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POTENTIALS OF RUDERAL PLANTS IN THE REMEDIATION OF POTENTIALLY TOXIC METAL-CONTAMINATED SITES IN KADUNA METROPOLIS, NORTHWESTERN NIGERIA

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ABSTRACT

River channels in urban centres are polluted by some heavy metals mainly through runoff of surface waters or agricultural activities. The potential of some ruderal plants growing by River Kaduna to remediate potentially toxic elements was assessed. Concentration of Cd, Ni, Cr, Cu, Fe, Mn, and Zn in soil and plant samples was determined using Energy Dispersive X-ray Fluorescence.Tenspecies of plants namely, *Salix leadermanii*, *Ceruanapra tensis*, *Polygonum lanigerum*, *Physalis angulata*, *Polygonum limbatum*, *Cymbopogon giganteum*, *Heliotropium indicum*, *Croton lobatus*, *Hypoethes cancellata* and *Mimosa pigra* that generally produce high above-ground biomass with bioconcentration factor >1were identified as phytoextractors of Cu. No hyper accumulator of other heavy metals were identified in this study. There are 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.

Keywords: Ruderals, phytoremediation, heavy metals, Kaduna river, Nigeria

INTRODUCTION

Trace elements occur naturally in the terrestrial ecosystem (An'ongo*et al*., 2005; Lar, 2013; Souza *et al*., 2021) and some of them like zinc (Zn), iro (Fe), manganese (Mn), and copper (Cu) are essential plant nutrients while others like lead (Pb), mercury (Hg), and chromium (Cr) are not of any known benefits to plants (Bako *et al*., 2005; Tanimu *et al*., 2013; Sabreena *et al*., 2022). All metals become Potentially Toxic Elements (PTEs) at concentration high

above the threshold the environment can handle. Human activities have been implicated for the increase in heavy metal concentration in many environments (Maine *et al*., 2004; Bako *et al*., 2008; Tanimu *et al*., 2013; Wei *et al*., 2021). PTEs are important components of agro-allied products such as pesticides, herbicides, fertilizers, and other synthetic products such as paints and batteries (USDA, 2000). Mining activities, industrial, municipal and domestic wastes are important sources of PTE pollution to the environment (Bako *et al*., 2005; Mathews-Amune and Kakulu, 2013; Ombugadu *et al*., 2014; Monaci *et al*., 2020).

An excessive concentration of PTEs in the environment is of great concern because of their non-biodegradability. Therefore, their persistence in the environment portends health hazard to plants, and animals and consequently trigger ecological imbalances in the ecosystem (Ekmekyaper *et al*., 2012; Olayinka *et al*., 2021). Another concern that high concentrations of PTEs is their ability to bioaccumulate across the food chain, with members that are high up the food chain having a 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).

Polluted soils are normally remediated by confinement, washing, thermal deposition or excavation. These methods are usually achieved at a very high cost with a consequent damage to soil structure, biology and fertility that is irreversible (Alkorta *et al*., 2010). Phytoremediation is achieved by taking advantage of the roles played by plants in the biogeochemical nutrient cycle (Robinson *et al*., 2009). In phytoremediation, tolerant plants that thrive in the presence of PTEs that are toxic to other plants are used to degrade, extract, hold, or immobilize such PTEs from soils (Souza *et al*., 2021; Wei *et al*., 2021). Phytoremediation may be achieved byphytostabilization (the reduction of mobility of toxic elements in contaminated soils or by phytoextraction (the plant absorbs and removes PTEs from the soil and takes them up into shoots and leaves (Awa and Hadibarata., 2020; Sabreena *et al*., 2022). The capacity to remove or tolerate PTEs in the shoot of plants depends on the extent of pollution in the soil, the physiological state of the species, and their selectivity for PTEs (Mandzhieva *et al*., 2016; Tapia *et al*., 2020). Considering this, bioprospecting of plants growing in polluted environments is an efficient approach for identifying plants that may be useful both for phytostabilization and phytoextraction purposes (Chapman *et al*., 2019; Monaci*et al*., 2020). Ruderal plants arise from strong environmental pressure due to the selection of tolerance mechanisms which allow these plants to grow under the stressful conditions prevailing at wastelands. A number of studies have shown that plant species from polluted areas have a higher exclusion efficiency, or higher accumulation and tolerance to potentially harmful concentrations of PTEs than those from non-polluted area as (Schat*et al*., 2000).Indigenous ruderal plants provide a naturally occurring gene pool for the 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. Examples of ruderals with tolerance of heavy metals include *Biscutella laevigata* (Pošćić*et al*., 2015), *Agrostis canina* (Bech*et al*., 2012a, 2012b), *Agrostis capillary s*(Teodoro*et al*., 2020) and *Lotus hispidus* (Matanzas *et al*., 2021).

