



## Speciation of Pb, Cu and Cd in Wildland Soil of (Oli Camp) Borgu Sector, Kainji Lake National Park

S. K. Omotugba<sup>1\*</sup>, C. E. Gimba<sup>2</sup>, E. B. Agbaji<sup>2</sup> and K. I. Omoniyi<sup>2</sup>

<sup>1</sup>Federal College of Wildlife Management (FRIN), P. M. B. 268, New Bussa, Nigeria.

<sup>2</sup>Department of Chemistry Ahmadu Bello University, Zaria, Nigeria.

### Authors' contributions

This work was carried out in collaboration between all authors. Authors SKO, CEG, EBA and KIO designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript and managed literature searches. Author SKO managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

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### ABSTRACT

The study carried out seasonal study of some potentially toxic heavy metals: Lead, copper, cadmium, chromium, Nickel, and zinc in soils was conducted in five different vegetation zones of (Oli Camp) Kainji Lake National Park at two different levels. The vegetations are *Isobertinia* woodland (S1), *Terminalia macroptera* woodland (S2), *Burkea African/Detarium microcarpum* woodland (S3), *Riparian* forest (S4) and *Diospyrus mespiliformis* (S5). The average values recorded for the wet season at 0-15cm depth in mg/Kg were in the order S1: Cd (10.73±2.00), Cu (34.21±0.00), Pb (20.08±3.40), Cr (39.39±2.30), Ni (29.14±2.90), and Zn (16.63±0.90); S2: Cd (11.56±4.00), Cu (24.11±2.78), Pb (18.97 ±4.50), Cr (47.34±6.70), Ni (12.03±3.45), and Zn (85.07±1.40); S3: Cd (7.17±2.45), Cu (47.52±2.10), Pb (19.73±1.00), Cr (37.48±2.22), Ni (24.67±1.20), and Zn (12.51±0.90); S4: Cd (8.00±1.30), Cu (35.21±0.00), Pb (19.74±1.00), Cr (37.96±3.00), Ni (10.93±1.00), and Zn (19.44±2.30); S5: Cd (1.95±0.00), Cu (7.92±0.40), Pb (10.74±1.20), Cr (40.35±2.60), Ni (25.27±1.80), and Zn (211.35±4.30). Generally, the trend showed a decreasing order for the sub surface soil (15-30 cm). Thus, the mean levels for the wet season at 15-30 cm depth followed the order of Zn>Cu>Cr>Ni >Pb>Cd in the vegetations investigated. The metal concentrations during dry season decreased at

\*Corresponding author: E-mail: omokay6@yahoo.com;

both depths with the ranges: Cd ( $0.74\pm 0.02$  to  $2.26\pm 0.01$ ); Cu ( $2.02\pm 0.02$  to  $6.72\pm 1.10$ ), Pb ( $9.18\pm 3.40$  to  $18.48\pm 1.45$ ) Cr ( $23.55\pm 2.00$  to  $51.94\pm 2.70$ ), Zn ( $160.06\pm 0.56$  to  $323.08\pm 2.10$ ), and Ni ( $14.03\pm 0.50$  to  $34.69\pm 1.00$ ) mg/g. The physico-chemical parameters of the soils in the wet and dry seasons was indicated that pH, 6.65 to 6.95 and 5.3 to 6.7; conductivity,  $10.00\pm 2.50$  to  $101.50\pm 2.12$   $\mu\text{Scm}^{-1}$ ; organic matter,  $1.79\pm 0.30$  to  $2.64 \pm 0.51$  among vegetations studied at 0-15 cm and 15-30 cm depths respectively; this trend is similar to that of the dry season. The range  $1.32\pm 0.25$  to  $2.11\pm 0.06$  were recorded against wet season at both depths. Generally, the speciation result revealed that the levels of these metals studied in both seasons were associated in the order: Residual > carbonate > Fe-MnO > Exchangeable > Organic > Water soluble fractions. The finding in this study has led to the better understanding of the metal levels and their sequential interaction with one another. This will aid in determining and to create awareness about the metal ion status of Oli Camp in Kainji Lake Nation Park to stakeholders in order to mitigate against metal pollution as it is barely monitored.

*Keywords: Soil; speciation; metal; wet and dry seasons; vegetation and wildlife; index enrichment goe-accumulation and mobility factors.*

## 1. INTRODUCTION

Heavy metal contamination in soils has received much attention and extensive research has been conducted on qualitative of metals in soils in some parts of Kainji Lake National Park. Several heavy metals are known to accumulate in water, soil, sediments and tissues of organism and cause acute toxicity when accumulated for a long period of time [1,2,3]. Total evaluation of heavy metals burden in the environment may not be completely understood until, the fact that the determination of total concentrations of these metals are not the best indicator is acknowledged [4,5,6].

Soil is a complex mixture of minerals and organic materials [7]. Soil has been described as a sink and source of contaminant and also a strong relationship between soil plants fauna composition and density in some ecosystems and how these biodiversities in the park is highly dependent on the soil properties has been acknowledged [8]. However, there was reported that it was not enough to only know the amount of these metals present in soils but also to know their chemical forms including the amount of it that is bioavailable [9].

Therefore, it is essential to establish the chemical forms and the amount of these metals that are bio-available to wildlife in the present study area. The various ways in which heavy metals associate with soil components determines their mobility and bioavailability [10,11] thus, to provide reliable information on the forms of association of heavy metals regarding their availability levels, a sequential procedure has been largely relied upon to partition heavy metals such that their chemical reactivity can be elucidated [12]. A universal problem associated with excessive presence of these heavy metals is toxic effects on living organisms. Heavy metals frequently reported in literature with regard to potential hazards and occurrence in contaminated soils, are Cd, Cr, Pb, Zn, Fe and Cu [13,14] but speciation study of Pb, Cu, Cd, Cr, Zn and Ni is reported in this work. Vehicle exhausts, as well as several industrial activities have been reported to be major sources of emitting these heavy metals into the soil [7] but contrary to the present study area where the source of the heavy metals detected has been solely natural. A natural process such as weathering of rocks and volcanic activities plays a noticeable role in enriching the soils with heavy metals [15,16].

All these facts above, informed the present research work to study the forms and quantify the physical and chemical compositions particularly the heavy metals (Pb, Cu, Ni, Cd, Cr and Zn) in Oli Base Camp a reserved area of Kainji lake National Park. The sequential extraction method of [17] with little modification was adopted considering five fractions describing the types of metal combinations in five different vegetation zones.

## 2. MATERIALS AND METHODS

### 2.1 Description of Study Area

The study area is Oli Base Camp, in Kainji Lake National Park (KLNP), Borgu sector. KLNP is the premier park in Nigeria covering a total area of 5340.82Km<sup>2</sup> and composed of two non-contiguous sectors, the Borgu and Zugurma sectors [18]. The Borgu sector covered an area of 3,970.02Km<sup>2</sup> while Zugurma sectors, covers an area of 1,370Km<sup>2</sup>. 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°40'N and 10°23'E and longitudes 3°30'N and 5°50'E [19]. The vegetation of the Borgu sector is differentiable by hydrological as well as soil factors into five major types viz: the *Isobertia woodland*, *Terminalia macroptera woodland*, *Burkea africana/Detarium microcarpum woodland*, *Riparian forest and the Diospyrus mespiliformis dry forest* [20,21].

