OPEN ACCESS

Haya: The Saudi Journal of Life Sciences
Abbreviated Key Title: Haya Saudi J Life Sci
ISSN 2415-623X (Print) | ISSN 2415-6221 (Online)
Scholars Middle East Publishers, Dubai, United Arab Emirates
Journal homepage: https://saudijournals.com

Original Research Article

Phytoremediation Potentials of Indigenous Ruderal Plants Growing on Soil Contaminated with Potentially Toxic Elements within a Petrochemical Refinery Complex

Sunday Paul Bako[1,2]*, Augustine Uwanekwu Ezealor[3], Yahuza Tanimu[2]

[1]Department of Biological Sciences, Faculty of Science, Taraba State University, Jalingo, Nigeria
[2]Department of Botany, Ahmadu Bello University, Zaria, Nigeria
[3]Department of Forestry and Environmental Management, Michael Okpara University of Agriculture, Umudike, Nigeria

DOI: https://doi.org/10.36348/sjls.2025.v10i03.002 | **Received:** 20.01.2025 | **Accepted:** 25.02.2025 | **Published:** 05.03.2025

***Corresponding author:** Sunday Paul Bako
Department of Biological Sciences, Faculty of Science, Taraba State University, Jalingo, Nigeria

Abstract

The utilization of indigenous plant species for remediation of polluted soils comes at a low economic and ecological cost when compared with traditional methods. In this study, the phytoremediation potential of indigenous ruderal plants in highly polluted soil within a petrochemical refinery complex was evaluated. First, a survey of the most abundant herbaceous plant species was carried out within the complex during the wet and dry seasons. The concentration of Cd, Ni, Cr, Cu, Fe, Mn, and Zn in soil and plant samples was determined using Energy Dispersive X-ray Fluorescence. Results show ten herbaceous plant species (*Calopogonium mucunoides*, *Terminalia macroptera*, *Centrosema pubescens*, *Piliostigma thonningii*, *Cochlospermum tinctorum*, *Isoberlinia tomentosa*, *Monotes kerstingii*, *Detarium microcarpum*, *Paspalum orbiculare*, *Borreria verticillata*) with accumulation factors (of Cd and/Cu) greater of than 1, thus revealing them as metal extractors. Furthermore, they have high above ground biomass due to their rapid vegetative growth, self-sustaining and easy to propagate. 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: Phytoremediation, Ruderal plants, soil pollution, Phytoextraction, Potentially Toxic Elements.

INTRODUCTION

Petrochemical refinery companies are designed to separate crude oil into several products like premium motor spirit (PMS), diesel, kerosene, lubricants, waxes, asphalt, ethylene, polyethylene chloride, vinyl chloride monomer (VCM), polyvinyl chloride (PVC), industrial grade methanol, ammonia and others (Odeyemi and Ogunseitan, 1985; Mustapah *et al*., 2015). The process of refining involves physical and chemical techniques such as fractionation, cracking, hydro-treating, and combination/blending processes which involve the use of several chemicals and may result in the release of environmental pollutants through gas flaring, oil spillage, effluent discharge, or sludge deposition (Asia *et al*., 2006; Uwidia *et al*., 2017). These pollutants have been characterised to include heavy metals, hydrocarbons, organic matter, oil and grease, salts, and other potentially toxic compounds (Pathak and Mandalia, 2012).

Although, trace quantities of heavy metals have been reported to occur naturally in the ecosystem (An'ongo *et al*., 2005; Lar, 2013), deposition of heavy metals in soils from anthropogenic activities has been implicated in 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). An 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, and animals and consequently trigger ecological imbalances in the ecosystem (Ekmekyaper *et al*., 2012; Olayinka *et* *al*., 2021). 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 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). 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 *et al*., 2013).

Contaminated soil is traditionally remediated through confinement, soil washing, thermal deposition, or excavation. These methods are expensive and the consequence is an irreversible damage to soil structure, biology, and fertility (Alkorta *et al*., 2010; Foroozanfar, 2017). Phytoremediation utilizes the roles of plants in the biogeochemical nutrient cycle and pollutants as a low-cost alternative (Robinson *et al*., 2009). Phytoremediation utilizes the ability of some tolerant plants and other microorganisms to grow in the presence of PTEs levels that are toxic to other plants and degrade, extract, hold, or immobilize Potentially Toxic Elements (PTEs) from soils (Souza *et al*., 2021; Wei *et al*., 2021). In some other cases, the reduction of the mobility of toxic elements in contaminated soils is achieved by phytostabilization, whereas in the case of phytoextraction, the plant absorbs and removes PTEs from the soil and takes them up into shoots and leaves (Awa and Hadibarata, 2020). The capacity to remove or tolerate PTEs in the shoot of plants is dependent on the level of pollution present in the soil, the physiological features 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). Spontaneous vegetation arises from strong environmental pressure due to the selection of tolerance mechanisms that allow these plants to grow under the stressful conditions prevailing at polluted sites. Several 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 areas (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 plants with remarkable tolerance of contaminated sites include *Biscutella laevigata* (Pošćić *et al*., 2015), *Agrostis canina* (Bech *et al*., 2012a, 2012b), *Agrostis capillaris* (Teodoro *et al*., 2020) and Lotus hispidus (Matanzas *et al*., 2021).

Mature plants of tolerant species which arise from the degradation of habitats could serve as candidates for phytoremediation programmes, especially when they are easy to propagate, self-sustaining, fast-growing, and possess a high above-ground biomass (Ligenfelter and Hartwig, 2007; Matanzas *et al*., 2021).

Soils and plants around the Kaduna Petrochemical and Refinery Company and River Kaduna have been reported to have concentrations of heavy metals above permissible limits (Bako *et al*., 2005; Ombugadu *et al*., 2014) but previous studies have focused on biomonitoring of air pollution by heavy metals (Bako *et al*., 2005, Bako *et al*., 2008; Bako *et al*., 2009a; Bako *et al*., 2009b) and documentation of visual symptoms expressed by some ruderal plant species (Bako *et al*., 2013).

