# Bioprospecting for Indigenous Ruderal Plants with Potentials for Phytoremediation of Soil Heavy Metals in the Southern Guinea Savanna of North Western Nigeria

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# Abstract

In a study to evaluate the response of indigenous ruderal plants to the metal deposition regime imposed by anthropogenic modification in the Southern Guinea Savanna of north Western Nigeria during the dry and wet seasons, herbaceous plants and samples of soils were collected in three 5m by 5m quadrats laid around the environs of the Kaduna Refinery and Petrochemical Company and the banks of River Kaduna. Heavy metal concentration (Cd, Ni, Cr, Cu, Fe, Mn and Zn) in soil and plant samples was determined using Energy Dispersive X-ray Fluorescence. Concentrations of heavy metals in soils were generally observed to be higher during the wet season in both locations although the differences were not statistically significant ($P > 0.05$). Concentrations of Cd, Zn, Cr, Cu and Ni in all the plants observed were found to be below levels described as phytotoxic to plants. However, above ‘normal’ concentrations of Cr was observed in most of the plant species sampled. The concentrations of Cr, Cu, Ni and Zn in soils around the KRPC and RKB were found to be above the acceptable limits. Although no hyper accumulator plant species was encountered in this study, twenty (20) plant species were identified to have high bioconcentration ($BCF > 1.0$) of Cd and Cu, which indicated tolerance of these plants to excessive or phytotoxic concentrations of these metals. In addition, they generally produce high above ground biomass, due to rapid vegetative growth. These are likely species for phytoextraction. Elevated concentration of metals in both soil and plant materials may cause a decrease in biodiversity due to direct toxicity. There are also risks to humans and other animals due to bioaccumulation across the food chain. There are further possibilities of further evaluating and genetically improving metal tolerance traits in some of these plant species in relation to their potential use in phytoremediation programmes in metal polluted sites.

# Introduction

Trace quantities of heavy metals have been reported to occur naturally in the ecosystem. (An’ongo et al. 2005; Lar 2013;). Depending on their concentration, some of them like Zn, Fe, Mn and Cu are essential plant nutrients, others like Pb, Hg and Cr do not have any known use to plants (Bako et al. 2005; Tanimu etal.2013). Deposition of heavy metals in soils from anthropogenic activities have been implicated for an increase in heavy metal concentration above background and recommended levels (Maine et al. 2004; Bako et al. 2008 ; Tanimu et al. 2013). Heavy metals are important components of agro-allied products such as pesticides, herbicides, fertilizers; manufacturing and other synthetic products such as paints and batteries (USDA, 2000). Mining activities, industrial, municipal and domestic wastes are important sources of heavy metal pollution to the environment (Mathews-Amune and Kakulu, 2013). Combustion of fuel from petroleum, abrasion of tyres, brake lining, corrosion of the body work of vehicles and engine wear have been associated with elevated concentrations of Cd, Cu, Mn, Ni, V and Zn (Albasel and Cottein 1985; Nyagababa and Hamya 1991; Menaci and Bargugli 1997; Munch 20l1).

Excessive concentration of heavy metals in the environment is of great concern because of their non-biodegradability. Therefore, their persistence in the environment portends health hazard to plants, animals and consequently trigger ecological imbalances in the ecosystem (Ekmekyaper et al. 2012).

Another concern that high concentrations of heavy metals raise is their ability to bioaccumulate across the food chain, with members that are high up the food chain having concentration of such metals several times higher than what is obtainable in the environment (Bako et al. 2009a; Bako et al. 2009b; Megateli et al. 2009; Kurhaluk et al. 2021).

The effect of metals in living organisms could be chronic, due to exposures over a long period of time as a result of food chain transfer or acute poisoning due to ingestion or dermal contact (Oti and Nwabue 2013). The concentration of heavy metals in the shoot of plants may vary with season as a result of inherent growth dynamics of the plant; metal concentration and its bio-availability in the environment. Data on the response of plants to anthropogenic modification of the environment, particularly in relation to soil and air pollution by heavy metals in northern Nigeria is limited and includes earlier assessments (Bako et al. 2005, Bako et al. 2008; Bako et al. 2009a; Bako et al. 2009b and more recently (Bako et al. 2013), in which an attempt was made to document the visual symptoms expressed by some ruderal plant species in relation to air pollution as a step towards developing a reference for field identification of metal pollution events (Bako et al. 2013). Indigenous ruderal plants provide a naturally occurring gene pool for selection of pollution tolerant species that have adapted to growth and development under less than ideal environments. Depending on their effectiveness, such plants may be exploited either in their natural state, or after genetic modification, as an alternative “green” technology for the clean-up strategies of metal polluted sites.

This study was therefore carried out to determine the spatial and seasonal variations of heavy metal deposition in soils and plants in Nigeria’s Southern Guinea Savanna in order to identify indigenous plant species that may be pollution tolerant and thus have potential for use in phytorememediation of heavy metal polluted sites.

## Materials And Methods

# Study Area

The two sampling sites are located in Kaduna metropolis, that falls within the Southern Guinea Savanna eco-region of northern Nigeria (See Figs. 1, 2 and 3). The first site is by the River Kaduna Bank (RKB), at Unguwan Rimi, near the Kaduna North Water Works, Malali, Kaduna. The River Kaduna is the major source of raw water treated for drinking and other uses.

The second is by the Kaduna Refinery and Petrochemical Company (KRPC), a subsidiary of the Nigerian National Petroleum Company (NNPC).

# Sample Collection

Soil and plant samples were collected in both dry and wet seasons from three sampling stations per location in 5m by 5m quadrats. A fourth sampling station was added at the KRPC site in the wet season due to the observance of a depression that collects surface runoff from a large area around the refinery.

Soil samples were collected at 0-15cm depth using a soil auger. The shoots of herbaceous plants with relative abundance greater than five per quadrat, were clipped with a pair of secateurs for heavy metal analysis. Identification of plant samples were confirmed in the herbarium of the Department of Biological Sciences, Ahmadu Bello University, Zaria.

# Sample Preparation

Plant samples were washed with tap water and then with distilled water to remove debris and surface contamination. Samples were then bulked and air dried to remove excess moisture. Similarly, samples of the soils collected were bulked into composite samples and air dried for three days (72 hours).

Dried plant and soil samples were ground using a porcelain mortar and pestle and sieved to attain a uniform particle size. Each sample was put in a small transparent polythene bag and labeled.

# Metal Analysis

Analysis of the elemental content of the samples was done using the Energy dispersive X-ray fluorescence Spectroscopy (EDXRF) method (Funtua 1999).

The samples were ground manually to powder with an agate mortar and pestle to grain size of less than 125µm. Pellets of 19mm diameter were prepared from 0.3-0.5kg powder mixed with three drops of organic liquid binder and pressed at 10 tons of pressure in a hydraulic press.

Measurements were performed using an annular 25mCi $^{109}$Cd as the excitation source, that emits Ag – K rays (22.1 KeV) in which case all elements with lower characteristic excitation energies are accessible for detection in the samples. The system consists furthermore of Si (Li) detector, with a resolution of 170eV for the 5.90KeV line, coupled to a computer controlled ADC – card.

