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STATUS OF HEAVY METALS AND REMEDIATION POTENTIAL OF INDIGENOUS PLANTS AT CONTAMINATED BENIN CITY AND ABUDU SITES OF EDO, NIGERIA

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Abstract

Assessment of heavy metals (HMs) concentrations and remediation potential of indigenous plants in urban environments are necessary for safeguarding and restoring soil quality. This study evaluated the status of total HMs and remediation potential of the predominant plant species growing at contaminated sites in both Benin City and Abudu. The species were sampled along with soil around auto-mechanic workshops and from two respective uncontaminated sites and analyzed for total concentrations of eight metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) with an Atomic Absorption Spectroscopy. The geo-accumulation index revealed that both sites were extremely polluted with four HMs in the order of Fe > Zn > Mn > Cu. Benin was severely polluted with Pb, Cd and Cr and moderately to highly polluted with Ni, while Abudu was moderately to severely polluted with Pb and Cd, moderately polluted with Cr and slightly polluted with Ni. *Eleucine indica* identified at Abudu and *Perperomia pellucida* in Benin City were both found to contain toxic levels of four HMs (Fe, Zn, Cd and Cr), only *E. indica* at Abudu was found to exceed the limit of Cu, Pb and Ni set for plants while the level of Mn in both species were far from the permissible limit set by WHO. No plant was proven to be a hyperaccumulator but such potential towards Zn, Pb and Cd was observed for *E. indica* while the same phenomenon could be ascribed to *P. pellucida* for Cu and Zn if assisted with soil amendment. Heavy metal pollution levels of the sites demand clean up and predominant indigenous plant species can be used to manage them.

Keywords: *Eleucine indica*; heavy metals; hyperaccumulator; *Perperomia pellucida*; pollution remediation

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Introduction

Soil pollution from waste generation and inappropriate disposal in urban areas of Edo State have become worrisome because of the concentrations of heavy metals (HMs) released into the environment. These non-biodegradable elements are usually transported through surface or ground water into surrounding soils where excessive levels could pose risks to humans and the ecosystem (McLaughlin *et al*., 2000). Interestingly, plant species that thrive in such soils (metallophytes) can be selected for remediation if they are hyperaccumulators (accumulate and tolerate up to 100 times metal(s) concentration(s) as much as normal plants in their shoots i.e. > 100 mg kg $^{-1}$ (0.01%) Cd or >1,000 mg kg^{-1} (0.1%) of Cu, Co, Cr, Ni or Pb, or >10,000 mg kg^{-1} (1%) of Fe, Mn or Zn on a dry matter basis (Baker and Brooks, 1989).

The most widely spread polluted sites with HMs in Nigeria could be auto-mechanic workshops due to prevalent activities which include repair of engine parts, panel beating, welding, disposal of batteries, and spent engine oil. Studies around such workshops for concentrations (mg kg^{-1}) of some HMs were reported to exceed established guideline at Ibadan (Adelekan and Abegunde, 2011) and in Port Harcourt (Warmate *et al*., 2011). Meanwhile, many of the technologies for the remediation of HM contaminated soils are very expensive and do not achieve a long-term or aesthetic solution (Cao *et al*., 2002), unlike when plants are used for the same purpose (phytoextraction): a process that utilizes hyperaccumulators. Identification of a hyperaccumulator requires assessing the potential of a plant for remediation by calculating its bioaccumulation factor (BAF), i.e., the metal concentration ratio in root to soil, and the translocation factor (TF), i.e., the ratio of metal concentration in shoot to root (Xiao *et al*., 2017; Swang et al., 2021). The biological accumulation coefficient (BAC), which is the metal content ratio in shoot to soil, may also be used. Over 400 plant species have been discovered in Europe, America, Australia and New Zealand and the use of native species are far preferred to exotic ones due to their relative chances of survival, growth and reproduction (Yoon *et al*., 2006).

