558	0.587	-0.713	-0.913*	-0.464	0.628	0.977**	0.815	-0.073
Ni	0.341	0.771	-0.853	-0.880*	-0.571	0.290	0.789	0.955*	0.278
Pb	0.541	0.127	-0.244	-0.884*	-0.129	0.680	0.686	0.489	-0.033
Zn	0.649	-0.124	-0.012	-0.304	-0.651	-0.383	-0.011	0.426	-0.343
Cu	0.563	0.699	-0.828	-0.818	-0.782	0.172	0.791	0.992**	-0.020

**. Correlation is significant at the 0.05 level (2-tailed).*
***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

Table 4.24 Correlation matrix between metals in the soil of Oli forest and the physicochemical parameters (15 – 30 cm) dry season of 2012

Parameter	Clay	Silt	Sand	pH_{H2O}	pH_{CaCl2}	EC	OM	CEC	AP
Cd	-0.464	-0.617	0.567	0.843	0.781	0.700	0.657	-0.584	-0.109
Cr	0.559	0.357	-0.442	-0.122	-0.181	0.352	0.488	0.235	-0.051
Ni	0.556	0.301	-0.406	0.014	-0.148	0.198	0.688	0.329	-0.318
Pb	0.082	0.384	-0.273	-0.316	-0.442	-0.348	-0.289	0.040	-0.223
Zn	0.845	0.961**	-0.932*	-0.678	-0.884*	-0.232	0.102	0.512	-0.332
Cu	0.437	0.189	-0.289	0.127	-0.015	0.331	0.709	0.185	-0.265

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

OM - Organic matter
EC - Electrical conductivity
CEC - Cations exchangeable capacity
AP - Available phosphorus

Table 4. 25: Correlation matrix of the metals in the soil of Oli forest (0 – 15 cm) in dry season of 2011

Parameter	Cd	Cr	Ni	Pb	Zn	Cu
Cd	1.000					
Cr	0.410	1.000				
Ni	-0.308	-0.425	1.000			
Pb	0.851	-0.066	-0.258	1.000		
Zn	-0.701	0.327	0.110	-0.964**	1.000	
Cu	0.489	-0.457	0.008	0.857	-0.935*	1.000

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

Table 4.26: Correlation matrix of the metals in the soil of Oli forest (15 – 30 cm) in dry season 0f 2011.

Parameter	Cd	Cr	Ni	Pb	Zn	Cu
Cd	1					
Cr	-0.323	1				
Ni	0.412	-0.447	1			
Pb	0.851	-0.648	0.201	1		
Zn	-0.909*	0.555	-0.286	-0.976**	1	
Cu	0.608	-0.531	-0.222	0.903*	-0.832	1

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

Table 4.27 Correlation matrix of the metals in the soil of Oli forest (0 – 15 cm) in wet season of 2012 .

Parameter	Cd	Cr	Ni	Pb	Zn	Cu
Cd	1.000					
Cr	-0.205	1.000				
Ni	-0.401	0.055	1.000			
Pb	0.603	-0.864	-0.182	1.000		
Zn	-0.551	0.894*	0.404	-0.902*	1.000	
Cu	0.377	-0.920*	-0.363	0.811	-0.974**	1.000

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

Table 4.28: Correlation matrix of the metals in the soil of Oli forest (15 - 30 cm) in wet season of 2012

Parameter	Cd	Cr	Ni	Pb	Zn	Cu
Cd	1.000					
Cr	-0.727	1.000				
Ni	0.371	-0.415	1.000			
Pb	-0.200	-0.049	-0.861	1.000		
Zn	-0.932*	0.905*	-0.283	-0.045	1.000	
Cu	0.646	-0.643	-0.292	0.533	-0.782	1.000

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

Table 4.29: Correlation matrix of the metals in the soil of Oli forest (0 – 15 cm) in dry season of 2012

Parameter	Cd	Cr	Ni	Pb	Zn	Cu
Cd	1.000					
Cr	-0.872	1.000				
Ni	-0.486	0.782	1.000			
Pb	-0.343	0.723	0.626	1.000		
Zn	0.193	0.135	0.448	0.416	1.000	
Cu	-0.647	0.840	0.941*	0.549	0.490	1.000

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

Table 4.30: Correlation matrix of the metals in the soil of Oli forest (15 -30 cm) in dry season of 2012

Parameter	Cd	Cr	Ni	Pb	Zn	Cu
Cd	1.000					
Cr	0.407	1.000				
Ni	0.462	0.955*	1.000			
Pb	-0.651	-0.650	-0.639	1.000		
Zn	-0.508	0.303	0.275	0.506	1.000	
Cu	0.581	0.955*	0.988**	-0.691	0.181	1.000

**. Correlation is significant at the 0.05 level (2-tailed).*

***. Correlation is significant at the 0.01 level (2-tailed).*

4.5 Spiking Experiment

The validity of the precision and accuracy of the atomic absorption spectrophotometer were tested by spiking experiment. The results of the spiking of the Cd, Cr, Ni, Pb, Cu and Zn are as shown on Table 4.1. The recovery varied between 89.67 – 108.67% for the soil. The highest % recovery of 108.67% was recorded for Zn in soil, while lowest % recoveries of 89.67% was recorded for Ni in soil. The pattern of recovery efficiency for the soil samples of Oli forest was found to follow the decreasing orders: Zn > Cu > Cr = Pb > Cd > Ni.

Table 4.31: Percentage recovery of heavy metals in soil samples

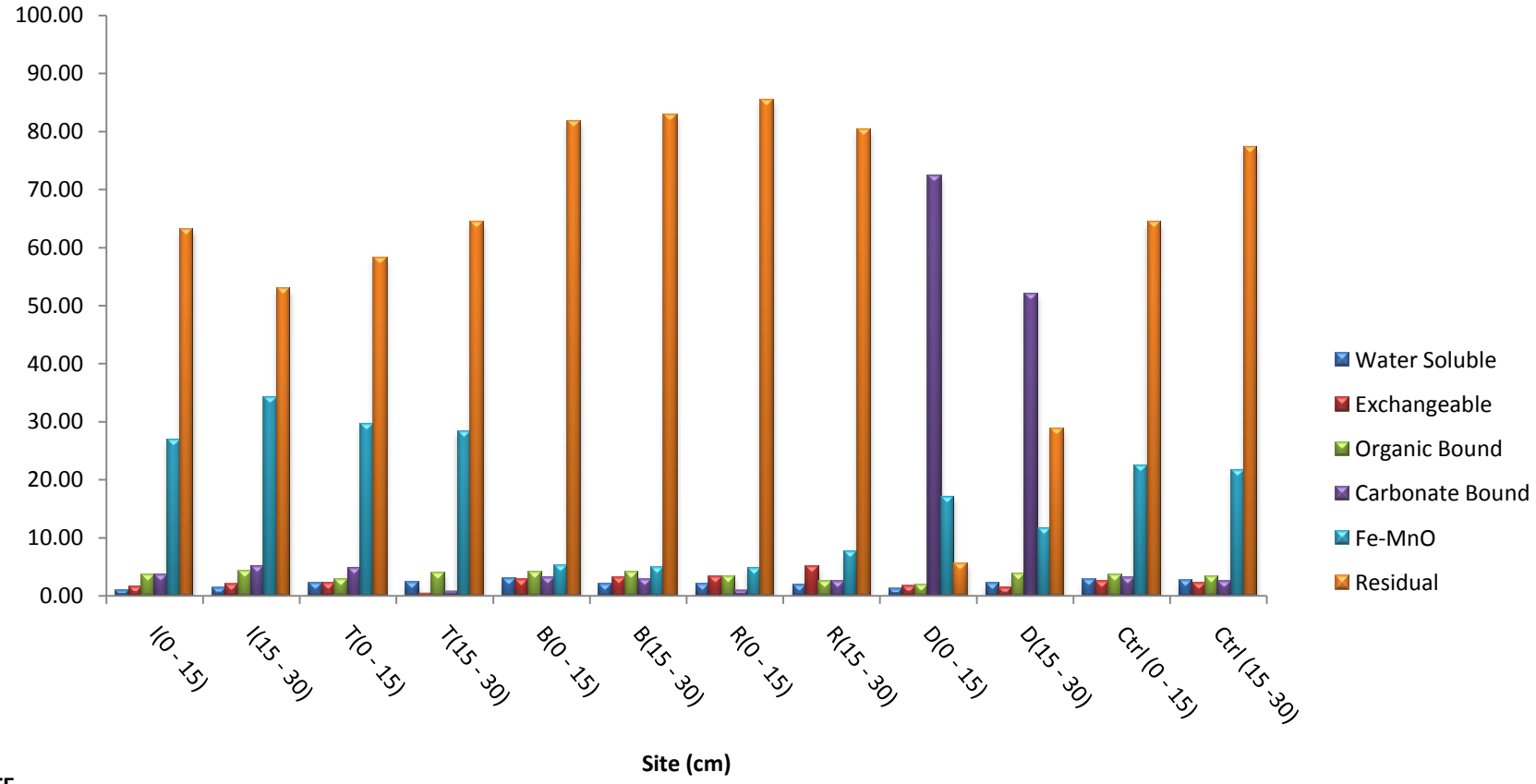
Metals	Soil Samples
Cd	90.67±1.00
Cr	93.00±1.20
Zn	108.67±1.00
Cu	98.00±2.00
Ni	89.67±1.00
Pb	93.00±1.30

4.6 Speciation of the Metals in the soils of the vegetation zones of Oli forest

The range, mean and standard deviation of Cd, Cr, Ni, Pb, Zn, and Cu concentrations at 0 -15 cm and 15 - 30 cm depths in the soil samples of the five vegetation zones studied during wet and dry seasons of 2011 and 2012 are presented in Tables 4.13 to 4.16. There was decreasing trend in the mean concentration of all the metals studied at depths 0 – 15 cm and 15 – 30 cml. The concentrations for the surface soil 0 – 15 cm ranged from 1.72 ± 0.59 to 213.93 ± 3.64 for, during wet season and from 0.69 ± 0.11 to 412.99 ± during dry season.

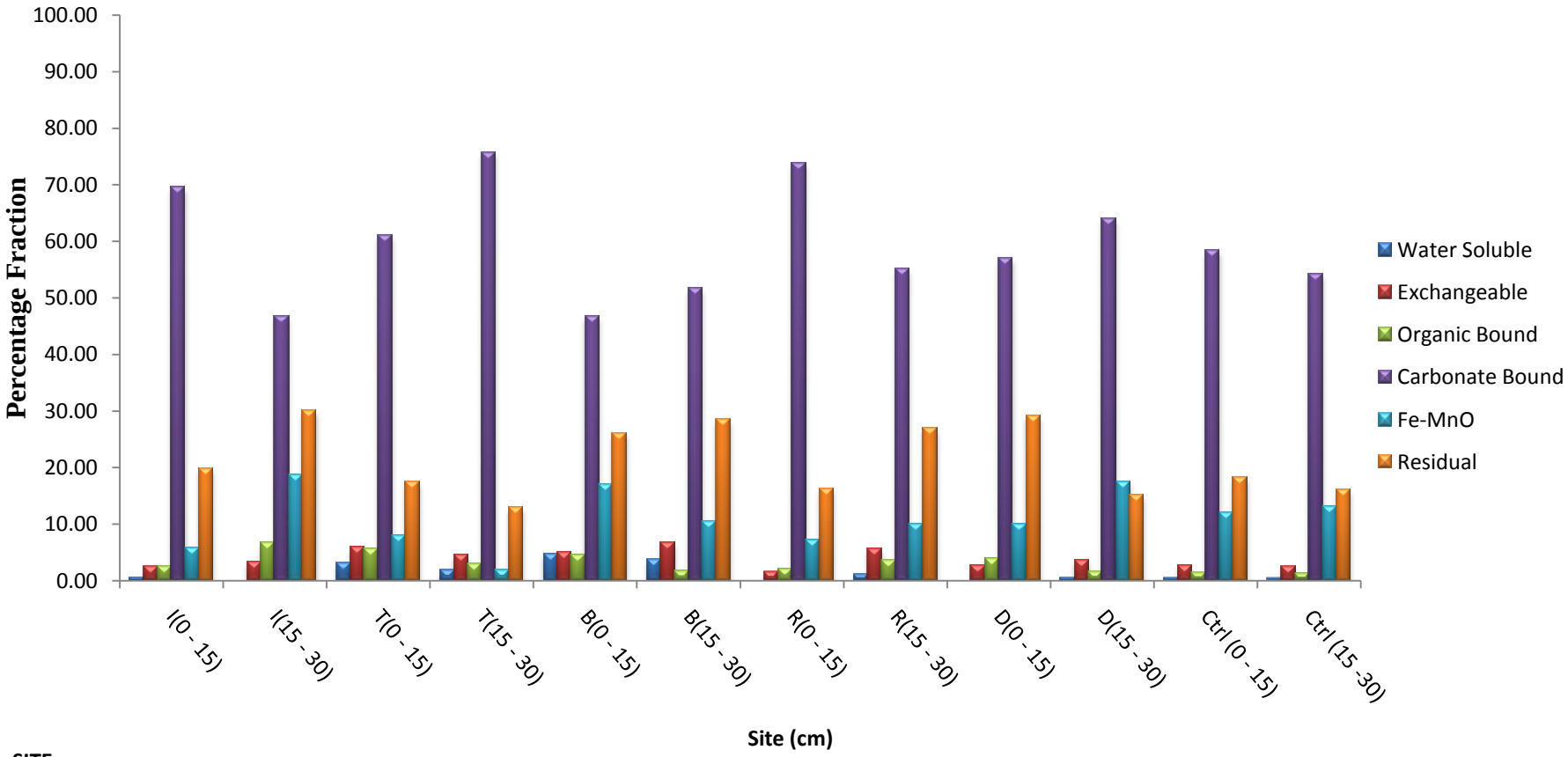
The concentrations of all the metals were found to decrease generally with increasing soil depth with Cu having by far the highest concentration followed by Pb, while Cr, Ni, Zn and Cd have the least and in the same order of magnitude.

The result for different fractions from sequential extraction were presented inFigures 4.1a to 4.6b and Appendix I – XII for both wet and dry season of year 2011while 2012 wet and dry season were presented in Figures 4.7a to 4.12b and Appendix XIV – XXV. The highest percentage of metals concentrations were mostly resided in the residual fractions for all the vegetation zones in both wet and dry season of 2011 and 2012. The trend observed is in order: RES > FMO > CB > OB > EX > WS. Contrary observation was recorded for Cadmium in dry season of 2011 with order: EX > RES > FMO > CB >OB > WS also Chromium had a pattern order: OB > CB > FMO > RES > EX > WS. Percentage range of 1 to 50(%) was recorded for Nickel and lead during wet dry season of 2011 and 2012. The values for the control soil samples were also mostly resided in the residual bound and the order is: RES > FMO > OB = EX > CB = WS for both seasons.



SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis

Figure 4.1a: Chemical fraction of Cadmium in soils of the different vegetations of Oli forest in wet season of 2011



SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis

Figure 4.1b. Chemical fraction of Cadmium in soils of the different vegetations of Oli forest in dry season of 2011

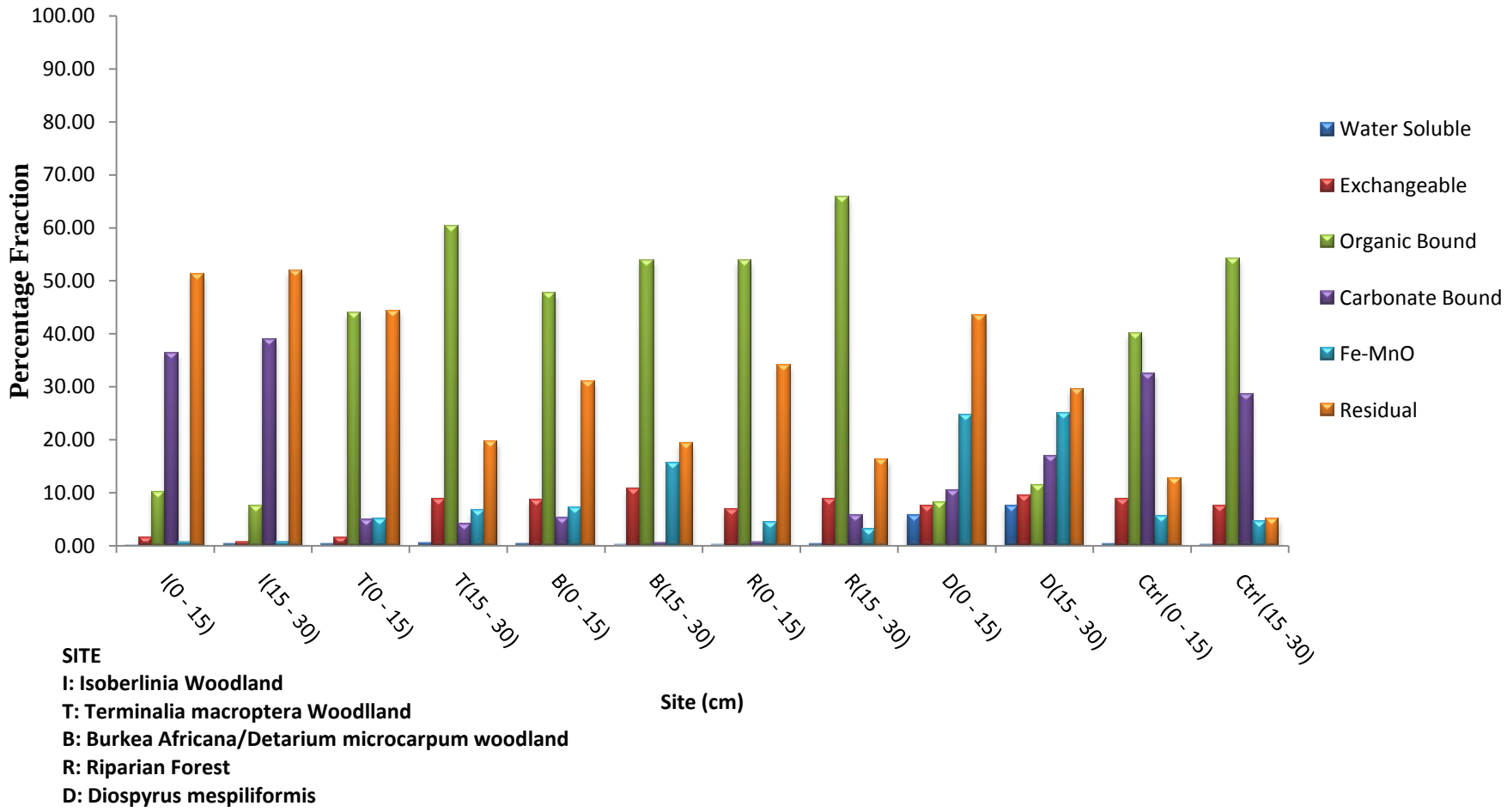
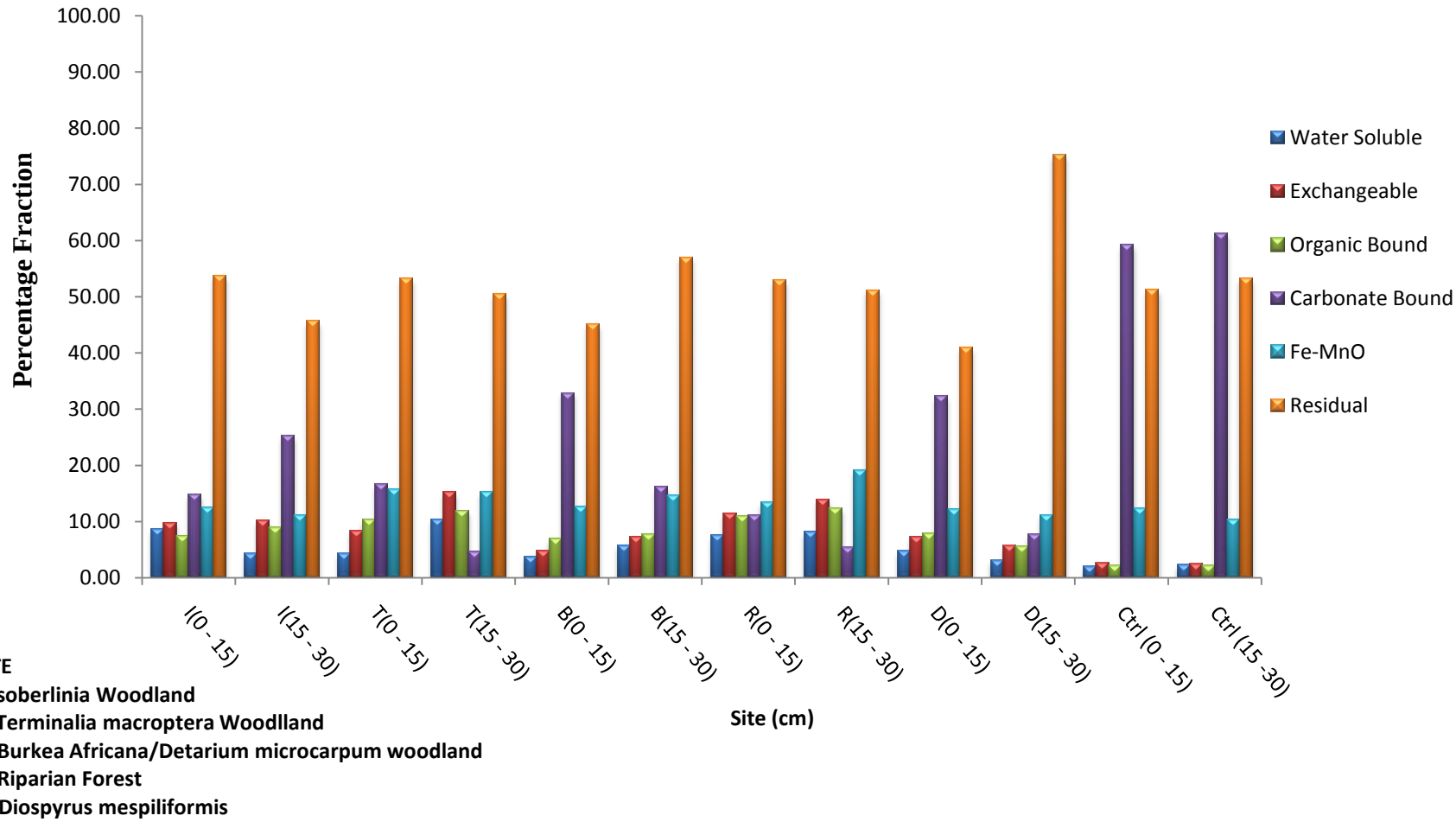
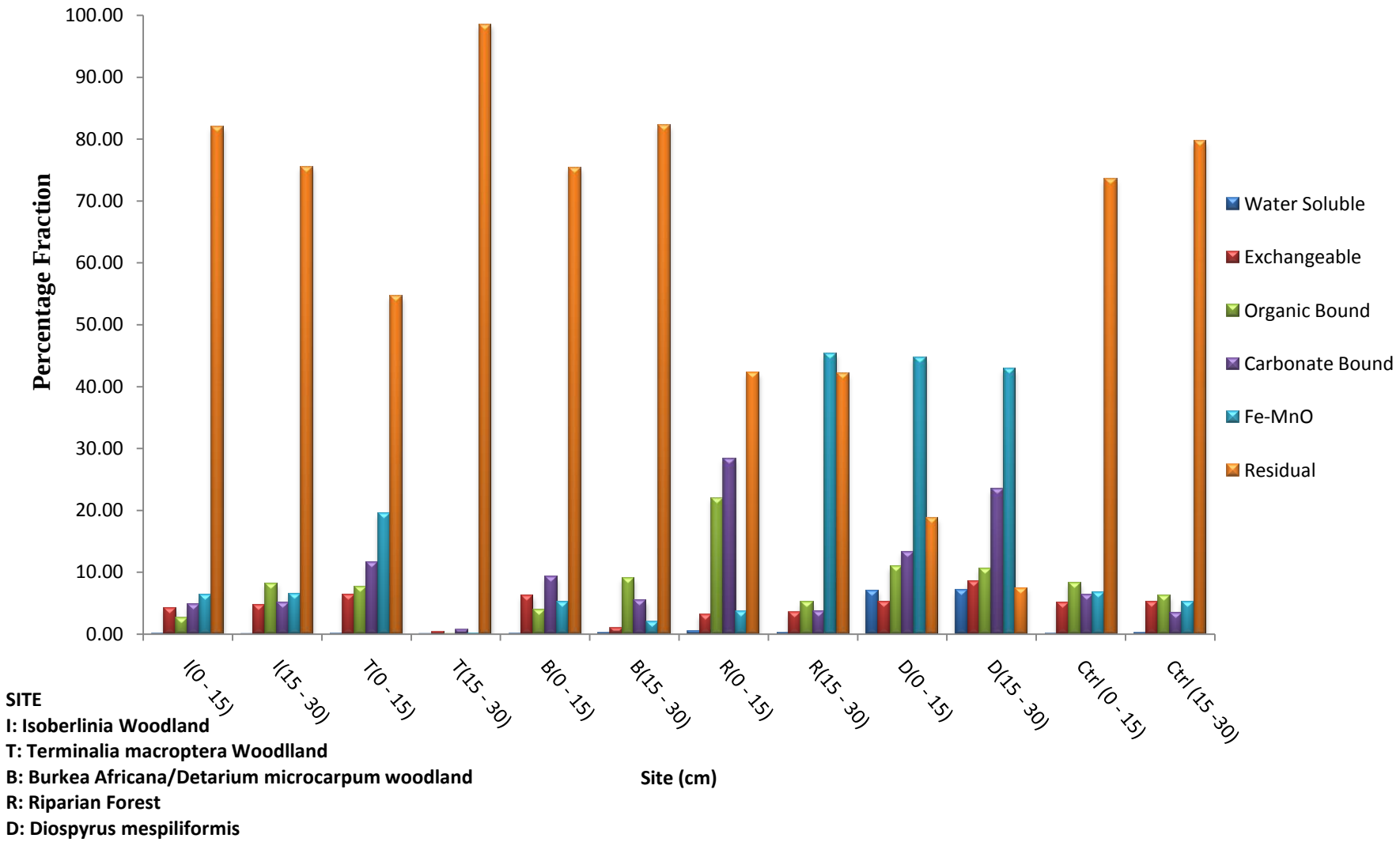


Figure 4.2a: Chemical fraction of Chromium in soils of the different vegetations of Oli forest in wet season of 2011



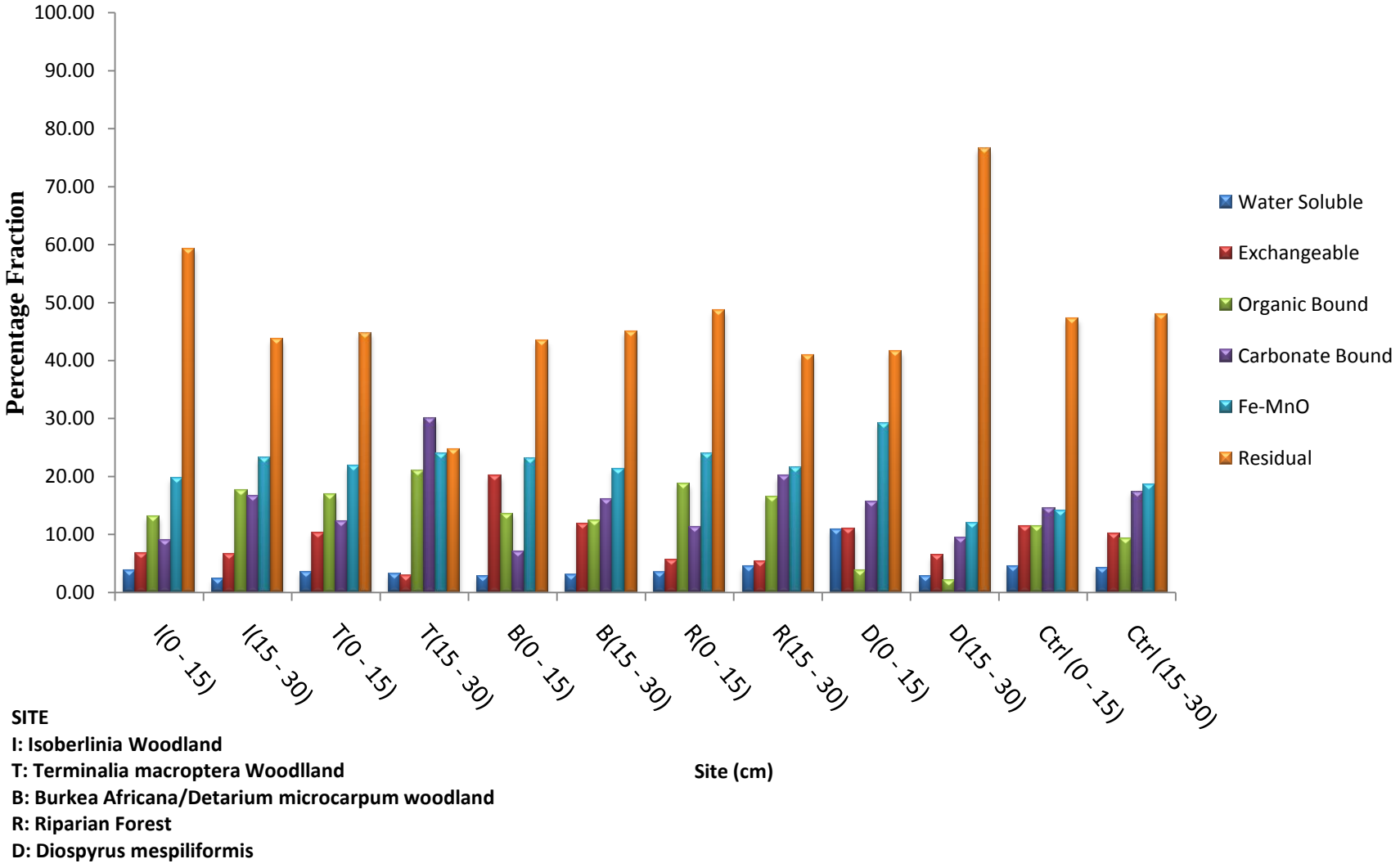
SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis

Figure 4.2b. Chemical fraction of Chromium in soils of the different vegetations of Oli forest in dry season of 2011



SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis

Figure 4.3a. Chemical fraction of Nickel in soils of the different vegetations of Oli forest in wet season of 2011



SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis

Figure 4.3b: Chemical fraction of Nickel in soils of the different vegetations of Oli forest in dry season 2011

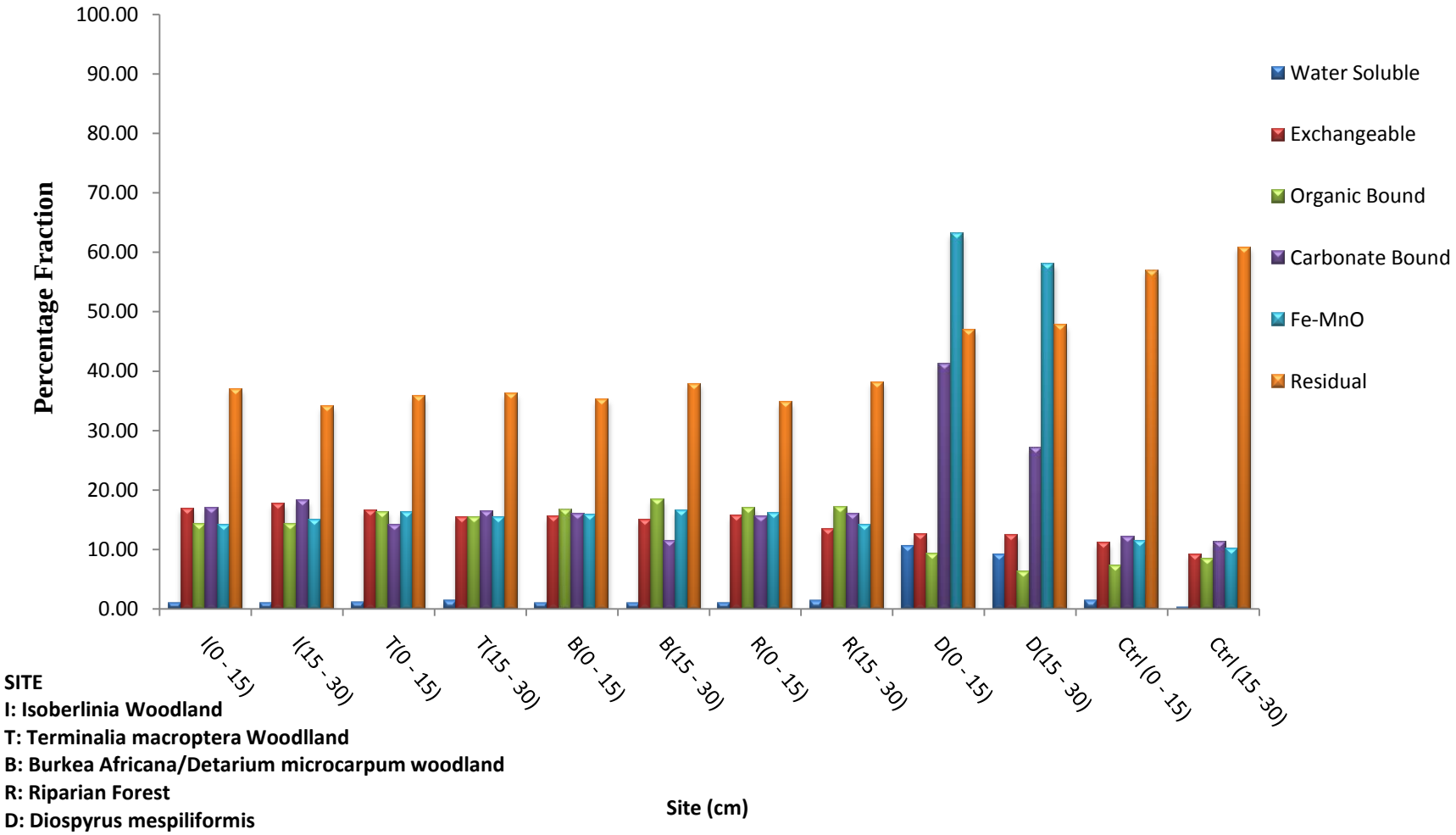
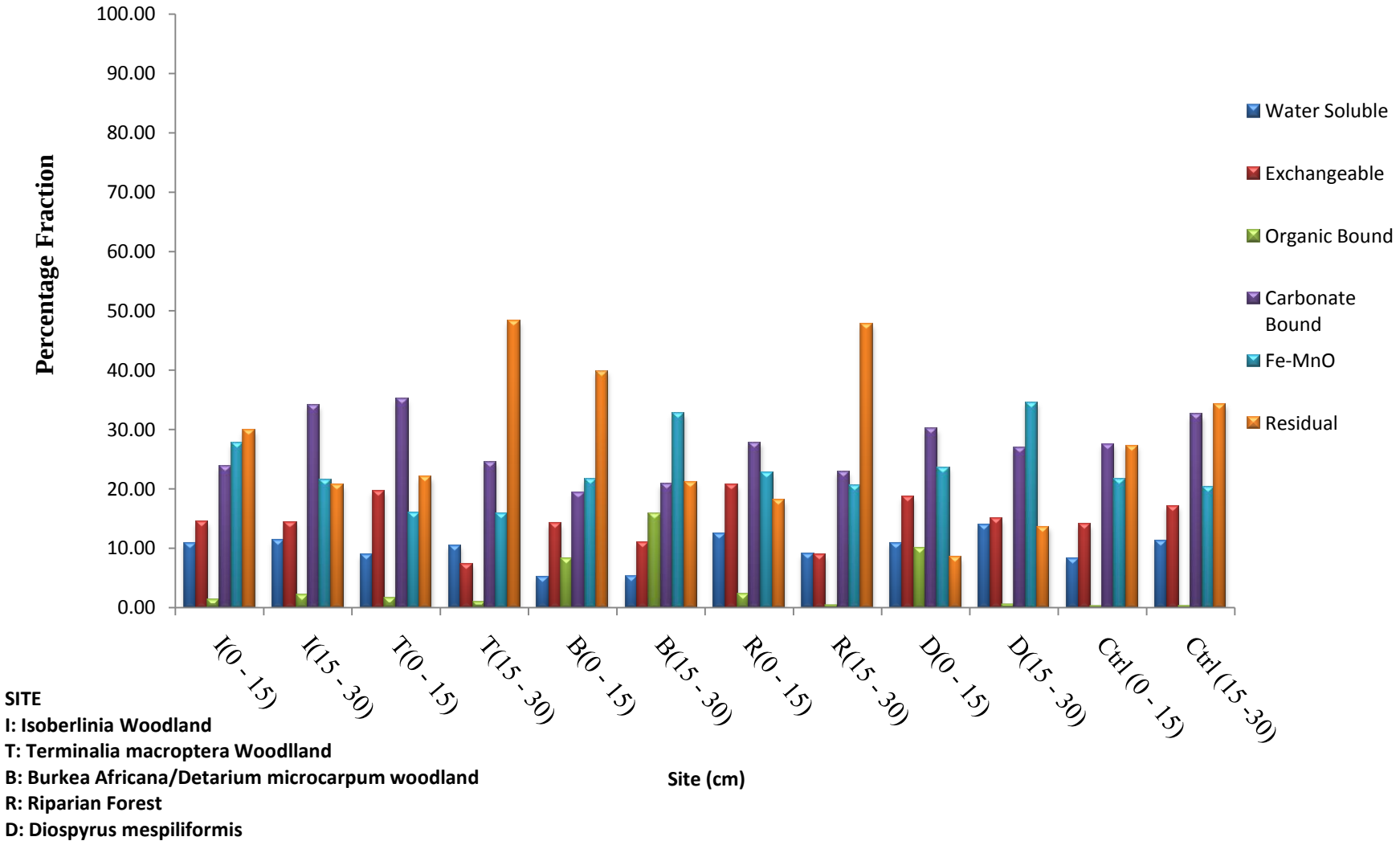


Figure 4.4a: Chemical fraction of Lead in soils of the different vegetations of Oli forest in wet season of 2011



SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis

Figure 4.4b: Chemical fraction of Lead in soils of the different vegetations of Oli forest in dry season of 2011

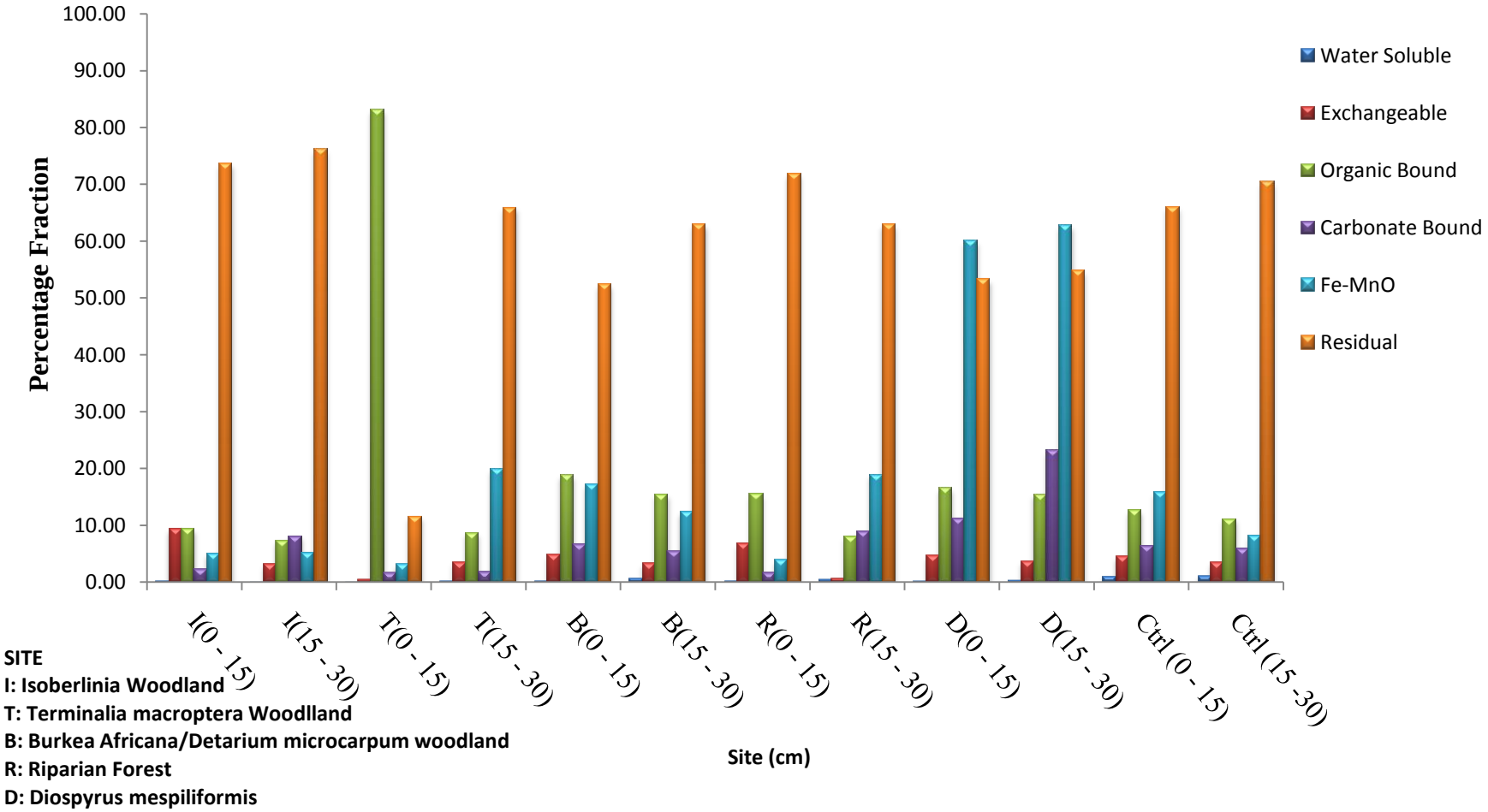


Figure 4.5a. Chemical fraction of Zinc in soils of the different vegetations of Oli forset in wet season of 2011

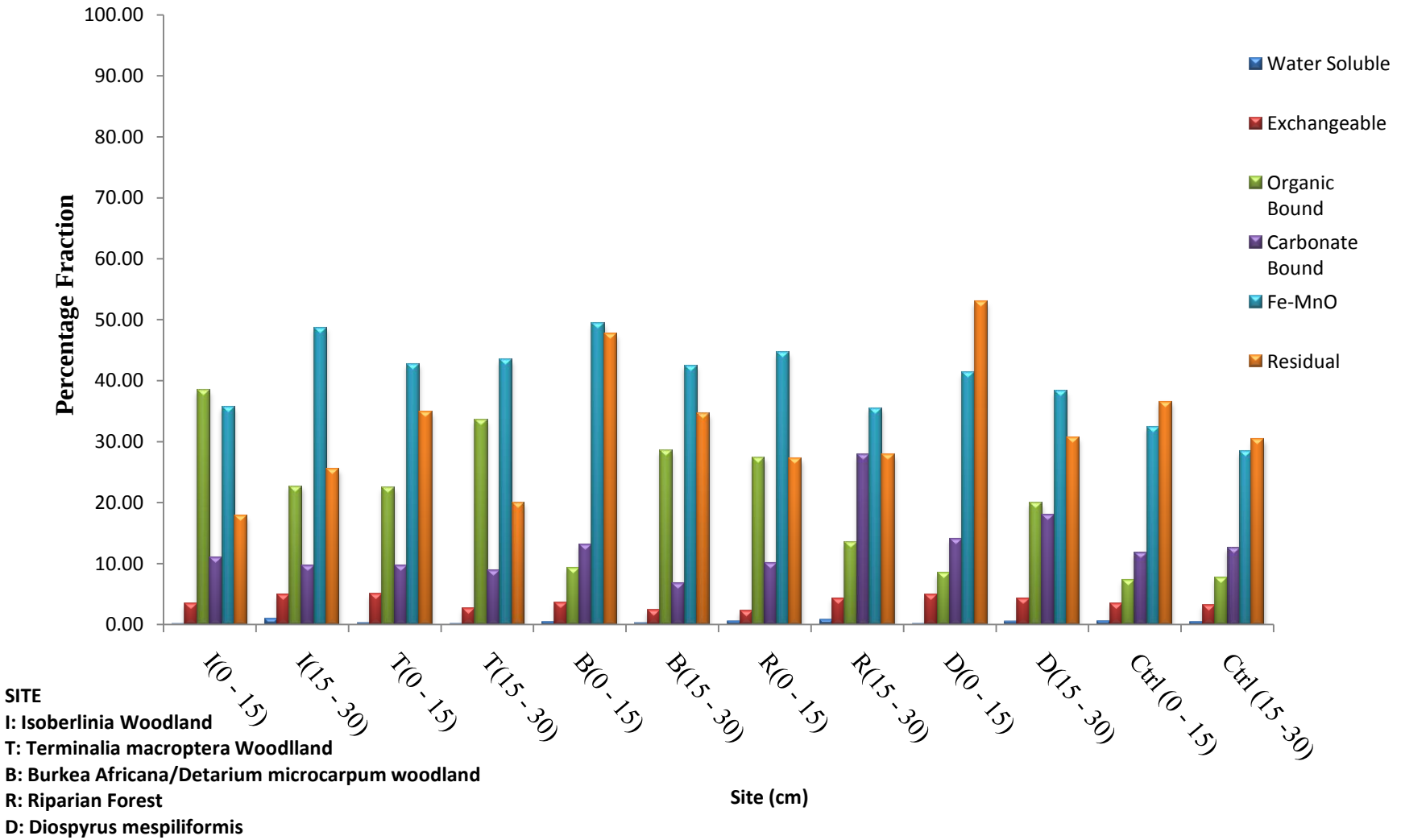
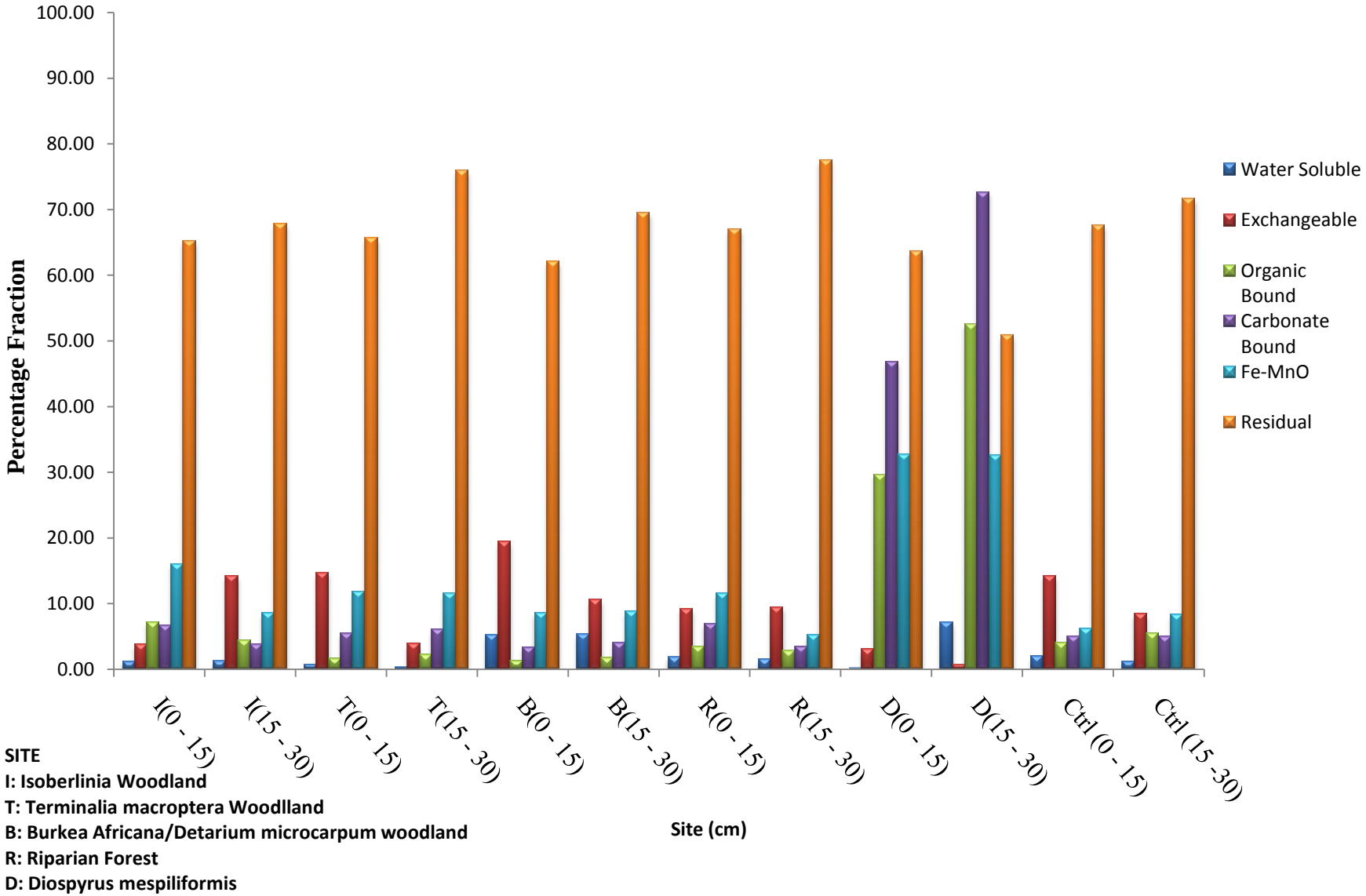
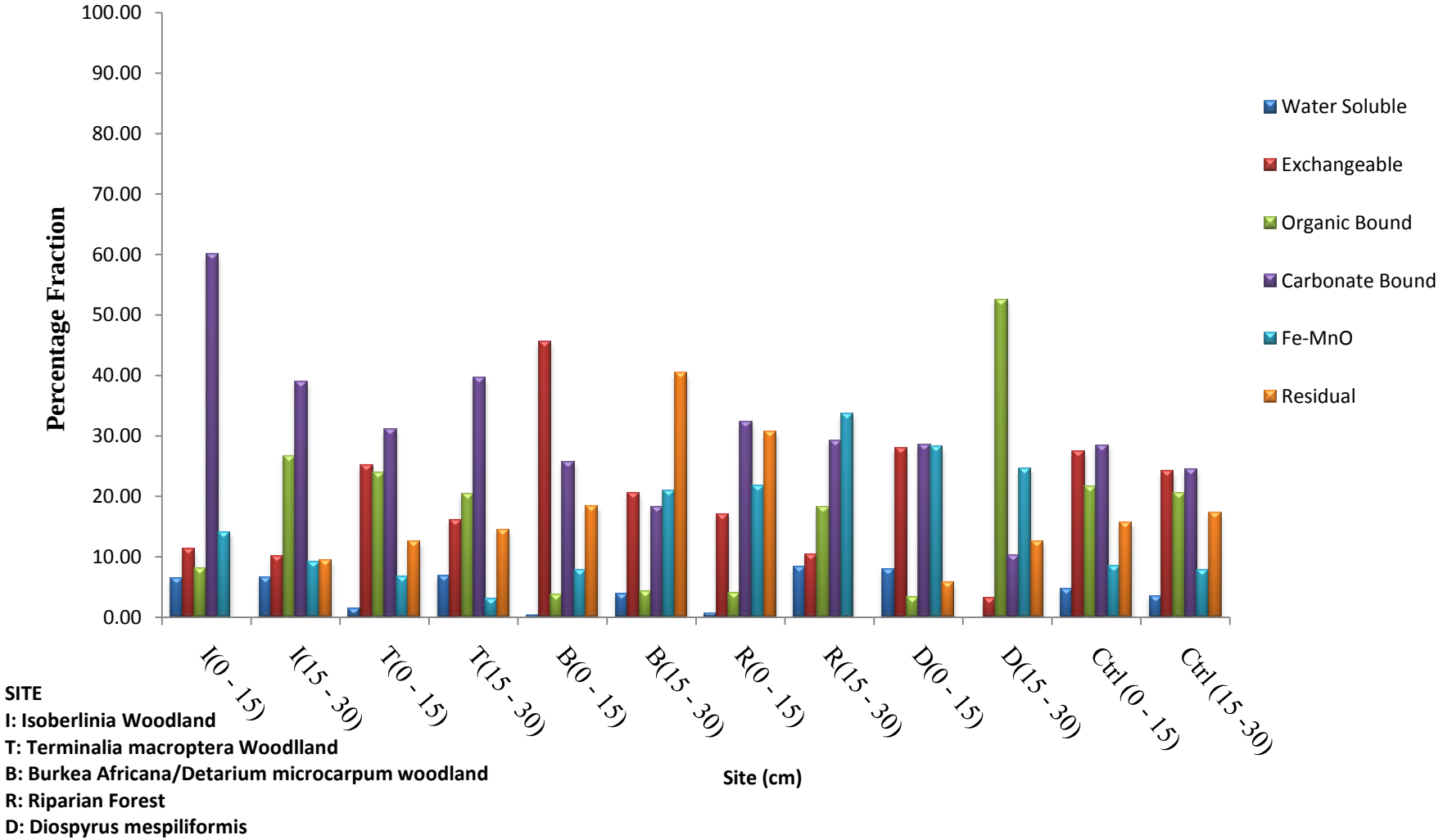


Figure 4.5b: Chemical fraction of Zinc in soils of the different vegetations of Oli forest in dry season of 2011



SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis

Figure 4.6a: Chemical fraction of Copper in soils of the different vegetations of Oli forest in wet season of 2011



SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis

Figure 4.6b: Chemical fraction of Copper in soils of the different vegetations of Oli forest in dry season of 2011