### 2.2 Sampling Sites Description

The entire sample sites are reserved region of the park. Agriculture is the most important economic activity and engages more than 75 percent of the active labour force. Besides crop production, the people of the area also engage in fishing and livestock production. Increasing population and unrestrained anthropogenic activities are impacting negatively on the rich biodiversity of the area. Illegal grazing, poaching, burning, farming, fishing and general encroachment into these protected areas are human activities threatening the protection of flora and fauna in the area.

### 2.3 Sample Collection

Five plots each was established in the five vegetation zones. Each plot was separated by a fire trace of 5m to prevent fire occurrence. To describe the soil properties of the different vegetation, soil samples were collected from each site during rainy and dry seasons using a metal auger from the randomised observation points at 0-15cm and 15-30cm into a transparent polyethylene bags, labelled and taken to the laboratory for treatment and analysis.

### 2.4 Sample Pre-treatment

All soil samples were homogenised and air dried, sieved via 2mm mesh and another portion through 0.5mm mesh [8] to remove rock fragments, surface plant litter and coarse root materials.

### 2.5 Methods

The analytical speciation extraction procedure by [17] with slightly modification was used. In this scheme heavy metals were separated into six operationally defined fractions (F): water

soluble (F1), exchangeable (F2), bound to organic matter (F3), carbonate (F4), bound to Fe/Mn (F5), and bound to residual (F6).

One gram of each soil sample was weighed and extractions were made through steps (F) by centrifugation and filtration at 4500 rpm. Deionised water was used to wash the residues following subsequent extractions in order to ensure selective dissolution and avoid possible inter-phase mixing between the extractants. All samples were run in duplicates.

### **2.5.1 Fraction 1: Water Soluble Metals**

#### *2.5.1.1 Water soluble*

Soil sample was extracted with 15ml of deionized water for 2hrs [22].

### **2.5.2 Fraction 2 exchangeable phase**

The residue from water soluble was shaken at room temperature with 16ml of 1M Mg (NO<sub>3</sub>)<sub>2</sub> at pH 7.0 for 1hr, centrifuged and supernatant decanted and made up to 40ml with double distilled water prior to analysis.

### **2.5.3 Fraction 3 oxidizable phase (bound to organic matter)**

The residue from exchangeable fraction + 10 ml H<sub>2</sub>O<sub>2</sub> 8.8 ML<sup>-1</sup> +6ml HNO<sub>3</sub> 0.02ML<sup>-1</sup>, was shaken for 5 + 1 hr at 98°C. 10 ml CH<sub>3</sub>COONH<sub>4</sub> 3.5ML<sup>-1</sup> was added as extracting agent, centrifuged and supernatant made up to 40ml with distilled deionized water prior to analysis.

### **2.5.4 Fraction 4 acid soluble phase (bound to carbonate)**

25ml of 0.05ML<sup>-1</sup> Na<sub>2</sub>EDTA was added to the residue from oxidizable phase, shaken for 6hrs and centrifuged and supernatant made up to 40 ml with distilled water prior to analysis.

### **2.5.5 Fraction 5 reducible phase (bound to Fe/Mn oxides and hydroxides)**

Residue from acid soluble phase + 17.5ml NH<sub>2</sub> OH.HCl 0.1ML<sup>-1</sup> + 17.5ml CH<sub>3</sub>COONH<sub>4</sub> 3.5ML<sup>-1</sup>, shaken for 4 + 1hr at 98°C. Extracted with 10 ml CH<sub>3</sub>COONH<sub>4</sub> 3.5ML<sup>-1</sup>, shaken for 1hr, centrifuged, the supernatant decanted and made up to 40ml with distilled water prior to analysis.

### **2.5.6 Fraction 6 residual fraction (bound to silicates and detrital materials)**

Residue from reducible phase was digested using HCl-HNO<sub>3</sub>/HF (0.35:12 w/v) Soil/solution ratio) in acid digestion Teflon cups. It was dried to ash for 2 hrs and evaporated to dryness. The residue was diluted to 40ml with distilled water prior to analysis. After each successive extraction, the samples were centrifuged at 4500 rpm for 15min [23]. The supernatants were removed with pipette and filtered with Whatman No. 42 filter paper. The residue was washed with deionized water followed by vigorous hand shaking and then followed by 15min of centrifugation before next extraction. The volume of rinse water used was kept to a minimum to avoid excessive solubilization of solid materials.

## **2.6 Instrumentation and Statistical Analysis of Data**

The metal concentrations of all the extracts in the centrifuged solutions were determined using Atomic absorption Spectrophotometer (AAS) at the Kaduna State University, Kaduna, Nigeria.

The coefficient variation, measure the strength of a linear relationship between any two variables on a scale of -1 to (perfect inverse relation) through zero (no relation) to +1(perfect sympathies relation). In this study, raw data was used in calculating the correlation coefficient using the SPSS computer software package 17.0 for window evaluation version. Both descriptive and inferential statistical analyses were used to interpret the data, also Pearson correlation analysis was also carried out in this study.

## **4. RESULTS AND DISCUSSION**

### **4.1 Total Metal Concentration**

There was wider variation in the concentration of metals. The metal concentrations for soil as shown in Tables 1 and 2 below during wet and dry season ranged from 1.72 to 11.56 mg/kg and 0.81 to 2.26mg/kg for Cd; 29.35 to 47.34mg/kg and 23.55 to 51.94mg/kg for Cr; 10.93 to 204.37mg/kg and 14.03 to 34.69mg/kg for Ni; 10.74 to 20.08mg/Kg and 8.43 to 18.48 mg/kg for Pb; 10.68 to 199.53mg/kg and 160.06 to 416mg/kg for Zn; and 6.67 to 38.82 mg/kg and 2.02 to 6.72mg/kg for Cu respectively. In general, there was slight decrease although, not regular from upper to lower portions of the soil. It was equally noticed that the concentrations of the six metals examined varied among the vegetation zones investigated with zinc having the highest mean concentration followed by chromium, lead, copper nickel and cadmium in that order. Due to the fact that 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 [24]. It is therefore necessary to pay a closer attention to the speciation study of these metals (Figs. 1-11) present the distribution of the trace metal studied in five different fractions.