However, the accumulation of metals by plants is affected by soil factors such as pH, organic matter, cation exchange capacity, as well as the species, cultivars and age of plant (Yoon *et al*., 2006). Useful information on the abilities of diverse plant species to absorb and transport metals under different soil conditions will enable the selection of ideal plants for remediation of polluted soils (Nouri *et al*., 2009) and set up legislature or guidelines on disposal of these metals in such environment.

Environmental and atmospheric deposition of metals in Southern Edo is on the increase and there is a dearth of knowledge on the suitability of native plants for remediation purpose. Appropriate protection and restoration of soil quality contaminated by these xenobiotics require their description and remediation. Consequently, the objectives of this study are to: (1) determine the total concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn at the study sites, (2) evaluate the severity of soil contamination, (3) identify the indigenous dominant plants and quantify concentrations of the test metals in them. (4) assess the remediation potential of the dominant plant species, and (5) assess the factors that influence the metals concentrations in soils, and their uptake by the plant species.

Materials and Methods

The study area

The study was carried out at Benin City and Abudu town in Edo State, Nigeria (Figure 1) which lies between latitude 5° 35′ N -7° 3′ N and longitude 5° 00′ E –6° 32′ E (Imadojemu *et al*., 2018). Rainfall is between 2000 –2540 mm with a mean monthly temperature of 28°C which may reach 34°C between the months of February and March. The humidity usually records highest value of 80 -90% around August and lowest of 40 –50% from November-March. The landscape range from gentle slope to uplands and the major geological materials from which soils are formed are sand, shale and limestone. However, the Benin area, generally marked by top Red Tropical Soils, is underlain by sands, sandy clays and ferruginous sandstone (Andre-Obayanju *et al*., 2017) and drained by two major rivers – Ikpoba River, towards the Northeast, and Ogba River, in the southwest of the city. While Abudu is generally a lowland (plain) area, primarily sands (mainly yellowish due to limonite content) and sandstone (90%) with a few shale intercalations devoid of mountainous hills and drained by tributaries of the River Niger (Asadu, 2015).

Site characterization and sample collection

A total of twelve plant species along with soil samples were collected around two auto-mechanic workshops which have existed for over 2 decades. Such sites are usually contaminated with heavy metals because of indiscriminate dumping of waste from the maintenance and repair of vehicles. First of all, assessment of the distribution of plant species was undertaken to identify the predominant one as *Peperomia pellucida* in Benin City and three of them were sampled along with soil from the root zone (0 - 20 cm). Another three species of the same plant were sampled along with soil from an uncontaminated site located at about 300 m away to serve as control. A similar process was carried out at Abudu town where the predominant plant was identified as *Eleusine indica,* also around an auto- mechanic workshop. Three of the species were sampled along with soil as described before and another three were sampled from a distant uncontaminated site discovered at about 250 m away.