Quantitative analysis of the sample was done using the Emission Transmission (E-T) method and that involves the use of pure target material (Mo) to measure the absorption factors in the sample.

The Mo target served as a source of monochromatic X-rays, which are excited through the sample by primary radiation and then penetrate the samples on the way to the detector. In this way, the absorption factor is experimentally determined. The program uses this in the quantification of concentration of the elements. In addition, the contribution to the Mo-K peak intensity by the Zr-K is subtracted for each sample.

Sensitivity calibration of the system was performed using thick pure metal foils (Ti, Fe, Co, N, Zn, Nb, Zr, Mo, Sn, Ta and Pb) and stable chemical compounds ($K_2CO_3$), $CaCO_3$, $Ce_2O_3$), $WO_3$, $ThO_2$, $U_3O_3$). The spectra for the samples were collected for 3000s with the $^{109}$Cd source and the spectra were then evaluated using the AXIL-QXAS program (Bernasconi 1996). $^{109}$Cd source was used for the analysis of K, Th, Y, Zr, Nb and Mo.

The accuracy and precision of the measurements was confirmed though an analysis of IAE – V10 (hay powder) and IAEA – 259 (cabbage) certified reference material, distributed by International Atomic Energy Agency (IAEA).

## Bioconcentration Factor (Enrichment Coefficient) (Zu et al.2005)

This estimates the capacity of plants to accumulate metals, and was computed for each species as:

$$\text{BCF} = \frac{\text{Mean concentration of metal in the plant}}{\text{Mean concentration of metal in the soil}}$$

### Results

## Metal concentration in Soils and Plant samples

In the soils sampled from the two sites, the mean concentration of metals in the wet season generally followed this order Fe > Mn > Zn > Ni > Cr > Cu > Cd. In the dry season the mean metal concentration in the soil followed this order Fe > Mn > Zn > Cr > Cu > Ni > Cd in KRPC and Fe > Mn > Zn > Cu > Ni > Cd > Cr in the samples collected from the River Kaduna Bank (Table 2).

## Chromium

The soil around the KRPC had a mean Cr concentration of 68.87 mg/kg and 45.60mg/kg, in dry and wet seasons respectively (Table 2). The mean Cr concentration in the River Kaduna Bank was below detectable limit in the dry season and 54.05mg/kg in the wet season. The dry season concentration of Cr in the KRPC soils was observed to be higher than the acceptable limits for Agricultural and Residential/park soils in Canada; and in soils of Germany, The Netherlands and Sweden. While the wet season concentrations of Cr were observed to be higher than acceptable limits for soils in the Netherlands in both sites (Table 3).

In the plant samples, the highest concentration of Cr was recorded in *Spermacose verticellata* (3.76 mg/kg) in the dry season and *Cochlospermum tinctorum* (6.71 mg/kg) in the KRPC site. While by the River Kaduna Bank, the highest concentration of Cr was recorded in *Polygonum lanigerum* (2.46 mg/kg) in the dry season and *Salix leadermanii* (3.2 mg/kg) (Fig. 5). “Normal” concentration of Cr in plants is described as being from 0.1 to 0.5 mg/kg, while concentrations between 5 to 30 mg/kg as “Excessive” and 75 to 100 mg/kg, “Phytotoxic” (Table 4).

## Copper

Mean concentrations of Cu in the soils samples collected around the KRPC was 45.50mg/kg in the dry season and 4.85 mg/kg in the wet season. While around at the RKB, the mean Cu concentration in soil samples observed was 23.37 mg/kg in the dry season and 5.95 mg/kg in the wet season (Table 2)

(Fig. 1). Only soil samples collected from the KRPC in the dry season was observed to have mean Cu concentration above the acceptable limits of the WHO (30 mg/kg), Germany, The Netherlands and Sweden (40 mg/kg) (Table 3).

In plant samples collected, the highest concentration of Cu was observed in *Spermacose verticellata*, 20 mg/kg in the dry season and *Isoberlinia tomentosa* 30mg/kg in the wet season, the concentration of Cu was generally higher in the plants during the wet

season (Fig. 5). Concentrations between 20 to 100 mg/kg in plants have been described as being excessive (Table 4).

## Nickel

In the wet season, the Ni concentration in soil samples was found to be higher (192.04 and 118.5 mg/kg) than what was observed in the dry season (24.89 and 21.1 mg/kg for KRPC and RKB, respectively (Table 2) (Fig. 1). The concentrations observed during the dry season were below the maximum permissible limit in all the countries on table for except the Netherlands and above all the limits, except the limit for Mexican Agricultural soils (Table 4) *Dichrostachys cinerea* was observed to accumulate the highest concentration of 4.95mg/kg of Ni in the dry season, while *Piliostigma thonningii* accumulated a highest concentration of 6.56 mg/kg in the wet season (Fig. 5). Normal concentration of Ni in plants has been described to be between 0.1 to 5 mg/kg, whereas concentrations between 10 to 100 mg/kg as excessive (Table 4).

## Cadmium

Mean dry season concentrations of Cd in soil samples were observed to be lower than those observed in the wet season. Mean Cd concentrations at the KRPC were 0.39 and 0.64 while in the RKB, 1.035 and 3.94 mg/kg in dry and wet seasons, respectively (Fig. 4). The above mean concentrations were found to be within the acceptable limits of the WHO and the Countries listed in Table 3.

*Sida acuta* was observed to have the highest concentration of 0.9 mg/kg in the dry season, whereas, *Centrosema pubescens* was observed to have the highest concentration of 1.3 mg/kg in the wet season (Fig. 5).

## Iron

Soils in the two study sites were observed to have a higher concentration of Fe in the dry season than in the wet season. Soils from the KRPC and the RKB were observed to have means of 22,166 and 498, 26.13 mg/kg; and 21,850 and 55,944 mg/kg for Fe, in dry and wet seasons, respectively (Fig. 4).

*Ludwigia repens* was observed to be the highest accumulator of Fe with a concentration of 287 mg/kg in the dry season while *Hydrocotyle bonariensis* was observed to be the highest accumulator of Fe with a concentration of 329.49 mg/kg in the wet season (Fig. 6).

# Manganese

The mean concentration of Manganese in soils was also observed to be higher in the wet season (1003.45 and 1503 mg/kg) than in the dry season (300.67 and 442.5 mg/kg) for KRPC catchment and RKB respectively.

*Ludwigia abbysinica* (208 mg/kg) was observed to have the highest Mn concentration during the dry season. In the wet season, *Detarium microcarpum* (355 mg/kg) was observed to have the highest concentration of Mn (Fig. 6).

# Zinc

Zn concentrations in soils showed a similar pattern with Mn and Fe, being higher in the wet (816.33 and 491.1 mg/kg) than the dry season (248.17 and 293 mg/kg for KRPC and RKB). These observed mean concentrations of Zn were higher than the 200 mg/kg acceptable limit of the WHO.

*Isoberlinia doka* (63 mg/kg) was observed to have the highest concentration of Zn in the dry season while *Detarium microcarpum* (341.56 mg/kg) was observed to have the highest concentration of Zn in the wet season (Fig. 6). Normal concentrations of Zinc in plants fall between 27 to 150 mg/kg. However, concentrations between 100 to 400 mg/kg may be considered Excessive, while from 70 to 400 mg/kg, as Phytotoxic (Table 4). This is dependent on the plant species in question.