### **4.2 Chemical Speciation of Metals in Soil Samples**

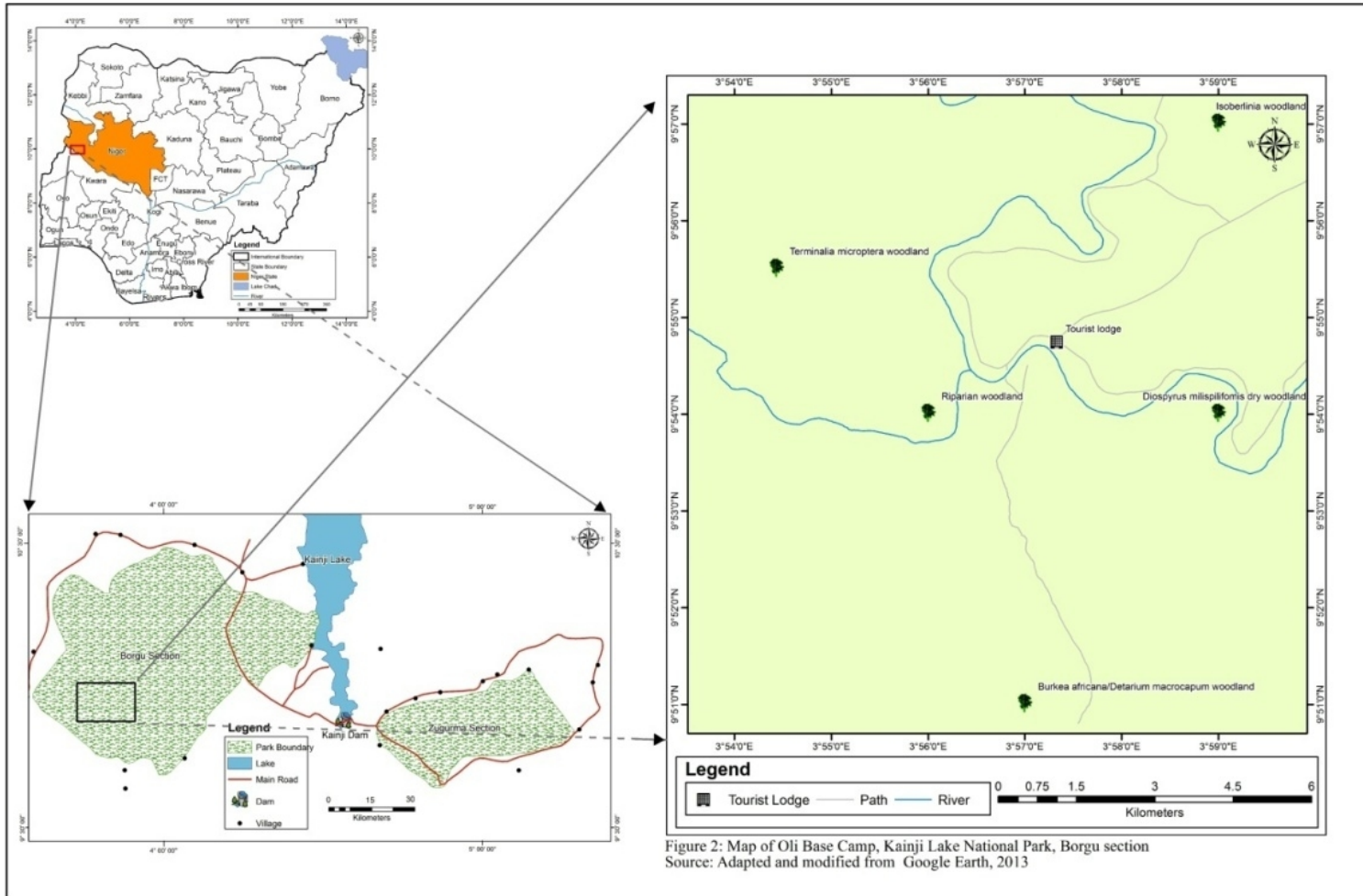
Metal chemical speciation carried out by sequential extraction of metals is essential to the metal mobility [17]. In all the soil samples subjected to chemical speciation, Cd, Cr, Ni, Pb, Zn and Cu were found to be most associated with the residual fraction than all other fractions during wet season but in dry season contrary observation was made, Zn was found to be most associated with Fe-Mn oxide while, Pb, Cu and Cd were found to be most associated with carbonate bound. The high content of carbonate fraction during dry season in the studied sites might be due to carbonate rocks. Many researchers have reported varying concentrations of these metals in different fractions, [25] reported 13% abundance of Cu in the carbonate bound, [26] reported 83% abundance of Cu in immobilized fraction, [27] reported Cu to be most associated with organic fractions. However, the findings from this present work, agrees very well with the report of those researchers enumerated above.

**Table 1. Total metal concentration in soils of different vegetation in wet season (mg/kg)**

Sample location	Metal					
	Cd	Cr	Ni	Pb	Zn	Cu
Isobertinia Woodland						
0 – 15cm	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 – 30cm	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 Woodland						
0 – 15cm	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 – 30cm	10.11±1.20	31.02±2.00	20.37±2.89	18.63±2.90	17.01±1.00	23.27±10.87
Burkea Africana/Detarium microcarpum woodland						
0 – 15cm	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 – 30cm	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 – 15cm	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 – 30cm	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 – 15cm	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 – 30cm	1.72±0.59	36.66±3.20	18.29±1.56	13.79±0.50	199.53±10.15	5.76±1.00

**Table 2. Total metal concentration in soils of different vegetation in dry season (mg/kg)**

Sample location	Metal					
	Cd	Cr	Ni	Pb	Zn	Cu
Isobertinia Woodland						
0 – 15cm	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 – 30cm	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 Woodland						
0 – 15cm	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 – 30cm	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 – 15cm	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 – 30cm	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 – 15cm	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 – 30cm	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 – 15cm	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 – 30cm	2.26±0.89	51.94±2.70	34.69±1.00	11.08±1.89	203.63±6.70	5.50±0.92



**Fig. 1. Map of Oli Base Camp, Kainji Lake National park, Borgu section**  
 Source: Adapted and modified from the administrative map of Nigeria and Google Earth. 2013