Mature ruderal plants with high above ground biomass which arise from the degradation of habitats could be utilized for phytoremediation programmes, especially when they are easy to propagate, self-sustaining and fast growing (Ligenfelter and Hartwig, 2007; Matanzas *et al*., 2021).

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;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).

This study was therefore carried out to identify indigenous ruderal plant species that are pollution tolerant and have the potential for use in phytoremediation of sites that are polluted with potentially toxic elements.

MATERIALS AND METHODS

Study Area

The sampling site is located in the Kaduna metropolis, which is home to many industries ranging from petrochemical refinery, fertilizer blending plants, textile and breweries. These industries and other small scale and medium industries, residential areas as well as urban markets discharge their wastewaters into the river Kaduna through more than fifty (50) drainage systems. These drainages have been reported to be polluted with heavy metals, oil and grease, excessive nutrients among other pollutants; the river serves as a sink for these pollutants. Kaduna falls within the Southern Guinea Savanna eco-region of northern Nigeria (Figure 1) and has distinct wet and dry seasons. The wet season starts from May to October whereas the dry season is from November to April.

Sample Collection

Samples were collected by the River Kaduna Bank (RKB), at UnguwanRimi, near the Kaduna North Water Works, Malali, Kaduna. These locations though not far apart, represent a unique ecosystem that has natural vegetation growing along the River Kaduna Bank within the Kaduna metropolis. Soil and plant samples were collected in both dry and wet seasons from three sampling stations (RBK1, RBK2 and RBK3)in three 5m by 5m quadrats. Soil samples were collected at 0-15cm depth using a soil auger. The shoots of herbaceous plants with relative abundance greater than five per quadrant were clipped with a pair of secateurs for heavy metal analysis. Identification and authentication of plant samples was done in the herbarium of the Department of Botany, Ahmadu Bello University, Zaria using Hutchinson and Dalziel (1952) as guide. The plants were assigned Accession Numbers and Voucher specimens were deposited in the herbarium.

Sample Preparation

Plant samples were washed with tap water and then with distilled water to remove debris and surface contaminants . 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 of less than 125micrometer. 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).

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 109Cd as the excitation source, that emits Ag elements were pKeV in which case all elements with lower characteristic excitation energies are accessible for detection in the samples. Furthermore, the system consists of Si (Li) detector, with a resolution of 170eV for the 5.90KeV line, coupled to a computer controlled
ADC quantitative analysis of the sample was done using the Emission Transmission (E-T) method 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 which the program uses 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 109Cd source and the spectra were then evaluated using the AXIL-QXAS program 109Cd 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 –the accuracy and precision IAEA of the measurements was confirmed though an analysis of IAE 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:

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

Student t-test was used to compare the heavy metal concentration in the soil between the wet and dry seasons

RESULTS

Metal concentration in Soil and Plant samples

The mean concentration of metals in the soils sampled were generally higher in the wet season and followed the trend Mn>Zn>Fe>Cu>Ni>Cd>Cr. In the dry season, the mean metal concentration in the soil followed the order Mn>Fe>Zn>Ni>Cr>Cu>Cd in the samples collected from the River Kaduna Bank. Concentration of Cr in the soil was observed to be below detectable limits in the dry season. Only the concentration of Cu did not vary significantly between seasons (Table 1).
Sixteen plant species were collected belonging to eleven families (Table 2). The concentration of Cr, Cu and Cd in the plants varied from below detectable limit to 3,200, 18000 and 4000 mg/kg, respectively.
Ni was observed to have the lowest concentration of 140 and a highest concentration of 4670 mg/kg, the highest concentrations of Fe, Mn and Zn in the plants were 329,490, 369,800 and 84,400 mg/kg, respectively (Table 3).
None of the plants had bioconcentration factor (BCF) greater than 1 for Cr, Ni, Cd, Fe, Mn and Zn. *Salix leadermanii, Ceruana pratensis, Polygonum lanigerum, Physalis*

angulata, Polygonum limbatum, Cymbopogon giganteum, Heliotropium indicum, Croton lobatus, Ludwigia repens, Hupethes cancellata and *Mimosa pigra* had BCF greater than 1 for Cu (Table 4).