# Bioconcentration Factor (BCF) of Heavy Metals in Plants

### Chromium

BCF for Cr was generally low across seasons and sites. In the two study areas, the BCF of Cr ranged between 0.00 to 0.12 in the dry season, while in the wet season it varied between 0.00 and 0.06. *Spermacose verticellata* was observed to have the highest BF value (Fig. 7).

### Nickel

Highest BCF of Ni was observed in *Spermacose verticellata* (0.32) in the dry season and *Detarium microcarpum* (0.11) in the wet season (Fig. 7).

### Copper

BCF for Cu was generally higher in the wet season than in the dry season, with *Dichrostachys cinerea* having the highest value of 0.87 in the dry season. *Terminalia macroptera* was observed to have the highest BCF in the wet season (7.32). Other plants observed to have a BCF of Cu above one (1.0) include *Centrosema pubescens*, *Piliostigma thonningii, Cochlospermum tinctorium, Isoberlinia tomentosa, Monotes kerstingii, Detarium microcarpum, Paspalum orbiculare, Borreria verticelata, Salix leadermanii, Ceruana pratensis, Polygonum lanigerum, Physalis angulata, Polygonum limbatum, Cymbopogon* *giganteum, Heliotropium indicum, Croton lobatus and Mimosa pigra* distributed across seasons and sites (Fig. 4).

### Cadmium

*Hypoethes cancellata, Centrosema pubescens*, *Polygonum lanigerum* and *Ludwigia repens* were observed to have considerably high BCF of 4.40, 1.39, 1.43 and 1.98 respectively. Most of the other plants were observed to have recorded higher BCF in the wet season than the dry season. (Fig. 8).

### Iron

BCF of Fe was generally low, with the highest value of 0.01 observed in *Isoberlinia doka Calopogonium mucunoides, Spermacose verticellata, Mariscus alternifolius, Ludwigia repens, Hypoethes cancellata, Ageratum conyzoides, Hydrocotyle asiatica, Hydrocotyle bonariensis*, *Polygonum lanigerum* and *Ludwigia abbysinica* distributed across seasons and sites (Fig. 9).

### Manganese

For Manganese, BCF was generally low ($< 1.0$) (Fig. 3) across seasons and sites. In the wet season, *Detarium microcarpum* was observed to show a high BF of 0.59. *Polygonum lanigerum* was observed to accumulate Mn to a BF of 0.43 in the dry season (Fig. 9).

### Zinc

For Zinc, BCF was also generally low ($< 1.0$) (Fig. 3) across seasons and sites. The highest BCF of Zn were observed in *Detarium microcarpum* (0.74), *Isoberlinia tomentosa* (0.36) *Calopogonium mucunoides* (0.26) and *Isoberlinia doka* (0.21) (Fig. 9).

## Discussion

Concentrations of heavy metals in soils were generally observed to be higher during the wet season in both locations although the differences were not statistically significant ($P > 0.05$). This differs somewhat with the findings of (Najib et al., 2012), who observed a higher concentration of these metals in the dry season than the wet season. Seasonal variations in patterns of metal deposition could be related to the intensity and duration of climatic variables such as precipitation, temperature etc., that interface with topography, drainage, soil structure/texture etc., to determine the physicochemical properties of the soil in a particular location. Soil physicochemical properties have complex, interdependent effects on metal solubility, with the most important of these including solution composition (inorganic and organic solubles), Eh, and pH; type and density of charge on soil colloids; and reactive surface area, that interact with factors like metal concentration and form, particle size distribution, quantity and reactivity of hydrous oxides, mineralogy, degree of aeration and microbial activity (Cataldo and Widung 1987). The aggregate effects of these complex interactions determine the bioavailabilty of metals to plants.

The above acceptable limits of the observed concentrations of Cr, Cu, Ni and Zn may be attributed to some of the human activities (mainly agriculture and industrial) going on around the sites. This presents health risks to humans and other animals as the metals contaminate both aquatic and terrestrial ecosystems. Above background values of these metals may have resulted from metal smelting and electroplating activities, burning of fossil fuels, application of phosphate fertilizers, disposal of solid wastes, and quarry activities (Kabata-Pendias and Pendias, 1992; Knox et al., 1999; Alloway, 1995; Liu et al., 2005). High levels of heavy metals in terrestrial or aquatic ecosystems ultimately end up being transmitted and accumulated in the food chain. Health risks to humans arise when metal polluted water is used as drinking water or when animals that have consumed vegetative materials in which metals have accumulated, are used for food. Furthermore, cultivation of crops on metal polluted soils indicates a possibility of consuming crops in which metals have accumulated. Although, specific effects of the various metals on human health have been discussed by several authors, the biotoxic effects of metals to humans have generally been outlined as ranging from gastrointestinal disorders, diarrhoea, stomatitis, tremor, hemoglobinuria, ataxia, paralysis, vomiting and convulsion, depression, coughing and wheezing, respiratory inflammation, dermatitis, leukocytis, low blood pressure, jaundice haemolytic anemia pneumonia and coma to death (Cd, Pb, As, Hg, Zn, Cu, Cr, Ni and Al). The nature of these effects could be toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or teratogenic. For example, see Duruibe et al. (2007);Bako et al. (2009a); Bako et al. (2009b); and Friends of Nature (2010).

Concentrations of Cd, Zn, Cr, Cu and Ni in all the plants observed were found to be below levels described as phytotoxic to plants. However, above ‘normal’ concentrations of Cr was observed in most of the plant species sampled (Galfata et al., 2013). This may be a consequence of the high values observed in the soils or direct deposition from the atmosphere (Jankowski et al. 2019). In addition to soil concentrations of metals, other factors that determine the uptake, translocation and accumulation of metals in plants include soil pH, cation exchange capacity, organic matter content, soil texture and interaction with other metals, as well as translocation factor (rate of movement of metals between root and shoot tissues) for the particular metal (Yoon et al., 2006; Baker and Brooks, 1989; Jung, 2010; Nwachukwu and Agbede, 2010; Guala et al., 2010, Addo et al., 2010). Heavy metals in toxic concentrations have inhibitory effects on enzymatic activity, stomatal function, photosynthesis and nutrient uptake, which may be expressed visually as chlorosis, reduced/stunted growth and yield depression. Plants vary widely in their ability to tolerate high concentrations of metals in their tissues. This variation is usually natural and dependent on inherent genetic factors. The genetic disposition confers the ability to employ a range of avoidance/exclusion or detoxification mechanisms that enable the plants cope with high metal loads. These may include the binding of metals (eg Ni and Cr) with amino acids, peptides and organic acids to form low molecular weight compounds, formation of phytochelatins, by binding (e.g. Cu and Pb) with sulphur-rich proteins and cellular adaptations. Other strategies may involve roles for mychorrhiza, the cell wall, extra-cellular exudates, efflux pumping mechanisms in the plasma membrane and formation of stress proteins etc (Bako et al., 2005; Kotrba et al., 2009).