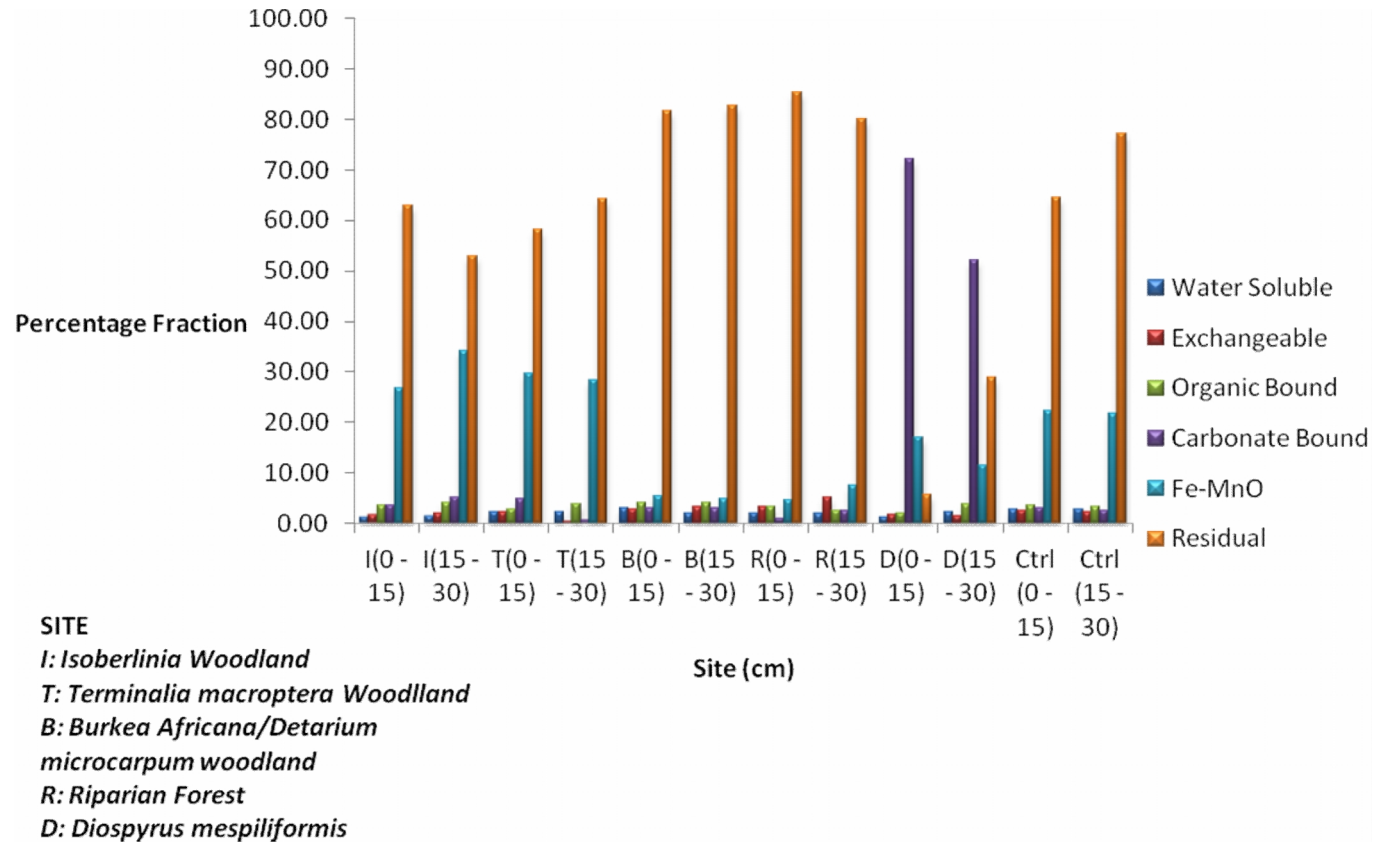


Fig. 2. Chemical fraction of Cadmium in soils of different