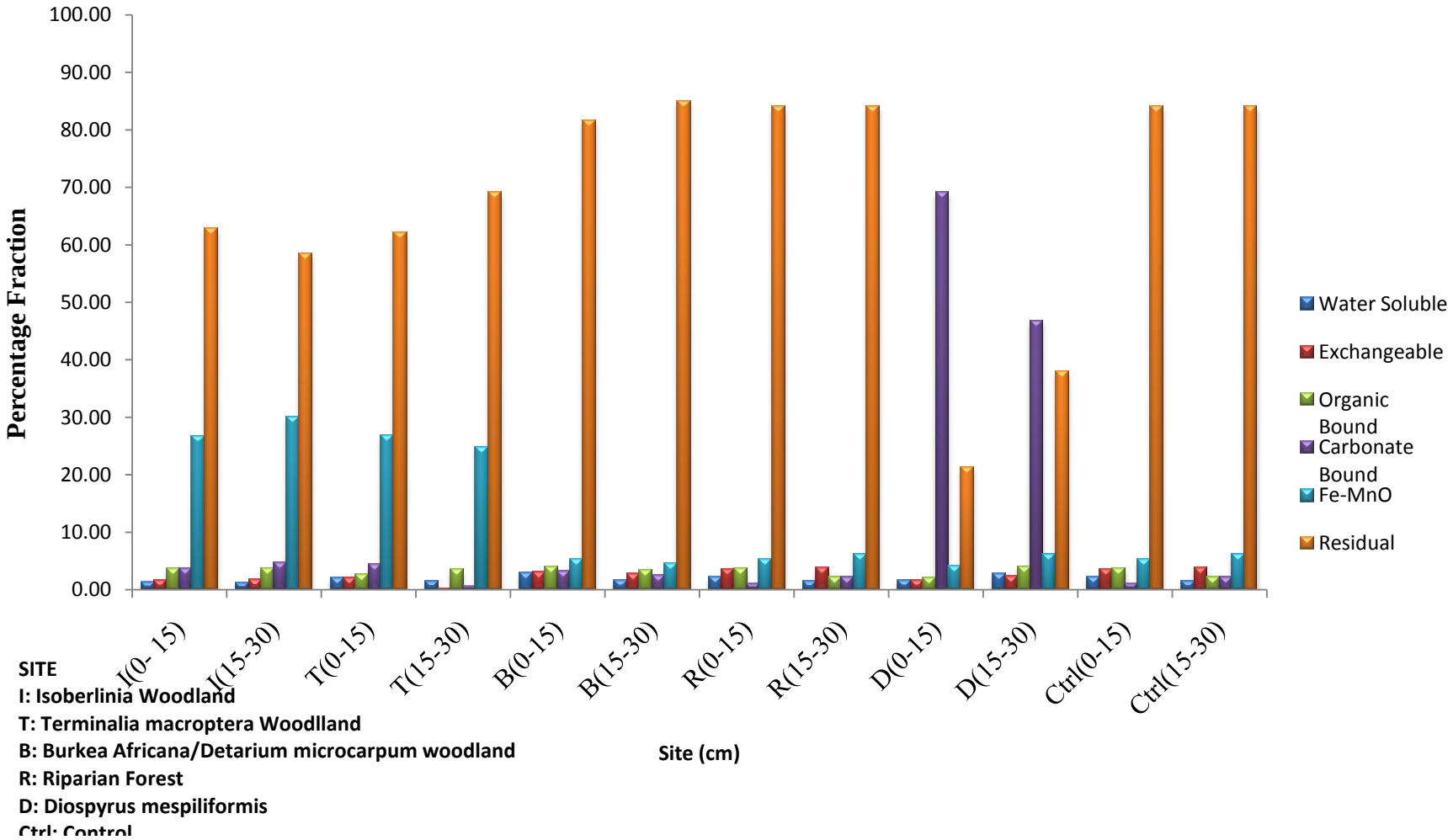
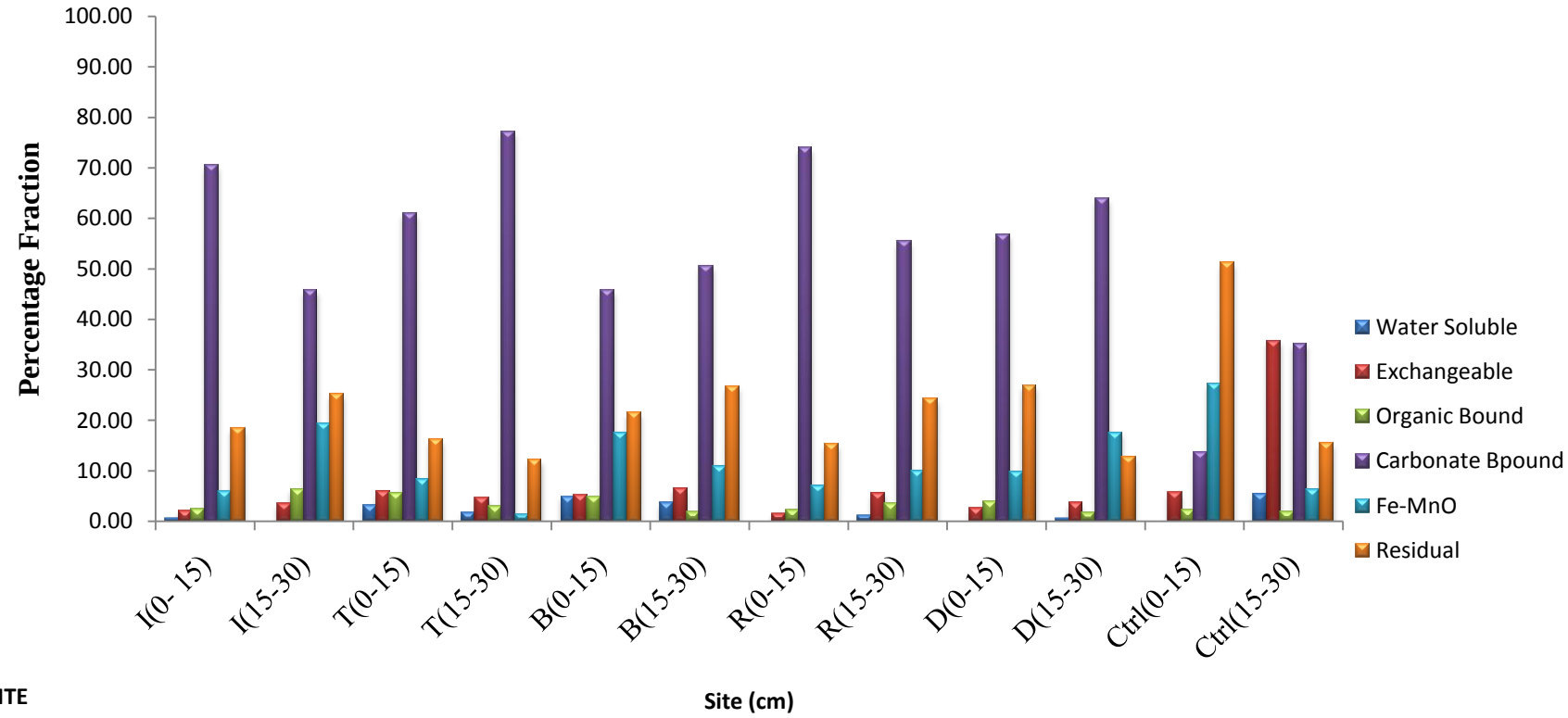
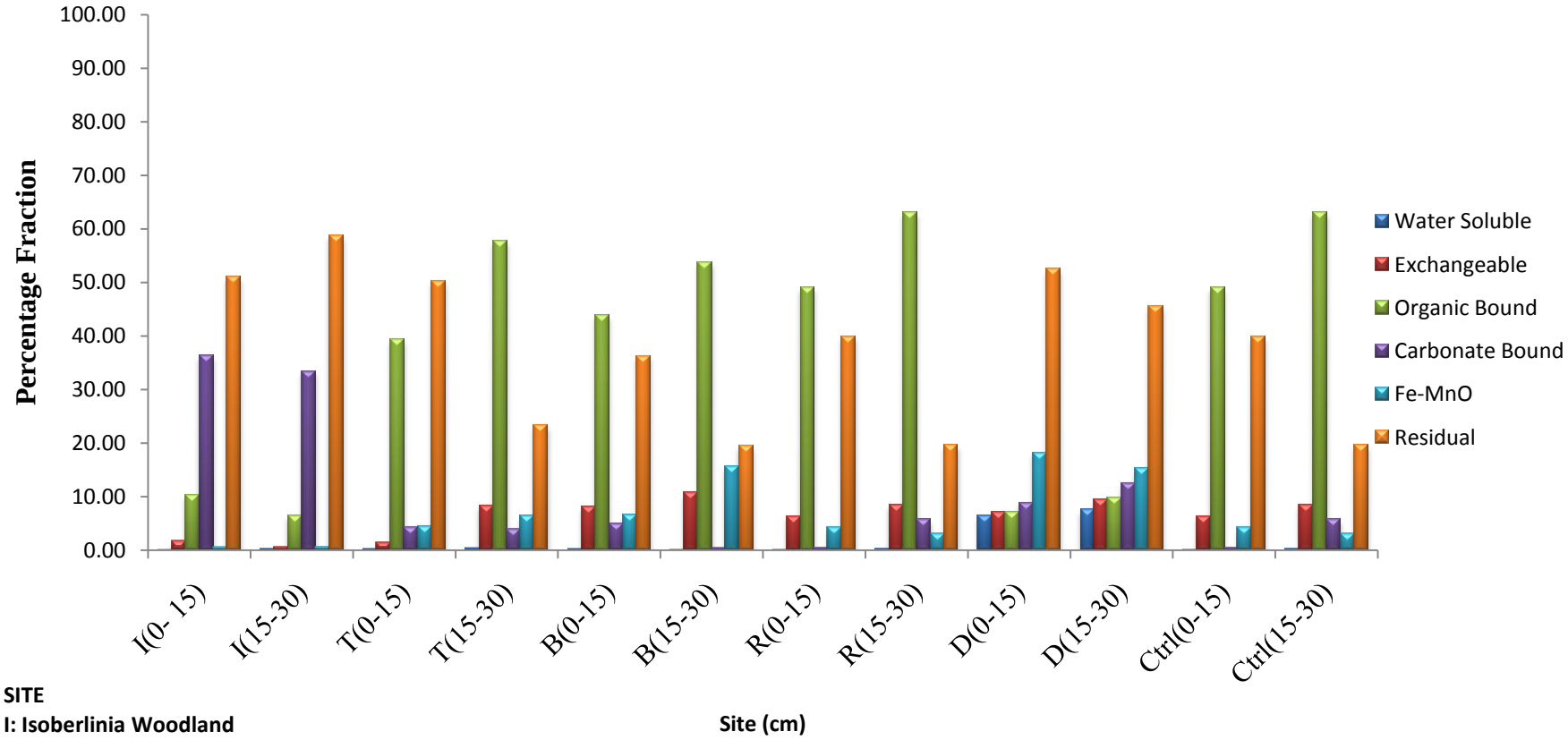


Figure 4.7a: Chemical fraction of Cadmium in soils of the different vegetations of Oli forest in wet season of 2012



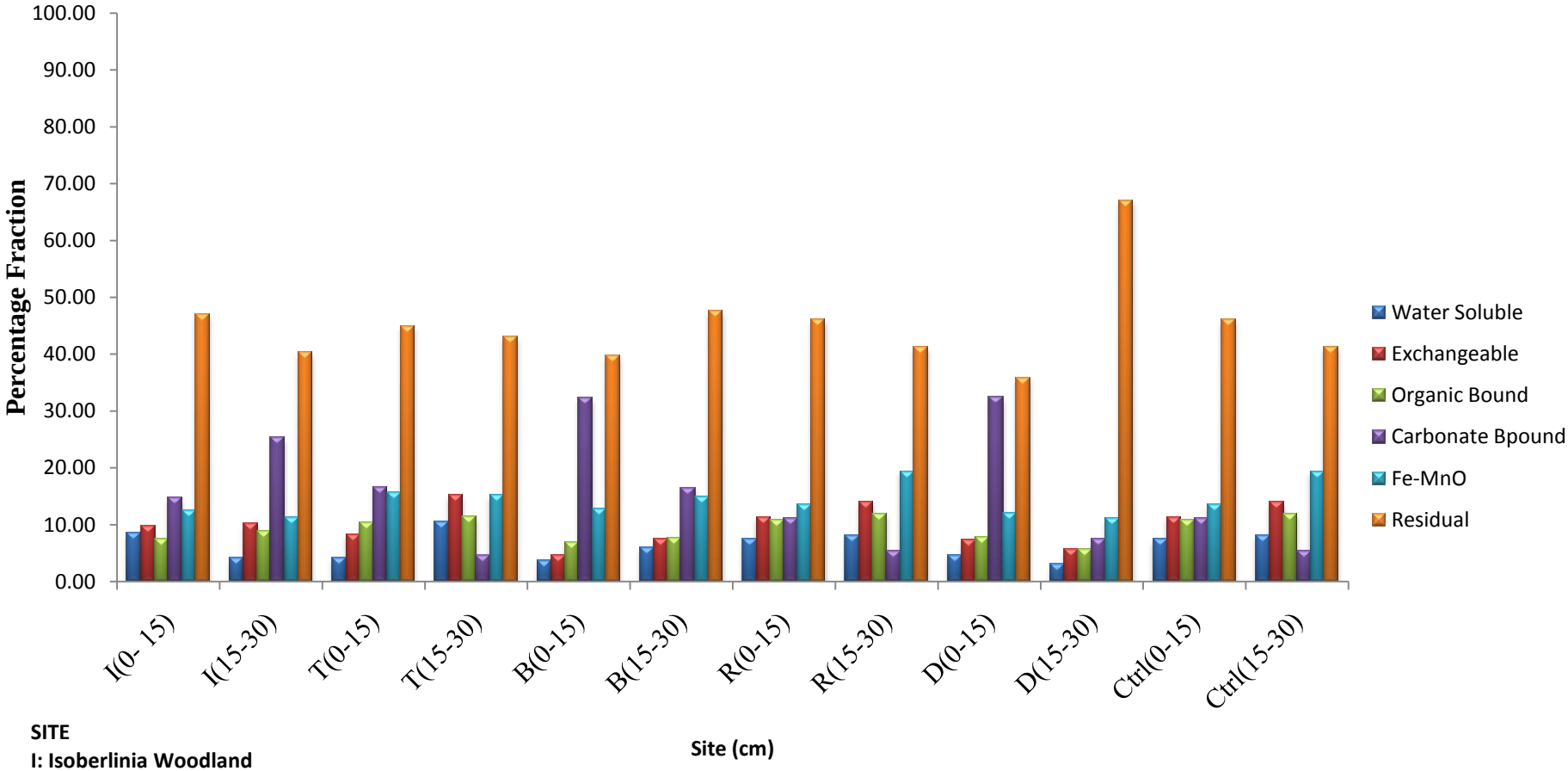
SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis
Ctrl: Control

Figure 4.7b: Chemical fraction of Cadmium in soils of the different vegetations of Oli forest in dry season of 2012



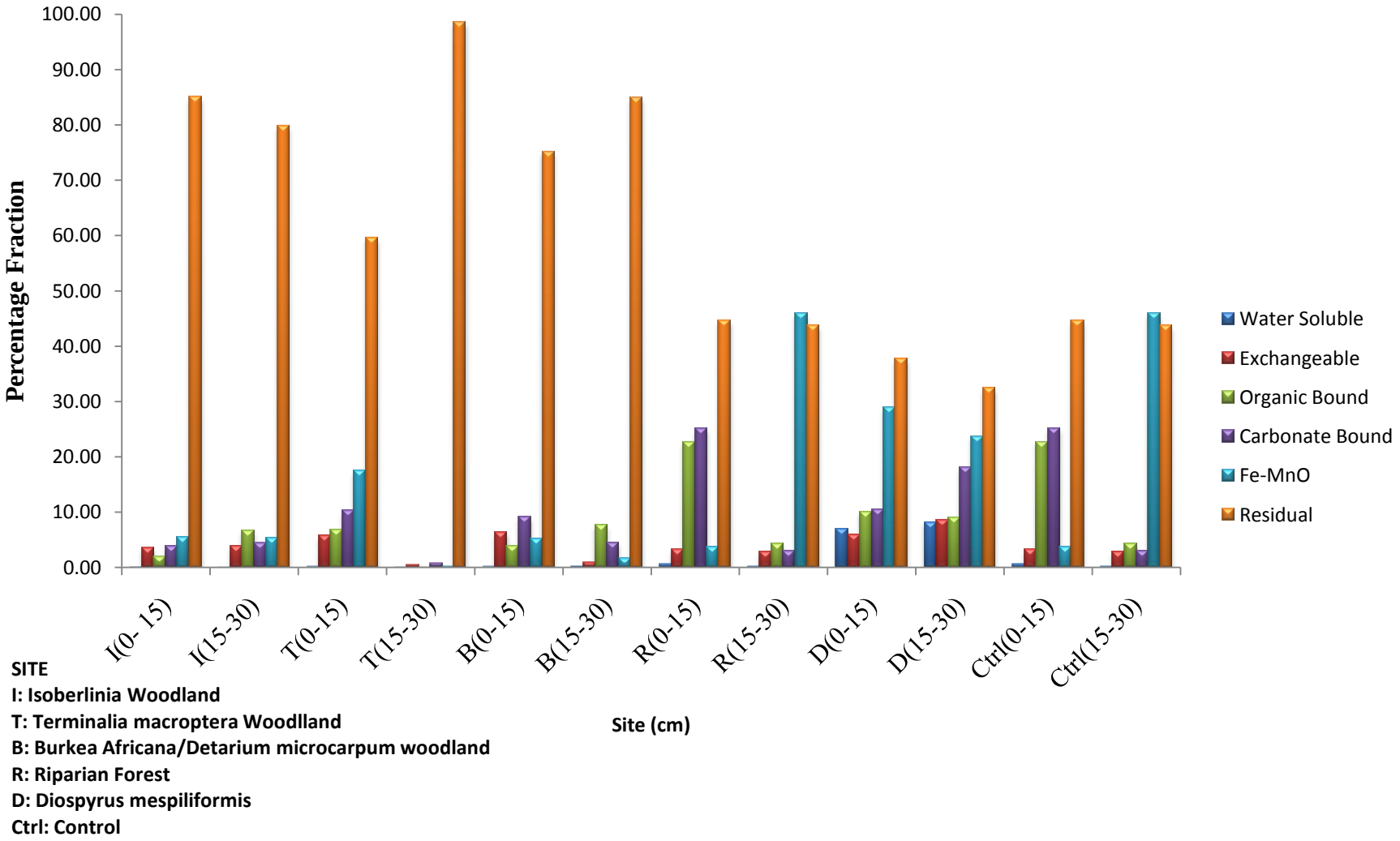
SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis
Ctrl: Control

Figure 4.8a. Chemical fraction of Chromium in soils of the different vegetations of Oli forest in wet season of 2012



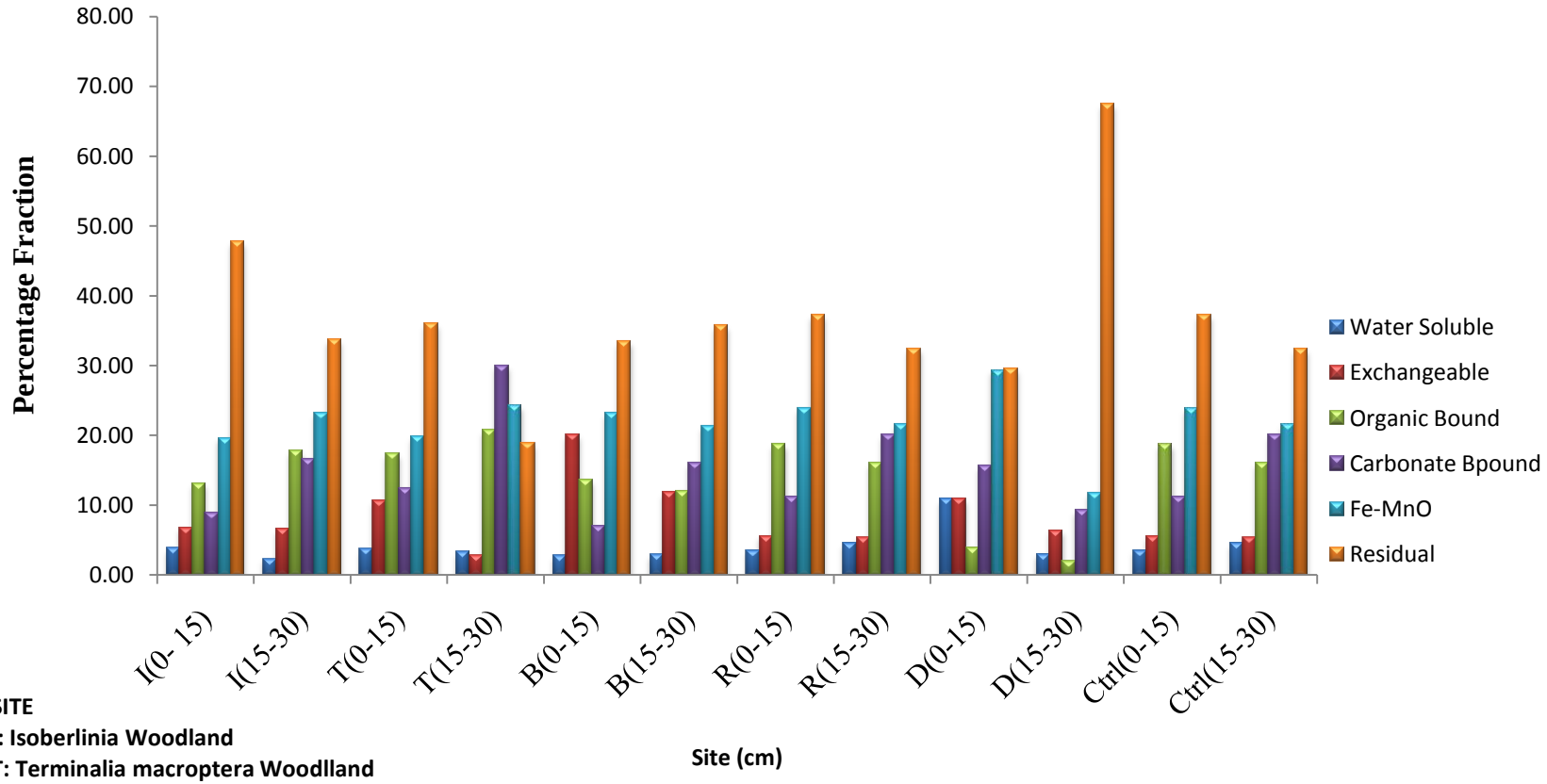
SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis
Ctrl: Control

Figure 4.8b: Chemical fraction of Chromium in soils of the different vegetations of Oli forest in dry season of 2012



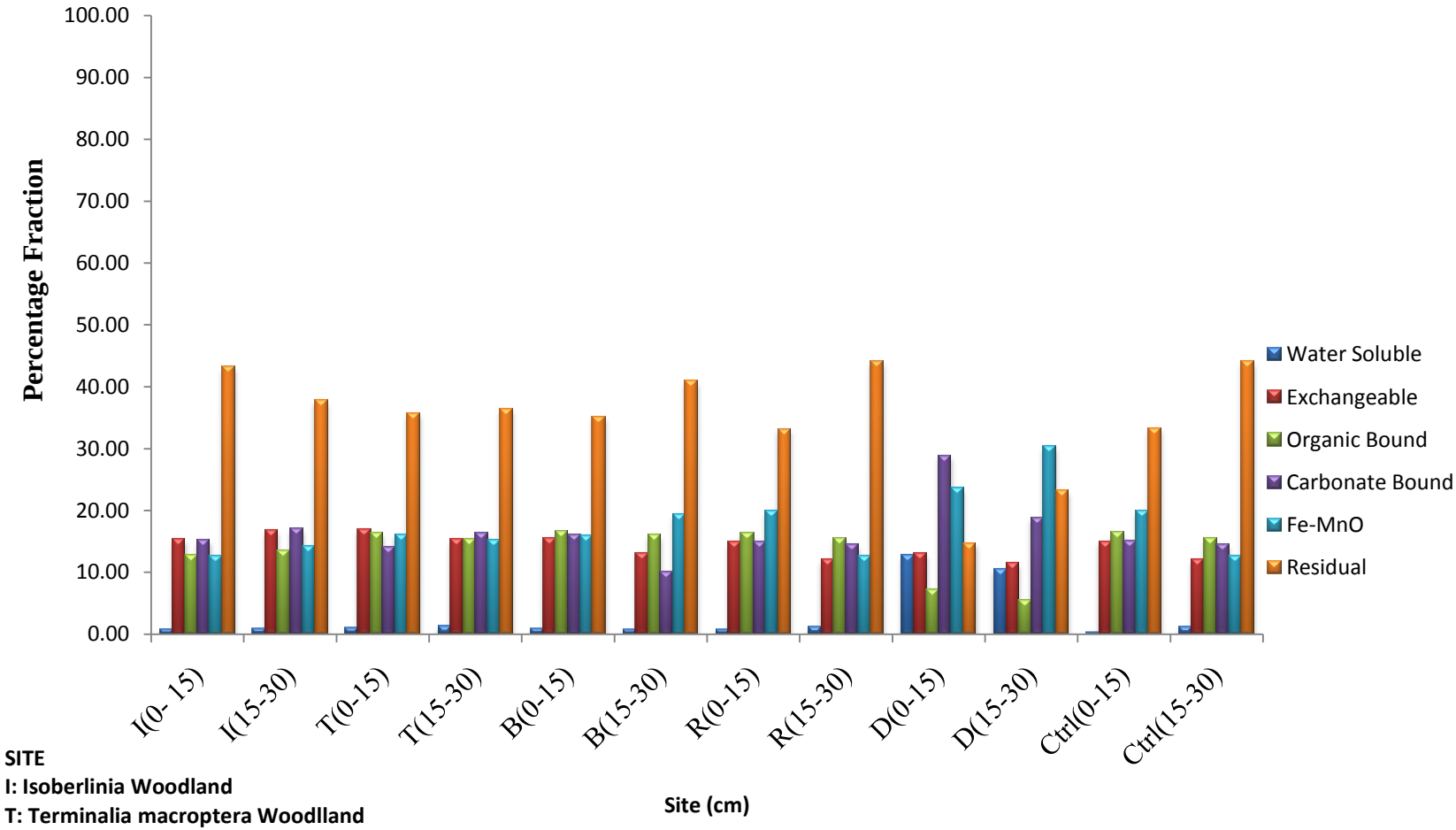
SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis
Ctrl: Control

Figure 4.9a: Chemical fraction of Nickel in soils of the different vegetations Oli forest in wet season of 2012



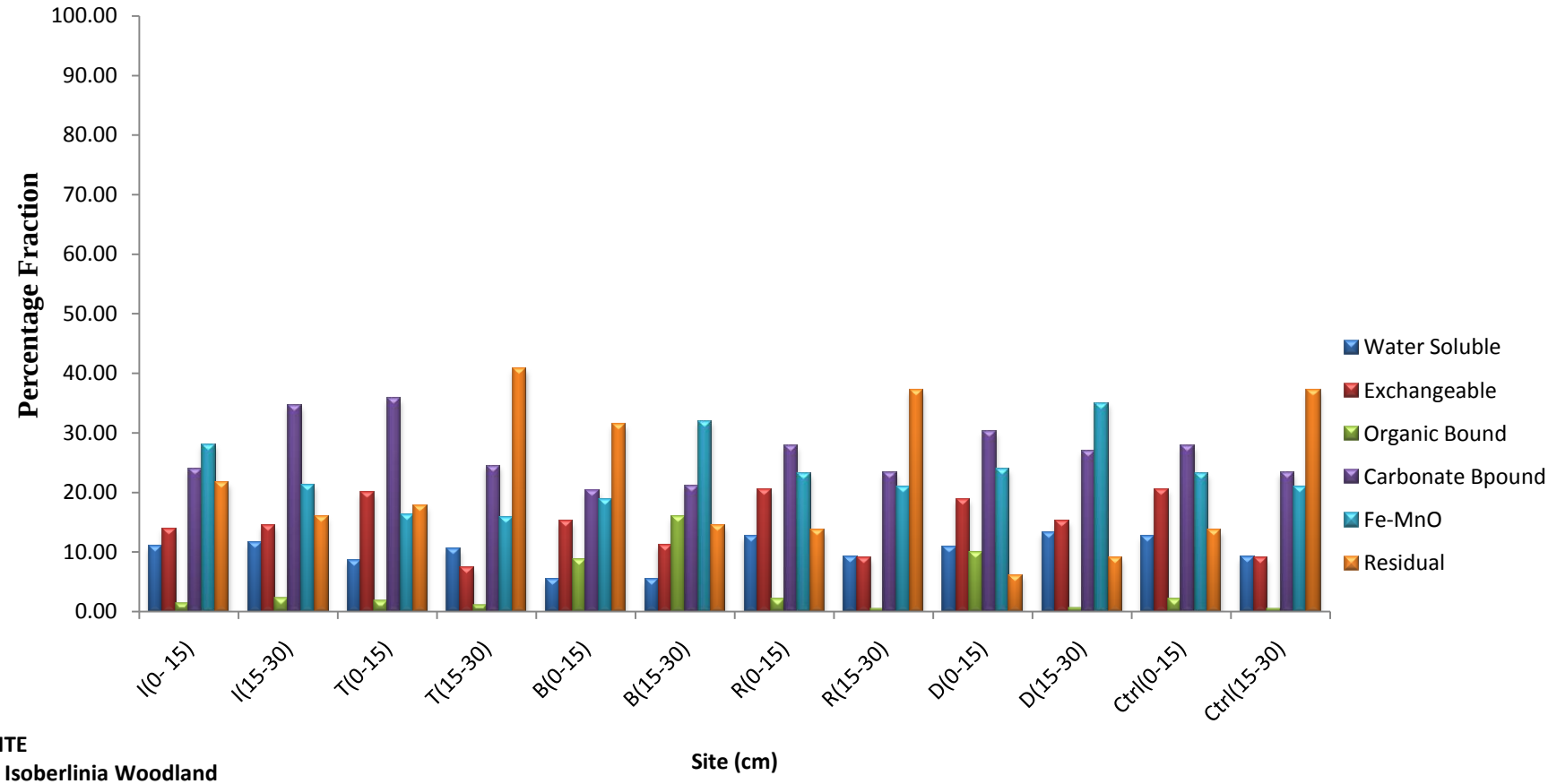
SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis
Ctrl: Control

Figure 4.9b: Chemical fraction of Nickel in soils of the different vegetations Oli forest in dry season of 2012



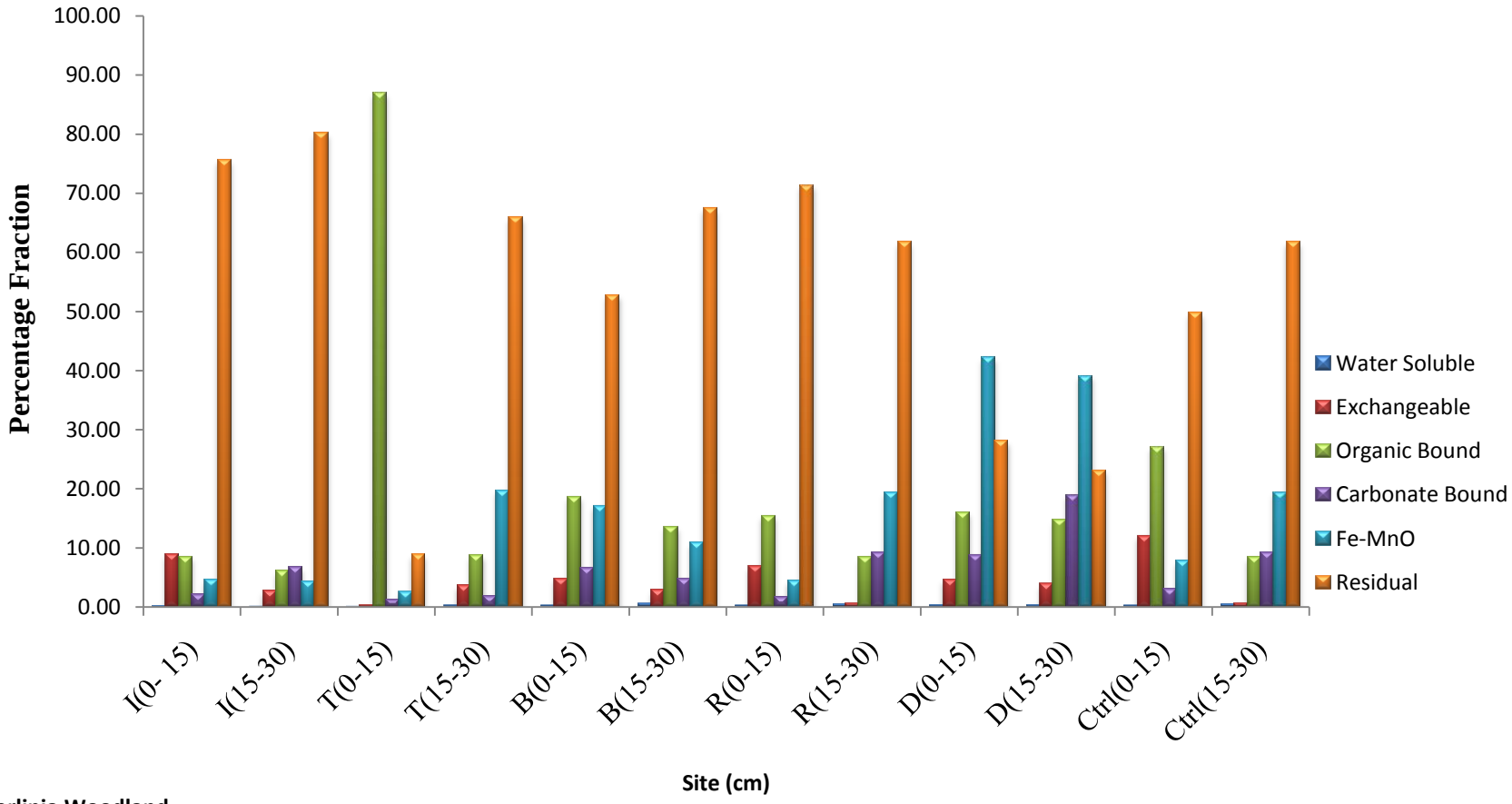
SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis
Ctrl: Control