Plants with BCF of metals > 1.0, have been described as suitable for phytoextraction. Some of the plants observed in this study with this potential include; *Terminalia macroptera, Centrosema pubescens*, *Piliostigma thonningii, Cochlospermum tinctorum, Isoberlinia tomentosa, Monotes kerstingii, Detarium microcarpum, Paspalum orbiculare, Borreria verticelata, Salix leadermanii, Ceruana pratensis, Polygonum lanigerum, Physalis angulata, Polygonum limbatum, Cymbopogon giganteum, Heliotropium indicum, Croton lobatus* and *Mimosa pigra* for Cu; and *Centrosema pubescens, Hypoethes cancellata* and *Polygonum lanigerum* for Cd. The ability of these plants to concentrate high levels of these metals suggests that they may have a good potential for phytoremediation.

No hyper-accumulator was observed in this study. Hyper-accumulators are plants that can accumulate at least 0.1% wt of Cu, Cd, Cr, Pb, Ni and Co or 1% wt of Zn and Mn (Baker and Brooks, 1989). There are possibilities for genetic modification of plants to enhance their capacity for metal tolerance (Kotrba et al., 2009).

### RECOMMENDATIONS FOR FURTHER RESEARCH

There is a great need to establish environmentally safe limits for metals in plant and soils of the various eco-regions in Nigeria. This need is emphasized by the observed variations in published background values from one country to another and even within the same country. These background values are often dependent on the geological history of the area. A comparison of observed field values with national recommended levels for heavy metals, developed from the background values will give a more realistic assessment of the pollution status. Furthermore, the search for alternative green technology that can be employed in remediation of pollution events must necessarily be a continuous one, due to the relative low cost and environmental friendliness of this option as compared to others. In this regard, ruderal species rather than those with agricultural value must be the candidates of choice for avoidance of obvious conflicts.

## Conclusion

The concentrations of Cr, Cu, Ni and Zn in soils around the KRPC and RKB were found to be above the acceptable limits. This presents health risks to humans and other animals as the metals contaminate both aquatic and terrestrial ecosystems.

Although no hyper accumulator plant species was encountered in this study, twenty (20) plant species were identified to have high bioconcentration of metals, particularly Cd and Cu which indicated tolerance to excessive or phytotoxic metal concentrations of these metals. In addition, they generally produce high above ground biomass, due to rapid vegetative growth. These plants include: *Terminalia macroptera, Centrosema pubescens*, *Piliostigma thonningii, Cochlospermum tinctorum, Isoberlinia tomentosa, Monotes kerstingii, Detarium microcarpum, Paspalum orbiculare, Borreria verticelata, Salix leadermanii, Ceruana pratensis, Polygonum lanigerum, Physalis angulata, Polygonum limbatum, Cymbopogon giganteum, Heliotropium indicum, Croton lobatus, Hypoethes cancellata* and *Mimosa pigra.* These present further possibilities for evaluating metal tolerance in relation to their potential use in phytoremediation programmes in metal polluted sites.

# Declarations

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## Competing Interest

*The authors have no relevant financial or non-financial interests to disclose.*

## Author Contribution

*All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Sunday Paul Bako, Augustine U. Ezealor and Yahuza Tanimu The first draft of the manuscript was written by Yahuza Tanimu and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.*

## Data Availability

*The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request*

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## Tables

Tables 1-4 are not available with this version.

## Figures

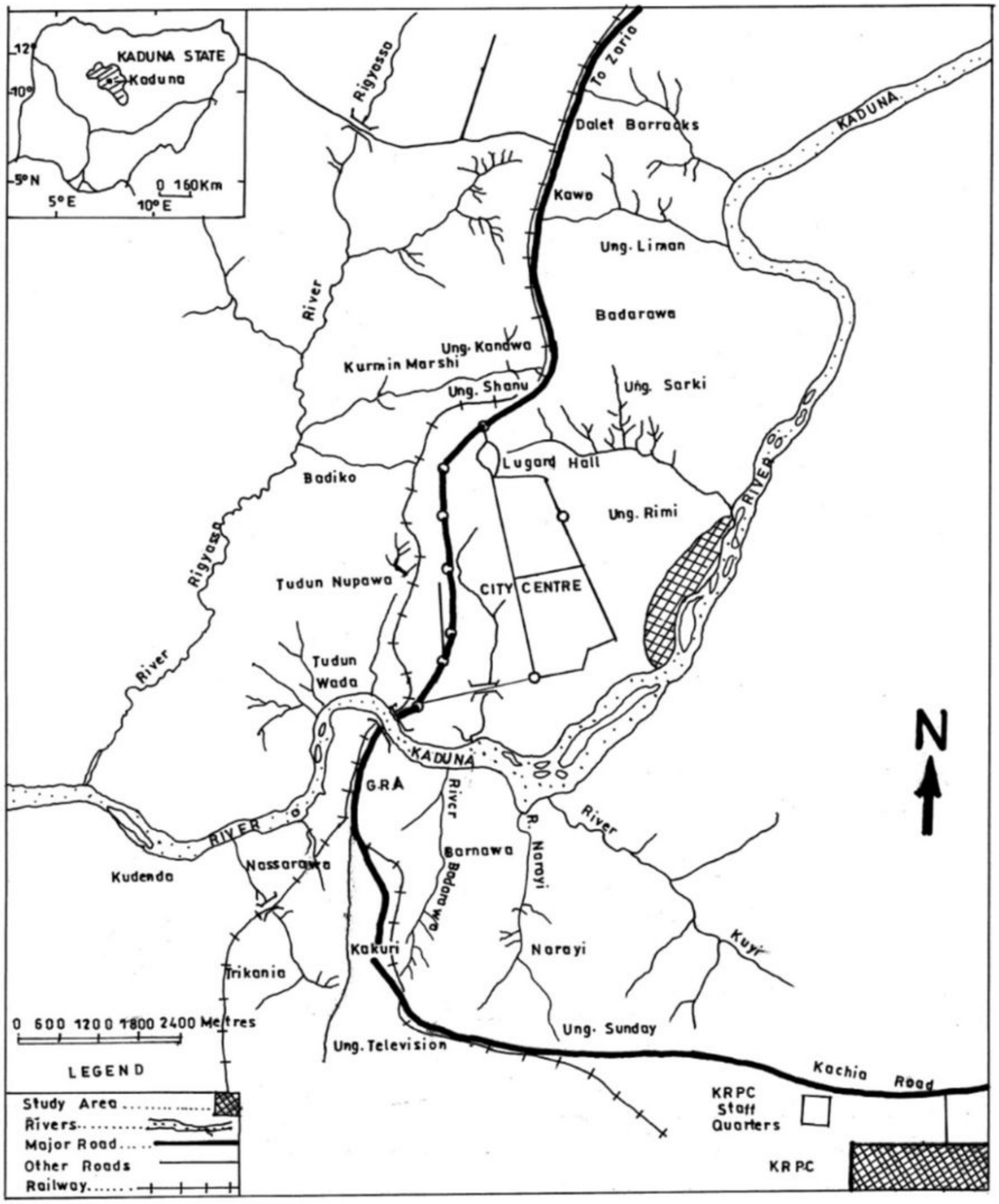

Fig.1 : Kaduna Metropolis Showing Approximate Locations of Kaduna Refinery and Petrochemical Company (KRPC) and Bank of River Kaduna at Unguwan Rimi.