In this study, we hypothesize that indigenous ruderal plants growing on soils contaminated with PTEs will bioaccumulate PTEs to concentrations that are considered phytotoxic in their shoots. This study was therefore carried out to identify the most suitable indigenous ruderal plant species thriving in soils contaminated with PTEs as candidates for phytoremediation programmes.

MATERIALS AND METHODS

Study Area

The Kaduna Refinery and Petrochemical Company (KRPC) is located on Long. 7 29' 01.5"E, Lat. 10 33' 08.96"N and an altitude of 615m above sea level and is a subsidiary of the Nigerian National Petroleum Company (NNPC). It has a capacity of refining 100, 000 barrels of crude oil per day, started operations in 1980. It is capable of refining both light and naphthenic Nigerian crude oil and the heavier paraffinic crude oils imported from Brazil, Venezuela, and Kuwait for the production of asphalt, lubricants, and waxes. It is built inland in Kaduna town and fed by a 600 km pipeline from the Niger-Delta oil fields (Odeyemi and Ogunseitan, 1985) (Figure 1). Kaduna is located in the Southern Guinea savannah ecological zone of Nigeria, with distinct wet and dry seasons. The wet season in Kaduna runs from May to October and is warm and humid, while the dry season from November to April, is cold and dry due to the harmattan wind that blows from the northeast toward the southwest. The average monthly temperature of Kaduna is between 26 to 34 °C (Bununu *et al*., 2015).

Sample Collection

Soil and plant samples were collected in both dry and wet seasons from triplicate 5m by 5m quadrats in four sampling locations within the KRPC complex. 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 of plant samples was confirmed in the herbarium of the Department of Botany, 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 from each location 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 as described by Funtua (1999).

Bioconcentration Factor (Enrichment Coefficient)

This estimates the capacity of plants to accumulate metals and was computed as previously reported (Zu *et al.*, 2005) for each species as:

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

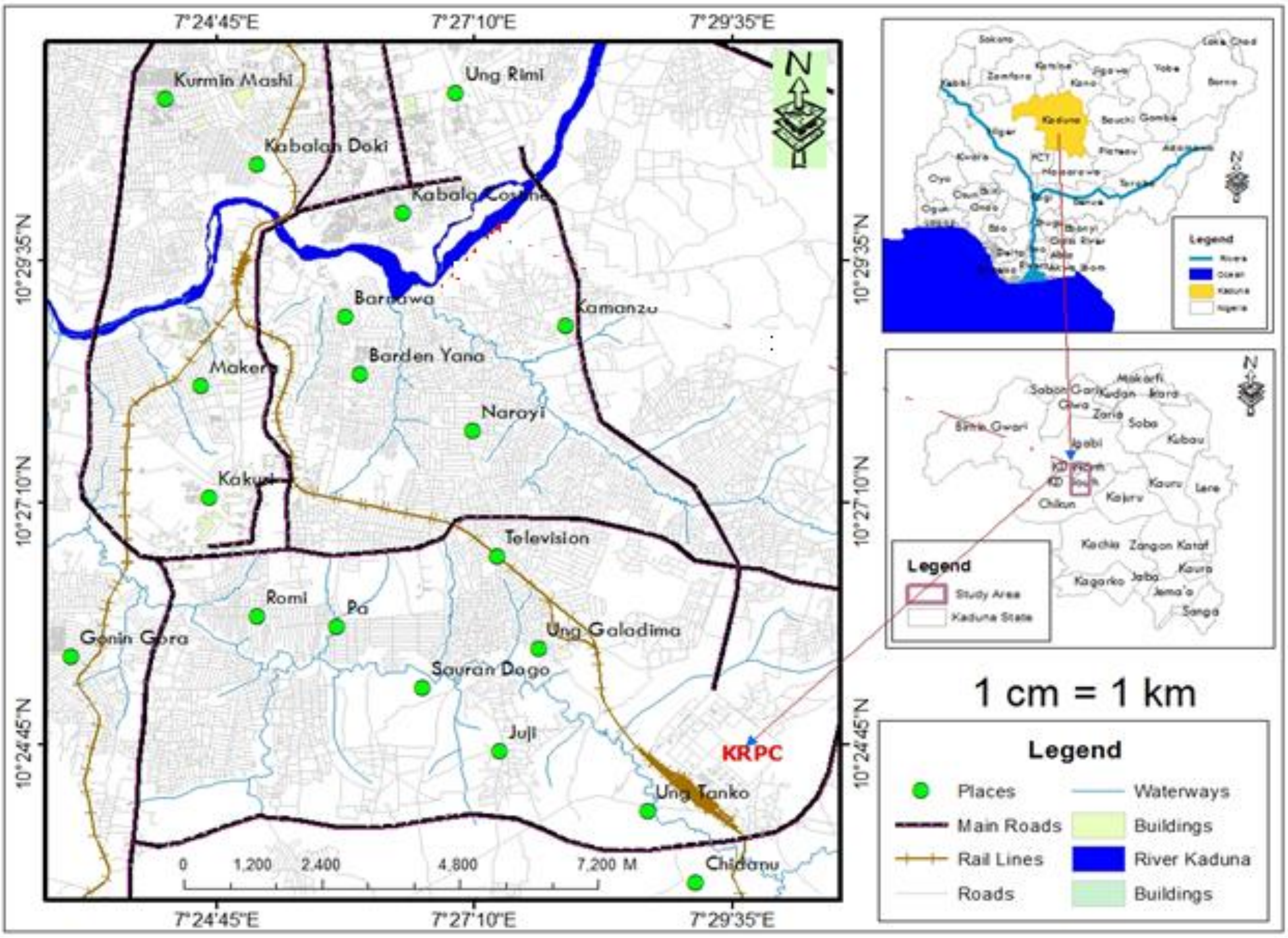

Figure 1: Map of Kaduna Metropolis Showing Kaduna Refinery and Petrochemical Company (KRPC)
Source: GIS Lab Department of Geography and Environmental Management A.B.U. Zaria

RESULTS

Plant species and their relative frequency

A total of 19 plant species belonging to 11 boatanic families which had a relative abundance of 5 per quadrat were collected for this study (Table 1).