Figure 4.10a: Chemical fraction of lead in soils of the different vegetations Oli forest in wet season of 2012



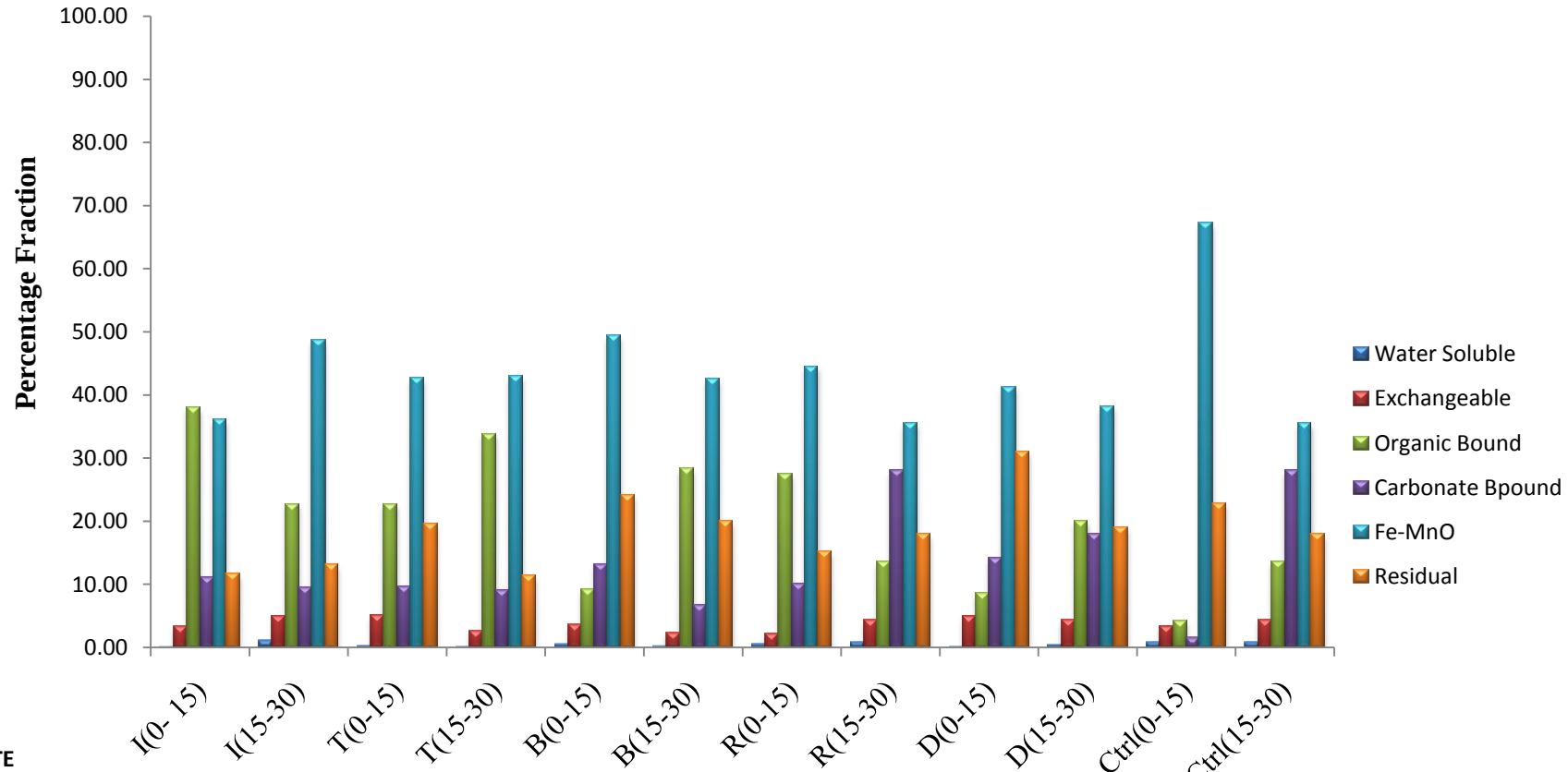
SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis
Ctrl: Control

Figure 4.10b: Chemical fraction of lead in soils of different vegetations of Oli forest in dry season of 2012



SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis
Ctrl: Control

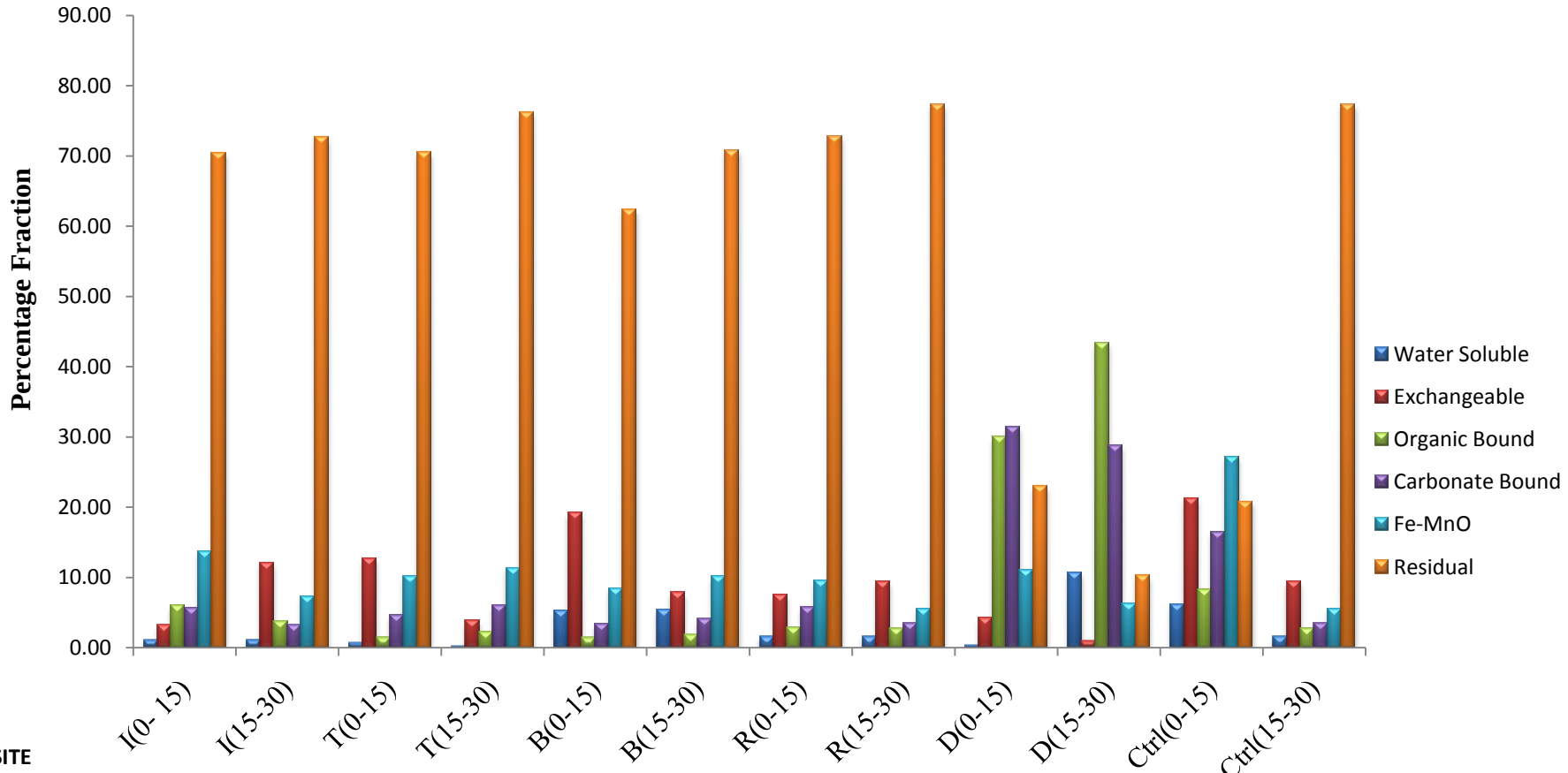
Figure 4.11a: Chemical fraction of Zinc in soils of the different vegetations of Oli forest in wet season of 2012



SITE

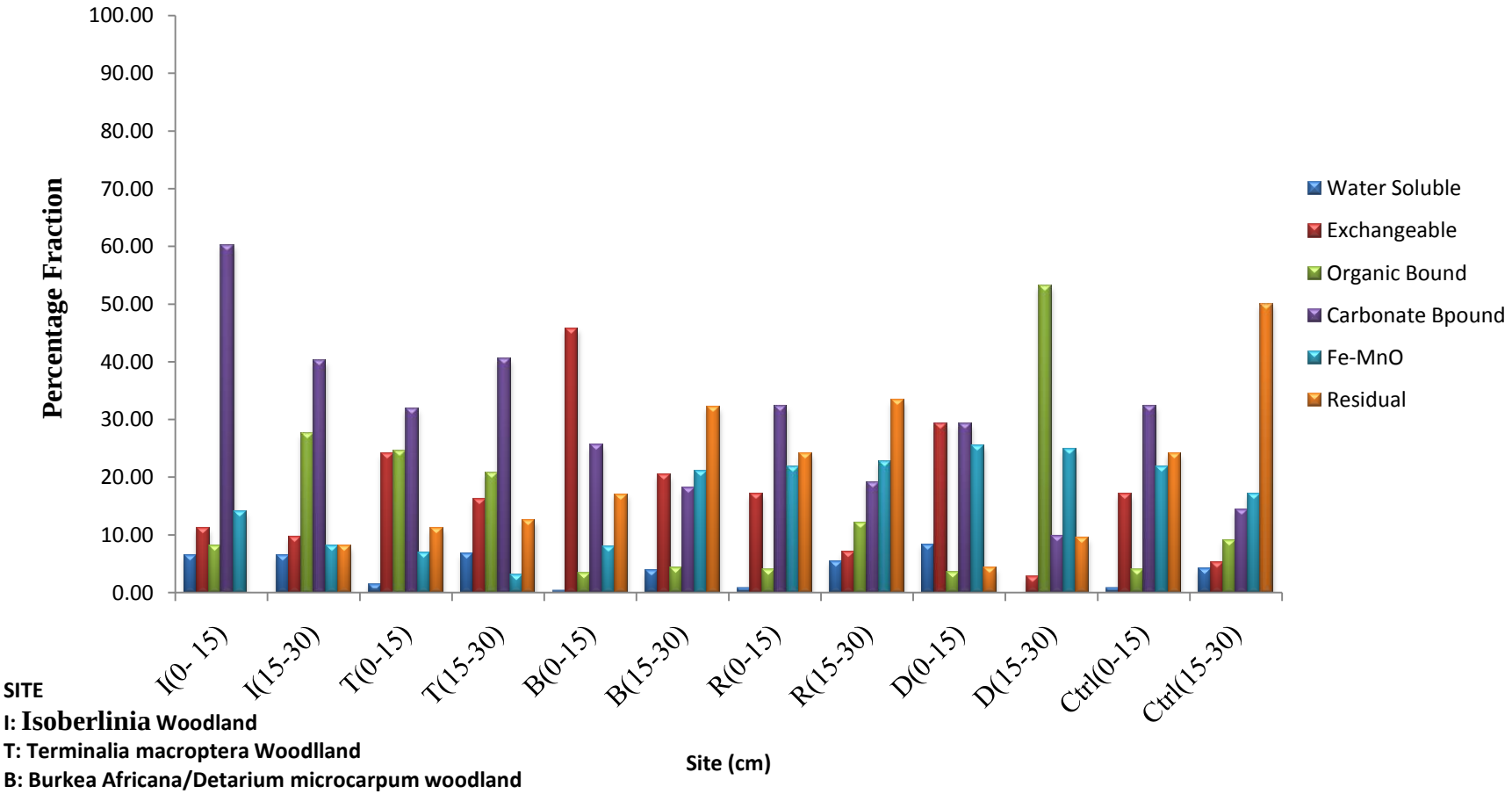
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis
Ctrl: Control

Figure 4.11b: Chemical fraction of Zinc in soils of the different vegetations of Oli forest in dry season of 2012



SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis
Ctrl: Control

Figure 4.12a:s Chemical fraction of copper in soils of the different vegetations of Oli forest in wet season of 2012



SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis
Ctrl: Control

Figure 4.12b: Chemical fraction of copper in soils of the different vegetations of Oli forest in dry season 2012

4.7: Pollution Indices for the Assessment of the soils of the Vegetation Zones in Oli Forest

Mobility factor (MF) is an index for assessing the mobility of metal ions in soil (Ogunfowokan *et al.,* 2009), values for 2011 seasons in the soil of Oli forest are presented in (Fig 4.13 – 4.17), on the basis of the absolute and relative values of the fractions (F1, F2 and F3) which were weakly bound to the soil components using the relationship:

$$MF = \frac{F1 + F2 + F3}{F1 + F2 + F3 + F4 + F5 + F6} X\,100$$

MF = Mobility Factor
F1 = Fraction soluble in soil solution
F2 = Exchangeable Fraction
F3 = Carbonate bound fraction
F6 = Residual fraction.

The values of the mean percentage mobility factor (MF) for the various metals at different vegetations of Oi forest during the wet season of 2011 at the 0 - 15 cm depth for Cadmium had an overall MF mean of 8.87, the value obtained decreased in the order: *Terminalia macroptera* woodland (14.55) □ *Burkea africana* woodland (13.94) > *Diospyrus mespilisformis* woodland (6.47) > *Isoberlinia* woodland (5.71) > *Riparian forest* (3.72). An overall mobility factor of 7.36 at depth (15-30cm) in the same dry season of 2011 was in the order:

Burkea africana woodland (11.92) > *Riparian forest* (10.20) >*Terminalia macroptera woodland* (9.55) > *Isoberlinia woodland* (9.54) > *Diospyrus mespiliformis woodland* (5.79). In the wet season, there was little variation in MF values between the two depths $7.46_{(0-15\ cm)}$ and $8.13_{(15-30\ cm)}$ and also among the sites investigated.

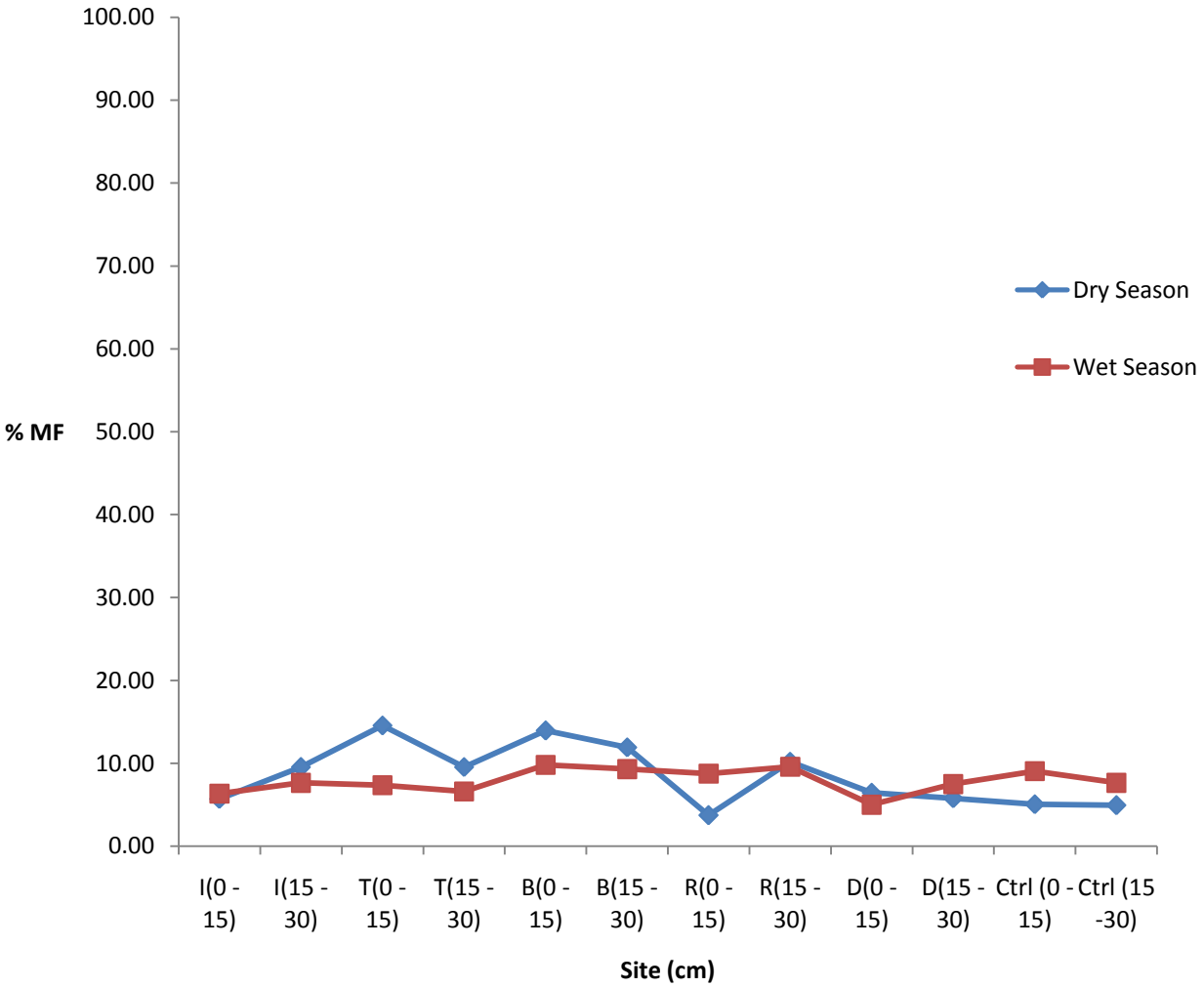
The overall percentage MF means for chromium $24.22_{(0 - 15\ cm)depth}$ and $24.04_{(15 - 30\ cm)depth}$ for different vegetations for the two depths and seasons studied were found higher than the values obtained for cadmium.. The decreasing order for the two depths follows as

Riparian (27.80) > *Isoberlinia* (24.08) > *Terminalia* (21.08) > *Diospyrus* (18.68) > *Burkea*(14.48)

and *Terminalia* (34.74) > Riparian (31.11) > *Isoberlinia* (22.05) > *Burkea* (19.02) > Diospyrus (13.30) respectively.

and *Riparian forest*. The decreasing order for both depths 0 – 15 cm and 15 - 30 cm followed *Riparian* (25.69) > *Diospyrus* (23.23) > *Terminalia* (14.22) > *Burkea* (10.27) > *Isoberlinia* and *Diospyrus* (26.26) > *Isoberlinia* (12.89) > *Terminalia* (10.51) > *Burkea* (10.33) > *Riparian* (8.90) respectively.

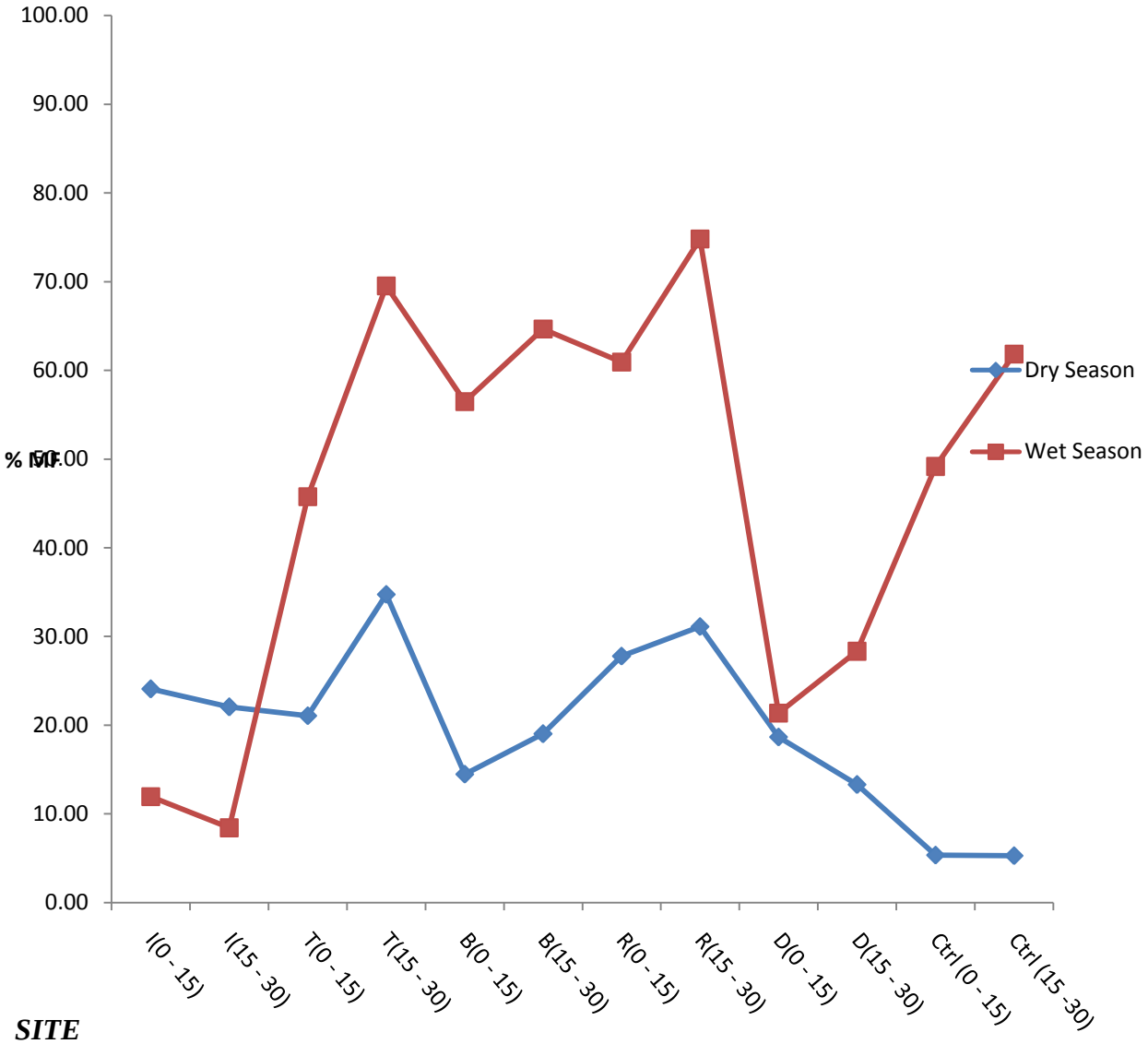
Lead, zinc and copper had similar mean values of mobility factor 30.53, 22.46, 36.76 in dry season respectively and 30.04, 32.59, 17.67 in wet season respectively at the same depth 0 - 15 cm. Considering 15 – 30 cm depth, mobility factor values were lower than the values obtained at 0 - 15 cm depth in dry season: Pb (23.93), Zn (25.00) and Cu (40.77). In wet season the values correspond to Pb (29.67), Zn (12.74) and Cu (17.13). In the dry season of 2012 from Appendix XXVI, the decreasing order for the metals followed order of pattern: For Pb at *Isoberlinia* woodland (26.34), *Burkea* (29.40), T (30.30) *Riparian* forest (35.31) *Diospyrus m* woodland (39.86) and Control (35.31); Cu at *Burkea* woodland (13.25), *Diospyrus melispiformis* (13.52) *Termilania macroptera* woodland (28.05), *Riparian* forest (30.21) *Isoberlinia* woodland (41.38) and Control (35.31), and control (18.36); Ni at *Isoberlinia* woodland (23.70), *Detarium* (25.94), *Riparian* (27.87), *Terminalia macroptera* (31.73), *Burkea* (36.42) and Control (27.87).



SITE

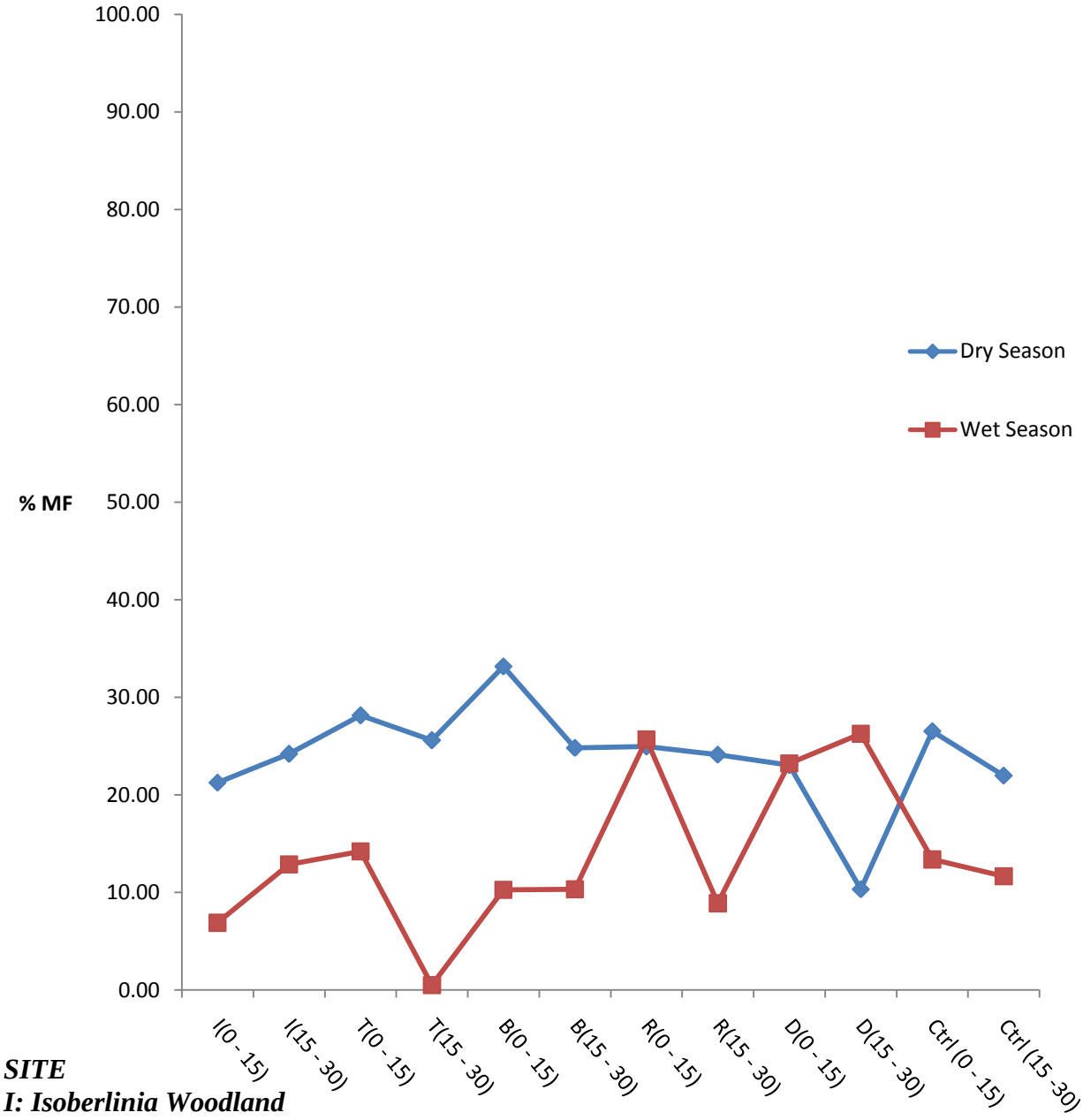
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis

Figure 4.13: Mobility factor for Cd in the soils of the different vegetations of Oli forest in 2011



SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis

Figure 4.14: Mobility factor for Cr in the soils of the different vegetations of Oli forest in 2011



SITE
I: Isoberlinia Woodland
T: Terminalia macroptera Woodlland
B: Burkea Africana/Detarium microcarpum woodland
R: Riparian Forest
D: Diospyrus mespiliformis

Figure 4.15: Mobility factor for Ni in the soils of the different vegetations of Oli forest in 2011