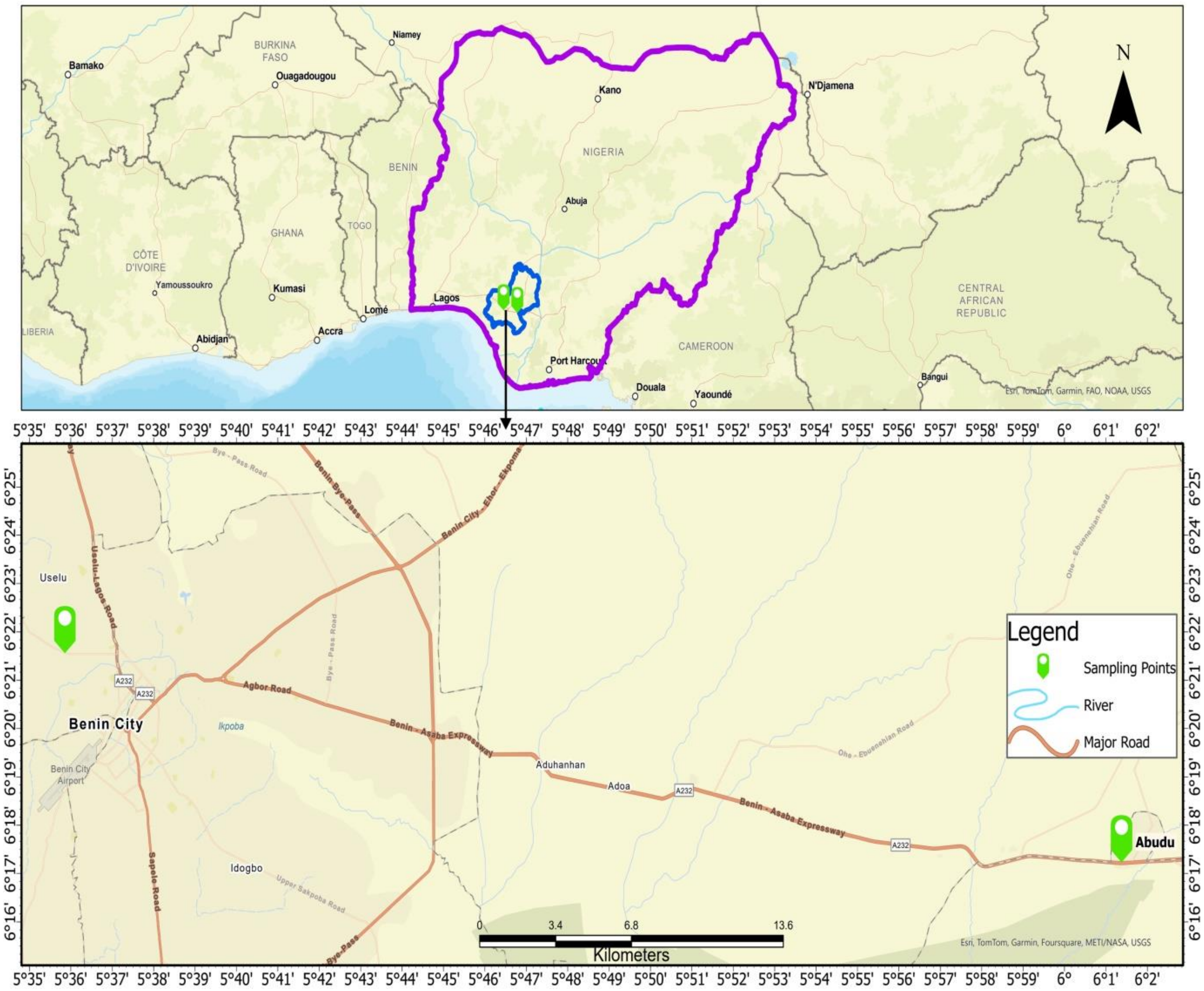


Figure 1: Location map of the study area

All soil and plant samples were sealed in clean polythene bags, labelled appropriately and transported to the laboratory. Thereafter, the plants samples were divided into roots and shoots, washed gently with distilled water and air-dried at room temperature for two weeks before they were ground to powder using a Wiley Mill. The soil samples were air-dried at room temperature for two weeks and then sieved by a 2-mm stainless steel sieve and stored in polyethylene bags until analyzed.

Chemical analysis of plant and soil samples

The plant samples were analyzed for the HMs based on the procedure of Akan *et al.* (2009) before their content on each of the final digest (with a mixture of $HNO_3 + H_2SO_4 + HClO_4$ acids) were determined using Perkin-Elmer Analyst 300 AAS (Yoon *et al.*, 2006). Determination of the total metal content of the soil was assessed by weighing 0.5 g of the sieved soil sample into a 125 cc conical flask and heating with a mixture of 20 ml conc. HNO_3 + 5 ml $HClO_4$ + 2 ml of H_2SO_4 until dense fumes were driven off (Hossner, 1996). Then, the digest was cooled, diluted to 50 ml and filtered into a 100 ml volumetric flask. Thereafter, 10 ml of each of the digested sample were analyzed for the test metals using an Atomic Absorption Spectroscopy (AAS).