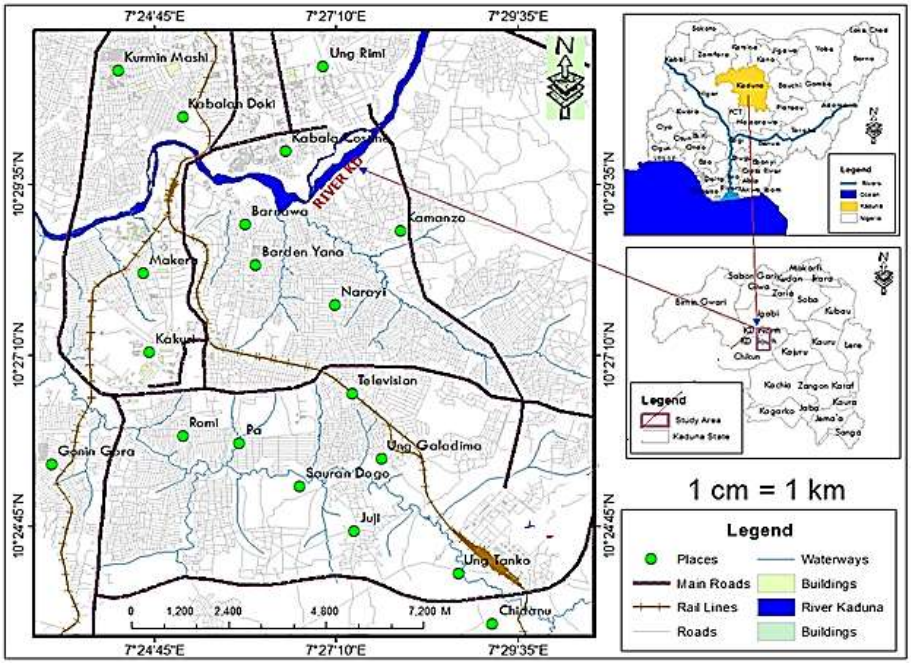


Fig. 1: Map of Kaduna Metropolis Showing River Kaduna (Nigeria and Kaduna State inset)

Source: GIS Lab, Department of Geography and Environmental Management, A.B.U. Zaria.

Table 1: Mean seasonal concentrations of heavy metals (mg/kg) in soils collected from River Kaduna Bank

	Metals						
	Cr	Cu	Ni	Cd	Fe	Mn	Zn
Dry	0	23,370	21,100	1,035	218,500	442,500	293,000
Wet	54,050	5,945	118,455	3,940	559,440	1,503,250	491,130
p-value		0.09ns	0.01*	0.00**	0.01*	0.01*	0.01*
WHO limits (Olayinka-Olagunju, 2021)	0.03-0.3	0.05-0.15	-	0.1	5	0.2	≤1
WSRA (Martin and Maybeck, 1979)	71	32	68	0.3	35900	750	127
Toxic Response factror (Sagagi *et al.* 2021)	2	5	5	30	-	1	1

ns, not significant p≥0.05, * significant p<0.05, ** significant p<0.01, WSRA- World Surface Rock Average (Background values)

Table 2: Plant species collected along River Kaduna Bank

	Plants	Family	Voucher Number
1	*Ageratum conyzoides*ex. Steud	Asteraceae	ABU09005
2	*Ceruanapra tensis*Forssk	Asteraceae	ABU4623
3	*Croton lobatus*L.	Euphorbiaceae	ABU04230
4	*Cymbopogon giganteum*(L) Spreng	Poaceae	ABU07231
5	*Heliotropium indicum* L.	Bignoniaceae	ABU07457
6	*Hydrocotyle bonariensis* Lam	Araliaceae	ABU8349
7	*Hypoethes cancellata*Sol,ex R.Br	Acanthaceae	ABU04601
8	*Ludwigia abbysinica*A.Rich	Orgnanceae	ABU0517
9	*Ludwigia decurrens W*alter.	Orgnanceae	ABU06001
10	*Ludwigia repens*J.R.forst	Orgnanceae	ABU04381
11	*Mariscus alternifolius*Rottb.	Cyperaceae	ABU090051
12	*Mimosa pigra* L.	Mimosaceae	ABU09083
13	*Physalis angulata* L.	Solanaceae	ABU090446
14	*Polygonum lanigerum* L	Polygonaceae	ABU0803
15	*Polygonum limbatum* H.Hara	Polygonaceae	ABU04691
16	*Salix leadermanii* Seemen	Salicaceae	ABU00081