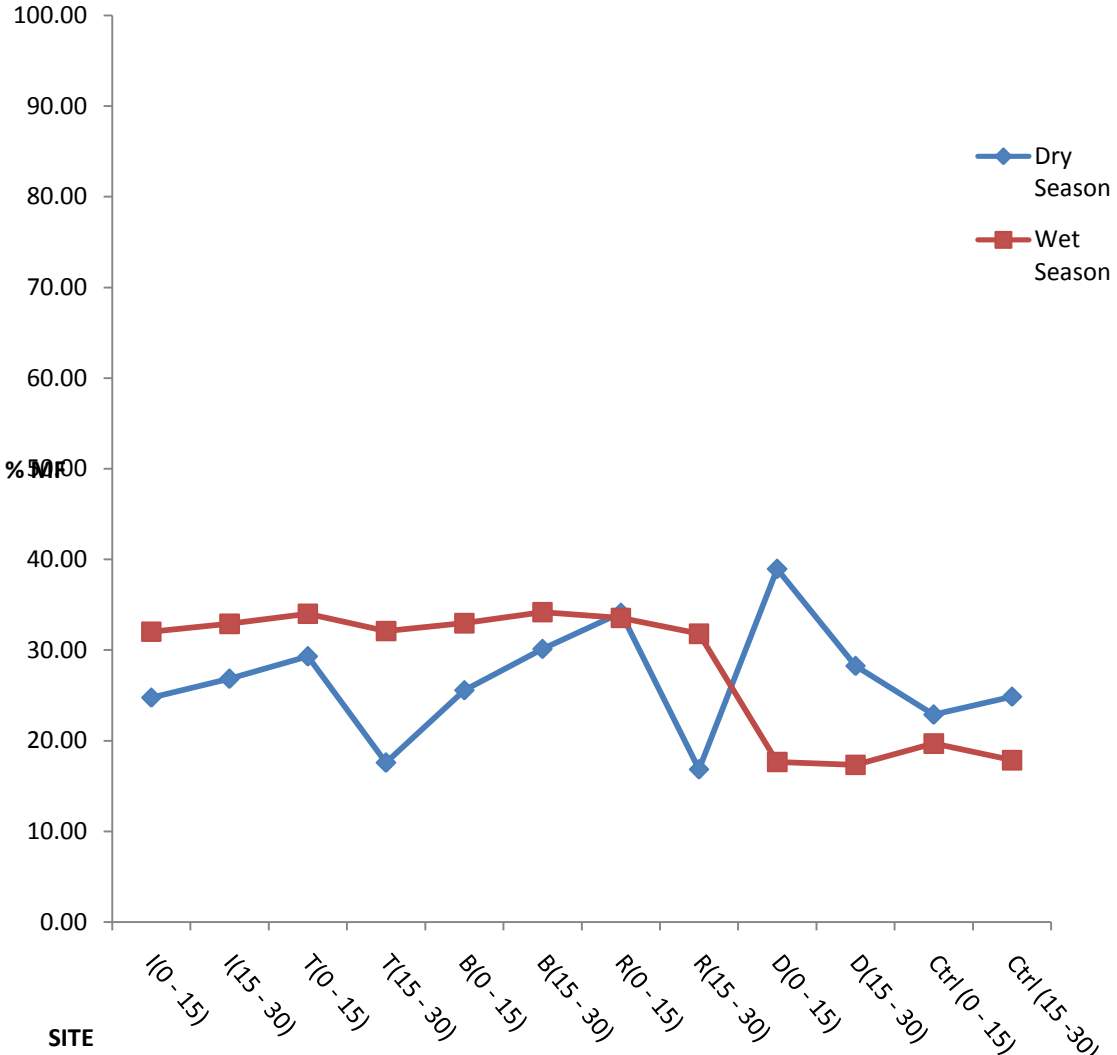


Figure 4.16: Mobility factor for Pb in the soils of the different vegetations of Oli forest in 2011

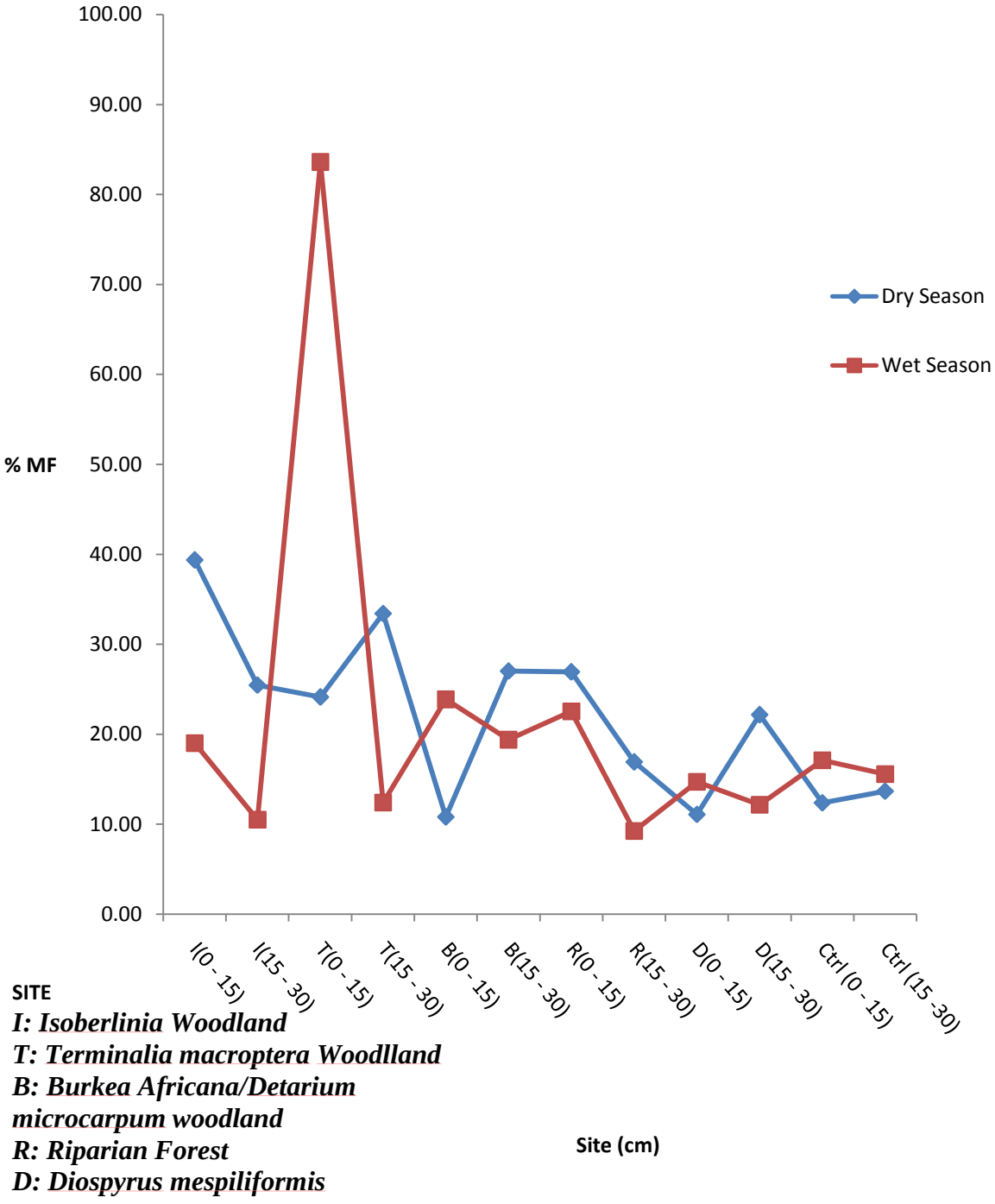


Figure 4.17: Mobility factor for Zn in the soils of the different vegetations of Oli forest in 2011

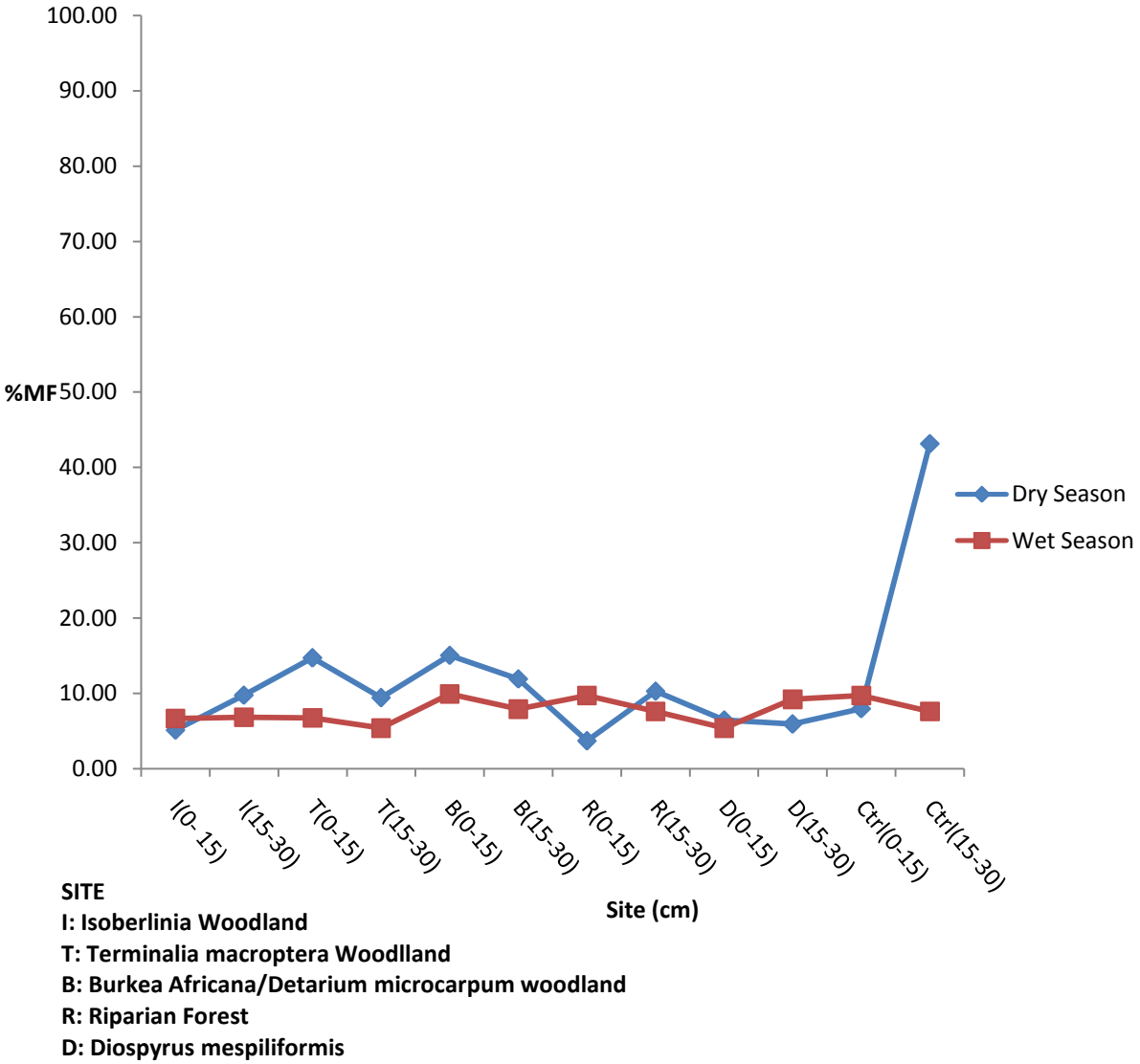


Fig 4.18: Mobility factor for Cd in the soils of the different vegetations of Oli forest in 2012

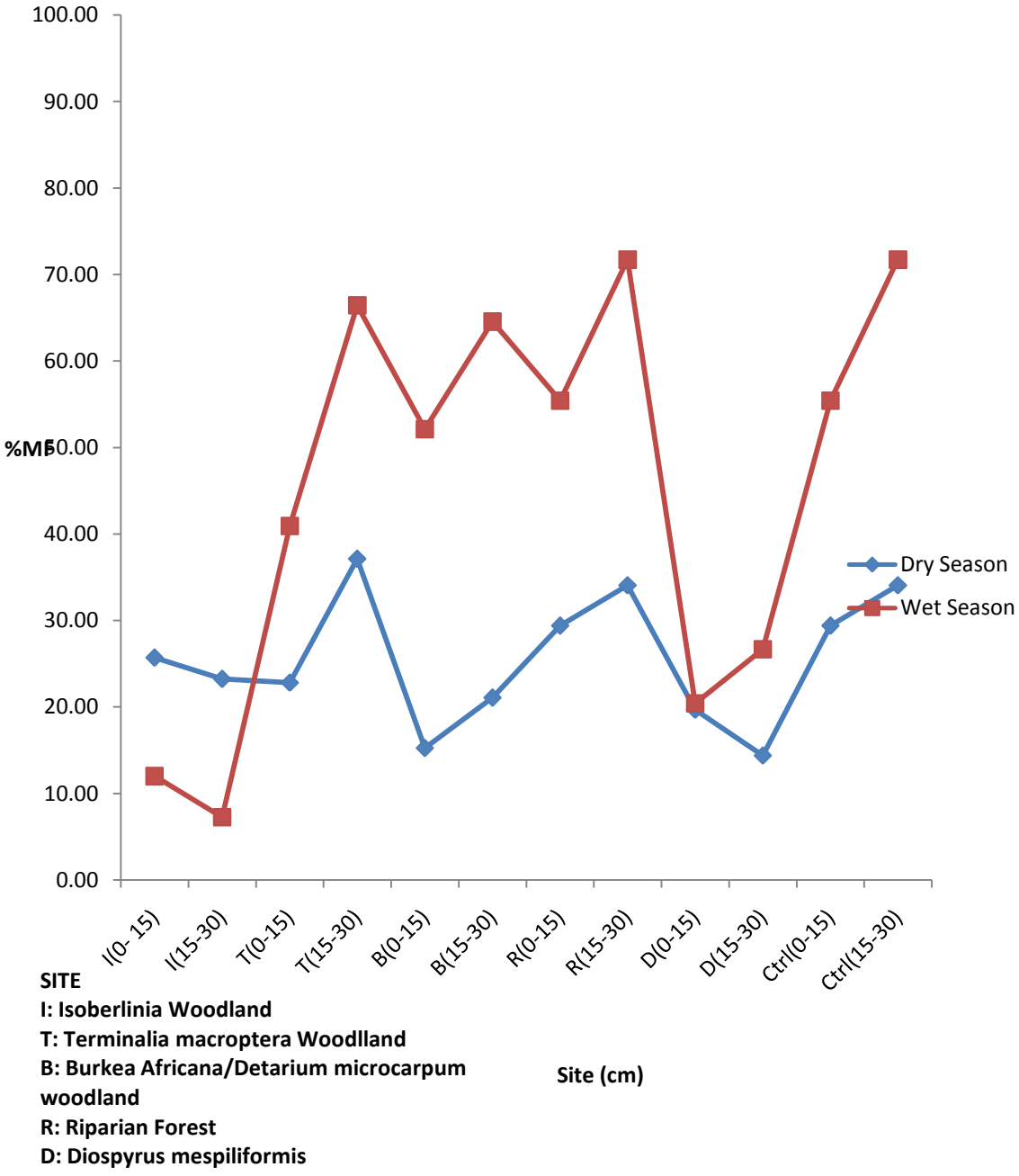


Fig 4.19: Mobility factor for Cr in the soils of the different vegetations of Oli forest in 2012

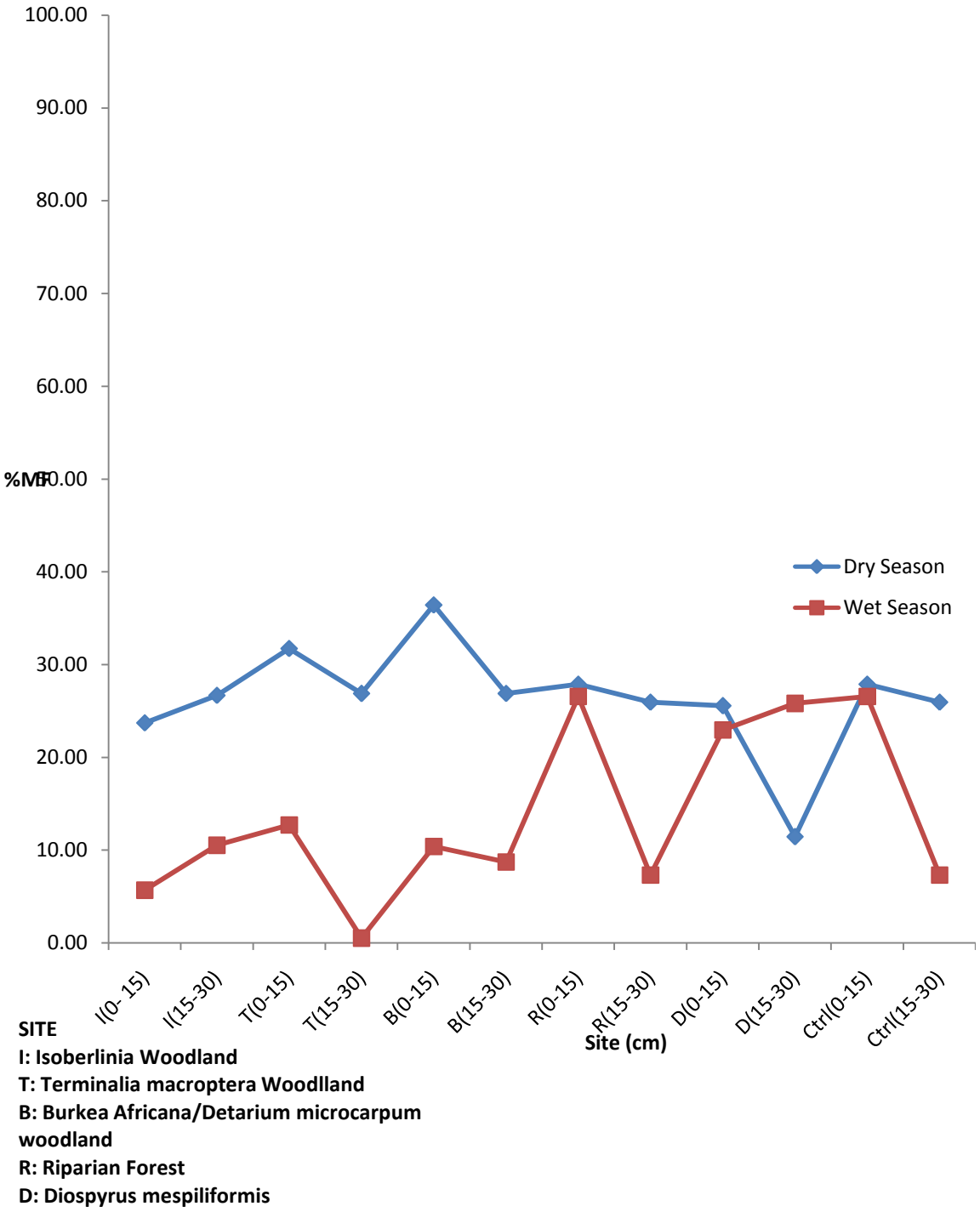


Fig 4.20: Mobility factor for Ni in the soils of the different vegetations of Oli forest in 2012

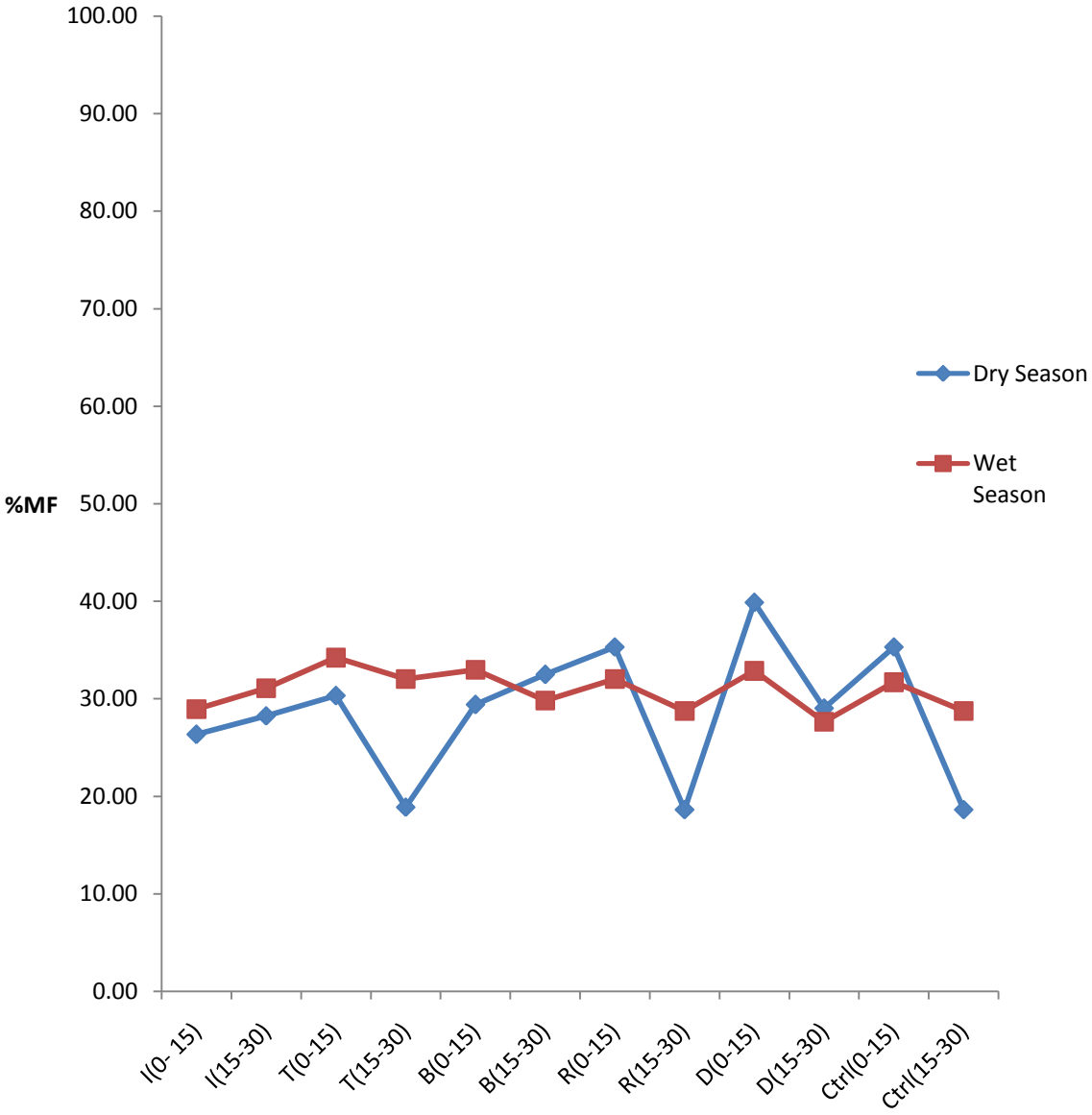


Fig 4.21: Mobility factor for Pb in the soils of the different vegetations of Oli forest in 2012

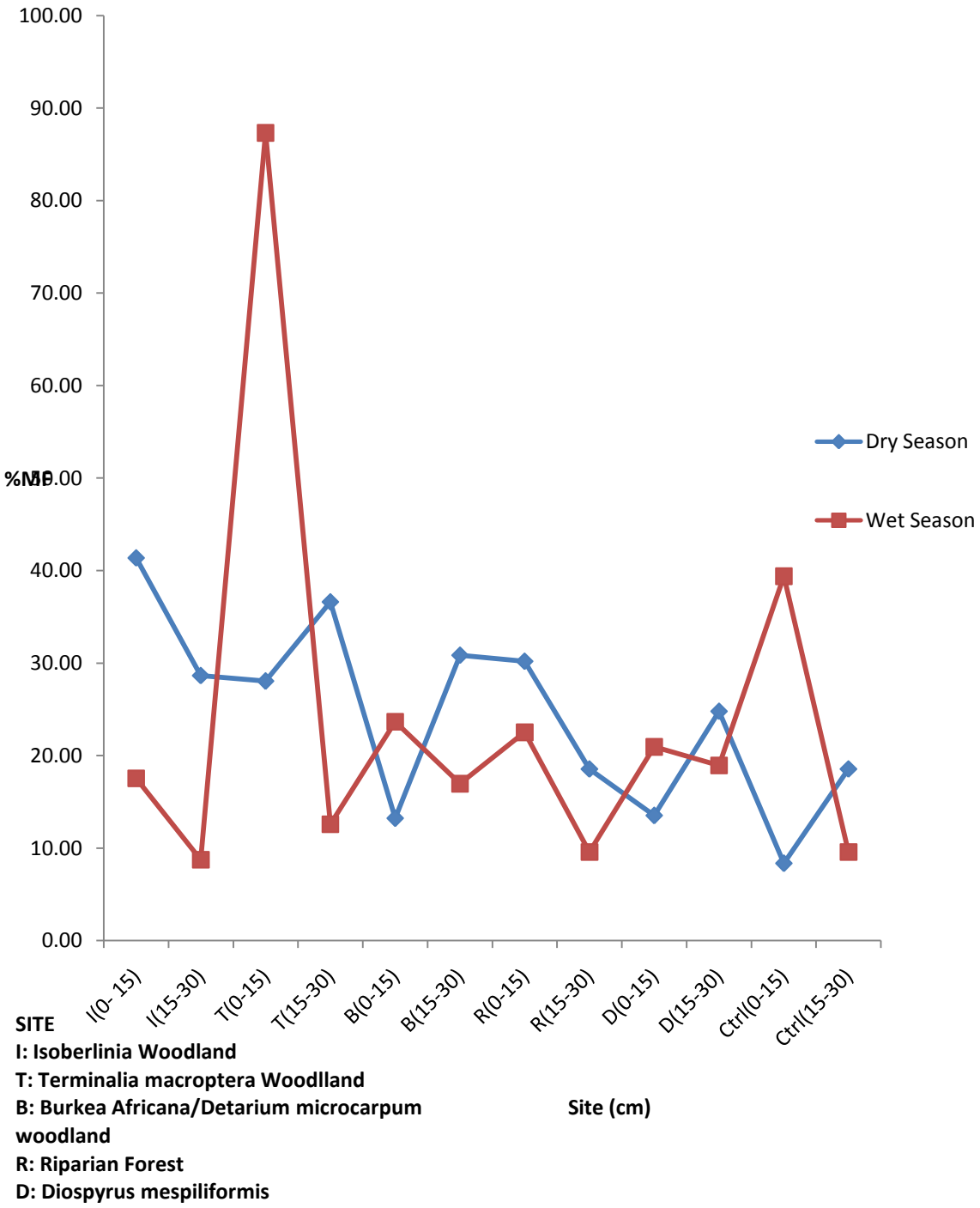


Fig 4.22: Mobility factor for Zn in the soils of the different vegetations of Oli forest in 2012

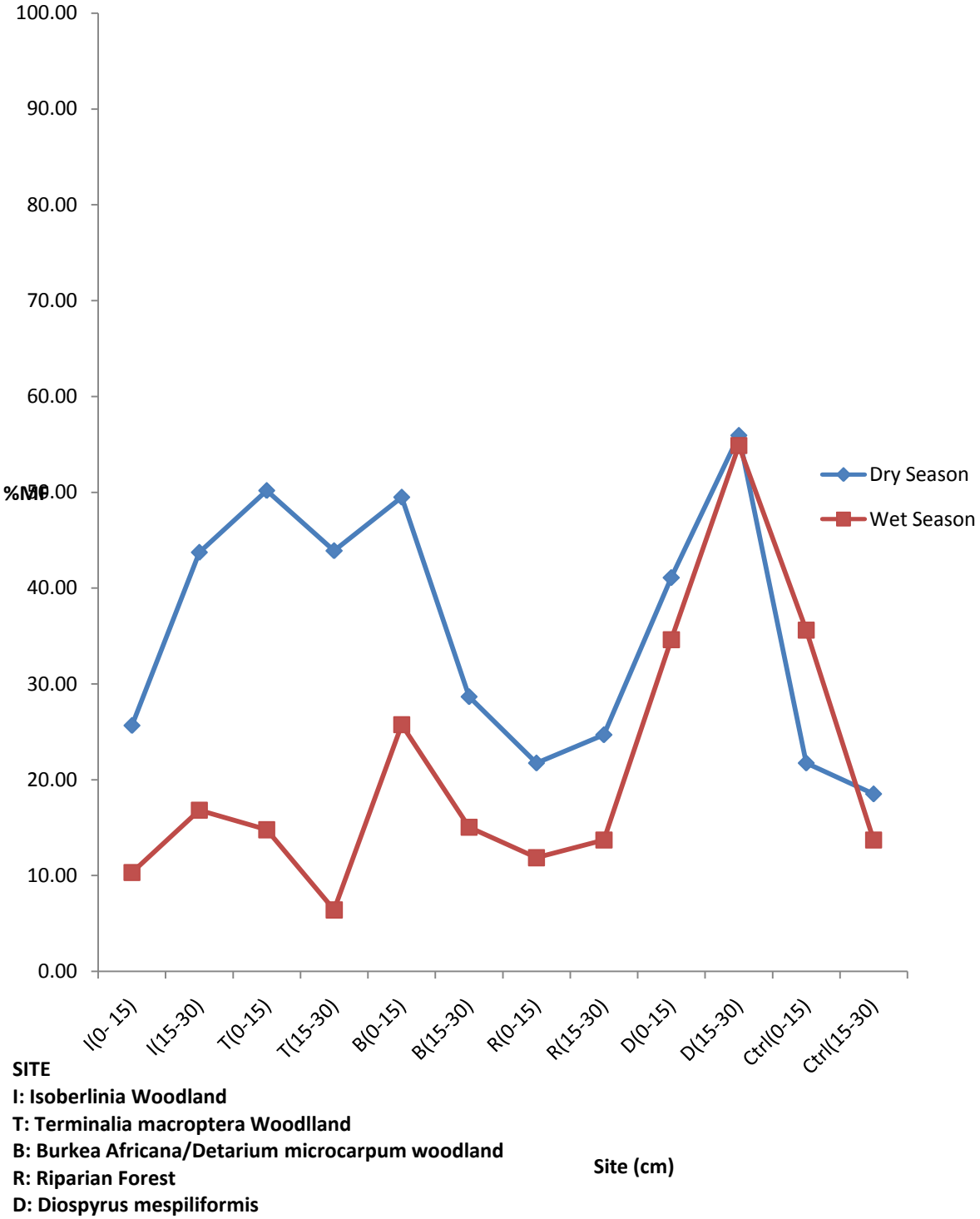


Fig 4.23. Mobility factor for Cu in the soils of the different vegetations of Oli forest in 2012

4.8 Index Analysis Approach for the Soils of Oli forest at different vegetations

Three different indices analysis were used to test the quality of all the soil samples collected at different vegetation zones of Oli Camp in Kainji Lake National Park and studied for the period of two years (2011 and 2012). The indices employed are enrichment index (EI), geo-accumulation index (I_{geo}), (Idris *et-al., 2006*) and mobility factors MF., (Ogunfowokan *et al*., 2009).