Soil particle-size distribution was assessed by the technique described by Rowell (1994), soil pH was measured in a 1:2 soil to deionized water and the saturated extract was used for measuring the electrical conductivity (EC) with a conductivity meter. Total N were calculated by the micro-Kjeldhal method (Bremner, 1996); Organic carbon was determined using the modified Walkley – Black method (Nelson and Sommers, 1996); available P was determined following Bray No 1 method (Kuo, 1996), exchangeable bases (Ca, Mg, K and Na) were extracted with 1 N NH_4OAC (ammonium acetate) buffered at pH 7. Exchangeable K and Na were read on a flame emission photometer while Ca and Mg were determined with an AAS. Effective cation exchange capacity (ECEC) was calculated by addition of exchangeable bases (Ca, Mg, K, and Na) and exchange acidity ($Al^{3+} + H^{+}$) (Anderson and Ingram, 1993).

Data Analysis

Calculation of phytoremediation potential

The remediation potential of the plants was assessed by calculating bioaccumulation factor (BAF), the efficiency of plants to accumulate HMs from soil to root and translocation factor (TF), the ability of plants to translocate heavy metals from roots to shoots, based on the formula by Xiao *et al.* (2017).

BAF=*C*root/*C*soil and TF=*C*shoot/*C*root; Where Croot is metal concentration in root, *C*soil is metal concentration in soil, and *C*shoot is metal concentration in plant shoot. Plants with both TF and BAF > 1 have phytoextraction potential while those with BCF >1 and TF < 1have the potential to be used for phytostabilization. The biological accumulation coefficient (BAC) was also used to calculate the ability of a plant to absorb and transport HMs from soil and store in shoot, i.e., ratio of metal concentration in shoot to that in soil, *C*shoot/*C*soil as described by Branquinho *et al.* (2007).

Assessment of heavy metal pollution

Geoaccumulation factor

The geoaccumulation index (Igeo) was used to assess the degree of metal pollution in soils (Muller, 1969). It is expressed as: $I_{geo} = \log_2 (C_n/1.5B_n)$. C_n and B_n are concentrations of metal in sample and background, respectively. Factor 1.5 is the surroundings matrix correction factor owing to lithogenic effect. The index is made up of 7 grades (Table 1.).

Contamination factor

The contamination factor (Cf) is the ratio of targeted metal in the soil to its background value, as provided by Hakanson (1980). It is calculated as $Cf_i = Cs_i/Cb_i$; where Cs_i and Cb_i are the measured concentrations of the examined metal in the contaminated sample and the control, respectively. Classification of the values is shown in Table 1.

Degree of contamination

The degree of contamination (C_{deg}) is defined as the sum of the contamination factors (Cf) for all trace elements (Hakanson, 1980) as shown in Table. It was designated as the summation of Cf of each sample which describes the degree of pollution of a site caused by all the metals analyzed. A value of C_{deg} which exceeds 20 suggests the need to reduce heavy metal from soil (Ghazaryan, 2015).

Pollution load index

Pollution load index (PLI) was deduced for each site to assess the extent of HM contamination as developed by Tomlinson (1980) as: $PLI = {}^{n}\sqrt{(Cf_1 x\ Cf_2 x \ldots x\ Cf_n)}$; where n = number of HMs considered, and Cf is the contamination factor. Interpretations of the classes are displayed in Table 1.