Metal concentration in Soils and Plant samples

The mean concentration of metals generally followed this order Fe>Mn>Zn>Ni>Cr>Cu>Cd in the wet season and this order Fe>Mn>Zn>Cr>Cu>Ni>Cd. Only Fe showed significant variation between seasons (Table 2). In general terms, the soil samples analysed showed high contamination with Cr, Cu, Ni, Cd, and Zinc when compared to guideline values on Table 3.

Table 1: Herbaceous plant species collection from Kaduna Refinery and Petrochemical Company, Kaduna, Nigeria

S/No.	Plant	Family	Voucher Number
1	*Alichunea caudifolia* (Schum &Thonn)	Euphorbiaceae	ABU09001
2	*Borreria verticillata L.*	Rubiaceae	ABU0372
3	*Calopogonium mucunoides* Desv.	Papilionaceae	ABU07940
4	*Centrosema pubescens* Mart.ex.Benth	Papilionaceae	ABU05231
5	*Cochlospermum tinctorum Perr.ex*	Cochlospermaceae	ABU06512
6	*Detarium microcarpum Guill. & Perr.*	Caesalpiniaceae	ABU03421
7	*Dichrostachys cinerea* (L.) Wight & Arn.	Mimosaceae	ABU03491
8	*Euphorbia hyssopifolia* L.	Euphorbiaceae	ABU06023
9	*Hyptis suaveolens* Lam	Lamiaceae	ABU08231
10	*Isoberlinia doka Craib & Stapf*	Caesalpiniaceae	ABU09005
11	*Isoberlinia tomentosa (Harms) Craib & Stapf*	Caesalpiniaceae	ABU01103
12	*Monotes kerstingii A.Dc*	Dipterocarpaceae	ABU04251
13	*Paspalum orbiculare Bergius*	Poaceae	ABU01849
14	*Piliostigma thonningii (Schumach.)MilneRedh*	Caesalpiniaceae	ABU02089
15	*Securinega virosa (Roxb.ex Wild.) Baill*	Euphorbiaceae	ABU07812
16	*Setaria barbata* (Lam) Kunth	Poaceae	ABU090032
17	*Sida acuta* Bunrn f.	Malvaceae	ABU08021
18	*Spermacoce verticellata L.*	Rubiaceae	ABU01649
19	*Terminalia macroptera* L	Combretaceae	ABU09024

Table 2: Mean concentration of Potentially Toxic Elements (mg/kg) of soils collected from Kaduna Refinery and Petrochemical Company (KRPC)

		Cr	*Cu*	*Ni*	*Cd*	*Fe*	*Mn*	*Zn*
Dry	Mean	6.65E+04	4.55E+04	2.49E+04	3.87E+02	2.22E+07	3.01E+05	2.48E+05
	Standard Error	1.99E+04	2.07E+04	7.84E+03	3.87E+02	6.98E+06	9.88E+04	6.04E+04
Wet	Mean	4.56E+04	4.85E+03	1.92E+05	6.37E+02	4.98E+07	1.00E+06	8.16E+05
	Standard Error	1.08E+04	1.61E+03	5.24E+04	3.18E+02	5.02E+06	2.97E+05	1.95E+05
p value		0.32ns	0.19ns	0.09ns	0.64ns	0.03*	0.09ns	0.05ns

ns: not significant $p \geq 0.05$, *: significant $p<0.05$

Table 3: Recommended Levels of Heavy Metals in Soils (mg/kg)

Recommending Agencies		Cr	Cu	Ni	Cd	Fe	Mn	Zn
WHO (WHO, 1996)		100	30	80	NA	NA	NA	200
Mexican Agricultural soils (ppm) (Davila *et al.*, 2012)				1600.00	37.00	NA	NA	NA
USEP (USEP 1993)		3,000	4,300	75.00		NA	NA	7500
Japan (MOE Japan 2006)		250			150	NA	NA	NA
Canada (Canadian Council of Ministers of Environment 2009)	Agricultural	64	63	50	14	NA	NA	NA
	Residential/Park	64	63	50	10	NA	NA	NA
	Commercial	87	91	50	22	NA	NA	NA
	Industrial	87	91	50	22	NA	NA	NA
Austria (ECDGE 2010)		100	60- 100	50- 70	1 - 2	NA	NA	NA
Germany (ECDGE 2010)		60	40	50	1	NA	NA	NA
France (ECDGE 2010)		150	100	50	2	NA	NA	NA
Luxembourg (ECDGE 2010)		100-200	50 – 140	30 – 75	1-3	NA	NA	NA
Netherlands (ECDGE 2010)		30	40	15	0.5	NA	NA	NA
Sweden (ECDGE 2010)		60	40	30	0.4	NA	NA	NA
United Kingdom (ECDGE 2010)		400	135	75	3	NA	NA	NA

Plant species showed concentration of Cr from below detectable limits to 6,710 mg/kg; Cu from 2,550 to 86,970 mg/kg; Ni from 640 to 12, 600 mg/kg; Cd from below detectable limits to 1,320 mg/kg; Fe from 31 to 208,800 mg/kg; Mn from 21,100 to 115,200 mg/kg; and Zn from 1,200 to 341,560 mg/kg (Table 4). These high concentrations of this metals falls above what is considered to be phytotoxic to plants (Table 5).

Bioconcentration Factor (BCF) of Metals in Plants

Based on the BCF, the plants studied showed variable accumulation of the metals from the soil. None of the 19 plants had BCF greater than 1 for Cr, Ni, Fe, Mn and Zn. Only *Centrosema pubescent* had a BCF > 1 for Cd, while Calopogonium mucunoides, *Borreria verticelata, Terminalia macroptera, Centrosema pubescens, Piliostigma thonningii, Isoberlinia tomentosa, Monotes kerstingii, Detarium microcarpum,* and *Paspalum orbiculare* had BCF > 1 for Cu (Table 6).