SOURCE: MODIFIED FROM STREET GUIDE MAP OF KADUNA BY KADUNA ENVIRONMENTAL PROTECTION AUTHORITY (KEPA).

Figure 1

See image above for figure legend.

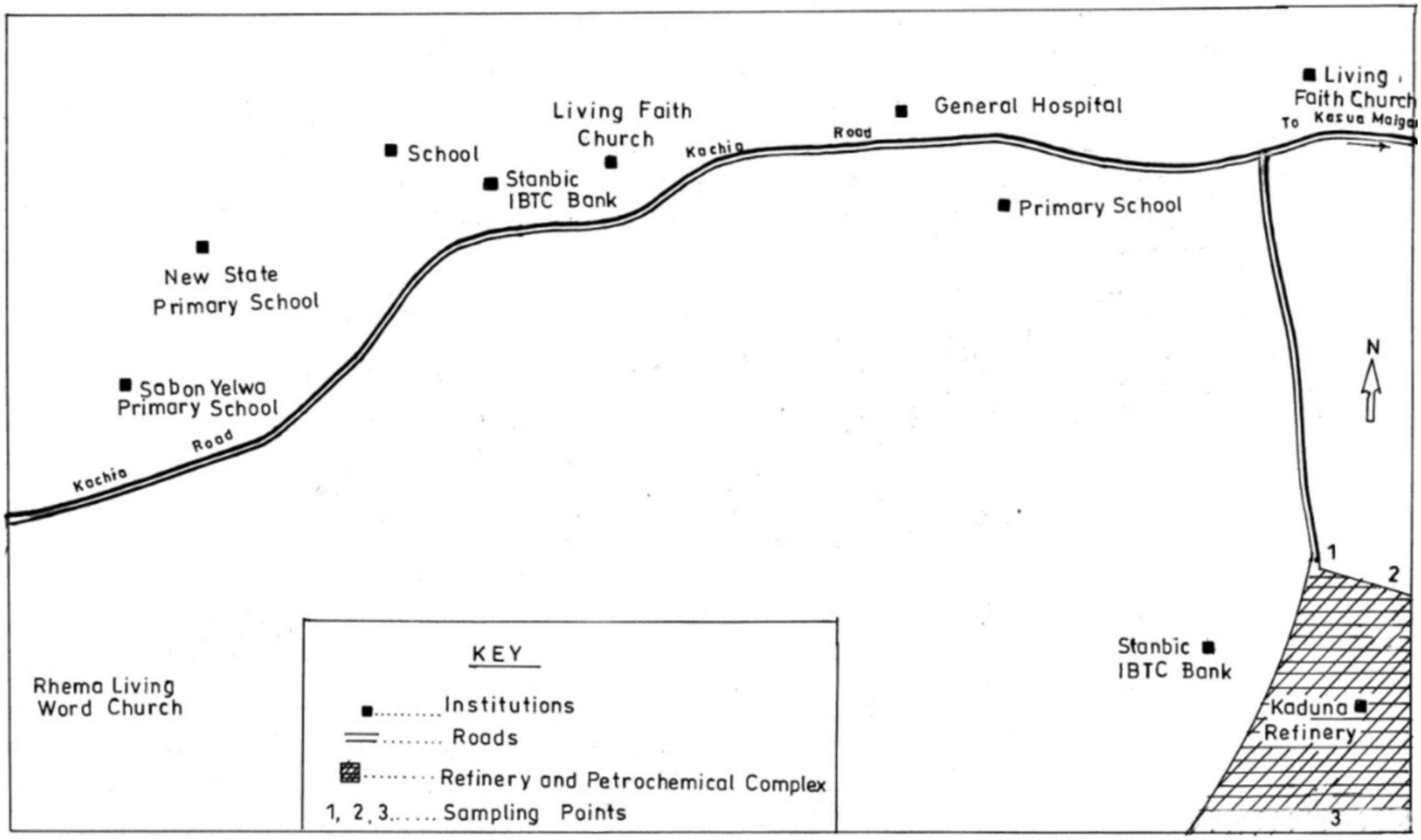

Fig. 2: Environs of the Kaduna Refinery and Petrochemical Complex (KRPC) Showing Sampling Points

### Figure 2

See image above for figure legend.

### Figure 3

See image above for figure legend.