Table 3: Metalconcentrations (mg/kg)in Plants collected along River Kaduna Bank

Season	Sampling Station	Plants	Cr	Cu	Ni	Cd	Fe	Mn	Zn
Wet	RKB1	*Physalis angulata*	710	4740	170	960	145000	30100	7330
		Hydrocotyle bonariensis	280	1280	2000	1190	329490	126990	61700
		Cymbopogon giganteum	650	5000	2530	440	156800	101500	84400
		Salix leadermanii	3200	18000	460	0	149700	197000	14330
	RKB 2	*Ceruana pratensis*	1200	6500	2110	300	167390	69830	43960
		Polygonum lanigerum	1600	9000	560	50	150510	153000	22210
		Physalis angulata	1100	9100	220	410	145780	26000	7470
		Polygonum limbatum	2000	9180	1100	290	149560	191000	40330
		Cymbopogon giganteum	0	10920	140	120	148600	22450	0
	RKB3	*Polygonum limbatum*	0	15000	4670	1110	236000	369800	43100
		Heliotropium indicum	0	6120	1530	740	146920	31670	38770
		Croton lobatus	1540	8160	1320	100	149000	78860	49690
		Mimosa pigra	2800	14560	2300	70	160270	138160	66810
Dry	RKB1	*Mariscus alternifolius*	2200	7200	1650	450	107200	57000	40420
		Ludwigia repens	820	4400	610	1800	287200	65640	33000
		Hypoethes cancellata	600	0	600	4000	135800	119000	23450
		Ageratum conyzoides	900	7200	800	850	109600	59040	32040
		Hydrcotyl asiatica	1600	9800	2100	300	135000	81570	15910
		Heliotropium indicum	500	4400	1100	850	88600	57000	38000
		Polygonum lanigerum	1230	8000	1410	1300	117600	177000	35000
	RKB2	*Polygonum lanigerum*	2460	11200	2600	110	109400	93280	15000
		Ludwigia decurrens	1200	8400	1260	900	60500		50500
		Ludwigia abbysinica	1730	10800	1260	500	123500		31210

Table 4: Heavy metal BCF of plants collected by River Kaduna

		Plants	Cr	Ni	Cd	Cu	Fe	Mn	Zn
Wet	RKB1	*Physalis angulata*	0.01	0.00	0.24	**0.80**	0.00	0.02	0.02
		Hydrocotyle bonariensis	0.01	0.02	0.30	0.22	0.01	0.08	0.13
		Cymbopogon giganteum	0.01	0.02	0.11	**0.84**	0.00	0.06	0.17
		Salix leadermanii	0.06	0.00	0.00	**3.03**	0.00	0.12	0.03
	RKB 2	*Ceruana pratensis*	0.02	0.02	0.08	**1.09**	0.00	0.05	0.09
		Polygonum lanigerum	0.03	0.00	0.01	**1.51**	0.00	0.11	0.04
		Physalis angulata	0.02	0.00	0.11	**1.53**	0.00	0.02	0.02
		Polygonum limbatum	0.03	0.01	0.07	**1.54**	0.00	0.14	0.08
		Cymbopogon giganteum	0.00	0.00	0.03	**1.84**	0.00	0.02	0.00
	RKB3	*Polygonum limbatum*	0.00	0.04	0.29	**2.52**	0.00	0.27	0.09
		Heliotropium indicum	0.00	0.01	0.19	**1.03**	0.00	0.02	0.08
		Croton lobatus	0.03	0.01	0.03	**1.37**	0.00	0.06	0.10
		Mimosa pigra	0.05	0.02	0.02	**2.45**	0.00	0.10	0.13
Dry	RKB1	*Mariscus alternifolius*	-	0.09	0.34	0.49	0.01	0.14	0.15
		Ludwigia repens	-	0.03	0.21	**1.98**	0.01	0.16	0.12
		Hypoethes cancellata	-	0.03	0.00	**4.40**	0.01	0.29	0.09
		Ageratum conyzoides	-	0.04	0.34	**0.93**	0.01	0.14	0.12
		Hydrcotyl asiatica	-	0.11	0.47	0.33	0.01	0.20	0.06
		Heliotropium indicum	-	0.06	0.21	**0.93**	0.00	0.14	0.14
		Polygonum lanigerum	-	0.07	0.38	**1.43**	0.01	0.43	0.13
	RKB2	*Polygonum lanigerum*	-	0.11	0.44	0.09	0.00	0.19	0.05
		Ludwigia decurrens	-	0.05	0.33	0.78	0.00	0.19	0.16
		Ludwigia abbysinica	-	0.05	0.42	0.43	0.01	0.43	0.10

Metal below detectable limit

DISCUSSION

Concentrations of heavy metals in soils generally observed to be higher during the wet season in both locations differs somewhat from the findings of Oluyemi *et al*.(2008) and Najib *et al*. (2012) who observed a higher concentration of these metals in the dry season Seasonal variations in patterns of metal deposition could be related to the intensity and duration of climatic variables such as precipitation and temperature that interface with topography, drainage, soil structure and texture 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 being solution composition and pH, type and density of charge on soil colloids, and reactive surface area that interact with factors like metal concentration, form, particle size distribution, quantity and reactivity of hydrous oxides, mineralogy, degree of aeration and microbial activity (Cataldo and Widung, 1987; Edokpayi *et al*., 2017). The aggregate effects of these complex interactions determine the bioavailability of metals to plants.