Table 4: Metal concentration of Potentially Toxic Elements (mg/kg) in plants collected from Kaduna Petrochemical and Refinery complex, Kaduna

Season	Location	Plant/Soil	Cr	Cu	Ni	Cd	Fe	Mn	Zn
Dry	KRPC 1	*Isoberlinia tomentosa*	1,230	5,200	1,020	300	31,000	44,500	46,440
		Isoberlinia doka	2,260	11,200	2,040	1,300	117,400	39,000	63,000
	KRPC2	*Calopogonium mucunoides*	1,400	10,000	1,730	720	177,500	50,430	34,420
		Spermacoce verticellata	3,760	20,000	4,400	-	208,800	39,330	12,670
	KRPC3	*Spermacoce verticellata*	-	6,800	640	-	107,100	42,510	12,670
		Hyptis suaveolens	910	6,400	770	800	168,000	37,000	29,000
		Dichrostachys cinerea	1,110	22,000	4,950	-	139,400	30,250	23,200
		Sida acuta	2,260	11,600	2,440	900	81,700	33,420	12,000
		Euphorbia hyssopifolia	1,430	9,600	1,180	850	137,300	70,840	54,140
Wet	KRPC 1	*Calopogonium mucunoides*	2,420	11,200	950	130	190,320	44,000	38,420
		Setaria barbata	730	2,550	1,230	520	169,470	87,980	35,400
		Borreria verticillata	2,300	12,500	810	30	157,880	90,820	28,350
		Centrosema pubescens	-	7,650	3,400	1,320	186,000	103,000	80,900
	KRPC 2	*Terminalia macroptera*	1,600	19,100	1,970	90	157,630	71,470	66,810
		Piliostigma thonningii	-	11,730	6,560	830	154,300	82,100	164,000
	KRPC 3	*Cochlospermum tinctorum*	6,710	19,380	1,190	-	150,000	40,390	41,340
		Isoberlinia tomentosa	-	31,000	15,000	600	165,440	61,070	137,580
		Terminalia macroptera	-	18,200	1,670	-	153,220	21,100	15,470
		Monotes kerstingii	1,060	8,670	5,460	80	165,000	70,590	165,130
		Detarium microcarpum	-	15,800	12,600	280	161,700	355,000	341,560
	KRPC 4	*Paspalum orbiculare*	1,600	8,500	1,960	110	149,690	108,400	58,510
		Alichunea caudifolia	1,100	7,500	1,850	170	163,420	115,200	49,600
		Securinega virosa	-	8,500	1,200	-	151,260	24,990	10,430
		Boreria verticellata	2,750	10,200	2,000	70	-	79,900	70,900

- BCF not computed because metal concentration in soil/plant is below detectable limit

Table 5: Range Values for Heavy Metals in Vegetation (mg/kg)

Metals	NORMAL	DEFICIENCY	EXCESSIVE	PHYTOTOXIC
Cd	NA	NA	NA	5 – 30
Zn	27-150	10 -20	100 – 400	70 – 400
Cr	0.1- 0.5	NA	5- 30	75-100
Cu	5.1-30	2 – 5	20-100	60-125
Ni	0.1 -5	NA	10-100	100

Table 6: Bioconcentration factor of metals in plant samples collected from the complex of Kaduna Refinery and Petrocheical Company, Kaduna

		Plant species	Cr	Ni	Cd	Cu	Fe	Mn	Zn
Wet	KRPC 1	*Calopogonium mucunoides*	0.06	0.01	0.14	2.83	0.00	0.05	0.05
		Setaria barbata	0.02	0.01	0.55	0.64	0.00	0.11	0.04
		Borreria verticillata	0.06	0.00	0.03	3.16	0.00	0.11	0.03
		Centrosema pubescent	0.00	0.02	1.39	1.93	0.00	0.12	0.09
	KRPC 2	*Terminalia macroptera*	0.05	0.01	0.09	7.32	0.00	0.05	0.06
		Piliostigma thonningii	0.00	0.02	0.86	4.49	0.00	0.05	0.14
	KRPC 3	*Cochlospermum tinctorium*	0.10	0.01	-	2.43	0.00	0.07	0.09
		Isoberlinia tomentosa	0.00	0.13	-	3.89	0.00	0.10	0.30
		Terminalia macroptera	0.00	0.01	-	2.28	0.00	0.04	0.03
		Monotes kerstingii	0.02	0.05	-	1.09	0.00	0.12	0.36
		Detarium microcarpum	0.00	0.11	-	1.98	0.00	0.59	0.74
	KRPC 4	*Paspalum orbiculare*	0.02	0.02	-	1.07	0.00	0.18	0.13
		Alichunea caudifolia	0.02	0.02	-	0.94	0.00	0.19	0.11

		Plant species	**Cr**	**Ni**	**Cd**	**Cu**	**Fe**	**Mn**	**Zn**
		Securinega virosa	0.00	0.01	-	1.07	0.00	0.04	0.02
		Borreria verticellata	0.04	0.02	-	1.28	0.00	0.13	0.15
Dry	KRPC 1	*Isoberlinia tomentosa*	0.02	0.03	0.06	-	0.00	0.21	0.14
		Isoberlinia doka	0.03	0.05	0.13	-	0.01	0.18	0.19
	KRPC2	*Calopogonium mucunoides*	0.04	0.13	0.41	0.62	0.01	0.26	0.26
		Spermacoce verticellata	0.12	0.32	0.83	0.00	0.01	0.20	0.10
	KRPC3	*Spermacoce verticellata*	0.00	0.03	0.27	-	0.00	0.09	0.05
		Hyptis suaveolens	0.01	0.04	0.25	-	0.00	0.07	0.10
		Dichrostachys cinerea	0.01	0.24	0.87	-	0.00	0.06	0.08
		Sida acuta	0.02	0.12	0.46	-	0.00	0.07	0.04
		Euphorbia hyssopifolia	0.01	0.06	0.38	-	0.00	0.14	0.19

Bold values signify high bioconcentration factors

DISCUSSIONS

The higher concentration of metals in soil during the wet season may be attributed to climatic variables such as precipitation, and temperature which interface with topography, drainage, soil structure/texture to determine the physicochemical properties of the soil in a particular location. This differs somewhat from the findings of Najib *et al*., (2012), who observed a higher concentration of these metals in the dry season than in the wet season in Kangar, Perlis, Malaysia. The bioavailability of metals depends on the aggregate effects of the complex interactions between moisture availability and soil physicochemical properties, metal solubility, pH, type and density of charge on soil colloids, reactive surface area of soil, 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 above acceptable limits of the observed concentrations of Cr, Cu, Ni, and Zn in soil may be attributed to petrochemical refining in the Refinery complex. Above background values of these metals have been reported wastes generated from petrochemical refineries (Asia *et al*., 2006; Erebho *et al*., 2017).