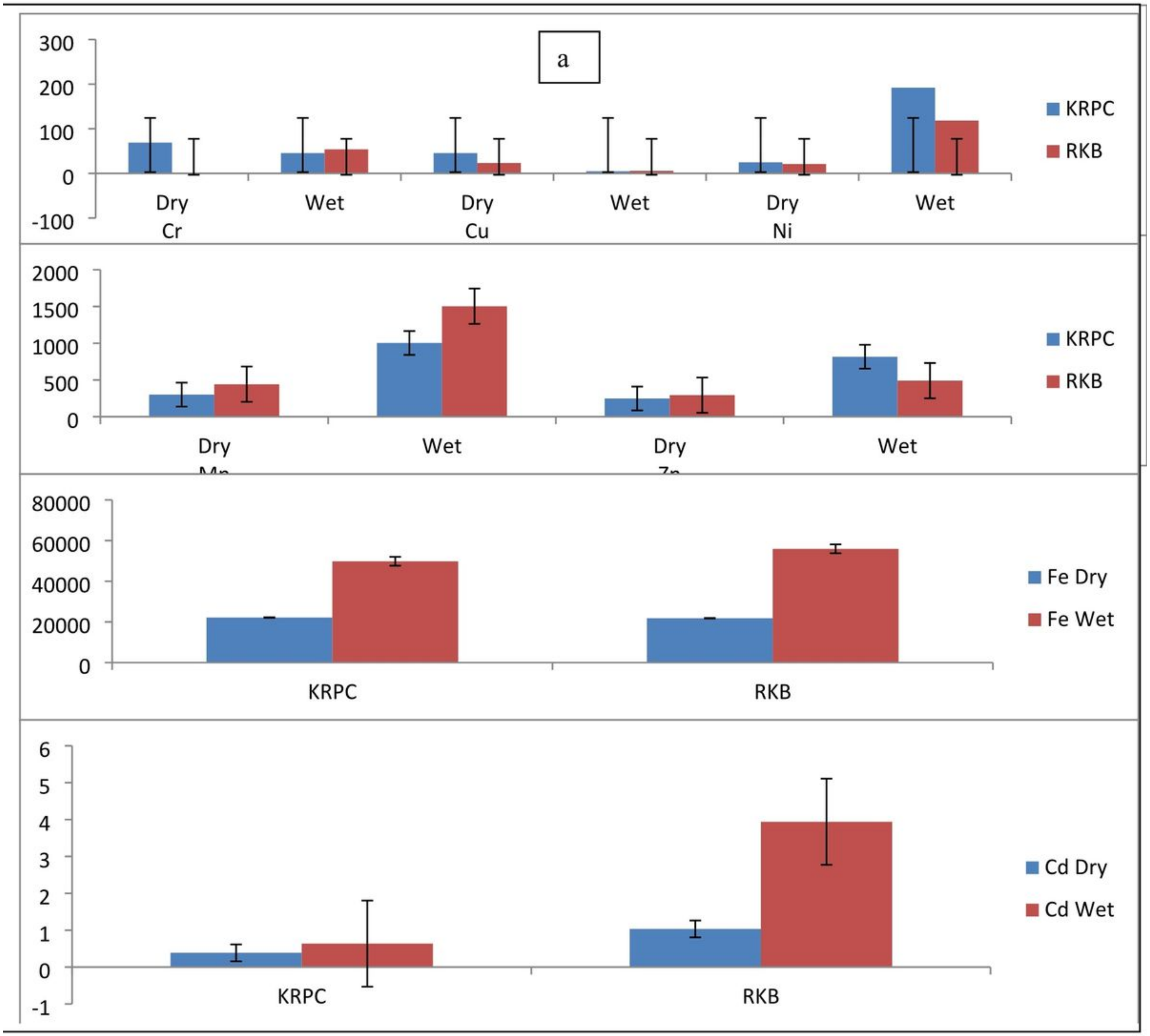

**Figure 4**

Seasonal variation in heavy metal concentration (mg/kg) in soils of Kaduna Refinery and Petrochemical Company (KRPC) and River Kaduna Bank (RKB) (**a**, Cu, Cr and Ni; **b**, Mn and Zn; **c**, Fe; and **d,** Cd).

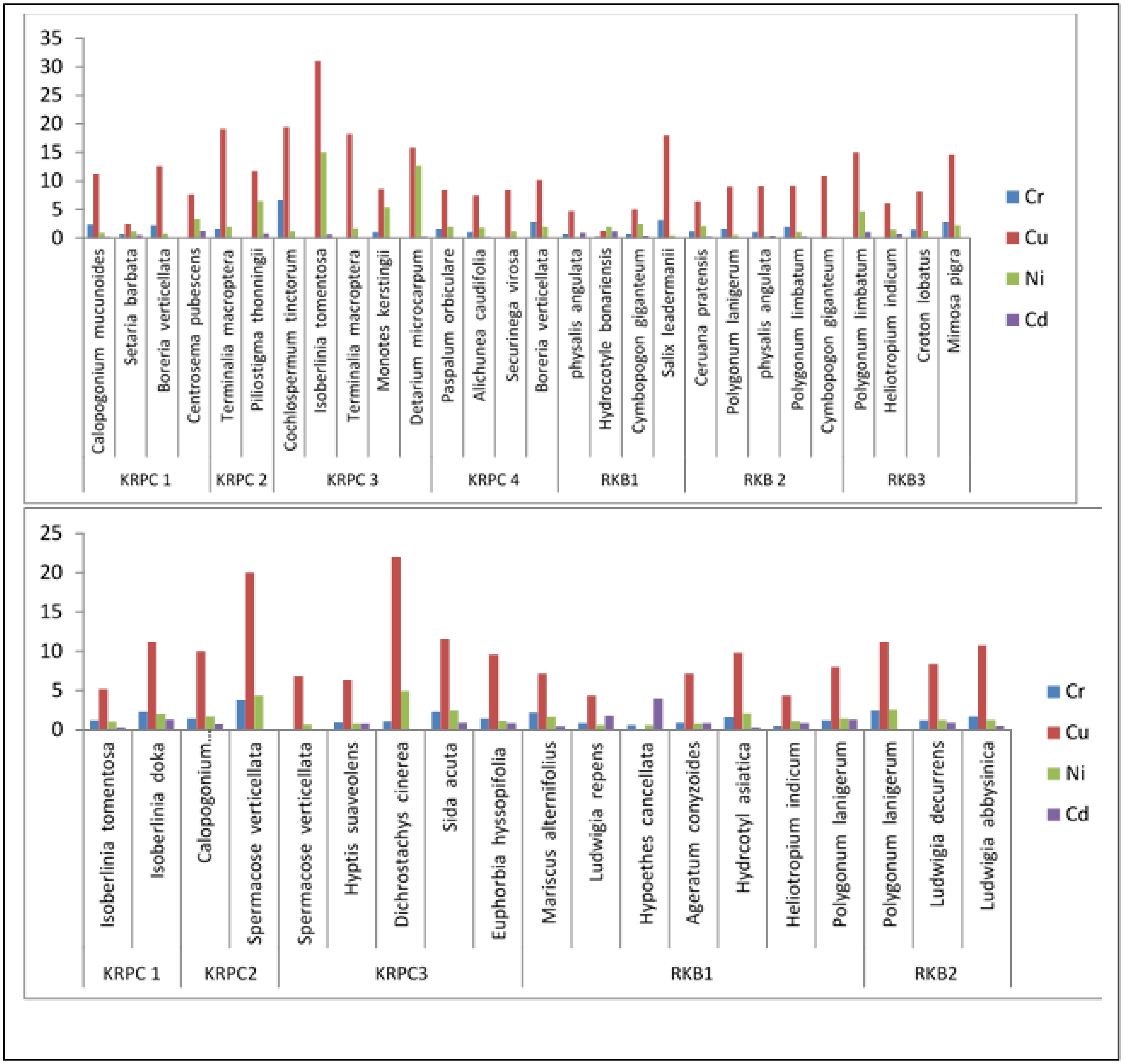

**Figure 5**

Concentration of Cr, Cu, Ni and Cd in plants collected from Kaduna Petrochemical and Refining Company Kaduna (KRPC) and River Kaduna Bank (RKB) during the Dry Season (a) and wet season (b)