vegetation in wet season



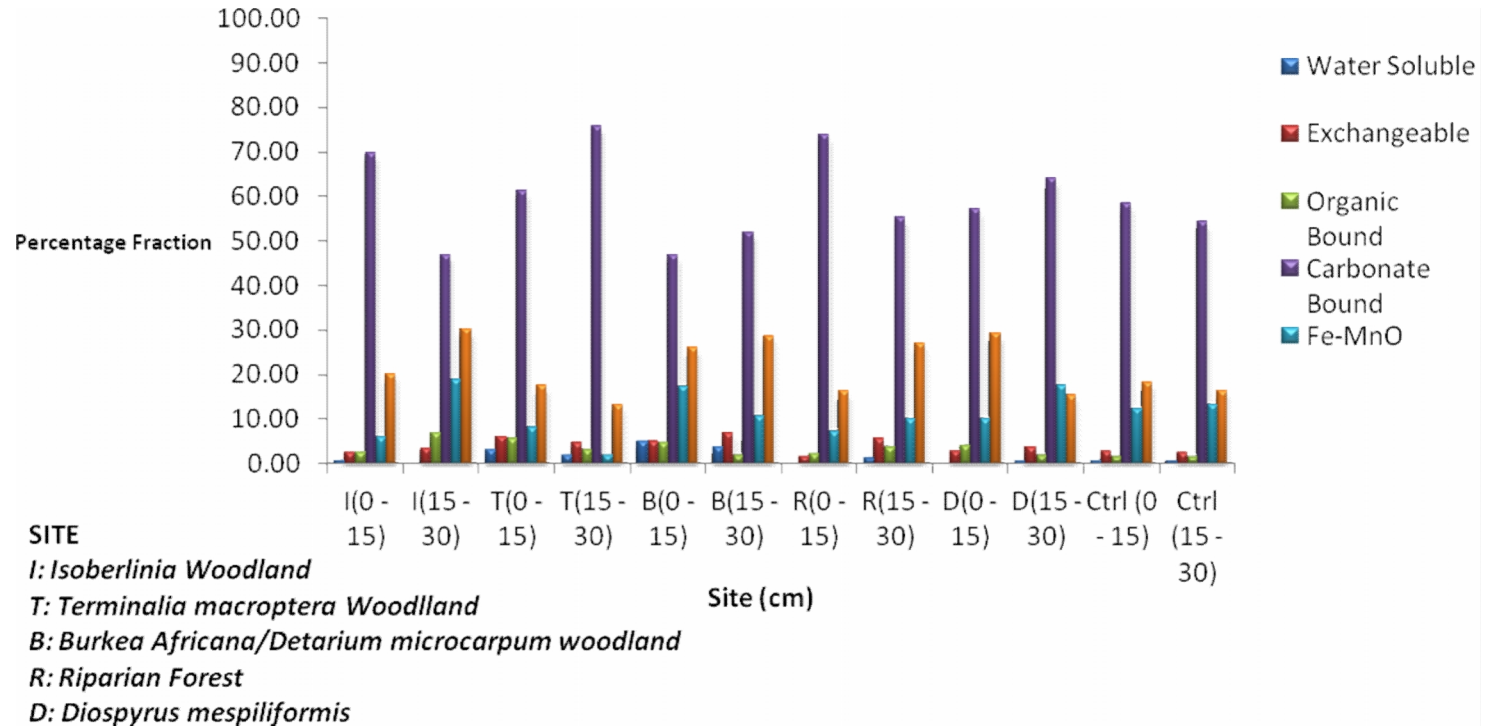
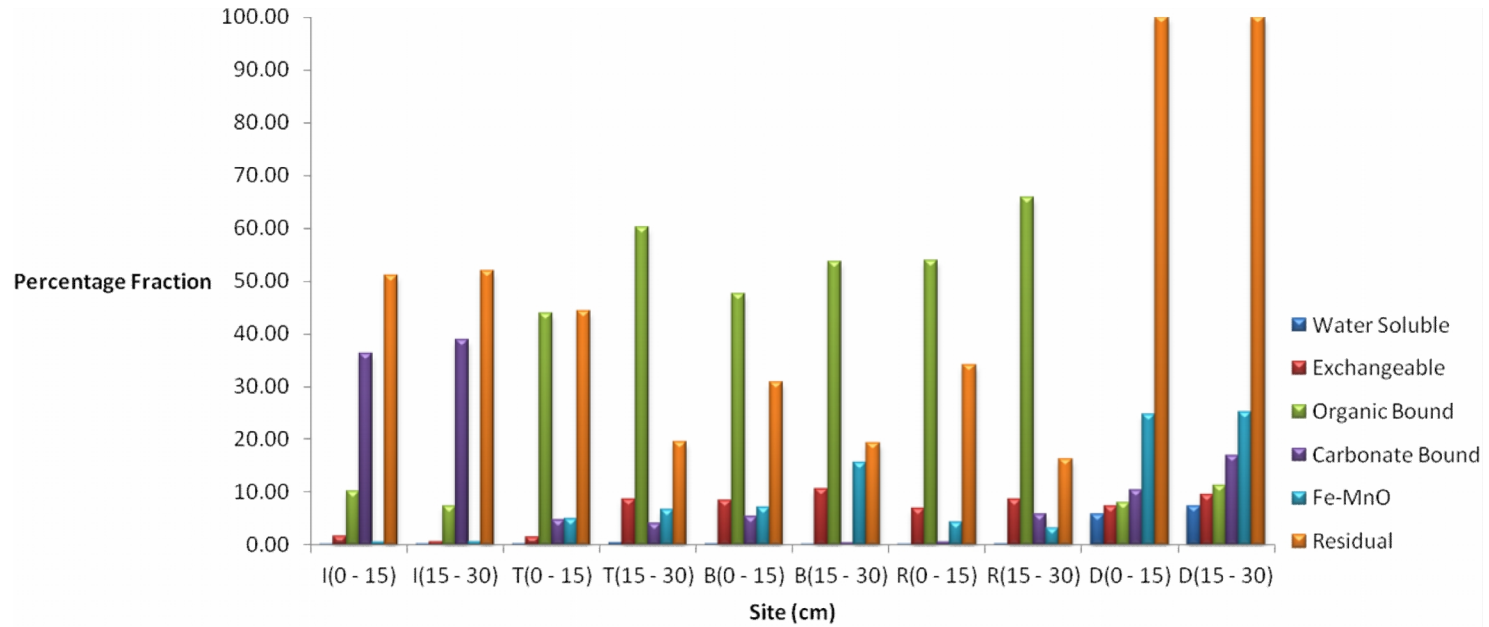