Despite the high concentrations of Cd, Zn, Cr, Cu, and Ni in the plants, they did not show any signs of toxicity.The high concentration may be a consequence of the high values observed in the soils or direct deposition from the atmosphere (Jankowski *et al*., 2019). 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 to 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, the 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 such as *Centrosema pubescens, Calopogonium mucunoides, Boreria verticellata, Termunalia macroptera, Piliostigma thonningii, Isoberlinia tomentosa, Monotes kerstingii, Detarium microcarpum, Paspalum orbiculare* and *Securinega virosa* with BCF of metals >1.0 have been described as suitable for phytoextraction of the metals for which they show such high BCF (Matanzas *et al*., 2021). Others that are tolerant to such high metal concentrations but have BCF < 1 may be classified as pseudometallophytes, the low accumulation may be as a result of the low bioavailability of the metals (Fedje *et al*., 2016; Mesa *et al*., 2017). These plants may show greater accumulation efficiency in metal availability is higher. The ability of these plants to accumulate high concentration 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).

Irrespective of metal concentration in the soil, some of the plants have been noted to show exceptional capacity to accumulate some of these metals and may constitute important excluders of these metals: *Cochlospermum tinctorum* for Cr; *Isoberlinia tomentosa,Spermacose verticellata, and Dichrostachys cinerea* for Cu; *Isoberlinia tomentosa* for Ni, *Isoberlinia doka* and *Centrosema pubescens* for Cd; *Centrosema pubescens* for Fe; and *Detarium microcarpum* for Mn and Zn.

The phytoremediation capacity of the plants studied herein has been reported by other scholars, which supports the findings in this study. For example*Centrosema pubescens* has been reported to decontaminate crude oil polluted soils (Nwaichi *et al*., 2011). Uwalaka *et al*., (2019) also reported the efficiency of *Centrosema pubescens* to remediate Pb, Cd, and Cu from polluted soils.

Calopogonium mucunoides have been shown to tolerate a high concentration of Boron and have the capacity as a phytostabiliser and phytoextractor of Boron polluted soils (DaSilva *et al*., 2021). Adewole and Bulu (2012) also reported the effectiveness of *C. mucunoides* in the phytoremediation of crude oil contaminated soil when compost organic fertilizer is applied. Arcanjo *et al*., (2016) reported the accumulation of Arsenic in roots of *Borreria verticillata* on an arsenic-contaminated site. Piliostigma thonningii has been reported as one of the early colonizers of abandoned mining sites and may thus have some tolerance to some heavy metals (Zine *et al*., 2020).

Regarding *Borreria verticilata, Cochlospermum tinctorum, Isoberlinia tomentosa, Monotes kerstingii, Detarium microcarpum, Paspalum orbiculare, Terminalia microcarpon* to the best of our knowledge, no specific studies have been done in their relation to phytoremediation.

CONCLUSION

The study of a petrochemical refinery complex that started operation in 1980 has high concentrations of Cr, Cu, Ni, Mn, Fe, and Zn in soils revealed diverse species of plants tolerant to heavy metals. Ten (10) plant species were identified as good candidates for phytoremediation because of their high bioconcentration factors. In addition, they generally produce high above-ground biomass, due to rapid vegetative growth. These plants include *Calopogonium mucunoides*, *Terminalia macroptera*, *Centrosema pubescens*, *Piliostigma thonningii*, *Cochlospermum tinctorum*, *Isoberlinia tomentosa*, *Monotes kerstingii*, *Detarium microcarpum*, *Paspalum orbiculare*, *Borreria verticilata*.

ACKNOWLEDGMENTS

The authors thank the University Board of Research (UBR) of the Ahmadu Bello University, Zaria for providing funds for this research.

Statements and Declarations

Funding: This work was supported by the Ahmadu Bello University Board of Research.

No competing Interests: The authors have no relevant financial or non-financial interests to disclose.