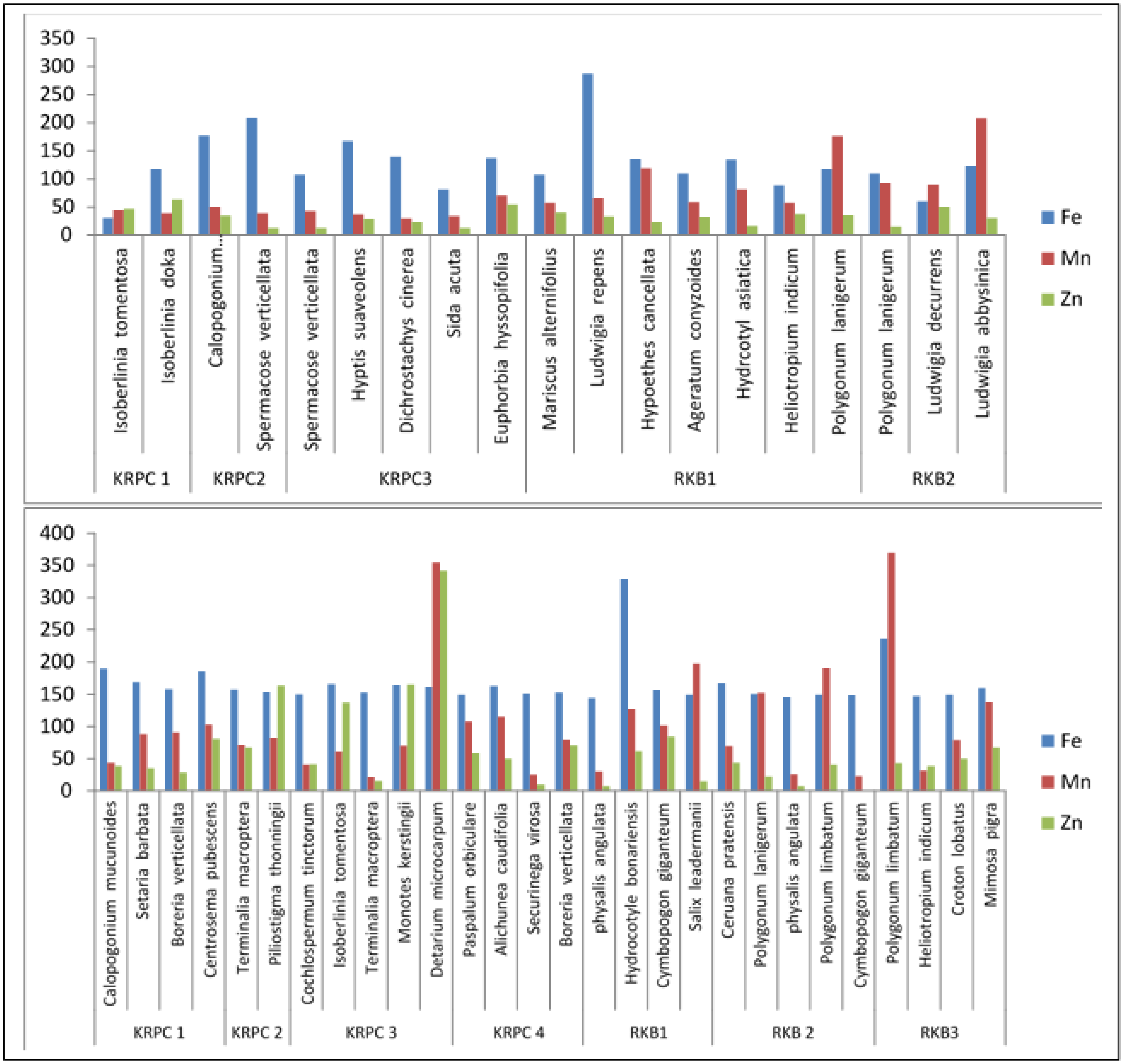

Figure 6

Concentration of Fe, Mn and Zn in plants collected from Kaduna Petrochemical and Refining Company Kaduna (KRPC) and River Kaduna Bank (RKB) during the Dry Season (a) and wet season (b)

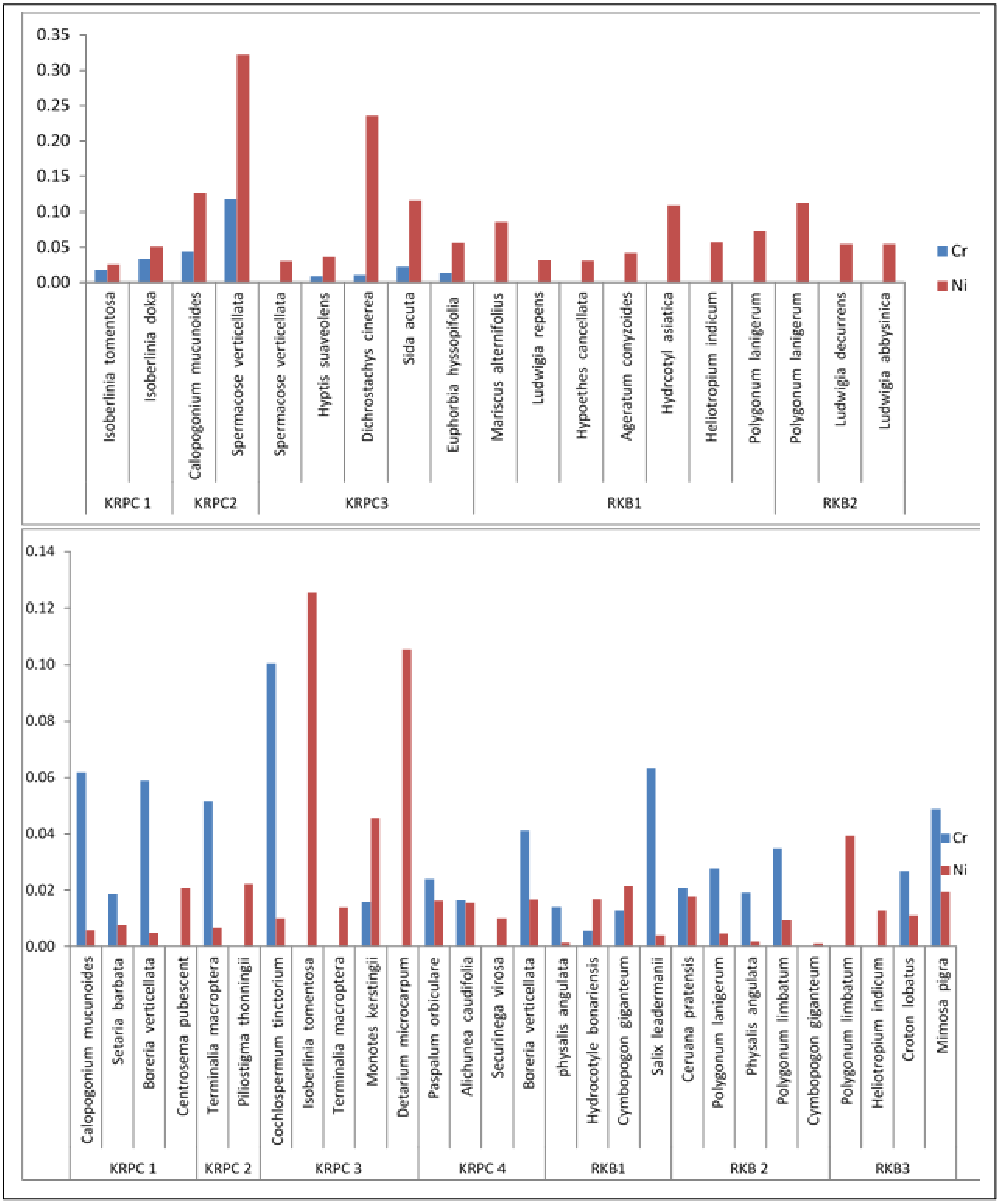

Figure 7

Bioconcentration of Cr and Ni in plants collected from Nigerian National Petrochemical Company Kaduna and River Kaduna Bank during the Dry Season (a) and wet season (b)