Fig. 3. Chemical fraction of Cadmium in soils of different vegetation in dry season



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

**Fig. 4. Chemical fraction of Chromium in soils of different vegetation in wet season**

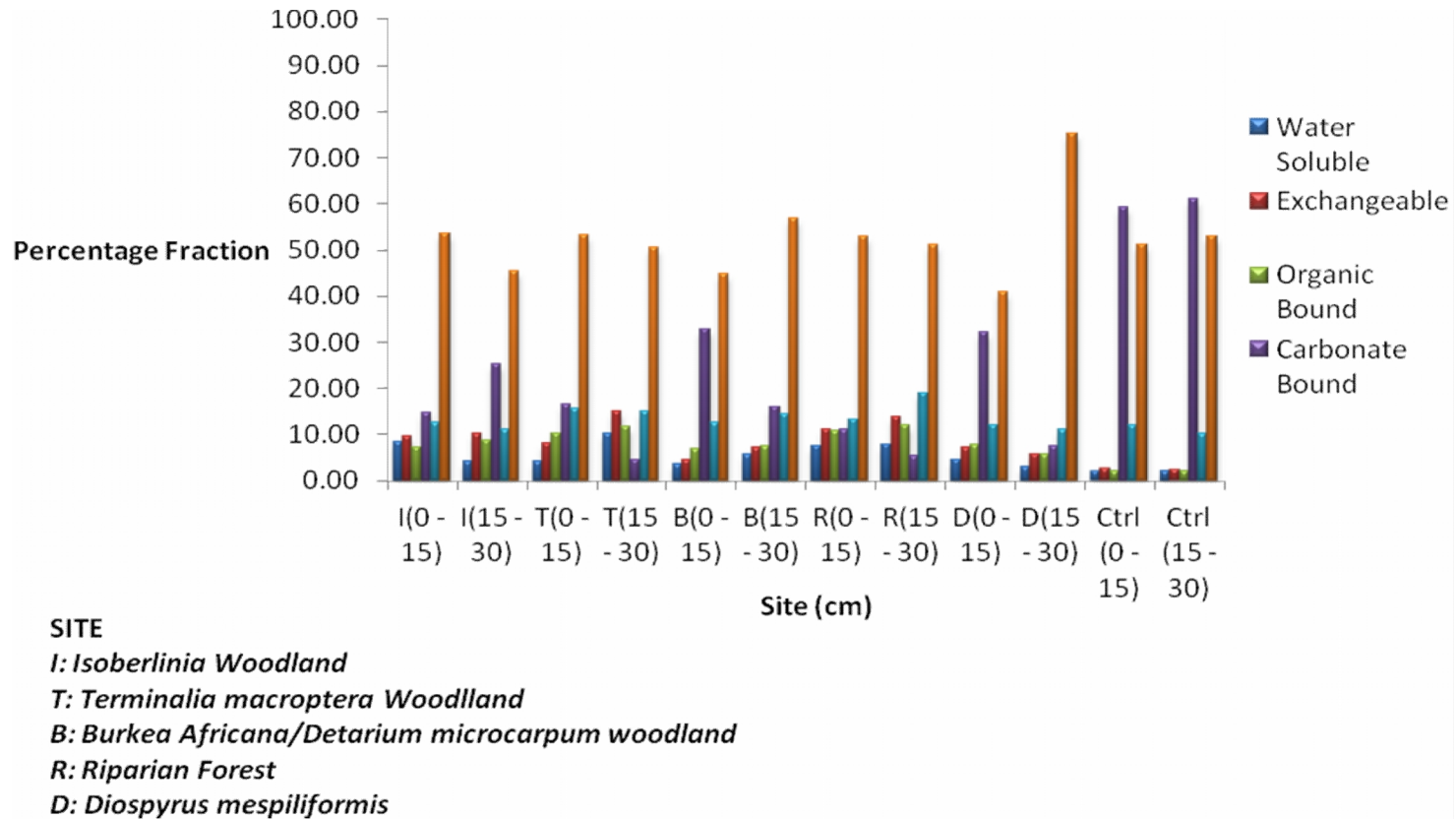
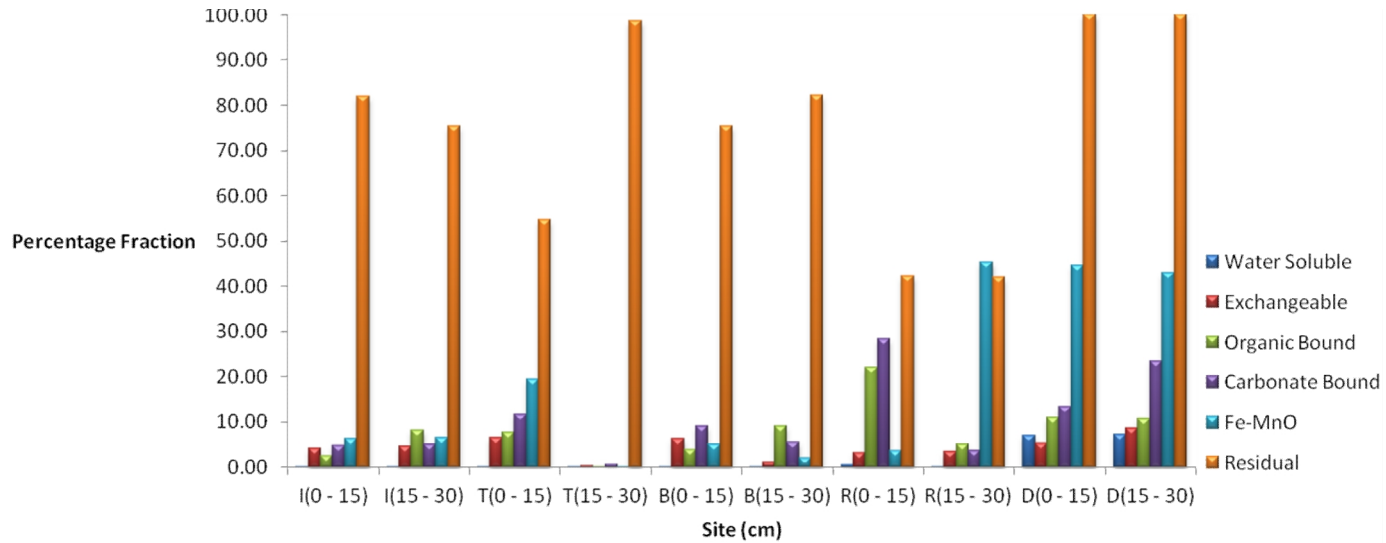
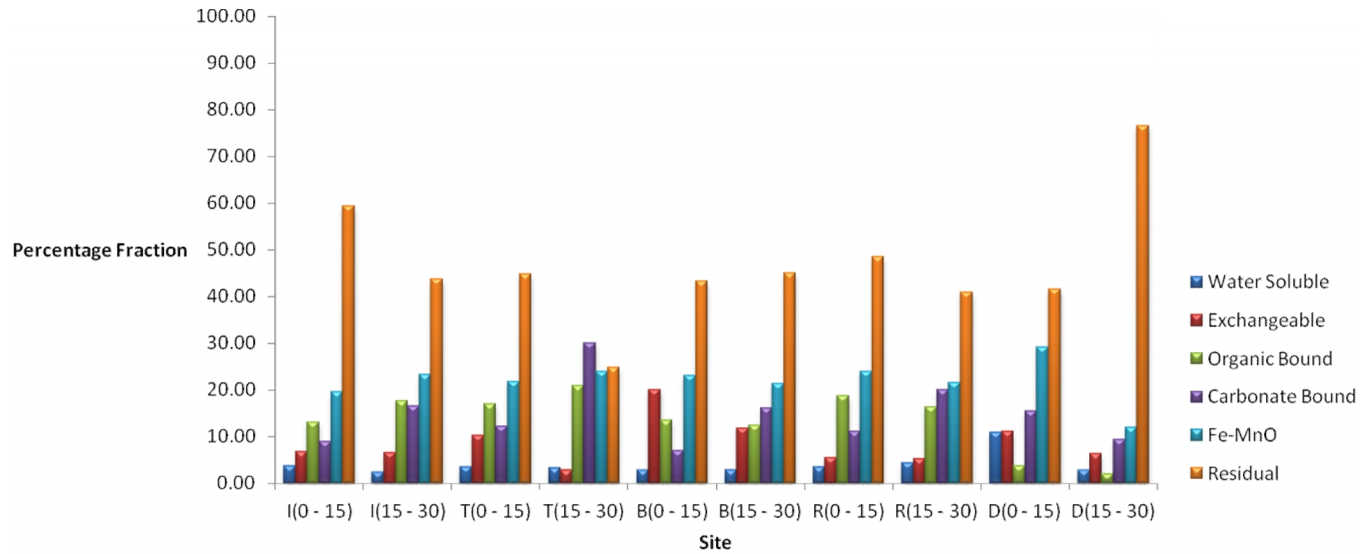


Fig. 5. Chemical fraction of Chromium in soils of different vegetation in dry season



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

Fig. 6. Chemical fraction of Nickel in soils of different vegetation in wet season



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

Fig. 7. Chemical fraction of Nickel in soils of different vegetation in dry season