Author Contributions

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

REFERENCES

- Adewole, M. B., & Bulu, Y. I. (2012). Influence of Different Organic-Based Fertilizers on the Phytoremediation Potential of Calopogonium mucunoides Desv. from Crude Oil Polluted Soils. *Journal of Bioremed Biodegrad*, 3, 144. doi:10.4172/2155-6199.1000144
- Alkorta, I., Becerril, J. M., & Garbisu, C. (2010). Phytostabilization of metal contaminated soils. *Review on Environmental Health, 25*(2), 135–146. https:// doi. org/ 10. 1515/reveh. 2010. 25.2. 135
- Alloway, B. J. (1995). The origins of heavy metals in soils. *In*: B. J. Alloway, (Ed.), *Heavy Metals in Soils*, Second Ed. Blackie Academic & Professional Publishers, 1995.
- An'ongo, M. C., Bako, S. P., & Ezealor, A. U. (2005). Trace metal content in relation to populations of micro-organisms in soils along some highways in Nigeria's Guinea Savanna. *Journal of Biological Sciences*, *5*(6), 703-706.
- Arcanjo, S., Campos, N. V., Becari-Viana, I., Azevedo, A., da Silva, L. C., & Ribeiro, C. (2016). Arsenic detoxification in two populations of Borreria verticillata (*Rubiaceae*) with differential tolerance to the metalloid. *Australian Journal of Botany*, *64*(6). DOI: 10.1071/BT16031
- Asia, I. O., Enweani, I. B., & Eguavoen, I. (2006). Characterization and treatment of sludge from the petroleum industry. *African Journal of Biotechnology*, *5*(5), 461-466.
- Awa, S. H., & Hadibarata, T. (2020). Removal of heavy metals in contaminated soil by phytoremediation mechanism: A review. *Water Air Soil Pollution*, 231, 47. https:// doi. org/10. 1007/ s11270- 020- 4426-0
- Bako, S. P., Odiwo, J. E., & Ezealor, A. U. (2008). Plant diversity in relation to anthropogenic Trace Metals in soils of selected sites in Nigeria's Guinea Savanna. *International Journal of Environmental Pollut*ion: Special issue on *Biogeochemistry of toxic trace metals in Water, Soil and Plant*, 33(2/3), 185-194.
- Bako, S. P., Bhwankot, E. S., Ezealor, A. U., Chia, A. M., & Funtua, I. I. (2009a). Human health implications of trace metal contents in parts of Maize (*Zea mays* L.) plants cultivated along highways in Nigeria's Guinea Savanna. *Soil RemediationSeries: Pollution Science, Technology and Abatement*. Lukas Aachen and Paul Eichmann (Eds). Nova Science Publishers, Inc. Hauppauge, New York, United States of America, pp. 345-356. (Available online at www.novapublishers.com)
- Bako, S. P., Bhwankot, E. S., Ezealor, A. U., Chia, A. M., & Funtua, I. I. (2009b). Human health implications of trace metal contents in parts of Cowpea (*Vignaunguiculata*L.Walp.) plants cultivated along highways in Nigeria's Guinea Savanna. *Soil RemediationSeries: Pollution Science, Technology and Abatement*. Lukas Aachen

and Paul Eichmann (Eds) Nova Science Publishers, Inc. Hauppauge, New York, United States of America 2009; pp.357-368. (Available on-lineatwww.novapublishers.com).

- Bako, S. P., Funtua, I. I., & Ijachi, M. (2005). Heavy metal content of some Savanna plant species in relation to air pollution. *Water Air Soil Pollut*ion, *161*(1-4), 125-136.
- Bech, J., Duran, P., Roca, N., Poma, W., Sánchez, I., Barceló, J., ... & Poschenrieder, C. (2012). Shoot accumulation of several trace elements in native plant species from contaminated soils in the Peruvian Andes. *Journal of Geochemical Exploration*, *113*, 106-111. https:// doi. org/ 10. 1016/j. gexplo. 2011. 04. 007
- Bech, J., Duran, P., Roca, N., Poma, W., Sánchez, I., Roca-Pérez, L., ... & Poschenrieder, C. (2012a). Accumulation of Pb and Zn in Bidens triplinervia and Senecio sp. spontaneous species from mine spoils in Peru and their potential use in phytoremediation. *Journal of Geochemical Exploration*, *123*, 109-113. https:// doi. org/ 10. 1016/j. gexplo. 2012. 06. 021
- Bernasconi, G. B. (1996). AXIL-QXAS, *Instruction Manual*. IAEA, Vienna, pp. 7-11.
- Bununu, Y. A., Ludin, A. N. M., & Hosni, N. (2015). City profile: Kaduna. *Cities*, 49, 53–65.
- Canadian Council of Ministers of the Environment. (2009). *Canada environment quality guidelines*. Published by the Canadian Council of Ministers of the Environment. Winnipeg, Canada pp. 8
- Cataldo, D. A., & Widung, R. E. (1978). Soil and plant factors influencing the accumulation of heavy metals by plants. *Environmental Health Perspective*, 27, 149-159.
- Chapman, E. E. V., Moore, C., & Campbell, L. M. (2019). Native plants for revegetation of mercury- and arsenic contaminated historical mining waste—can a low-dose selenium additive improve seedling growth and decrease contaminant bioaccumulation? *Water Air Soil Pollution*, 230, 225. https:// doi. org/ 10. 1007/ s11270- 019- 4267-x
- da Silva, V. N., Frachia, C. D. L., Barbosa, I. C. F., da Silva, M. B., de Paiva, W. D. S., Souza, L. A., ... & de Camargos, L. S. (2021). Tolerance and phytoremediation potential of Calopogonium mucunoides to boron. *Environmental Quality Management*, *30*(3), 27-36.
- Dávila, O. G., Gómez-Berna, B., & Ruíz-Huerta, E. S. (2012). Plants and Soil Contamination with Heavy Metals in Agricultural Areas of Guadalupe, Zacatecas, Mexico. Environmental Contamination. Dr.JatinSrivastava (Ed.), 2012; ISBN: 978-953-51-0120-8, INTECH Publishers, Available from: http://www.intechopen.com/books/environmental-contamination/plants-and-soil-contamination-with-heavymetals-
- Duruibe, J. O., Ogwuegbu, M. O. C., & Egwurugwu, J. N. (2007). Heavy metal pollution and human toxic effects. *International Journal of Physical Science*, *2*(5), 112-118.
- Ekmekyapar, F., Sabudak, T., & Seren, G. (2012). Assessment of heavy metal contamination in soil and wheat (*Triticumaestivum* L.) plant around the Corlu-Cerkezkoy highway in Thrace region. *Global Nest Journal*, *14*(4), 496-504.
- European Commission Director-General, Environment (ECDGE). (2010). *Heavy metals and organic compounds from wastes used as organic fertilizers. Final Report*, July 2010. WPA Consulting Engineers Inc. Ref. Nr. TEND/AML/2001/07/20, pp73-74. http;//ec.europa.eu/environment/waste/compost/pdf/hm_finalreport.pdf
- Fedje, K. K., Sierra, C., & Gallego, J. R. (2017). Enhanced soil washing for the remediation of a brownfield polluted by pyrite ash. *Soil and Sediment Contamination*, 26, 377– 390. https:// doi. org/ 10.1080/ 15320 383. 2017. 13193 35
- Foroozanfar, M. (2017). Environmental control in petroleum operations. *Journal Clean WAS*, 1(2), 18-22.
- Funtua, I. I. (1999). Application of the transmission emission method in ED-XRF for the determination of trace elements in geological and biological materials. *Journal of Trace and Microprobe Techniques*, 17, 293-297.
- Galfati, I., Bilal, E., Sassi, A. B., Abdallah, H., & Zaïer, A. (2011). Accumulation of heavy metals in native plants growing near the phosphate treatment industry, Tunisia. *Carpathian Journal of Earth and Environmental Sciences*, *6*(2), 85-100.
- Jankowski, K., Malinowska, E., Ciepiela, G. A., Jankowska, J., Wiśniewska-Kadżajan, B., & Sosnowski, J. (2019). Lead and cadmium content in grass growing near an expressway. *Archives of environmental contamination and toxicology*, *76*, 66-75. https://doi.org/10.1007/s00244-018-0565-3
- Kabata-Pendias, A., & Pendias, H. (1992). *Trace elements in soils and plants*. CRC Press, Boca Raton, USA. Pp. 365.
- Knox, A. S., Gamerdinger, A. P., & Adriano D. C. (1999). Sources and Practices Contributing to Soil Contamination. *In*: Adriano, D. C., Bollag, J. M., Frankenberg, W. T. Jr, Sims, R. C. (Eds.), *Bioremediation of the Contaminated Soils. Agronomy Series*, 37, 53-87.
- Kotrba, P., Najmanova, J., Macek, T., Ruml, T., & Mackova, M. (2009). Genetically modified plants in phytoremediation of heavy metal and metalloid soil and sediment pollution. *Biotechnology advances*, *27*(6), 799-810.
- Kurhaluk, N., Tkachenko, H., & Hetmański, T. (2021). Profile of Heavy Metals and Antioxidant Defense in the Muscle Tissues of Pigeons (*Columba livia*f. *Urbana*) from Anthropogenically Transformed Areas in the Pomeranian Region (Northern Poland), *Archives of Environmental*