4.8.1 Enrichment Index

Following from Table 4.27 during dry season of 2011, the enrichment factor (EI) values recorded at *Isoberlinia* woodland soil (S1) were in order: Cu (0.00); Ni (0.00); Pb (0.01); Zn (0.00) and Cr (0.07). *Terminalia/Detarium macrocarpum* woodland (S2) soil had order: Cu, Cd, and Ni (0.00) each; Pb (0.01); Zn (0.03) and Cr (0.06); at *Burkea africana/Detarium microcarpum woodland* soil (S3) the trend was in order: Cu (0.00); Ni (0.00); Pb (0.01); Zn (0.03) and Cr (0.06). *Riparian forest* soil (S4) had order Cd and Cu (0.00) each, Pb (0.01), Zn (0.03) and Cr (0.06). For *Diospyrous melispiformis* woodland soil (S5) the order was Cu and Cd (0.00), Ni and Pb (0.01), Zn (0.03) and Cr (0.06). During wet season of 2011 EI values for Cd was 0.02 at S1, S2, S3 and S4 while 0.00 EI value was recorded at S5. EI values for Cr at S1, S2 and S4 was 0.08 and 0.9 at S2 and S5 as presented in Table 4.28. Ni had EI value (0.01) in all the five vegetation zones studied. For Pb the order was: At S1 (0.02), S2 (0.01), S3 (0.01), S4 (0.02) and S5 (0.03); At S1 Zn (0.01), S2 (0.01), S3 (0.00), S4 (0.00) and S (0.03) while Cu had order: S1 (0.03), S2 (0.02) S3 (0.04) S4 (0.04) and S5 (0.01). The same trends of order were rcorded for all the metals studied during wet and dry seasons of year 2011 and 2012 EI < 1.5 in all the sites (S1, S2, S3, S4 and S5). Cr had the highest EI value (0.06) across the sites.

Table 4.27: Enrichment indices for the metals in the different vegetations of Oli forest during dry season of 2011

	Cd	Cr	Ni	Pb	Zn	Cu
S1	0.00	0.07	0.01	0.01	0.04	0.00
S2	0.00	0.06	0.01	0.01	0.03	0.00
S3	0.00	0.06	0.01	0.01	0.06	0.01
S4	0.00	0.06	0.01	0.01	0.03	0.00
S5	0.00	0.06	0.01	0.01	0.03	0.00

Table 4.28: Enrichment indices for the metals in the different vegetations of Oli forest during wet season of 2011

	Cd	Cr	Ni	Pb	Zn	Cu
S1	0.02	0.08	0.01	0.02	0.00	0.03
S2	0.02	0.9	0.01	0.01	0.01	0.02
S3	0.02	0.08	0.01	0.01	0.00	0.04
S4	0.02	0.08	0.01	0.02	0.00	0.04
S5	0.00	0.09	0.01	0.01	0.03	0.01

Table 4.29 Enrichment indices for the metals in the different vegetations of Oli forest during dry season of 2012

	Cd	Cr	Ni	Pb	Zn	Cu
S1	0.11	0.11	0.01	0.02	0.06	0.00
S2	0.09	0.09	0.01	0.02	0.05	0.00
S3	0.15	0.15	0.01	0.02	0.08	0.00
S4	0.09	0.09	0.01	0.01	0.05	0.00
S5	0.01	0.01	0.01	0.01	0.04	0.00

Table 4.30 Enrichment indices for the metals in the different vegetations of Oli forest during wet season of 2012

	Cd	Cr	Ni	Pb	Zn	Cu
S1	0.04	0.12	0.02	0.02	0.00	0.01
S2	0.04	0.13	0.05	0.02	0.01	0.00
S3	0.03	0.12	0.01	0.02	0.00	0.01
S4	0.03	0.11	0.01	0.02	0.00	0.01
S5	0.01	0.13	0.01	0.01	0.05	0.00

4.8.2 Geo-accumulation Index (I_{geo})

The Geo- accumulation indices for dry and wet seasons of the year 2011 and 2012 are presented in Table 4.31 to 4.34 respectively. In dry season of 2011 I_{geo} at *Isoberlinia* woodland (S1) is in order: Cu (0.03), Cd (0.12), Ni (0.13), Pb (0.18), Zn (0.33) and Cr (0.47); *Terminalia macroptera* woodland (S2) Cu (0.03), Cd (0.10), Ni (0.12), Pb (0.30), Zn (0.32) and Cr (0.43); *Burkea africana/Detarium microcarpum* woodland (S3) Zn (0.07), Cu (0.11), Ni (0.16), Pb (0.21), Cd (0.23) and Cr (0.50); Riparian forest (S4) Cd (0.10), Cu (0.12), Ni (0.13), Pb (0.20), Zn (0.33) and Cr (0.47); *Diospyrus melispiformis* dry forest(S5) Cu (0.04), Cd (0.11), Ni (0.14), Pb (0.17), Zn (0.30) and Cr (0.51). In wet season of 2011 Igeo values recorded at different vegetation zones were in order: *Isoberlinia* woodland (S1) Cu (0.03), Zn (0.09), Ni (0.16), Pb (0.26), Cd (0.27) and Cr (0.50); *Terminalia macroptera* woodland (S2) Cu (0.08), Ni (0.12), Zn (0.15) Pb (0.20), Cd (0.26) and Cr (0.51); *Burkea Africana/Detarium microcarpum* woodland (S3) Zn (0.07), Cu (0.11), Ni (0.16), Pb (0.21), Cd (0.32) and Cr (0.50); *Riparian* forest (S4) Cu (0.12), Ni (0.13), Pb (0.20), Zn (0.32), Cd (0.22) and Cr (0.47); *Diospyrus melipiformis* dry forest (S5) Cu (0.04), Cd (0.11), Ni (0.14), Pb (0.17), Zn (0.30) and Cr (0.51). The geo-accumulation indices obtained are similar and follows the order: Cd 0.07 – 0.12 and 0.07 – 0.10; Cr 0.42 – 0.55 and 0.42 - 0.55; Ni 0.12 – 0.15 and 0.12 – 0.15; Pb 0.16 – 0.30 and 0.16 – 0.19; Zn 0.30 – 0.41 and 0.09 – 0.41; Cu 0.02 - 0.04 and 0.02 – 0.04 in the wet and dry season of both 2011 and 2012 respectively (Table 4. 31 to 4.34). The same geo-accumulation indices trend was recorded for both dry and wet season of 2012 in the various vegetation zones. The average geo – accumulation for Cr (0.55) was costant for all the vegetation zones while Cu had the least value (0.01).

Table 4.31: Geo-accumulation indices of the metal in the different vegetation in Oli forest Kainji Lake National Park in dry season of 2011

	Cd	Cr	Ni	Pb	Zn	Cu
S1	0.12	0.47	0.13	0.18	0.33	0.03
S2	0.10	0.43	0.12	0.30	0.32	0.03
S3	0.07	0.55	0.15	0.19	0.41	0.04
S4	0.10	0.42	0.12	0.16	0.32	0.02
S5	0.10	0.55	0.15	0.16	0.30	0.03

Table 4.32: Geo-accumulation indices of the metal in the different vegetation in Oli forest Kainji Lake National Park in wet season of 2011

	Cd	Cr	Ni	Pb	Zn	Cu
S1	0.27	0.50	0.16	0.26	0.09	0.03
S2	0.26	0.51	0.12	0.20	0.15	0.08
S3	0.23	0.50	0.16	0.21	0.07	0.11
S4	0.22	0.47	0.13	0.20	0.27	0.12
S5	0.11	0.51	0.14	0.17	0.30	0.04

Table 4.33: **Geo-accumulation indices of the metal in the different vegetation in Oli forest Kainji Lake National Park in dry season of 2012**

	Cd	Cr	Ni	Pb	Zn	Cu
S1	0.10	0.47	0.13	0.18	0.33	0.03
S2	0.10	0.43	0.12	0.18	0.32	0.03
S3	0.07	0.55	0.15	0.19	0.41	0.04
S4	0.10	0.42	0.12	0.16	0.32	0.02
S5	0.10	0.48	0.15	0.16	0.09	0.03

Table 4.34: Geo-accumulation indices of the metal in the different vegetation in Oli forest Kainji Lake National Park in wet season of 2012

	Cd	Cr	Ni	Pb	Zn	Cu
S1	0.03	0.50	0.16	0.21	0.09	0.10
S2	0.27	0.51	0.31	0.20	0.15	0.08
S3	0.23	0.50	0.16	0.21	0.07	0.11
S4	0.222	0.47	0.13	0.21	0.08	0.01
S5	0.11	0.51	0.14	0.17	0.23	0.04

CHAPTER FIVE

5.0 DISCUSSION

5.1 Physical Parameters of the Soils of Oli forest at different vegetation zones

5.1.1 Particle Size Distribution

The soil was essentially sandy loam at depth (0 - 15 cm) and loamy sand at depth (15 - 30 cm) for *Terminalia macrocarpum* wood land soil and *Isoberlinia* wood land soil, *Detarium microptera* wood land soil, *Riparian* wood land, and *Diospyros mespiliformis dry forest* soil respectively. The result (Table 4.2 – 4.5) of the physical properties of the different soils analysed revealed that sand is the most variable among the soil depth both in the wet and dry season of 2011 and 2012, and silt was the least. Sand proportions decreased while those of silt increased with soil depth. The loamy-sand nature of the soils studied could be attributed to the widespread occurrence of sedimentary granitic and gneissic parent materials downward leaching of clay, differential soil erosion due to the high energy impact of rainstorms tending to remove fine particles in run-off water and, the possible chemical destruction of kaolinite in the top soil (Ahn, 1970).

The clay content is low but more varied than silt in amount.The content also increases with soil depth and collaborated Ubom (2006) report. Generally, average percentage of sand at 0 - 15 cm and 15 -3 0 cm soil depth was 68.70 ±3.06% and 78.50 ±0.85% respectively. This was relatively similar to the values (73.60% and 80.60%; 75% and 79%) previously reported (Ubom, 2006 and Akinyemi, 2007). The mean percentage of silt at soil depth 0-15cm (14.40 ±0.36%), 15-30cm (13.20 ±0.76%) also agreed with the low values (10% and 9.40%) reported by Akinyemi (2007) although the values were higher.

5.1.2 Soil pH

The soil pH in water was between 6.8 (*Burkea africana/Microptera* woodland soils) and 7.5 (*Diospyrus mespiliformis dry forest* soils) during dry season of 2011 while the wet season values were between 6.6 (*Isoberlinia* woodland) to 7.5 (*Terminalia macroptera* woodland soils); though these values are almost of the same magnitude. There was little or no variability in the soil pH at both depths studied in all the soils of the different vegetation zones during wet and dry seasons of the of years 2011 and 2012 (Tables 4.2 – 4.5). The pH values in water was slightly alkaline while in $CaCl_2$ was slightly acidic with values ranging from 5.30 ± 0.80 to 7.1 ± 0.1.3 and 5.15 ± 0.07 to 6.50 ± 0.14 for the dry and wet season of 2011 respectively.There was no significant difference among the pH values during the year 2012. The range was 4.85 ± 0.21 to 6.30 ± 0.00 and 5.15 ± 0.07 to 6.50 ± 0.14 for the dry and wet season of 2012 respectively. Akinyemi (2007), Kadeba (1974) and (Aremu *et al.,* 2007) have earlier reported that the soils of some villages surrounding the park is slightly acidic (6.3 – 6.7). This is in accord with the present result (Tables 4.2 to 4.5). This is likely due to parent sands derived from kaolinite and granite. It is also evident that the pH values obtained are within the tolerance limits for most plants (Landon, 1991). The result suggests that vegetation types did not have effect on soil pH but could be related to the similarities in terms of herbivores grazing intensity, trampling, defecation and urination. The result is supported by Zhao *et al.,* (2007) and Killham (1994) who reported that herbivore grazing, trampling defecation and urination could affect soil pH. The amount of acid (or alkali) in soils determines the availability of many nutrients for plant growth and maintenance (Arias *et al.,* 2005). Thus, pH being a key player in soil microbial reactions, the measured pH values may well have implications on the availability and uptake of metals by plants and micro - organisms.

5.1.3 Electrical Conductivity (EC)

The electrical conductivity values were similar at the 0 - 15 cm depth (50 – 60 (μScm^{-1}) though with little variation. The highest electrical conductivity EC 101.50 ±2.12 μScm^{-1} was obtained in *Terminalia Macroptera* woodland soil, and 50 and 80 (μScm^{-1}) were obtained for the other vegetation zones. This could be due to the soil physical properties at the vegetation zones. In support of this result, Corwin *et al.,* (2003) indicated that EC is influenced by water content, bulk density and texture. The EC of the soils ranged from 10.00 to 101.50 μScm^{-1} in wet season of 2011 and 0.02 to 0.12 μScm^{-1} in dry season of the year, 2011. The high conductivity of the soils of different vegetation zones during wet season could be attributed to good weathering of the parent rock and this is an indication that there are more soluble salts in the soil (Karaca, 2004, Arias *et al.,* 2005). The low values of EC in dry season of 2011 and 2012 (Tables 4.3 – 4.5) could be as a result of low water content (Uba, *et-al.,* 2008). This is also supported by positive correlation observed between pH and EC in dry season of 2011 Table 4.9 and in the dry and wet season of 2012 respectively, Table 4.10-4.13.

5.1.4 Soil Organic Matter (SOM) Content of Oli Forest Soil at the Different Vegetation Zones

Soil organic matter (SOM) and clay mineral are responsible for the CEC contents. The SOM decreased with depth within the soils of the vegetation zones investigated. During 2011 at 0 - 15 cm depth, the SOM ranged from 1.35 g/kg to 5.48 g/Kg in *Isoberlinia* woodland soils and *Diospyrus melispiformis dry* woodland. while the sub-soil (15 - 30 cm) depth recorded again 1.36 g/Kg to 2.99 g/kg for *Isoberlinia* woodland soils and *Diospyrus melispiformis dry* woodland in wet season of 2011 and during dry season of 2011 the values for 0 - 15 cm depth is 1.79 to 3.06 g/kg at *Riparian forest* and *Burkea africana/Detarium microcarpum* woodland, for 15 - 30 cm depth at *Isoberlinia*

woodland soils and *Diospyrus melispiformis dry* woodland is 1.32 to 2.11 g/kg (Tables 4.2 and 4.3). Similar result was obtained in the dry and wet season of 2012 with range 1.12 to 5.30 g/kg.

These values are relatively lower than the values (3.4 to 0.9g/ kg and 2.21 g/kg) reported by Graham (2010) for soils of Gayi area, North-western Nigeria and the result reported by Uba *et al*., (2008) with range (13.20 to 28.80 g/kg) although on slightly contaminated soil. It was revealed from the results that all the sites at the vegetation zones of Oli forest had very low organic matter contents. Since soil fertility is closely linked to soil organic matter, whose status depends on biomass input and management of mineralisation, leaching and erosion (Roose and Barthes, 2001; Nandwa, 2001).

It is well recognised that soil organic matter increases soils structure stability resistance to rainfall impact rate of infiltration and fauna activities (Roose and Barthes, 2001). The inherent levels of organic matter in West Africa savannas soils are very low (). Result from the present study are in line with what has been cited in literature (Jones and Wild, 1975; Kowal and Kassam, 1978). This had been attributed to low root growth of plants and natural vegetation and rapid turnover rates of organic materials with high soil temperature and microfauna, particularly termites (Bationo *et al;* 1991). While soil organic carbon is not a requirement for plant growth, the levels of **organic matter** in soils influence a number of soil chemical and physical processes, and is an important indicator of the soil as a rooting environment (Okalebo *et al*., 1993). However, the soil organic matter values is considered low based on the classification of soil organic matter given by Enwezor *et al.* (1998).

5.6 Cation Exchange Capacity (CEC)

The cation exchange capacity (CEC) of the various vegetation soils of Oli forest Kainji Game Reserve is low. The highest value being 6.75 ± 0.35 cmol/kg at *Burkea africana* zone and the least value was 3.75 ± 0.21 cmol/kg at *Terminalia macroptera* woodland soil in dry season of 2011, while it was 17.4 ± 3.00 cmol/kg and 4.45cmol/kg for *Diospyrus mespiliformis* woodland soils and *Isoberlinia* woodland soils respectively during wet season of 2011. During dry season of 2012, the highest CEC was 6.50 ± 0.00 cmol/kg at *Burkea africana/detarium microcarpum* woodland soils and least value 3.55 ± 0.07 cmol/kg at *Terminalia macroptera wooddland* soils while it was 16.95 ± 0.64 cmol/kg for *Diospyrus mespiliformis woodland* soils and 3.70 ± 0.99 cmol/kg for *Isoberlinia woodland* soils respectively during wet season of 2012. This finding collaborate report of Akinyemi (2007) and Shamshuddin and Paramananthan (1980).that mineralogy in which kaolinite and mica are found to be dominated in the clay fraction. The cation exchange capacity (CEC) values of the soils investigated rated marginally low and decreased with depth among the sites (Tables 4.1 to 4.5). The CEC ranges from 4.45 to 17.40 cmol/kg and 3.75 to 6.75 cmol/kg wet and dry season of 2011 respectively; while in 2012 the CEC values ranged from 4.20 ± 0.00 to 6.50 ± 0.01 and 3.70 ± 0.99 to 11.15 ± 0.21 for both dry and wet season of 2012 respectively. The low CEC values can be attributed to the low clay content. low organic content and the kaolinitic mineralogy of the soils.

However, Bationo and Mokwuye (1991) and Akinyemi (2007) reported that the CEC is more related to the organic matter content than to the clay in Sudano-Sahelian soils of West Africa. Meanwhile the variation in CEC between the studied sites implies that identical management practices at different vegetation types have effects on CEC of the soil. This fact could be attributed to the variation of rainfall and suggests that

exchangeable cations were leached, following the amount of rainfall for each vegetation zone as supported by Chadwick *et al.*, (1999); Luwing *et.al.*, (2001) and Yimer *et al.*, (2006) who reported that exchangeable cations are leached at high rainfall areas. Incorporation of organic manure (cow dung) and agricultural waste from buffer zone is considered essential to improve the organic matter of the soils. In so doing, soil structure development is encouraged and more nutrients are added (Paramananthan, 1980).

5.6 Available Phosphorous of Oli Camp Soil at the Different Vegetation Zones

Available phosphorous values in all the sites at 0 - 15 cm and 15 - 30 cm depths varied among the soils at the different vegetation zones studied (Tables 4.2). The values ranged from 6.57 to 85.88 and 8.75 to 66.50 mg/g in dry and wet season of 2011 respectively; and also from 7.69 ± 0.27 to 84.38 ± 1.94 and 9.75 ± 1.06 to 42.50 ± 3.54 mg/kg, for the dry and wet season of 2012 respectively. But there was report that vegetation types had no effect on available phosphorous, this could be attributed more to management practices such as routing, annual bush burning in the vegetation zone studied. Phosphorous has been reported to be one of the two major nutrients limiting plant yield (Falusi and Williams, 1981).

Available phosphorus concentrations in the surface and sub-surface soil of Oli forest being examined was generally low, but higher than the soil outside the park. This result is in conformity with the work of Akinyemi (2003), Milligan (1979); Okigbo (1989) and Kadeba (1978) on soils of savannah ecosystem. The phosphorus concentrations were inversely related to cation exchange capacity which implies that the soil with higher CEC have lower available phosphorus (Congdon and Herbohn, 1993). This could be attributed to phosphorus fixation as consistent with the work by Yimer *et al*., (2006).

5.2 Statistical Analysis for Physical Properties of the Soil

The physiochemical parameter data obtained from the soils of Oli forest at different zones were subjected to statistical analysis (Table 4.6 to 4.9) to establish the inter-parameter relationships of the soils. Pearson correlation two tailed was conducted on all the soil samples. The correlation was significant at $P < 0.05$ for clay, silt and sand. This is an indication of poor soil nutrients in the different vegetation studied. Available phosphorus was not significantly related to CEC. The implication is that phosphorus is a limiting nutrient. There was a strong negative relationship between clay and sand ($P < 0.01$, $r = 0.944$) and a significant positive correlation between clay and CEC $P < 0.01$, $r = 0.867$).

5.3 Total Metal Levels of Oli forest Soil at the Different Vegetation Zones

There was variation in the concentration of metals in the soils of the vegetation zones. The metal concentrations for the soil in 2011 for the wet and dry season ranged from 1.72 to 11.56 mg/kg and 0.81 to 2.26 mg/kg for Cd, 29.35 to 47.34 mg/kg and 23.55 to 51.94 mg/kg for Cr, 10.93 to 204.37 mg/kg and 14.03 to 34.69 mg/kg for Ni, 10.74 to 20.08 mg/kg and 8.43 to 18.48 mg/kg for Pb, 10.68 to 199.53 mg/kg and 160.06 to 416 mg/kg for Zn, and 6.67 to 38.82 mg/kg and 2.02 to 6.72 mg/kg for Cu respectively (Tables 4.13 and 4.14). The same trend was recorded in the wet and dry season of 2012 with slight decrease in the levels of these metals although, not regular from 15 - 30 cm to 0 – 15 cm depth of the different vegetation soils Tables 4.15 and 4.16.

It was equally noticed that the concentrations of the six metals examined varied among the vegetation zones investigated in wet season of 2011with zinc (211.35 mg/kg) having the highest mean concentration followed by nickel (204.37 mg/kg), chromium (47.34 mg/kg), copper (50.92 mg/kg), lead 20.08 mg/kg, and cadmium (11.56 mg/kg)

in decreasing order (Table 4.14). The same trend Zn > Ni > Cr > Cu > Pb > Cd was obtained in wet season of 2012. The concentration of the trace metals studied at different sites, were less when compared with that report by Okunola *et al.*, (2007). Due to fact that the total concentration of heavy metal is not sufficient to give information on the bioavailability and toxicity of heavy metal, mobility, bioavailability and toxicity of heavy metals have correlation with their speciation (Huang *et al*., 2009). It is therefore necessary to pay a close attention to the speciation study of these metals presented in (Fig 4.2 – 4.13)

5.4 Quality Assurance

According to Shriadah (1999) recovery of metals are as follows: 96.7% for Pb, 97.5% for Cd, 105.0% for Zn, 101.3% for Cu and 104.9% for Mn while Awofolu (2005), reported their trend in a decreasing order Cu > Zn > Cd > Pb for soil sample, although slight changes were observed in the sample which could be due to error due to experimental procedure. However, high percentage recoveries compared to the range 87.8 – 96.2% for soil sample reported by Awofolu (2005) could imply validation of the experimental protocol. From the results, the recovery varied between 89.67 - 108.67 (%) but the pattern of recovery efficiency in all cases for the soil samples of Oli forest was found to followed the decreasing order: Zn > Cu > Cr = Pb > Cd > Ni which validate the extraction procedure and the efficiency of the atomic absorption spectrophotometer.

5.5 Chemical Speciation of Metals of the Oli Camp Soil at the Different Vegetation Zones

Metal chemical speciation carried out by sequential extraction of metals is essential to the metal mobility (Tessier *et al*., 1979). In all the soil samples subjected to chemical speciation,

Cd: 60 - 65% at Isoberlinia woodland; 60 – 70% at *Terminalia macroptera* wood land*;* 80 - 90% at *Burkea africana/Detarium microcarpum woodland* and 65-90% at *Riparian forest in wet season* of 2011 Fig 4.1 and Appendix I.

For Cr: 45 - 60% at *Isobrliniaa woodland Terminalia macroptera woodland*, *Burkea africana/Detarium microcarpum and Riparian forest* repectively and 82% at *Diospyrus mespiliformis dry woodland* in dry season of 2011 Fig 4.2b and Appendix IV;

For Ni: 70 – 90% at *Isoberlinia woodland* in wet season of 2011 Fig 4.3a and Appendix V;

For Pb: 40 – 65% and 40 – 50% in wet season of 2011 and 2012 respectively, Fig 4.4a and 4.10a in all the soils of the different vegetation zones;

Zn and Cu had the same range of 70 – 89% in the wet season of 2011 being found to be most associated with the residual fraction than all other fractions during wet season of 2011 and 2012, but in the dry season of 2011 and 2012, a contrary observation was recorded, Zn (40 – 65%) and (55 – 95%) respectively was found to be associated with the Fe-Mn oxide fraction (Fig 4.5b and Fig 4.11b), while Pb (30 – 60% and 25 – 40%) Fig 4.4b , and 4.10b; Cu (20 - 60% and 30 - 60%) Figs 4.16b and 4.12b; and Cd 50 - 90% and 20 – 85%) Figs 4.1b and 4.7b were found to be most associated with carbonate bound. The high content of carbonate fraction during dry season of 2011 and 2012 in the vegetation zones studied might be due to carbonate rocks. Many work have reported

varying concentrations of these metals in different fractions, Olutona *et al*., (2012) reported high percentage of Cu in the carbonate bound, Sobczynski and Siepak (2001) also reported the highest percentage of Cu (83%) in the immobilized fraction, while Loska *et al.,* (2000) reported Cu to be most associated with organic fractions. However, the findings from this present work, agrees very well with the report of these researchers enumerated above.

In dry season of 2011 and 2012, Zn was found to be most associated with Fe-Mn oxide with abundance of 40 - 70% and 40 - 80% respectively and residual fractions with abundance of 70 - 90% and 40 - 90% in wet season of 2011 and 2012 respectively, an indication that Zn is more mobile in these geochemical phases. This is in agreement with the reports of Sobczynski and Siepak (2001) that highest percentage of Zn were found associated with Fe-Mn oxide and the lowest were found bounded to carbonate fraction. These results were different from the result reported by Wufem *et-al*. (2007) that the highest fraction of Zn was associated with carbonate fractions. Lim and Kiu (1994) had earlier concluded that irrespective of the sampling sites, the speciation pattern of zinc indicates that more than 50% of the metal was associated with the moderately and easily reducible fractions. Frostner and Wittmann (1983) and Alloway (1995) have reported the importance of co-precipitation of zinc and cadmium with carbonate minerals. The strong association in the residual was also confirmed by Fayun *et al.* (2008).

In all the soil samples studied, Pb was found to be most associated with residual fraction (40 - 80%) and (40 - 50%) in wet season of 2011 and 2012 respectively, and with carbonate fraction (25 - 42%) and (30 - 45%) during dry season of 2011 and 2012 respectively. Very low fraction was recorded for Pb in both organic bound fraction (3%) and water soluble fraction (10%) during dry and of 2011 and 2012 respectively. This

result is not in agreement with the report of Olutona (2012) that, the highest percentage of Pb was associated with exchangeable fractions, although the soil samples were collected from polluted region. Welte *et al.,* (2007) reported the highest association of Pb with hydrate Fe-Mn oxide, and the least with organic bound. This is an indication that Pb associated with residual fraction in the present study is strongly bound to the crystal lattices of minerals hence it will not be easily released into the environment. Metals present in the residual fraction are a measure of the degree of environmental pollution. The higher the metals present in this fraction, the lower the degree of pollution (Howari and Banat, 2001). Therefore, it is considered that Pb is not a threat to all the vegetation zones investigated. All analysed heavy metals Cd, Cr, Ni, Pb, Zn, and Cu in wet season were highly abundant in the residual fraction, this is an implication that they were not derived from anthropogenic sources thus, they could bee lithogenic (Ramirez *et al*., 2005).