The above acceptable limits of the observed concentrations of Cr, Cu, Ni, and Zn may be attributed to mainly agricultural activities going on along the River Kaduna bank. This presents health risks to humans and

other animals as the metals contaminate both aquatic and terrestrial ecosystems. Application of fertilizer, herbicides and pesticides has been implicated for increased metal concentration in soils (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, the 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 on humans have generally been outlined as ranging from gastrointestinal disorders, diarrhoea, stomatitis, tremor, haemoglobinuria, ataxia, paralysis, vomiting, and convulsion, depression, coughing and wheezing, respiratory tract inflammation, dermatitis, leukocytis, low blood pressure, jaundice haemolytic anaemia pneumonia, coma and death. The nature of these effects could be toxic (acute, chronic, or sub-chronic), neurotoxic, carcinogenic, mutagenic, or teratogenic (Duruibe *et al*., 2007; Bako *et al*., 2009a; Bako *et al*., 2009b; Friends of Nature. 2010).

The high concentration of these potentially toxic elements (Cd, Zn, Cr, Cu, and Ni) in plants along the banks of River Kaduna could be toxic to the plants (Galfata *et al*., 2013). Metal toxicity in plants may inhibit enzyme activity, stomatal function, photosynthesis, and nutrient uptake, which may be expressed visually as chlorosis, reduced or stunted growth, and yield depression. Jankowski *et al*. (2019) reported that direct atmospheric deposition of heavy metals could result in high concentration of heavy metals in plants. 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).

The variation in tolerance of plants to high concentrations of metals in their tissues depends on inherent genetic factors which confers the ability to employ a range of avoidance, exclusion or detoxification. This mechanisms enable the plants to cope with high metal loads, which may include the binding of metals like Ni and Cr with amino acids, peptides, and organic acids to form low molecular weight compounds, and 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 (Bako*et al*., 2005; Kotrba*et al*., 2009).

Plants with BCF of metals >1.0 have been described as suitable for phytoextraction (Baker and Brooks, 1989). Some of the plants observed in this study with this potential include *Salix leadermanii, Ceruanapra tensis, Polygonum lanigerum, Physalis angulata, Polygonum limbatum, Cymbopogon giganteum, Heliotropium indicum, Croton lobatus, Mimosa pigra, Ludwigia repens* and *Hypoethes cancellata.*

The ability of these plants to concentrate high levels of these metals suggests that they may have a good potential for phytoremediation. For example Ameh *et al* (2019) reported *Physalis angulata* as a potential phytoextractor of Cu; *Cymbopogon citratus* which belongs to the same genus

with *Cymbopogon giganteum* is a phytostabliser of Fe, Mn and Cu. Different species of the members of the genera *Salix* have been reported by Brkovic *et al*. (2021) to have phytoextractiveaction for Zn and Ca, and phytostabilisng potentials for Zn, Ca, Mn, Fe, Cr, Pb, Zn, and Ca.Pérez-Hernández *et al.* (2020) reported the capacity of *Mimosa pigra* to restore a contaminated soil with anthracene, phenanthrene, and other hydrocarbons.

In our extensive literature search we did not come across any work on the phytoremdiation potential of *Polygonum lanigerum, Polygonum limbatum, Cymbopogon giganteum, Heliotropium indicum, Croton lobatus ,Ludwigia repens, Ceruanapra tensis*and *Hypoethes cancellata.* 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. There are possibilities for genetic modification of plants to enhance their capacity for metal tolerance (Kotrba *et al*., 2009).

CONCLUSION

The concentrations of Cr, Cu, Ni, and Zn in soils around River Kaduna bank were found to be above the acceptable limit, which could present health risks to humans and other animals.

Ten (10) plant species were identified to have high bioconcentrations of 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 are *Salix leadermanii, Ceruana pratensis, Polygonum lanigerum, Physalis angulata, Polygonum limbatum, Cymbopogon giganteum, Heliotropium indicum, Croton lobatus, Hypoethe scancellata* and *Mimosa pigra.*

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