Contamination and Toxicology, 21, 825-830. https://doi.org/10.1007/s00244-021-00825-3

- Lar, U. A. (2013). Trace elements and health: an environmental risk in Nigeria. *Earth Sciences*, *2*(3), 66-72.
- Lars, J. (2003). Hazards of heavy metal contamination. *British Medical Bulletin*, 68, 167-182.
- Ligenfelter, D. D., & Hartwig, N. L. (2007). *Introduction to weeds and herbicides*. Pennsylvania State University: Publication Distribution Center, 1–28. Retrieved July 20, 2018. https:// exten sion. psu. edu/ intro ducti on- to- weeds- and- herbi cides
- Liu, X. M., Wu, Q. T., & Banks, M. K. (2005). Effect of simultaneous establishment of *Sedum afridi* and *Zea mays* on heavy metal accumulation in plants. *Int J Phytoremediation*, *7*(1), 43-53. doi: 10.1080/16226510590915800
- Maine, M. A., Sune, N. L., & Lagger, C. (2004). Chromium bioaccumulation: Comparison of the capacity of floating aquatic macrophytes. *Water Res*, 38, 1494-1501.
- Mandzhieva, S. S., Minkina, T. M., Chaplygin, V. A., Motuzova, G. V., Sushkova, S. N., Bauer, T. V., & Nevidomskaya, D. G. (2016). Plant contamination by heavy metals in the impact zone of Novocherkassk Power Station in the south of Russia. *Journal of soils and sediments*, *16*, 1383-1391. https:// doi. org/ 10. 1007/ s11368- 015- 1098-2
- Matanzas, N., Afif, E., Díaz, T. E., & Gallego, J. R. (2021). Phytoremediation potential of native herbaceous plant species growing on a paradigmatic brownfield site. *Water, Air, & Soil Pollution*, *232*(7), 290. https://doi.org/10.1007/s11270-021-05234-9
- Mathews-Amune, O. C., & Kakulu, S. (2013). Investigation of heavy metal levels in roadside agricultural soil and plant samples in Adogo, Nigeria. *Academic J Environ Sci*, *1*(2), 31-35.
- Megateli, S., Semsari, S., & Couderchet, M. (2009). Toxicity and removal of heavy metals (Cadmium, Copper, and Zinc) by *Lemnagibba*. *Ecotoxicol Environ Safety*, 72, 1774-1780.
- Mesa, V., Navazas, A., Gonzalez-Gil, R., Gonzalez, A., Weyens, N., Lauga, B., ... & Peláez, A. I. (2017). Use of endophytic and rhizosphere bacteria to improve phytoremediation of arsenic-contaminated industrial soils by autochthonous Betula celtiberica. *Applied and Environmental Microbiology*, *83*(8), e03411-16. https:// doi. org/ 10. 1128/ AEM. 03411- 16
- Monaci, F., Trigueros, D., & Mingorance, M. D. (2020). Phytostabilization potencial of *Erica australis L*. and *Nerium oleander L*.: A comparative study in the Riotinto mining area (SW Spain). *Environmental Geochemistry and Health*, 42, 2345–2360. https:// doi. org/ 10. 1007/ s10653- 019-00391-7
- Mustapha, H. I., van Bruggen, J. J. A., & Lens, P. N. L. (2015). Vertical subsurface flow constructed wetlands for polishing secondary Kaduna refinery wastewater in Nigeria. *Ecological Engineering*, 84, 588–595.
- Najib, N. W., Mohammed, S. A., Ismail, S. H., & Ahmad, W. A. (2012). Assessment of heavy metal in soil due to human activities in Kangar, Perlis, Malaysia. *Int J Civil Environ Eng [Internet]*, *12*(6), 28-33.
- Nouri, J., Khorasani, N., Lorestani, B., Karami, M., Hassani, A. H., & Yousefi, N. (2009). Accumulation of heavy metals in soil and uptake by plant species with phytoremediation potential. *Environmental earth sciences*, *59*, 315-323.
- Nwaichi, E. O., Osuji, L. C., & Onyeike, E. N. (2011). Evaluation and Decontamination of Crude Oil-Polluted Soils Using *Centrosema pubescen* Benth and Amendment- Support Options. *International Journal of Phytoremediation*, *13*(4), 373-382. http://dx.doi.org/10.1080/15226514.2010.495144
- Odeyemi, O., & Ogunseitan, O. A. (1985). Petroleum Industry and its Pollution Potential in Nigeria. *Oil and Petrochemical Pollution*, 2, 223-229.
- Olayinka-Olagunju, J. O., Dosumu, A. A., & Olatunji-Ojo, A. M. (2021). Bioaccumulation of Heavy Metals in Pelagic and Benthic Fishes of Ogbese River, Ondo State, South-Western Nigeria. *Journal of Water Air Soil Pollution*, 232, 44.
- Ombugadu, A., Mwansat, G. S., Manu, S. A., Chaskda, A. A., Ottosson, U., Njila, L. H., ... & Leventis, A. (2014). Comparison on bioaccumulation of heavy metals in birds and plants species in Amurum forest reserve and the Nigerian National Petroleum Corporation (NNPC) Refinery area of Kaduna, Nigeria. *Int J Adv Stud Eng Sci Invent*, *2*(1), 26-32.
- Pathak, C., & Mandalia, H. C. (2012). Petroleum Industries: Environmental Pollution Effects, Management and Treatment Methods. *International Journal of Separation for Environmental Sciences*, *1*(1), 55-61.
- Pošćić, F., Fellet, G., Vischi, M., Casolo, V., Schat, H., & Marchiol, L. (2015). Variation in heavy metal accumulation and genetic diversity at a regional scale among metallicolous and non-metallicolous populations of the facultative metallophyte Biscutella laevigata subsp. laevigata. *International Journal of Phytoremediation*, *17*(5), 464-475. https:// doi. org/ 10. 1080/ 15226 514. 2014. 922921
- Robinson, B. H., Bañuelos, G., Conesa, H. M., Evangelou, M. W., & Schulin, R. (2009). The phytomanagement of trace elements in soil. *Critical Reviews in Plant Sciences*, *28*(4), 240-266. https:// doi. org/ 10. 1080/ 07352 68090 30354 24
- Schat, H., Llugany, M., & Bernhard, R. (2000). Metal-specific patterns of tolerance, uptake, and