5.6 Potential Mobility of Heavy Metals in Soil of Oli Forest at different Vegetation Zones

Average potential mobility of the heavy metals in soil of Oli forest at different vegetation zones is shown graphically in (Fig 4.13 – 4.23) and also in (Appendix: XIII and XXVI). During wet season the mobility factor for Cd, Cr, Ni, Pb, Zn and Cu in vegetation soil samples investigated showed variation across the five different vegetation zones and between the two depths 0 - 15 cm and 15 - 30 cm. In the wet season of 2011 the range is in the order: 5.01 to 9.82%$_{0\text{ -}15\text{ cm}}$ and 6.01 to 9.59%$_{15\text{ -}30\text{ cm}}$ for Cd; 11.95 to 60.94% $_{0\text{- }15\text{ cm}}$ and 8.44 to74.80% $_{1\ 5\text{- }30\text{ cm}}$ for Cr; 6.90 to 25.69% $_{0\text{ - }15\text{ cm}}$; and 8.90 to 26.26%$_{15\ –\ 30\text{ cm}}$ for Ni; 17.66 to 34.00%$_{0\text{ -}15\text{ cm}}$ and 17.35 to 34.18%$_{15\ –\ 30}$

$_{cm}$ for Pb; 14.71 to 83.63%$_{0 - 15 cm}$ and 9.24 to 12.41%$_{15 -3 0cm}$ for Zn; 12.10 to 18.65%$_{0 - 15}$ and 6.51 to 27.89%$_{1 5- 30 cm}$ for Cu (Appendix XIII).

During dry season, the MF values have the range (0 - 15 cm and 15 - 30 cm) in the order as: 3.72 to 14.55%$_{0 - 15 cm}$ and 5.79 to 11.92%$_{15 - 30}$ cm for Cd;14.48 to 27.80%$_{0 – 15 cm}$ and 13.34 to 34.74$_{15 – 30 cm}$ for Cr; 21.26 to 33.17%$_{0 – 15 cm}$ and 10.34 to 25.59%$_{15 - 30 cm}$ for Ni; 24.75 to 38.93%$_{0 – 15 cm}$ and 17.58 to 30.11%$_{15 – 30 cm}$ for Pb, 10.79 to 39.36%$_{0 – 15 cm}$ and 16.91 to 33.42%$_{15 – 30 cm}$ for Zn; 20.53 to 50.15%$_{0 – 15 cm}$ and 26.57 to 54.11%$_{15 – 30 cm}$ for Cu respectively (Appendix XIII). The same trend was observed and recorded in the wet and dry season of 2012.

High MF values, give an indication of liability and biological availability of heavy metals (Ahumada et-al., 1999; Kabala and Singh, 2001; Yusuf, 2007). It also showed the extent of the vulnerability of living things generally to heavy metals (Ogunfowokan, et-al., 2009, Okunola et al, 2011) for different environment. Due to low percentage mobility of the metals studied, they are not likely to be available to the environment.

CHAPTER SIX

6.0 SUMMARY AND CONCLUSION

6.1 Summary

The concentration of all metals was found to decrease generally with increasing depth of the soil. Zn has the highest mean concentration 313.66 ± 2.05 mg/kg followed by Ni 107.29 mg/kg; Cr 48.18 mg/kg; Cu 25.78 mg/kg while Pb 18.47 mg/kg and Cd 6.41 mg/kg have the least and of the same order of magnitude. The result of this present work also revealed that the presence of these metals were mainly of natural origin. The mean values for surface and subsurface soils for the vegetation zones revealed that the soils were not contaminated with any of the metals investigated. However, Zn, Ni, and Cr exhibited the highest natural origin followed by Cu, Pb and cadmium Cd in that order. Lead is found to be highly toxic metals (Adekola *et al.*, 2012) but its low concentration in all the vegetation soils investigated would not pose any serious threat within and among the vegetation soils. This does not mean periodical research of these metals status in the studied areas should not be carried out, especially for Pb, Cd and Ni, because their high presence in the future could lead to serious health challenges to the wildlife in the Camp and the environment at large.

In all the soil samples on which speciation were conducted, almost all the metals were found to be mostly concentrated in the residual fraction and carbonate bound fraction during wet season of 2011 and 2012. This implies that, the metals are inert and could not be easily leached to the immediate environment, where they could get into the food chain of flora and fauna. In the dry seasons, Cu, Pb and Cd were retained predominantly by carbonate bound fractions. It was found that the concentrations in the water soluble, exchangeable and Fe - Mn bound fractions were generally low for the metals studied.

This is a clear evidence for the low metal level in the soils of Oli forest at the different vegetation zones.

6.2 CONCLUSION

The mean metal concentrations, mobility factors for various soil samples and enrichment index obtained indicates that activities due to poaching, illegal grazing in vegetation zones studied has not affected levels of the metal studied in the park.

The physical and chemical characteristics of the soils studied for the both wet and dry seasons were generally low. The physico - chemical parameters indicated that pH range of 5.15 to 6.80 at 0 - 15 cm and 5.90 to 6.80 at 15 - 30 cm were obtained for the wet season of 2012; these values were similar to those obtained during dry season with no significant different at ($P < 0.05$). Electric conductivity obtained has the range 0.01 ± 0.00 to 0.08 ± 0.02 (µS/cm) Organic matter contents obtained, has the range 1.12 ± 0.03 to 3.75 ± 0.35 (%) among the vegetation studied. Cations exchange capacity has average values ranging from 3.55 ± 0.07 to 16.95 ± 0.64. These values are in agreement with the report of Ubom *et al*. (2004).

Among the vegetations studied, Cu and Cr have the highest concentrations with range (5.76 ± 1.00 to 50.92 ± 1.01) and (29.35 ± 1.20 to 47.34 ± 1.01) mg/kg respectively in the wet season except for *Diospyrus melispiformis* forest, where Zn had the highest value with range 202.2956 ± 3.84 to 213.93 ± 3.64 mg/kg, and Cd has the least values. In the dry season, at both depths, Zn has the highest concentration (19.92 ± 0.35 to 312.55 ± 4.88)$_{0\text{-}15\ cm}$ and (15.90 ± 2.14 to 412.99 ± 6.81)$_{15\text{-}30\ cm}$ mg/kg. Percentages of the metal extracted in the sequential extraction, is in the order :

residual fractions carbonates bound fraction organic bound fractions Fe-Mn oxide fractions exchangeable fractions Water soluble.The knowledge of the metals studied with different soil phases is of major interest to assess the connections with other biotic and abiotic element of the environment. However, the enrichment factors and mobility factors calculated indicate that the trace metals investigated are below permissible level and hence the vegetation zones are not polluted.

6.3 RECOMMENDATIONS

Careful development and protection of the soil of different vegetations under the studied area is very important as it serves as habitant to wildlife and other biodiversity which are source of tourist attraction.

The burning of organic matter is a poor conservation practice which should be avoided as cumulative burning might have negative effect on the soil physical and chemical properties.

Further research could be carried out on the speciation of metals in other environmental components in the vicinity of the Kainji Lake National Park.

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APPENDIX I

Chemical fractionation of Cd (mg/kg) of the soils of Oli forest at different vegetation zones in wet season of 2011

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
***Isoberlinia* Woodland**						
0 – 15 cm	0.11±0.02	0.14±0.06	0.30±0.17	0.31±0.18	2.17±1.04	5.09±2.42
15 – 30 cm	0.12±0.06	0.16±0.08	0.35±0.20	0.43±0.24	2.75±1.31	5.35±0.49
***Terminalia macroptera* Woodlland**						
0 – 15 cm	0.20±0.10	0.20±0.10	0.25±0.14	0.43±0.23	2.59±1.29	6.00±1.41
15 – 30 cm	0.13±0.17	0.03±0.01	0.31±0.20	0.05±0.04	2.16±1.05	6.00±1.41
***Burkea africana/Detarium microcarpum* woodland**						
0 – 15 cm	0.16±0.08	0.17±0.12	0.22±0.11	0.18±0.11	0.29±0.16	4.50±2.12
15 – 30 cm	0.14±0.07	0.23±0.11	0.29±0.16	0.21±0.13	0.38±0.17	7.07±1.32
Riparian Forest						
0 – 15 cm	0.13±0.06	0.20±0.11	0.21±0.13	0.06±0.03	0.29±0.16	4.65±3.32
015– 30 cm	0.10±0.05	0.26±0.15	0.14±0.08	0.14±0.08	0.41±0.21	5.50±0.71
Diospyrus mespiliformis Forest						
0 – 15 cm	0.04±0.01	0.04±0.01	0.05±0.01	1.67±0.47	0.10±0.01	0.52±0.12
15 – 30 cm	0.06±0.02	0.05±0.02	0.08±0.03	0.92±0.12	0.12±0.04	0.74±0.08
Control						
0 – 15 cm	0.01±0.01	0.02±0.01	0.02±0.01	0.01±0.00	0.03±0.02	0.47±0.33
15 – 30 cm	0.01±0.00	0.03±0.01	0.01±0.01	0.01±0.01	0.04±0.02	0.55±0.07

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX II

Chemical fractionation of Cd (mg/kg) of the soils of Oli forest at different vegetation zones in dry season of 2011

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
***Isoberlinia* Woodland**						
0 – 15 cm	0.01±0.00	0.04±0.01	0.05±0.01	1.34±0.00	0.11±0.00	0.35±0.01
15 – 30 cm	0.00±0.00	0.04±0.00	0.07±0.00	0.51±0.02	0.22±0.00	0.28±0.01
***Terminalia macroptera* Woodland**						
0 – 15 cm	0.04±0.01	0.08±0.02	0.08±0.01	0.85±0.07	0.12±0.00	0.23±0.01
15 – 30 cm	0.03±0.01	0.07±0.01	0.04±0.01	1.07±0.03	0.02±0.01	0.17±0.19
***Burkea africana/Detarium microcarpum* woodland**						
0 – 15 cm	0.04±0.00	0.04±0.01	0.04±0.00	0.35±0.07	0.14±0.01	0.17±0.05
15 – 30 cm	0.03±0.01	0.05±0.01	0.01±0.00	0.35±0.07	0.08±0.01	0.19±0.02
Riparian Forest						
0 – 15 cm	0.00±0.00	0.03±0.01	0.04±0.00	1.26±0.34	0.12±0.04	0.26±0.06
15 – 30 cm	0.01±0.00	0.07±0.01	0.04±0.01	0.64±0.01	0.12±0.01	0.28±0.01
Diospyrus mespiliformis Forest						
0 – 15 cm	0.00±0.00	0.03±0.01	0.04±0.00	0.55±0.07	0.10±0.01	0.26±0.06
15 – 30 cm	0.01±0.00	0.08±0.01	0.04±0.00	1.42±0.09	0.39±0.01	0.28±0.01
Control						
0 – 15 cm	0.00±0.00	0.03±0.01	0.01±0.00	0.06±0.01	0.12±0.04	0.23±0.04
15 – 30 cm	0.01±0.00	0.07±0.01	0.00±0.00	0.06±0.00	0.01±0.00	0.03±0.00

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX III

Chemical fractionation of Cr (mg/kg) of the soils of Oli forest at different vegetation zones in wet season of 2011

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
***Isoberlinia* Woodland**						
0 – 15 cm	0.03±0.01	0.50±0.28	3.04±1.51	10.78±5.27	0.18±0.10	15.13±7.18
15 – 30 cm	0.09±0.05	0.19±0.12	1.93±0.90	10.10±4.81	0.19±0.09	17.75±1.06
***Terminalia macroptera* Woodlland**						
0 – 15 cm	0.10±0.05	0.58±0.28	15.66±7.69	1.72±0.82	1.80±0.99	20.05±1.48
15 – 30 cm	0.10±0.05	2.04±0.99	14.06±6.70	0.96±0.46	1.57±0.75	5.65±0.92
***Burkea africana/Detarium microcarpum* woodland**						
0 – 15 cm	0.04±0.02	1.99±0.97	15.40±7.50	0.17±0.12	1.34±0.48	12.50±0.71
15 – 30 cm	0.08±0.00	1.94±1.03	14.54±7.01	1.33±0.95	0.70±0.35	4.50±0.71
Riparian Forest						
0 – 15 cm	0.00±0.00	0.03±0.01	0.04±0.00	1.26±0.34	0.12±0.04	0.26±0.06
15 – 30 cm	0.01±0.00	0.07±0.01	0.04±0.01	0.64±0.01	0.12±0.01	0.28±0.01
Diospyrus mespiliformis Forest						
0 – 15 cm	2.67±0.47	2.92±0.11	2.93±0.10	3.70±0.42	7.58±0.60	21.89±0.16
15 – 30 cm	2.87±0.19	3.62±0.54	3.75±0.35	4.82±0.26	5.84±0.23	17.45±0.78
Control						
0 – 15 cm	0.00±0.00	0.20±0.10	1.54±0.75	0.02±0.01	0.13±0.05	1.25±0.07
15 – 30 cm	0.01±0.00	0.19±0.10	1.45±0.70	0.13±0.10	0.07±0.04	0.45±0.07

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX IV

Chemical fractionation of Cr (mg/kg) of the soils of Oli Camp at different vegetation zones in dry season of 2011

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
***Isoberlinia* Woodland**						
0 – 15 cm	2.75±0.35	3.16±0.06	2.38±0.03	4.75±0.07	4.05±0.07	15.15±0.07
15 – 30 cm	1.41±0.13	3.41±0.13	2.96±0.06	8.45±0.07	3.74±0.09	13.50±0.71
***Terminalia macroptera* Woodland**						
0 – 15 cm	1.41±0.13	2.74±0.09	3.39±0.16	5.48±0.32	5.17±0.19	14.84±0.37
15 – 30 cm	2.44±0.08	3.57±0.05	2.70±0.28	1.09±0.16	3.57±0.05	10.09±0.16
***Burkea africana/Detarium microcarpum* woodland**						
0 – 15 cm	1.71±0.15	2.20±0.14	3.23±0.18	15.05±0.78	5.96±0.20	18.55±0.64
15 – 30 cm	2.56±0.06	3.19±0.02	3.35±0.07	7.10±0.14	6.45±0.07	20.50±2.12
Riparian Forest						
0 – 15 cm	2.05±0.07	3.10±0.14	2.95±0.21	3.05±0.22	3.71±0.13	12.70±0.42
15 – 30 cm	1.94±0.23	3.35±0.21	2.85±0.35	1.28±0.11	4.62±0.54	9.85±0.92
Diospyrus mespiliformis Forest						
0 – 15 cm	1.75±0.35	2.74±0.37	2.95±0.21	12.25±0.35	4.56±0.62	13.50±0.71
15 – 30 cm	1.58±0.11	2.95±0.07	2.92±0.01	3.85±0.21	5.75±0.35	34.70±1.84
Control						
0 – 15 cm	0.21±0.01	0.31±0.01	0.30±0.02	0.30±0.02	0.37±0.01	1.27±0.04
15 – 30 cm	0.19±0.02	0.34±0.02	0.29±0.04	0.13±0.01	0.46±0.05	0.99±0.09

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX V

Chemical fractionation of Ni (mg/kg) of the soils of Oli forest at different vegetation zones in wet season of 2011

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.04±0.00	1.23±0.03	0.74±0.01	1.39±0.05	1.85±0.36	23.90±0.42
15 – 30 cm	0.01±0.00	1.32±0.04	2.28±0.04	1.42±0.04	1.82±0.04	21.09±0.16
Terminalia macroptera Woodlland						
0 – 15 cm	0.02±0.00	0.78±0.05	0.92±0.03	1.40±0.02	2.35±0.22	6.58±0.60
15 – 30 cm	0.05±0.01	0.85±0.03	0.14±0.00	1.48±0.04	0.36±0.03	201.50±0.71
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	0.03±0.00	1.54±0.19	0.97±0.02	2.27±0.05	1.27±0.04	18.60±0.57
15 – 30 cm	0.07±0.00	0.32±0.01	2.71±0.03	1.64±0.01	0.60±0.10	24.65±0.49
Riparian Forest						
0 – 15 cm	0.06±0.01	0.35±0.01	2.41±0.06	3.11±0.13	0.40±0.00	4.62±0.54
15 – 30 cm	0.06±0.01	0.92±0.01	1.34±0.08	0.97±0.05	11.79±0.30	10.95±0.07
Diospyrus mespiliformis Forest						
0 – 15 cm	1.78±0.56	1.23±0.50	2.44±1.00	2.64±1.00	7.68±2.56	9.50±3.00
15 – 30 cm	1.30±0.10	1.45±0.00	1.65±0.57	3.25±1.20	4.56±1.78	6.08±1.00

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX VI

Chemical fractionation of Ni (mg/kg) of the soils of Oli forest at different vegetation zones in dry season of 2011

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.71±0.28	1.25±0.07	2.43±0.10	1.65±0.07	3.63±0.18	8.84±0.23
15 – 30 cm	0.39±0.01	1.10±0.14	2.95±0.07	2.75±0.35	3.85±0.07	5.60±0.57
***Terminalia macroptera* Woodlland**						
0 – 15 cm	0.71±0.06	2.00±0.42	3.29±0.01	2.35±0.21	3.75±1.06	6.80±0.28
15 – 30 cm	0.46±0.06	0.40±0.04	2.85±0.49	4.13±0.18	3.35±0.21	2.60±0.14
***Burkea africana/Detarium microcarpum* woodland**						
0 – 15 cm	0.68±0.03	4.90±0.14	3.30±0.28	1.70±0.42	5.65±0.07	8.15±0.07
15 – 30 cm	0.82±0.05	3.25±0.35	3.30±0.28	4.40±0.14	5.85±0.21	9.79±0.30
Riparian Forest						
0 – 15 cm	0.56±0.06	0.89±0.02	2.95±0.07	1.75±0.35	3.75±0.35	5.86±0.20
15 – 30 cm	0.78±0.04	0.92±0.00	2.75±0.21	3.45±0.07	3.70±0.14	5.55±0.35
***Diospyrus mespiliformis* Forest**						
0 – 15 cm	1.70±0.43	1.70±0.42	0.61±0.13	2.45±0.07	4.60±0.28	4.63±0.11
15 – 30 cm	1.04±0.09	2.20±0.14	0.70±0.14	3.20±0.42	4.05±0.21	23.25±0.35
Control						
0 – 15 cm	0.06±0.01	0.09±0.00	0.30±0.01	0.18±0.04	0.38±0.04	0.59±0.02
15 – 30 cm	0.78±0.04	0.92±0.00	2.75±0.21	3.45±0.07	3.70±0.14	5.55±0.35

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX VII

Chemical fractionation of Pb (mg/kg) of the soils of Oli forest at different vegetation zones in wet season of 2011

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.15±0.86	2.57±15.31	2.15±12.78	2.56±15.22	2.13±12.66	7.25±43.18
15 – 30 cm	0.14±0.94	2.57±16.71	2.07±13.43	2.62±17.00	2.19±14.21	5.80±37.71
Terminalia macroptera Woodlland						
0 – 15 cm	0.15±1.04	2.43±16.85	2.35±16.33	2.01±13.97	2.32±16.09	5.14±35.72
15 – 30 cm	0.19±1.35	2.16±15.34	2.16±15.33	2.30±16.30	2.15±15.27	5.13±36.41
***Burkea africana/Detarium microcarpum* woodland**						
0 – 15 cm	0.14±0.94	2.30±15.45	2.47±16.59	2.38±16.02	2.36±15.88	5.22±35.13
15 – 30 cm	0.13±0.80	2.07±13.02	2.55±16.00	1.59±9.98	3.08±19.33	6.50±40.87
Riparian Forest						
0 – 15 cm	0.12±0.79	2.33±14.91	2.55±16.32	2.35±15.01	3.10±19.84	5.18±33.12
15 – 30 cm	0.21±1.25	1.99±12.07	2.54±15.44	2.39±14.50	2.09±12.67	7.25±44.07
Diospyrus mespiliformis Forest						
0 – 15 cm	1.57±12.69	1.61±12.97	0.**89**±**7**.19	3.57±28.86	2.92±23.57	1.82±14.71
15 – 30 cm	1.63±10.59	1.78±11.56	0.85±5.49	2.89±18.77	4.68±30.37	3.58±23.22
Control						
0 – 15 cm	0.00±0.31	0.23±14.99	0.26±6.40	0.23±15.08	0.31±19.94	0.52±33.28
15 – 30 cm	0.02±1.25	0.20±12.07	0.25±15.44	0.24±14.50	0.21±12.67	0.73±44.07

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX VIII

Chemical fractionation of Pb (mg/kg) of the soils of Oli forest at different vegetation zones in dry season of 2011

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
***Isoberlinia* Woodland**						
0 – 15 cm	1.46±0.06	1.85±0.21	0.19±0.02	3.17±0.11	3.72±0.12	2.88±0.11
15 – 30 cm	1.61±0.06	2.00±0.14	0.31±0.06	4.80±0.13	2.95±0.35	2.20±0.28
***Terminalia macroptera* Woodlland**						
0 – 15 cm	0.78±0.11	1.81±0.28	0.16±0.06	3.23±0.10	1.46±0.06	1.60±0.28
15 – 30 cm	1.94±0.37	1.35±0.21	0.19±0.08	4.50±0.71	2.91±0.03	7.51±0.69
***Burkea africana/Detarium microcarpum* woodland**						
0 – 15 cm	0.75±0.07	2.10±0.14	1.21±0.13	2.80±0.14	2.60±0.85	4.35±0.49
15 – 30 cm	0.89±0.08	1.85±0.21	2.65±0.07	3.50±0.14	5.30±0.42	2.40±0.28
Riparian Forest						
0 – 15 cm	1.04±0.23	1.70±0.14	0.18±0.11	2.30±0.42	1.91±0.06	1.13±0.18
15 – 30 cm	1.35±0.21	1.34±0.23	0.07±0.01	3.44±0.08	3.10±0.14	5.50±0.71
Diospyrus mespiliformis Forest						
0 – 15 cm	1.25±0.07	2.16±0.00	1.15±0.07	3.45±0.07	2.73±0.10	0.70±0.28
15 – 30 cm	1.45±0.21	1.66±0.06	0.07±0.01	2.95±0.07	3.83±0.10	0.99±0.02
Control						
0 – 15 cm	0.10±0.02	0.17±0.01	0.02±0.01	0.23±0.04	0.19±0.01	0.11±0.02
15 – 30 cm	0.14±0.02	0.13±0.02	0.01±0.00	0.34±0.01	0.31±0.01	0.55±0.07

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX IX

Chemical fractionation of Zn (mg/kg) of the soils of Oli forest at different vegetation zones in wet season of 2011

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.04±0.00	1.37±0.18	1.37±0.03	0.33±0.03	0.74±0.01	10.78±0.04
15 – 30 cm	0.01±0.00	0.61±0.11	1.41±0.02	1.55±0.01	1.00±0.07	14.64±0.51
Terminalia macroptera Woodlland						
0 – 15 cm	0.02±0.00	0.43±0.04	70.69±8.02	1.38±0.03	2.71±0.02	9.85±0.21
15 – 30 cm	0.05±0.01	0.59±0.12	1.48±0.04	0.32±0.01	3.38±0.03	11.20±0.42
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	0.03±0.00	0.60±0.03	2.36±0.05	0.83±0.04	2.15±0.07	6.55±0.64
15 – 30 cm	0.07±0.00	0.35v0.01	1.65±0.03	0.58±0.04	1.32±0.05	6.72±0.40
Riparian Forest						
0 – 15 cm	0.05±0.01	1.32±0.06	3.01±0.00	0.33±0.04	0.77±0.05	13.97±0.05
15 – 30 cm	0.06±0.01	0.08±0.01	1.02±0.12	1.13±0.11	2.38±0.18	7.90±0.14
Diospyrus mespiliformis Forest						
0 – 15 cm	0.53±0.02	9.81±1.20	33.33±2.89	18.75±0.98	89.55±2.00	59.38±0.00
15 – 30 cm	0.64±0.10	7.45±0.50	29.56±1.00	37.56±3.00	78.08±1.50	46.28±0.50
Control						
0 – 15 cm	0.40±0.01	0.27±0.20	1.02±0.20	2.09±1.17	1.16±1.00	3.10±1.00
15 – 30 cm	1.24±0.02	1.45±1.00	2.00±0.00	3.30±0.11	4.30±2.10	4.50±0.39

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX X

Chemical fractionation of Zn (mg/kg) of the soils of Oli forest at different vegetation zones in dry season of 2011

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.29±0.02	10.51±0.70	117.87±3.02	33.75±0.35	109.74±0.37	35.19±1.15
15 – 30 cm	1.94±0.09	9.23±0.39	42.52±0.68	17.92±0.12	91.34±0.94	24.52±0.69
Terminalia macroptera Woodlland						
0 – 15 cm	0.49±0.08	9.71±0.41	43.47±0.05	18.57±0.61	82.74±0.37	38.64±0.51
15 – 30 cm	0.39±0.01	7.03±0.04	88.75±0.36	23.54±0.65	115.12±0.16	29.93±0.11
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	1.58±0.59	11.75±0.35	29.75±0.35	42.54±0.66	159.57±0.61	77.89±0.16
15 – 30 cm	0.79±0.02	9.73±0.39	118.50±0.71	27.78±0.31	176.68±0.45	82.88±0.18
Riparian Forest						
0 – 15 cm	1.73±0.39	6.76±0.34	82.86±0.20	30.77±0.33	134.80±0.29	45.64±0.51
15 – 30 cm	1.27±0.04	6.90±0.14	21.58±0.59	44.66±0.48	56.83±0.24	28.82±0.26
Diospyrus mespiliformis Forest						
0 – 15 cm	0.29±0.02	9.56±0.62	16.59±0.58	27.54±0.65	80.78±0.32	60.80±0.28
15 – 30 cm	0.95±0.07	8.84±0.23	40.64±0.50	36.73±0.39	77.91±0.13	38.57±0.62
Control						
0 – 15 cm	2.40±0.50	3.20±1.000	3.00±1.20	4.11±2.23	2.10±2.00	5.20±2.00
15 – 30 cm	5.90±1.00	4.40±3.00	4.00±1.00	5.10±1.01	5.00±1.10	6.00±0.89

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX XI

Chemical fractionation of Cu (mg/kg) of the soils of Oli forest at different vegetation zones in wet season of 2011

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.42±0.01	1.29±0.01	2.44±0.05	2.29±0.01	5.49±0.02	22.29±0.08
15 – 30 cm	0.52±0.01	5.75±0.49	1.79±0.01	1.57±0.04	3.48±0.11	27.64±0.51
***Terminalia macroptera Woodla*nd**						
0 – 15 cm	0.19±0.01	3.55±0.21	0.40±0.03	1.31±0.02	2.85±0.07	15.82±0.26
15 – 30 cm	0.08±0.01	0.91±0.04	0.53±0.04	1.41±0.13	2.67±0.04	17.68±0.46
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	2.48±0.04	9.22±0.01	0.64±0.04	1.61±0.01	4.08±0.03	29.50±0.71
15 – 30 cm	1.99±0.01	3.93±4.54	0.66±0.01	1.49±0.01	3.28±0.03	25.87±0.19
Riparian Forest						
0 – 15 cm	0.65±0.08	3.23±0.11	1.23±0.00	2.45±0.07	4.07±0.05	23.59±0.58
15 – 30 cm	0.79±0.10	4.83±0.09	1.41±0.13	1.79±0.01	2.66±0.07	39.45±0.78
Diospyrus mespiliformis Forest						
0 – 15 cm	0.01±0.00	0.24±0.00	2.28±1.00	2.53±0.00	0.94±0.00	1.93±0.00
15 – 30 cm	0.41±0.00	0.04±0.00	2.79±0.00	1.83±0.00	0.23±0.00	0.46±0.00

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX XII

Chemical fractionation of Cu (mg/kg) of the soils of Oli forest at different vegetation zones in dry season of 2011

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.14±0.01	0.26±0.06	0.18±0.03	1.36±0.06	0.32±0.11	0.00±0.00
15 – 30 cm	0.21±0.12	0.33±0.11	0.86±0.05	1.26±0.06	0.29±0.01	0.28±0.04
***Terminalia macroptera Woodla*nd**						
0 – 15 cm	0.04±0.02	0.70±0.21	0.67±0.04	0.87±0.05	0.19±0.02	0.33±0.25
15 – 30 cm	0.19±0.01	0.46±0.06	0.58±0.03	1.13±0.10	0.09±0.02	0.40±0.14
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	0.02±0.01	3.06±0.19	0.25±0.14	1.72±0.25	0.53±0.10	1.14±0.09
15 – 30 cm	0.16±0.05	0.86±0.05	0.18±0.03	0.76±0.05	0.88±0.06	1.34±0.09
Riparian Forest						
0 – 15 cm	0.02±0.00	0.38±0.03	0.09±0.00	0.72±0.14	0.49±0.10	0.54±0.09
15 – 30 cm	0.17±0.04	0.21±0.12	0.37±0.04	0.59±0.08	0.68±0.10	0.00±0.00
Diospyrus mespiliformis Forest						
0 – 15 cm	0.17±0.04	0.59±0.08	0.07±0.01	0.61±0.06	0.60±0.14	0.09±0.02
15 – 30 cm	0.00±0.00	0.18±0.04	2.89±0.15	0.56±0.14	1.36±0.22	0.52±0.06

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX XIII

Percentage Mobility factor of metal of the soil of Oli forest at different vegetation zones in the dry and wet season of 2011