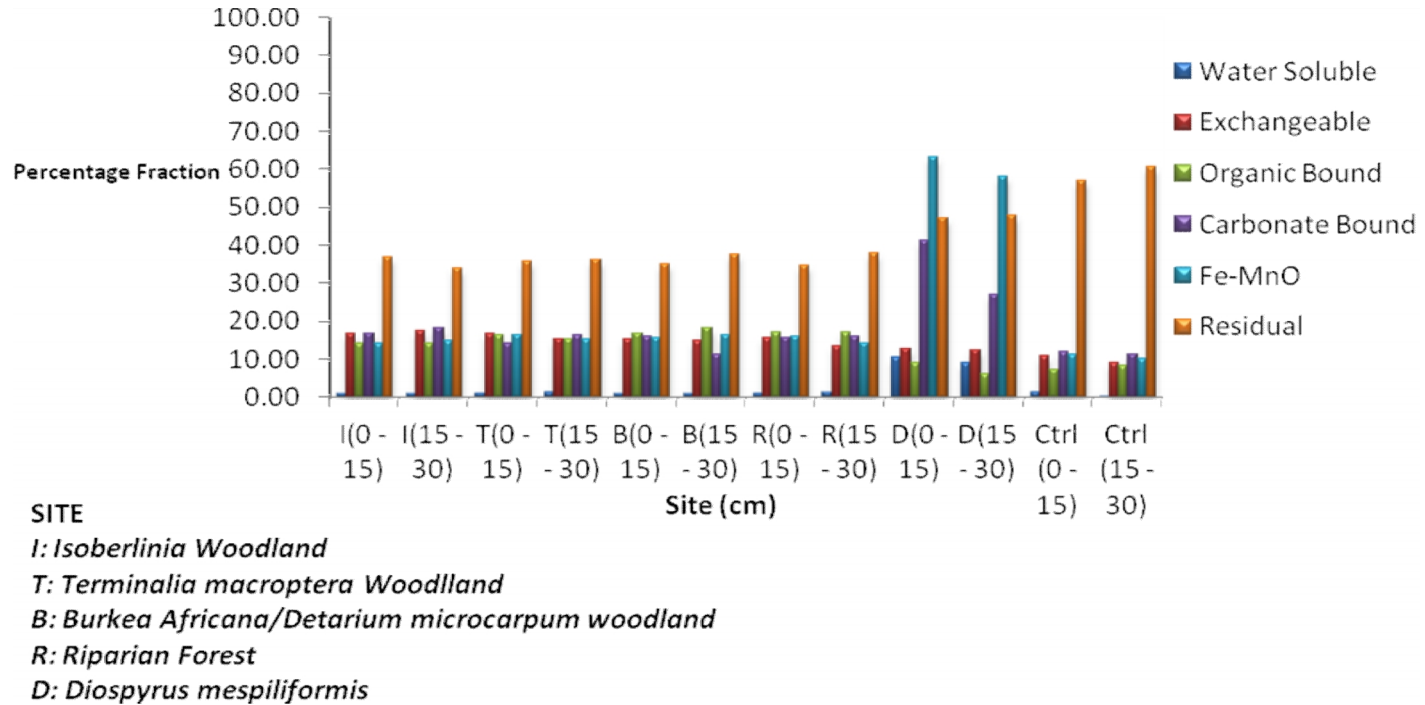


Fig. 8. Chemical fraction of Lead in soils of different vegetation in wet season

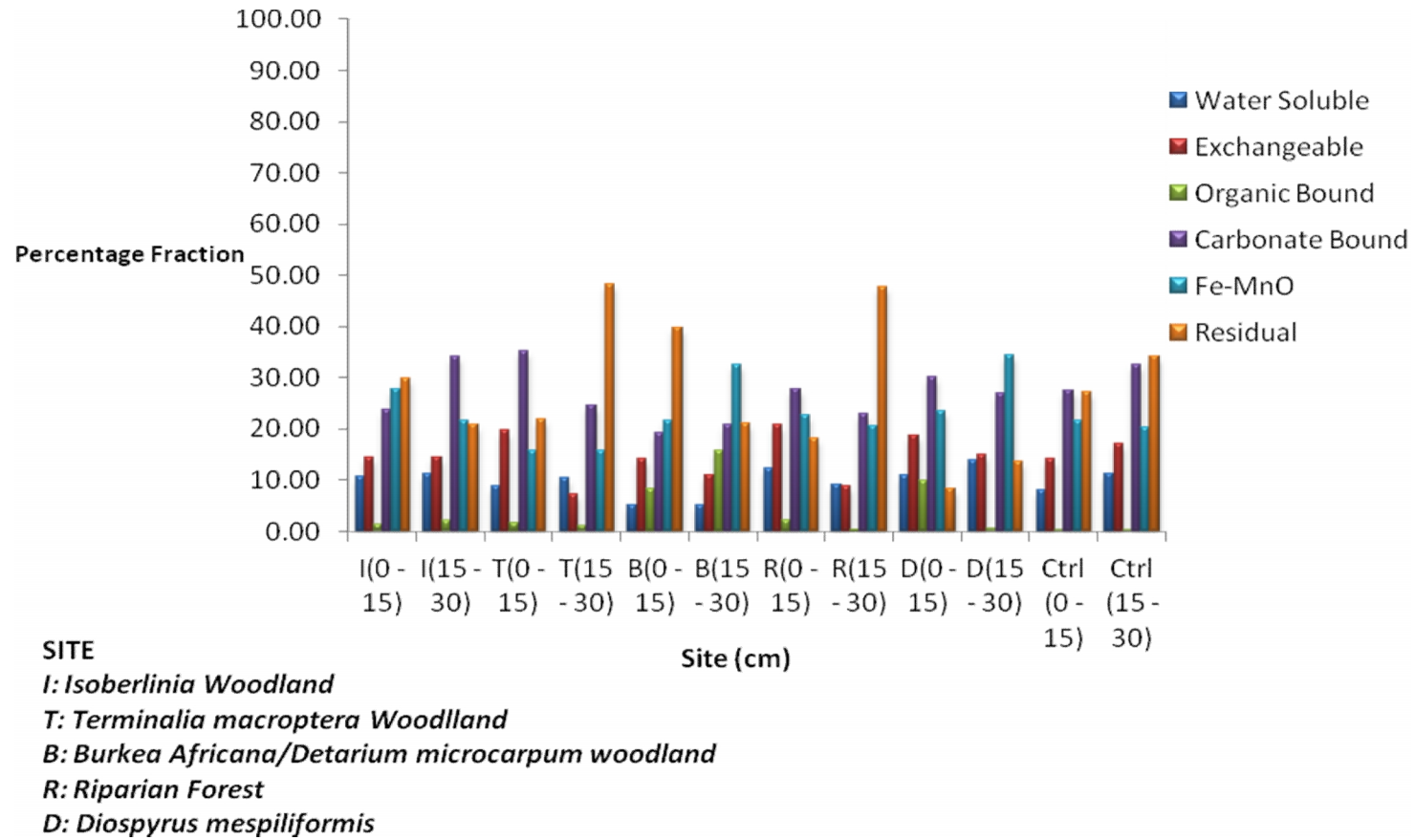
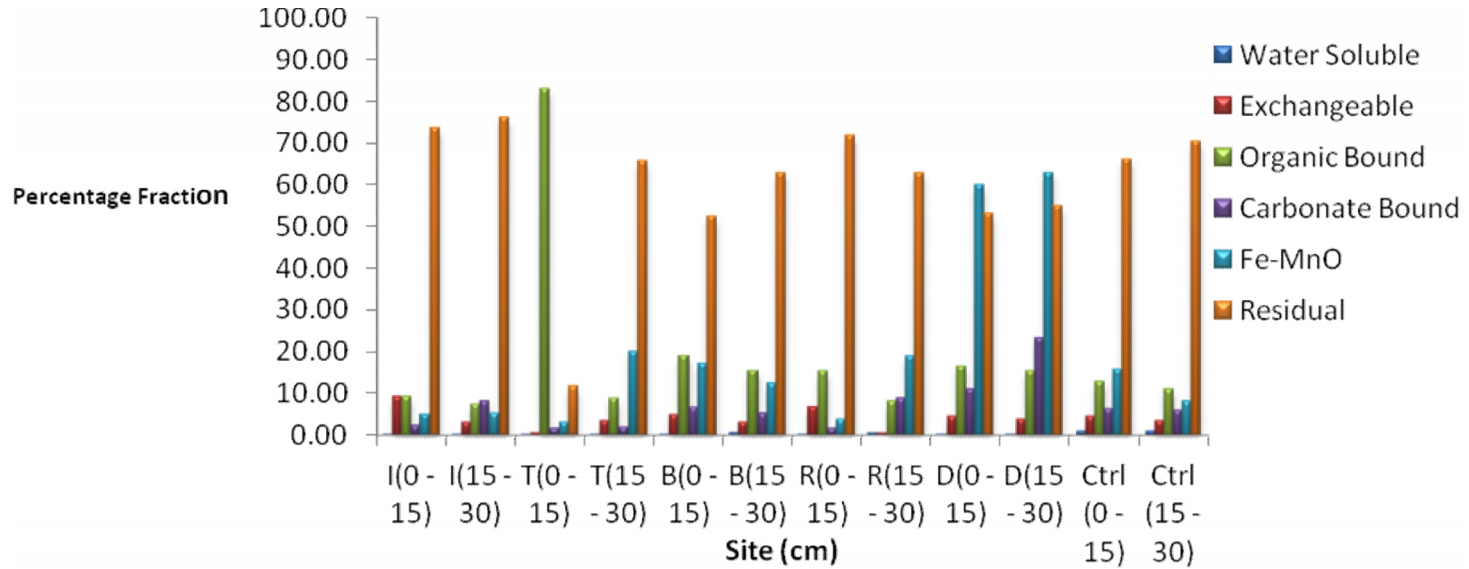