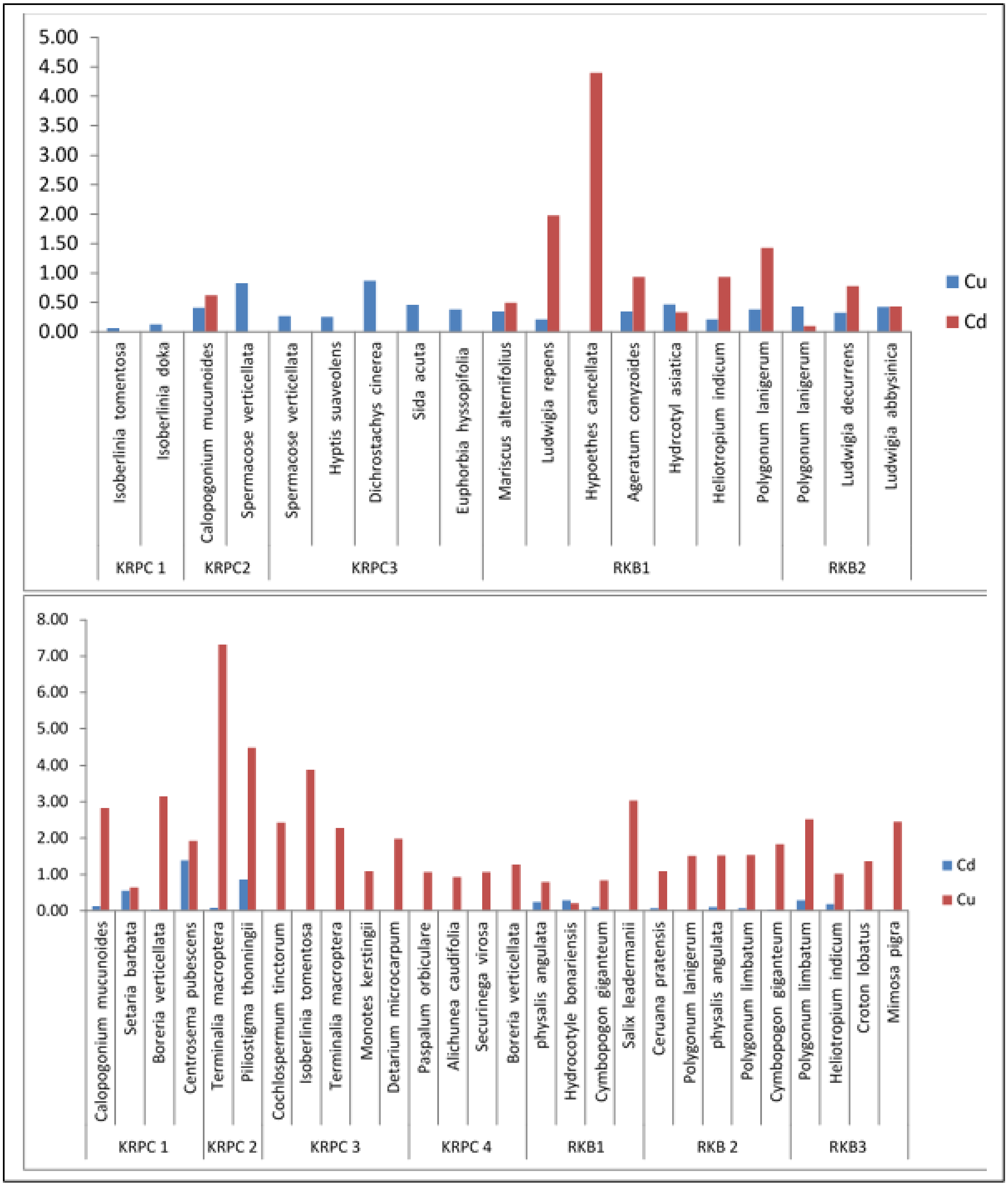

Figure 8

Bioconcentration of Cu and Cd in plants collected from Nigerian National Petrochemical Company Kaduna and River Kaduna Bank during the Dry Season (a) and wet season (b)

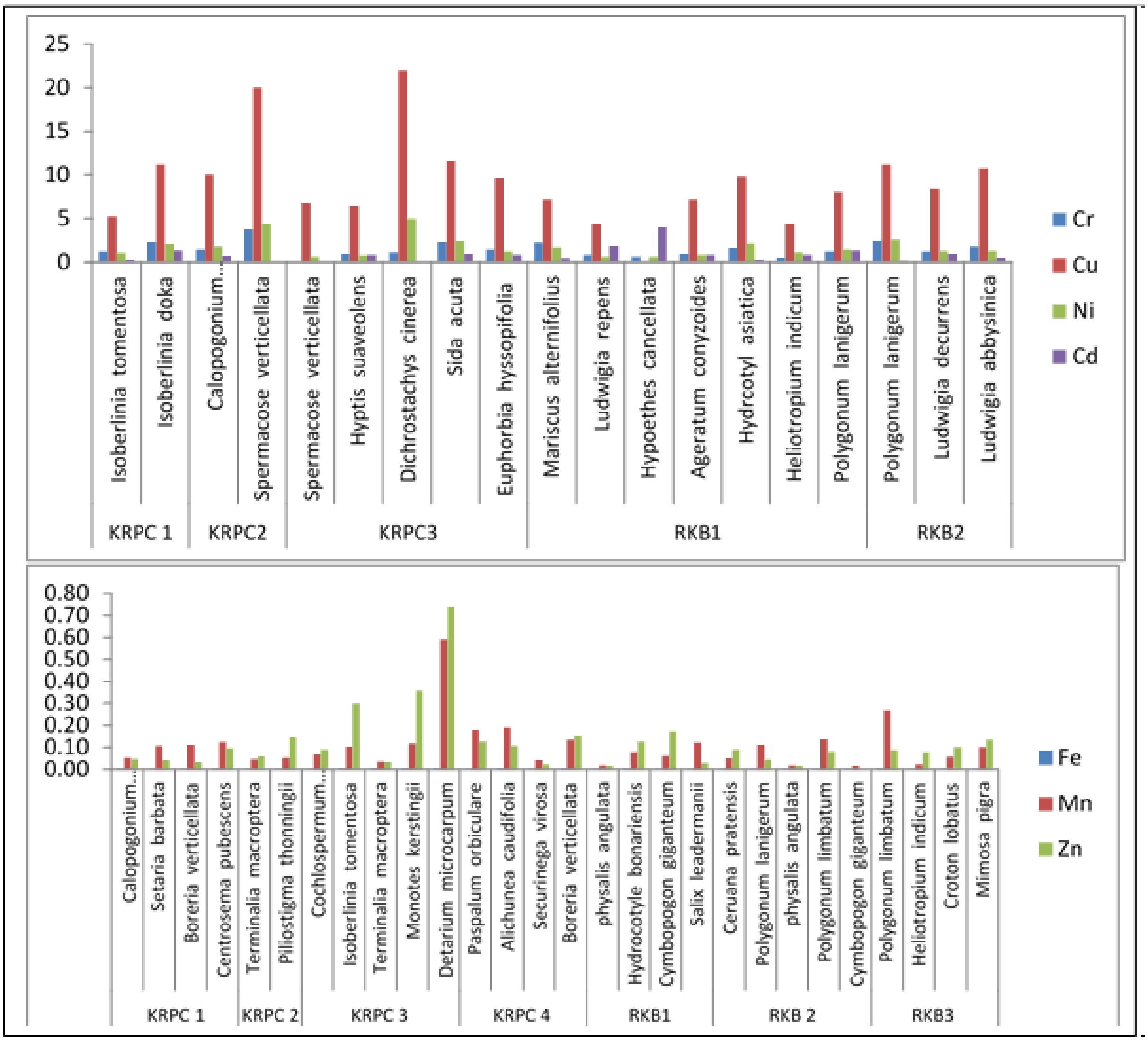

Figure 9

Bioconcentration of Fe, Mn and Zn in plants collected from Nigerian National Petrochemical Company Kaduna and River Kaduna Bank during the Dry Season (a) and wet season (b)