transport of heavy metals in hyperaccumulating and nonhyperaccumulating metallophytes. In N. Terry, G. Banuelos (Eds.), Phytoremediation of contaminated soil and water (1st ed. pp. 171-188). *CRC Press LLC.*

- de Souza, D. C., Fontaneli, A. C., Peron, A. P., & Froehner, S. (2021). Physiological effects of exposure to copper and chromium in three floating aquatic macrophyte species. *Water, Air, & Soil Pollution*, *232*, 1-12. https:// doi. org/10. 1007/ s11270- 020- 04960-w
- Tanimu, J., Uyovbisere, E. O., Lyocks, S. W. J., & Tanimu, Y. (2013). Cowdung management on the calcium and magnesium content and total microbial population in the Northern Guinea Savanna of Nigeria. *Global Journal of Biology, Agriculture and Health Sciences*, *2*(2), 7-11.
- Tanimu, Y., Bako, S. P., & Tiseer, F. A. (2013). Effects of sewage pollution on water quality of Samarustrea, Zaria, Nigeria. *In*: Fernando Sebastian Garcia Einschlag and Luciano Carlos (Eds). Waste Water: Treatment Technologies and Recent Analytical Developments, INTECH Publishers, Rijeka, Croatia, pp189-195.
- Tapia, Y., Loch, B., Castillo, B., Acuña, E., Casanova, M., Salazar, O., ... & Antilén, M. (2020). Accumulation of sulphur in Atriplex nummularia cultivated in mine tailings and effect of organic amendments addition. *Water, Air, & Soil Pollution*, *231*, 1-14. https:// doi. org/ 10. 1007/ s11270- 019- 4356-x
- Teodoro, M., Hejcman, M., Vítková, M., Wu, S., & Komárek, M. (2020). Seasonal fluctuations of Zn, Pb, As and Cd contents in the biomass of selected grass species growing on contaminated soils: Implications for in situ phytostabilization. *Science of the Total Environment*, *703*, 134710. https:// doi. org/ 10. 1016/j. scito tenv. 2019. 13471
- The United States Environmental Protection Agency (USEPA). (1993). *Clean Water Act*, Section, 503, 58(32). www.epa.gov.
- USDA (United States Department of Agriculture). (2000). Heavy metal soil contamination.Soil Quality. *Urban Technical Note*, 3, 1-7.
- Uwalaka, B. N., Osuagwu, G. G. E., & Udogu, O. F. (2018). Heavy Metal and Mineral Contents of *Centrosema pubescens* and *Pueraria phaseoloides* used as Phytoremediators in Crude Oil Polluted Soil. *Journal of Science and Sustainable Technology*, *1*(2), 328-344.
- Uwidia, I. E., Asia, I. O., & Jatto, O. E. (2017). Correlation Studies of Some Parameters in Petroleum Wastewater Obtained From Warri, Delta State. *Nigeria International Journal of Scientific & Engineering Research*, *8*(7), 380-385.
- Wei, Z., Van Le, Q., Peng, W., Yang, Y., Yang, H., Gu, H., ... & Sonne, C. (2021). A review on phytoremediation of contaminants in air, water and soil. *Journal of hazardous materials*, *403*, 123658. https://doi. org/ 10. 1016/j. jhazm at. 2020. 123658
- World Health Organization, (WHO). (1996). *World Health Organization Guidelines for Drinking-Water Quality*.1996; 2nd Ed., Vol. 2. Health Criteria and Supporting Information, WHO, Geneva.
- Zine, H., Midhat, L., Hakkou, R., Mariam, M. E., & Ouhammou, A. (2020). Guidelines for a phytomanagement plan by the phytostabilization of mining wastes. *Scientific African*, 10, 1-20.
- Zu, Y., Li, Y., Chen, J., Chen, H., Qin, L., & Christian, S. (2005). Hyperaccumulation of Pb, Zn, and Cd in herbaceous plants grown on lead-zinc mining area in Yunnan, China. *Environ International*, *31*(5), 755–762.