Fig. 9. Chemical fraction of Lead in soils of different vegetation in dry season



**SITE**

*I: Isoberlinia Woodland*

*T: Terminalia macroptera Woodland*

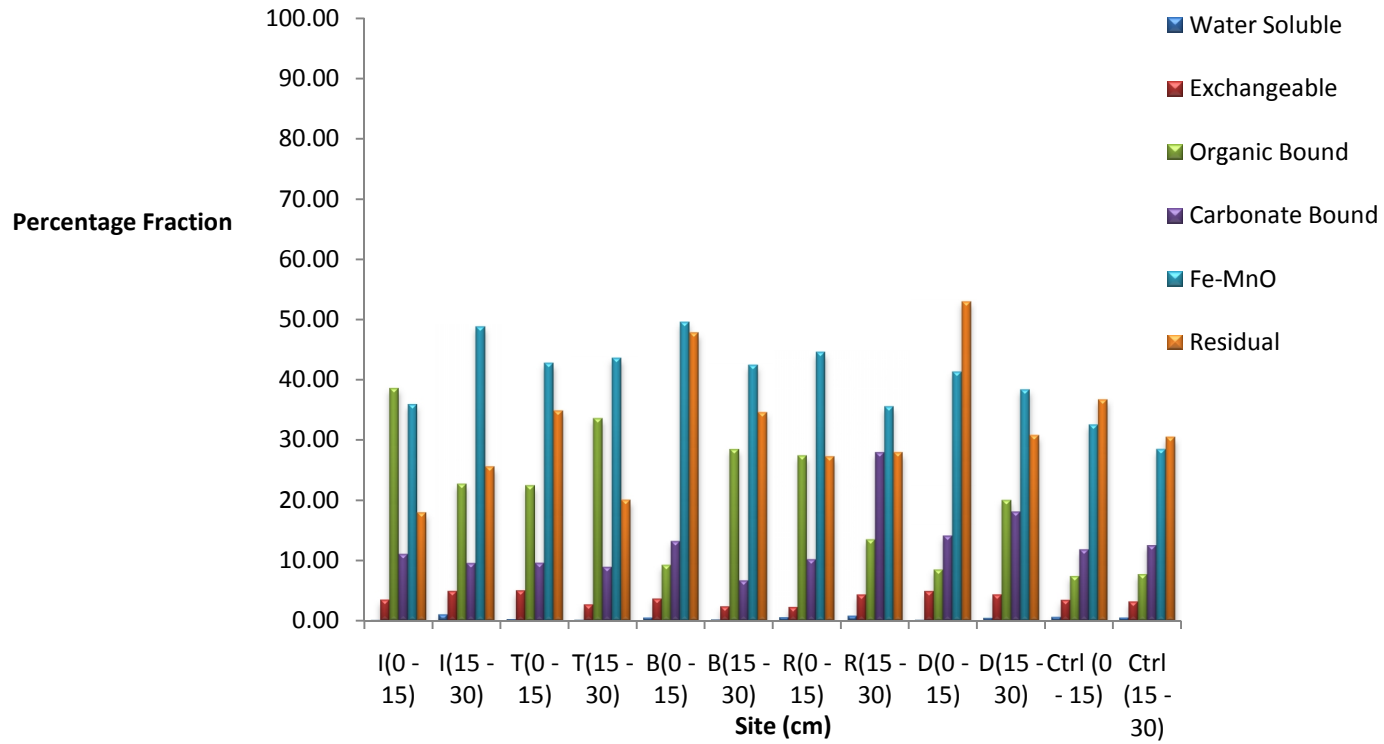
*B: Burkea Africana/Detarium microcarpum woodland*

*R: Riparian Forest*

*D: Diospyrus mespiliformis*

**Fig. 10. Chemical fraction of Zinc in soils of different vegetation in wets season**





**SITE**

**I: *Isoberlinia* Woodland**

**T: *Terminalia macroptera* Woodland**

**B: *Burkea Africana*/*Detarium microcarpum* woodland**

**R: Riparian Forest**

**D: *Diospyrus mespiliformis***

**Fig. 11. Chemical fraction of Zinc in soils of different vegetation in dry season**

In dry season Zn was found to be most associated with Fe-Mn oxide with abundance of 39% and residual with abundance of 36% in wet season an indication that Zn is more mobile in these geochemical phases. This agreement with the reports of [26] 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 [28] that the highest fraction of Zn was associated with carbonate fractions. [4] 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. The importance of co-precipitation of zinc and cadmium with carbonate minerals had been reported [15,14]. The strong association in the residual was also confirmed [29].

In all the soil samples studied Pb was found to be most associated with residual fraction in wet season, and with carbonate fraction during dry season and the least fractions in both organic bound and water soluble during dry and wet season respectively. This result is not in agreement with the report of [25] that, the highest percentage of Pb was associated with exchangeable fractions, although in that study, the soil samples were collected from polluted region. [30] 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 is a measure of the degree of environmental pollution. The higher the metals present in this fraction, the lower the degree of pollution [31]. 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 be lithogenic [32].

## **5. CONCLUSION**

The concentration of all the metals were found to decrease generally with increasing depth of the soil. Zn has by far the largest concentration followed by Cr, and Cu while Ni and Cd 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 all the metals investigated. However, Cr, Zn and Cu exhibited the highest natural origin followed by lead Pb, nickel Ni and cadmium Cd in that order. Lead is found to be highly toxic metals [33] but its low concentration in all the vegetations investigated would not pose any serious threat within and among the vegetations soil though, that does not depute periodical research of these metals status in the studied areas, especially for Pb, Cd and Ni because their high presence could lead to serious health challenges.

In all the soil samples on which speciation were conducted, almost all metals were found to be most concentrated in the residual fraction and carbonate bound fraction during wet season. During dry season the group of 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 metals studied.

## **COMPETING INTERESTS**

Authors declare that there are no competing interests.

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