Metal/Season	Site (cm)											
Cd	I(0 - 15)	I(15 - 30)	T(0 - 15)	T(15 - 30)	B(0 - 15)	B(15 - 30)	R(0 - 15)	R(15 - 30)	D(0 - 15)	D(15 - 30)	Ctrl (0 - 15)	Ctrl (15 -30)
Dry Season	5.71	9.54	14.55	9.55	13.94	11.92	3.72	10.20	6.47	5.79	5.06	4.94
Wet Season	6.36	7.65	7.35	6.61	9.82	9.31	8.77	9.59	5.01	7.50	9.06	7.65
Cr												
Dry Season	24.08	22.05	21.08	34.74	14.48	19.02	27.80	31.11	18.68	13.30	5.37	5.29
Wet Season	11.95	8.44	45.75	69.51	56.48	64.65	60.94	74.80	21.37	28.34	49.17	61.82
Ni												
Dry Season	21.26	24.20	28.14	25.59	33.17	24.82	24.96	24.13	23.04	10.34	26.52	21.98
Wet Season	6.90	12.89	14.22	0.51	10.27	10.33	25.69	8.90	23.23	26.26	13.39	11.67
Pb												
Dry Season	24.75	26.83	29.29	17.58	25.56	30.11	34.11	16.83	38.93	28.26	22.87	24.85
Wet Season	32.03	32.90	34.00	32.10	32.97	34.18	33.55	31.81	17.66	17.35	19.69	17.85
Zn												
Dry Season	39.36	25.47	24.13	33.42	10.79	27.02	26.93	16.91	11.09	22.17	12.39	13.67
Wet Season	19.01	10.50	83.62	12.41	23.88	19.40	22.54	9.24	14.71	12.17	17.12	15.58
Cu												
Dry Season	25.80	43.02	50.15	43.03	48.87	26.57	20.53	37.10	38.58	54.11	50.56	49.30
Wet Season	12.10	19.77	17.15	6.51	25.96	17.67	14.49	13.79	18.65	27.89	20.36	14.99

APPENDIX XIV

Chemical fractionation of Cd (mg/kg) of the soils of Oli forest at different vegetation zones in wet season of 2012

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.11±0.02	0.14±0.06	0.30±0.17	0.31±0.18	2.17±1.04	5.09±2.42
15 – 30 cm	0.12±0.06	0.16±0.08	0.35±0.20	0.43±0.24	2.75±1.31	5.35±0.49
Terminalia macroptera Woodlland						
0 – 15 cm	0.20±0.10	0.20±0.10	0.25±0.14	0.43±0.23	2.59±1.29	6.00±1.41
15 – 30 cm	0.13±0.17	0.03±0.01	0.31±0.20	0.05±0.04	2.16±1.05	6.00±1.41
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	0.16±0.08	0.17±0.12	0.22±0.11	0.18±0.11	0.29±0.16	4.50±2.12
15 – 30 cm	0.14±0.07	0.23±0.11	0.29±0.16	0.21±0.13	0.38±0.17	7.07±1.32
Riparian Forest						
0 – 15 cm	0.13±0.06	0.20±0.11	0.21±0.13	0.06±0.03	0.29±0.16	4.65±3.32
15 – 30 cm	0.10±0.05	0.26±0.15	0.14±0.08	0.14±0.08	0.41±0.21	5.50±0.71
Diospyrus mespiliformis Forest						
0 – 15 cm	0.04±0.01	0.04±0.01	0.05±0.01	1.67±0.47	0.10±0.01	0.52±0.12
15 – 30 cm	0.06±0.02	0.05±0.02	0.08±0.03	0.92±0.12	0.12±0.04	0.74±0.08
Control						
0 – 15 cm	0.01±0.01	0.02±0.01	0.02±0.01	0.01±0.00	0.03±0.02	0.47±0.33
15 – 30 cm	0.01±0.00	0.03±0.01	0.01±0.01	0.01±0.01	0.04±0.02	0.55±0.07

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX XV

Chemical fractionation of Cd (mg/kg) of the soils of Oli forest at different vegetation zones in dry season of 2012

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.01±0.00	0.04±0.01	0.05±0.01	1.34±0.00	0.11±0.00	0.35±0.01
0 – 30 cm	0.00±0.00	0.04±0.00	0.07±0.00	0.51±0.02	0.22±0.00	0.28±0.01
Terminalia macroptera Woodland						
0 – 15 cm	0.04±0.01	0.08±0.02	0.08±0.01	0.85±0.07	0.12±0.00	0.23±0.01
15 – 30 cm	0.03±0.01	0.07±0.01	0.04±0.01	1.07±0.03	0.02±0.01	0.17±0.19
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	0.04±0.00	0.04±0.01	0.04±0.00	0.35±0.07	0.14±0.01	0.17±0.05
15 – 30 cm	0.03±0.01	0.05±0.01	0.01±0.00	0.35±0.07	0.08±0.01	0.19±0.02
Riparian Forest						
0 – 15 cm	0.00±0.00	0.03±0.01	0.04±0.00	1.26±0.34	0.12±0.04	0.26±0.06
15 – 30 cm	0.01±0.00	0.07±0.01	0.04±0.01	0.64±0.01	0.12±0.01	0.28±0.01
Diospyrus mespiliformis Forest						
0 – 15 cm	0.00±0.00	0.03±0.01	0.04±0.00	0.55±0.07	0.10±0.01	0.26±0.06
15 – 30 cm	0.01±0.00	0.08±0.01	0.04±0.00	1.42±0.09	0.39±0.01	0.28±0.01
Control						
0 – 15 cm	0.00±0.00	0.03±0.01	0.01±0.00	0.06±0.01	0.12±0.04	0.23±0.04
15 – 30 cm	0.01±0.00	0.07±0.01	0.00±0.00	0.06±0.00	0.01±0.00	0.03±0.00

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX XVI

Chemical fractionation of Cr (mg/kg) of the soils of Oli forest at different vegetation zones in wet season of 2012

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.03±0.01	0.50±0.28	3.04±1.51	10.78±5.27	0.18±0.10	15.13±7.18
0 – 30 cm	0.09±0.05	0.19±0.12	1.93±0.90	10.10±4.81	0.19±0.09	17.75±1.06
Terminalia macroptera Woodland						
0 – 15 cm	0.10±0.05	0.58±0.28	15.66±7.69	1.72±0.82	1.80±0.99	20.05±1.48
15 – 30 cm	0.10±0.05	2.04±0.99	14.06±6.70	0.96±0.46	1.57±0.75	5.65±0.92
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	0.04±0.02	1.99±0.97	15.40±7.50	0.17±0.12	1.34±0.48	12.50±0.71
15 – 30 cm	0.08±0.00	1.94±1.03	14.54±7.01	1.33±0.95	0.70±0.35	4.50±0.71
Riparian Forest						
0 – 15 cm	0.00±0.00	0.03±0.01	0.04±0.00	1.26±0.34	0.12±0.04	0.26±0.06
15 – 30 cm	0.01±0.00	0.07±0.01	0.04±0.01	0.64±0.01	0.12±0.01	0.28±0.01
Diospyrus mespiliformis Forest						
0 – 15 cm	2.67±0.47	2.92±0.11	2.93±0.10	3.70±0.42	7.58±0.60	21.89±0.16
15 – 30 cm	2.87±0.19	3.62±0.54	3.75±0.35	4.82±0.26	5.84±0.23	17.45±0.78
Control						
0 – 15 cm	0.00±0.00	0.20±0.10	1.54±0.75	0.02±0.01	0.13±0.05	1.25±0.07
15 – 30 cm	0.01±0.00	0.19±0.10	1.45±0.70	0.13±0.10	0.07±0.04	0.45±0.07

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX XVII

Chemical fractionation of Cr (mg/kg) of the soils of Oli forest at different vegetation zones in dry season of 2012

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	2.75±0.35	3.16±0.06	2.38±0.03	4.75±0.07	4.05±0.07	15.15±0.07
0 – 30 cm	1.41±0.13	3.41±0.13	2.96±0.06	8.45±0.07	3.74±0.09	13.50±0.71
Terminalia macroptera Woodland						
0 – 15 cm	1.41±0.13	2.74±0.09	3.39±0.16	5.48±0.32	5.17±0.19	14.84±0.37
0 – 30 cm	2.44±0.08	3.57±0.05	2.70±0.28	1.09±0.16	3.57±0.05	10.09±0.16
Burkea Africana/Detarium microcarpum woodland						
0 – 15 cm	1.71±0.15	2.20±0.14	3.23±0.18	15.05±0.78	5.96±0.20	18.55±0.64
0 – 30 cm	2.56±0.06	3.19±0.02	3.35±0.07	7.10±0.14	6.45±0.07	20.50±2.12
Riparian Forest						
0 – 15 cm	2.05±0.07	3.10±0.14	2.95±0.21	3.05±0.22	3.71±0.13	12.70±0.42
0 – 30 cm	1.94±0.23	3.35±0.21	2.85±0.35	1.28±0.11	4.62±0.54	9.85±0.92
Diospyrus mespiliformis Forest						
0 – 15 cm	1.75±0.35	2.74±0.37	2.95±0.21	12.25±0.35	4.56±0.62	13.50±0.71
0 – 30 cm	1.58±0.11	2.95±0.07	2.92±0.01	3.85±0.21	5.75±0.35	34.70±1.84
Control						
0 – 15 cm	0.21±0.01	0.31±0.01	0.30±0.02	0.30±0.02	0.37±0.01	1.27±0.04
0 – 30 cm	0.19±0.02	0.34±0.02	0.29±0.04	0.13±0.01	0.46±0.05	0.99±0.09

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

Appendix XVIII

Chemical fractionation of Ni (mg/kg) of the soils of Oli forest at different vegetation zones in wet season of 2012

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.03±0.11	0.93±3.53	0.54±2.03	1.02±3.88	1.45±5.48	22.40±84.97
15 – 30 cm	0.00±0.02	1.00±3.86	1.71±6.63	1.12±4.35	1.38±5.33	20.60±79.81
Terminalia macroptera Woodlland						
0 – 15 cm	0.02±0.15	0.59±5.76	0.70±6.79	1.05±10.25	1.80±17.55	6.10±59.50
15 – 30 cm	0.04±0.02	0.65±0.41	0.10±0.07	1.12±0.72	0.28±0.18	153.50±98.60
Burkea Africana/Detarium microcarpum woodland						
0 – 15 cm	0.03±0.14	1.19±6.34	0.73±3.91	1.71±9.14	0.99±5.30	14.05±75.18
15 – 30 cm	0.06±0.21	0.24±0.90	2.04±7.61	1.24±4.61	0.47±1.75	22.75±84.91
Riparian Forest						
0 – 15 cm	0.05±0.57	0.26±3.26	1.82±22.73	2.00±25.05	0.30±3.76	3.57±44.64
15 – 30 cm	0.05±0.19	0.69±2.88	1.02±4.23	0.74±3.06	11.00±45.86	10.50±43.77
Diospyrus mespiliformis Forest						
0 – 15 cm	1.89±6.97	1.62±5.95	2.72±10.02	2.82±10.39	7.84±28.89	10.25±37.77
15 – 30 cm	1.65±8.19	1.73±8.56	1.83±9.06	3.63±17.99	4.78±23.73	6.54±32.46
Control						
0 – 15 cm	0.00±0.57	0.03±3.26	0.18±22.73	0.20±25.05	0.03±3.76	0.36±44.64
15 – 30 cm	0.00±0.19	0.07±2.88	0.10±4.23	0.07±3.06	1.10±45.86	1.05±43.77

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX XIX

Chemical fractionation of Ni (mg/kg) of the soils of Oli forest at different vegetation zones in dry season of 2012

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.71±0.28	1.25±0.07	2.43±0.10	1.65±0.07	3.63±0.18	8.84±0.23
15 – 30 cm	0.39±0.01	1.10±0.14	2.95±0.07	2.75±0.35	3.85±0.07	5.60±0.57
Terminalia macroptera Woodland						
0 – 15 cm	0.71±0.06	2.00±0.42	3.29±0.01	2.35±0.21	3.75±1.06	6.80±0.28
0 – 30 cm	0.46±0.06	0.40±0.04	2.85±0.49	4.13±0.18	3.35±0.21	2.60±0.14
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	0.68±0.03	4.90±0.14	3.30±0.28	1.70±0.42	5.65±0.07	8.15±0.07
15 – 30 cm	0.82±0.05	3.25±0.35	3.30±0.28	4.40±0.14	5.85±0.21	9.79±0.30
Riparian Forest						
0 – 15 cm	0.56±0.06	0.89±0.02	2.95±0.07	1.75±0.35	3.75±0.35	5.86±0.20
15 – 30 cm	0.78±0.04	0.92±0.00	2.75±0.21	3.45±0.07	3.70±0.14	5.55±0.35
Diospyrus mespiliformis Forest						
0 – 15 cm	1.70±0.43	1.70±0.42	0.61±0.13	2.45±0.07	4.60±0.28	4.63±0.11
15 – 30 cm	1.04±0.09	2.20±0.14	0.70±0.14	3.20±0.42	4.05±0.21	23.25±0.35
Control						
0 – 15 cm	0.06±0.01	0.09±0.00	0.30±0.01	0.18±0.04	0.38±0.04	0.59±0.02
15 – 30 cm	0.78±0.04	0.92±0.00	2.75±0.21	3.45±0.07	3.70±0.14	5.55±0.35

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX XX

Chemical fractionation of Pb (mg/kg) of the soils of Oli forest at different vegetation zones in wet season of 2012

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.15±0.86	2.57±15.31	2.15±12.78	2.56±15.22	2.13±12.66	7.25±43.18
15 – 30 cm	0.14±0.94	2.57±16.71	2.07±13.43	2.62±17.00	2.19±14.21	5.80±37.71
Terminalia macroptera Woodland						
0 – 15 cm	0.15±1.04	2.43±16.85	2.35±16.33	2.01±13.97	2.32±16.09	5.14±35.72
15 – 30 cm	0.19±1.35	2.16±15.34	2.16±15.33	2.30±16.30	2.15±15.27	5.13±36.41
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	0.14±0.94	2.30±15.45	2.47±16.59	2.38±16.02	2.36±15.88	5.22±35.13
15 – 30 cm	0.13±0.80	2.07±13.02	2.55±16.00	1.59±9.98	3.08±19.33	6.50±40.87
Riparian Forest						
0 – 15 cm	0.12±0.79	2.33±14.91	2.55±16.32	2.35±15.01	3.10±19.84	5.18±33.12
15 – 30 cm	0.21±1.25	1.99±12.07	2.54±15.44	2.39±14.50	2.09±12.67	7.25±44.07
Diospyrus mespiliformis Forest						
0 – 15 cm	1.57±12.69	1.61±12.97	0.**89**±**7**.19	3.57±28.86	2.92±23.57	1.82±14.71
15 – 30 cm	1.63±10.59	1.78±11.56	0.85±5.49	2.89±18.77	4.68±30.37	3.58±23.22
Control						
0 – 15 cm	0.00±0.31	0.23±14.99	0.26±6.40	0.23±15.08	0.31±19.94	0.52±33.28
15 – 30 cm	0.02±1.25	0.20±12.07	0.25±15.44	0.24±14.50	0.21±12.67	0.73±44.07

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX XXI

Chemical fractionation of Pb (mg/kg) of the soils of Oli forest at different vegetation zones in dry season of 2012

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	1.46±0.06	1.85±0.21	0.19±0.02	3.17±0.11	3.72±0.12	2.88±0.11
15 – 30 cm	1.61±0.06	2.00±0.14	0.31±0.06	4.80±0.13	2.95±0.35	2.20±0.28
Terminalia macroptera Woodland						
0 – 15 cm	0.78±0.11	1.81±0.28	0.16±0.06	3.23±0.10	1.46±0.06	1.60±0.28
15 – 30 cm	1.94±0.37	1.35±0.21	0.19±0.08	4.50±0.71	2.91±0.03	7.51±0.69
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	0.75±0.07	2.10±0.14	1.21±0.13	2.80±0.14	2.60±0.85	4.35±0.49
15 – 30 cm	0.89±0.08	1.85±0.21	2.65±0.07	3.50±0.14	5.30±0.42	2.40±0.28
Riparian Forest						
0 – 15 cm	1.04±0.23	1.70±0.14	0.18±0.11	2.30±0.42	1.91±0.06	1.13±0.18
15 – 30 cm	1.35±0.21	1.34±0.23	0.07±0.01	3.44±0.08	3.10±0.14	5.50±0.71
Diospyrus mespiliformis Forest						
0 – 15 cm	1.25±0.07	2.16±0.00	1.15±0.07	3.45±0.07	2.73±0.10	0.70±0.28
15 – 30 cm	1.45±0.21	1.66±0.06	0.07±0.01	2.95±0.07	3.83±0.10	0.99±0.02
Control						
0 – 15 cm	0.10±0.02	0.17±0.01	0.02±0.01	0.23±0.04	0.19±0.01	0.11±0.02
15 – 30 cm	0.14±0.02	0.13±0.02	0.01±0.00	0.34±0.01	0.31±0.01	0.55±0.07

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX XXII

Chemical fractionation of Zn (mg/kg) of the soils of Oli forest at different vegetation zones in wet season of 2012

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.03±0.01	1.06±0.62	1.01±0.54	0.26±0.13	0.56±0.27	9.05±2.47
15 – 30 cm	0.01±0.00	0.47±0.29	1.05±0.52	1.17±0.56	0.77±0.40	14.00±1.41
Terminalia macroptera Woodland						
0 – 15 cm	0.01±0.01	0.33±0.18	70.35±98.51	1.04±0.51	2.03±0.97	7.18±4.00
15 – 30 cm	0.04±0.03	0.46±0.30	1.13±0.53	0.24±0.11	2.54±1.22	8.50±4.24
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	0.03±0.01	0.46±0.23	1.78±0.87	0.63±0.32	1.63±0.81	5.03±2.79
15 – 30 cm	0.06±0.03	0.26±0.13	1.24±0.60	0.44±0.23	1.00±0.50	6.20±1.13
Riparian Forest						
0 – 15 cm	0.04±0.02	1.00±0.51	2.26±1.06	0.25±0.14	0.65±0.21	10.45±5.02
15 – 30 cm	0.05±0.03	0.06±0.03	0.79±0.45	0.87±0.47	1.82±0.97	5.78±3.14
Diospyrus mespiliformis Forest						
0 – 15 cm	0.77±0.33	9.91±0.13	34.17±1.18	18.88±0.18	90.28±1.03	59.94±0.79
15 – 30 cm	0.82±0.25	7.73±0.39	29.78±0.31	38.28±1.02	79.04±1.36	46.64±0.51
Control						
0 – 15 cm	0.00±0.00	0.10±0.05	0.23±0.11	0.03±0.01	0.07±0.02	0.42±0.39
15 – 30 cm	0.00±0.00	0.01±0.00	0.08±0.04	0.09±0.05	0.18±0.10	0.58±0.31

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX XXIII

Chemical fractionation of Zn (mg/kg) of the soils of Oli forest at different vegetation zones in dry season of 2012

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.29±0.02	10.00±1.41	115.00±7.07	33.50±0.71	109.00±1.41	35.00±1.41
15 – 30 cm	1.94±0.09	9.20±0.42	42.50±0.71	17.90±0.14	91.00±1.41	24.50±0.71
Terminalia macroptera Woodland						
0 – 15 cm	0.49±0.08	9.70±0.42	43.45±0.07	18.57±0.61	81.50±2.12	37.50±2.12
15 – 30 cm	0.39±0.01	7.03±0.04	88.50±0.71	23.95±0.07	112.50±3.54	29.50±0.71
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	1.55±0.64	11.50±0.71	29.50±0.71	42.50±0.71	159.00±1.41	77.50±0.71
15 – 30 cm	0.79±0.02	9.70±0.42	117.00±2.83	27.50±0.71	175.50±2.12	82.50±0.71
Riparian Forest						
0 – 15 cm	1.65±0.49	6.75±0.35	82.50±0.71	30.50±0.71	134.00±1.41	45.50±0.71
15 – 30 cm	1.27±0.05	6.75±0.35	21.50±0.71	44.50±0.71	56.50±0.71	28.50±0.71
Diospyrus mespiliformis Forest						
0 – 15 cm	0.29±0.02	9.56±0.62	16.50±0.71	27.50±0.71	80.50±0.71	60.50±0.71
15 – 30 cm	0.90±0.14	8.80±0.28	40.60±0.57	36.50±0.71	77.50±0.71	38.50±0.71
Control						
0 – 15 cm	0.17±0.05	0.68±0.04	0.83±0.01	0.31±0.01	13.40±0.14	4.55±0.07
15 – 30 cm	0.13±0.00	0.68±0.04	2.15±0.07	4.45±0.07	5.65±0.07	2.85±0.07

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX XXIV

Chemical fractionation of Cu (mg/kg) of the soils of Oli forest at different vegetation zones in wet season of 2012

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.32±0.15	0.97±0.47	1.84±0.90	1.72±0.82	4.12±1.95	21.29±1.50
15 – 30 cm	0.39±0.18	4.40±2.40	1.35±0.64	1.19±0.59	2.63±1.32	26.50±2.12
Terminalia macroptera Woodlland						
0 – 15 cm	0.14±0.07	2.70±1.41	0.31±0.16	0.98±0.48	2.15±1.06	15.00±1.41
15 – 30 cm	0.05±0.06	0.69±0.35	0.41±0.22	1.08±0.60	2.01±0.98	13.50±6.36
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	1.88±0.88	6.92±3.27	0.50±0.25	1.23±0.53	3.07±1.46	22.50±10.61
15 – 30 cm	1.50±0.71	2.14±2.02	0.51±0.23	1.12±0.54	2.78±0.74	19.50±9.19
Riparian Forest						
0 – 15 cm	0.50±0.28	2.40±1.06	0.93±0.43	1.85±0.92	3.08±1.45	23.50±0.71
15 – 30 cm	0.61±0.35	3.64±1.77	1.08±0.60	1.35±0.64	2.16±0.78	30.00±14.14
Diospyrus mespiliformis Forest						
0 – 15 cm	0.04±0.00	0.37±0.18	2.64±0.51	2.77±0.33	0.97±0.04	2.02±0.12
15 – 30 cm	0.71±0.42	0.06±0.03	2.90±0.15	1.92±0.12	0.42±0.26	0.68±0.31
Control						
0 – 15 cm	0.07±0.00	0.24±0.11	0.09±0.04	0.19±0.09	0.31±0.14	0.24±0.01
15 – 30 cm	0.06±0.04	0.36±0.18	0.11±0.06	0.13±0.06	0.22±0.08	3.00±1.41

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX XXV

Chemical fractionation of Cu (mg/kg) of the soils of Oli forest at different vegetation zones in dry season of 2012

Sample Location	Fractions					
	WS	**EX**	**OB**	**CB**	**FMO**	**RES**
Isoberlinia Woodland						
0 – 15 cm	0.15±0.01	0.25±0.07	0.18±0.03	1.35±0.07	0.32±0.12	0.00±0.00
15 – 30 cm	0.20±0.14	0.30±0.14	0.86±0.06	1.25±0.07	0.25±0.07	0.25±0.07
Terminalia macroptera Woodland						
0 – 15 cm	0.04±0.03	0.65±0.28	0.67±0.05	0.86±0.06	0.19±0.02	0.30±0.28
15 – 30 cm	0.19±0.01	0.46±0.06	0.58±0.03	1.13±0.10	0.09±0.02	0.35±0.21
Burkea africana/Detarium microcarpum woodland						
0 – 15 cm	0.02±0.01	3.05±0.21	0.23±0.18	1.70±0.28	0.53±0.10	1.14±0.09
15 – 30 cm	0.16±0.06	0.85±0.07	0.18±0.03	0.75±0.07	0.88±0.06	1.34±0.09
Riparian Forest						
0 – 15 cm	0.02±0.01	0.38±0.03	0.09±0.01	0.72±0.14	0.49±0.11	0.54±0.09
15 – 30 cm	0.17±0.05	0.21±0.13	0.37±0.05	0.58±0.11	0.68±0.10	1.00±0.41
Diospyrus mespiliformis Forest						
0 – 15 cm	0.17±0.05	0.58±0.11	0.07±0.01	0.58±0.11	0.50±0.28	0.09±0.02
15 – 30 cm	0.00±0.00	0.15±0.07	2.89±0.16	0.53±0.18	1.35±0.21	0.52±0.06
Control						
0 – 15 cm	0.00±0.00	0.04±0.00	0.01±0.00	0.07±0.01	0.05±0.01	0.05±0.01
15 – 30 cm	0.02±0.00	0.02±0.01	0.04±0.00	0.06±0.01	0.07±0.01	0.20±0.00

WS: *Water Soluble;* ***EX:*** *Exchangeable;* ***OB:*** *Organic Bound;* ***CB:*** *Carbonate Bound;* ***FMO:*** *Fe-MnO;* ***RES:*** *Residual*

APPENDIX XXVI

Percentage Mobility factor of metal of the soil of Oli forest at different vegetation zones in the dry and wet season of 2012

Metal/Season	Site (cm)											
Cd	I(0 - 15)	I(15 - 30)	T(0 - 15)	T(15 - 30)	B(0 - 15)	B(15 - 30)	R(0 - 15)	R(15 - 30)	D(0 - 15)	D(15 - 30)	Ctrl (0 - 15)	Ctrl (15 -30)
Dry Season	5.12	9.76	14.70	9.40	15.03	11.91	3.67	10.27	6.46	5.91	7.95	43.13
Wet Season	6.67	6.82	6.75	5.39	9.92	7.90	9.72	7.59	5.38	9.21	9.72	7.59
Cr												
Dry Season	25.70	23.24	22.83	37.12	15.27	21.07	29.40	34.09	19.70	14.39	29.40	34.09
Wet Season	12.01	7.26	40.94	66.46	52.12	64.57	55.43	71.73	20.43	26.69	55.43	71.73
Ni												
Dry Season	23.70	26.68	31.73	26.86	36.42	26.88	27.87	25.94	25.54	11.43	27.87	25.94
Wet Season	5.67	10.52	12.70	0.50	10.38	8.72	26.55	7.30	22.94	25.81	26.55	7.30
Pb												
Dry Season	26.34	28.25	30.30	18.89	29.40	32.49	35.31	18.62	39.86	29.02	35.31	18.62
Wet Season	28.95	31.08	34.22	32.02	32.97	29.81	32.03	28.75	32.86	27.64	31.70	28.75
Zn												
Dry Season	41.38	28.68	28.05	36.63	13.23	30.87	30.21	18.56	13.52	24.80	8.36	18.56
Wet Season	17.55	8.76	87.34	12.59	23.67	16.97	22.53	9.58	20.96	18.95	39.41	9.58
Cu												
Dry Season	25.67	43.73	50.19	43.91	49.48	28.67	21.74	24.70	41.09	55.93	21.74	18.52
Wet Season	10.31	16.83	14.78	6.41	25.75	15.05	11.86	13.70	34.62	54.87	35.62	13.70

APPENDIX XXVII

Analysis of Difference in Parameters between horizons in wet season 2011

Parameter	t	Df	Sig. (2-tailed)
Cd	-0.276	8	0.600
Cr	1.424	8	0.111
Ni	-1.617	8	0.456
Pb	-0.766	8	0.444
Zn	0.902	8	0.090
Cu	0.018	8	0.234
Clay	-0.823	8	0.352
Silt	0.146	8	0.531
Sand	-.176	8	0.123
pH_{H2O}	-1.723	8	0.290
pH_{CaCl2}	-1.315	8	0.300
EC	-.621	8	0.451
OM	1.222	8	0.421
CEC	0.123	8	0.231
AP	0.023	8	0.677

APPENDIX XXVIII

Analysis of Difference in Parameters between horizons in wet season 2012

Parameter	t	Df	Sig. (2-tailed)
Cd	-.376	8	.717
Cr	1.624	8	.143
Ni	-1.217	8	.258
Pb	-.766	8	.466
Zn	.292	8	.778
Cu	.038	8	.971
Clay	-.915	8	.387
Silt	.460	8	.658
Sand	-.776	8	.460
pH_{H2O}	-1.251	8	.246
pH_{CaCl2}	-1.194	8	.267
EC	-.346	8	.738
OM	1.144	8	.286
CEC	.785	8	.455
AP	.633	8	.544

APPENDIX XXVIX

Analysis of Difference in Parameters between horizons in dry season 2011

Parameter	t	Df	Sig. (2-tailed)
Cd	0.113	8	0.121
Cr	0.049	8	0.192
Ni	-0.770	8	0.178
Pb	-1.141	8	0.134
Zn	0.327	8	0.782
Cu	-0.533	8	0.902
Clay	-1.340	8	0.103
Silt	1.234	8	0.041
Sand	-1.567	8	0.600
pH_{H2O}	-0.431	8	0.626
pH_{CaCl2}	0.876	8	0.005
EC	0.651	8	0.123
OM	1.345	8	0.002
CEC	0.720	8	0.692
AP	-0.800	8	0.420

APPENDIX XXX

Analysis of Difference in Parameters between horizons in dry season 2012

Parameter	t	Df	Sig. (2-tailed)
Cd	0.103	8	0.921
Cr	0.049	8	0.962
Ni	-0.770	8	0.463
Pb	-2.241	8	0.055
Zn	0.327	8	0.752
Cu	-0.533	8	0.608
Clay	-1.124	8	0.293
Silt	1.012	8	0.341
Sand	-0.408	8	0.694
pH_{H2O}	-0.419	8	0.686
pH_{CaCl2}	1.527	8	0.165
EC	0.552	8	0.596
OM	2.918	8	0.019
CEC	0.410	8	0.692
AP	-0.849	8	0.420