Table 1: Models and categories for the description of soil contamination

Model	Class	Description
Contamination factor [1]	$Cf < 1$	Low contamination
	$1 \leq Cf < 3$	Moderate contamination
	$3 \leq Cf < 6$	Considerable contamination
	$Cf \geq 6$	Very high contamination
Degree of contamination [1,2]	$C_{deg} < 6$	Low contamination
	$6 \leq C_{deg} < 12$	Moderate contamination
	$12 \leq C_{deg} < 24$	Considerable contamination
	$C_{deg} \geq 24$	Very high contamination
Pollution load index [3]	$PLI < 1$	Perfection contamination
	$PLI = 1$	Baseline level of pollution
	$PL1 > 1$	Deterioration of site quality
Geoaccumulation index [4]	$Igeo \leq 0$	Unpolluted
	$0 < I_{geo} \leq 1$	Unpolluted to moderately polluted
	$1 < I_{geo} \leq 2$	Moderated polluted
	$2 < I_{geo} \leq 3$	Moderately to severely polluted
	$3 < I_{geo} \leq 4$	Severely polluted
	$4 < I_{geo} \leq 5$	Severely to extremely polluted
	$1_{geo} > 5$	Extremely polluted

[1] Hakanson, 1980; [2] Ghazaryan, 2015; [3] Tomlinson, 1980); [4] Muller, 1969.

Statistical analysis

All data were processed using Microsoft Excel and SPSS (Statistic Programme for Service and Solutions) statistical program package (Release 21.0) was used to analyze them. Pearson product moment correlation coefficients (r) were employed to determine the relationships of quantitative variables at 0.05 and 0.01 probability levels.

Results

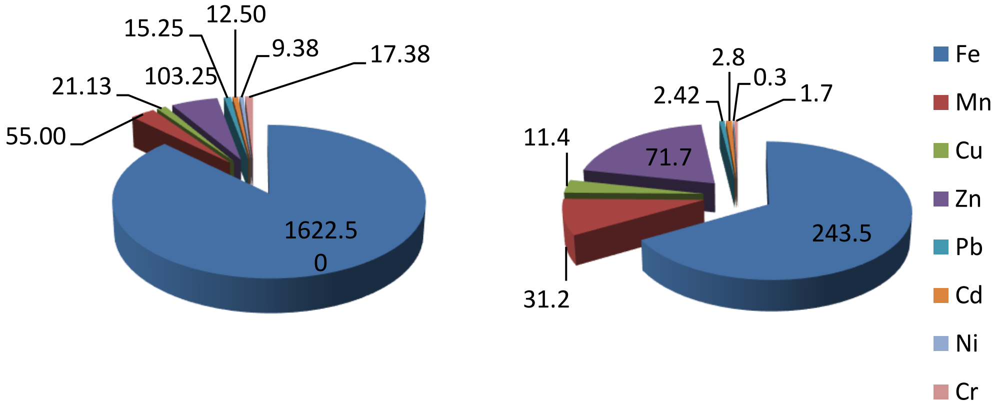
The soil physical and chemical properties are shown in Table 2. The texture of Benin was sandy loam while Abudu with relatively more percentage of sand was loamy sand. The soil pH of Benin was slightly acid (6.1) while Abudu was neutral (6.7) as rated by Batjes (1995) in comparison to their control sites which were very strongly acid. Although the values of their available P were close, soil in Benin was low, < 15 mg/kg $^{-1}$, while Abudu was moderate (15.93 mg/kg). Organic C content of the polluted soil at Abudu was moderate (12.82) while in Benin was low (9.25). The ECEC of the soils were low, all < 10.0 cmol kg^{-1} based on the rating by Landon (1991).

Table 2: Soil physicochemical properties of the study areas

Region	Status	Sand	Silt	Clay	Texture	pH	Org. C	N	Av. P	ECEC
			(g kg^{-1})				g kg^{-1}		(mg kg^{-1})	
Benin	Polluted	810	50	140	SL	6.1	9.25	2.16	14.02	4.96
	Control	820	40	140	SL	4.7	7.89	1.83	19.84	4.44
Abudu	Polluted	870	63	67	LS	6.7	12.82	0.52	15.93	2.66
	Control	860	40	100	LS	4.6	7.26	2.32	13.47	3.76

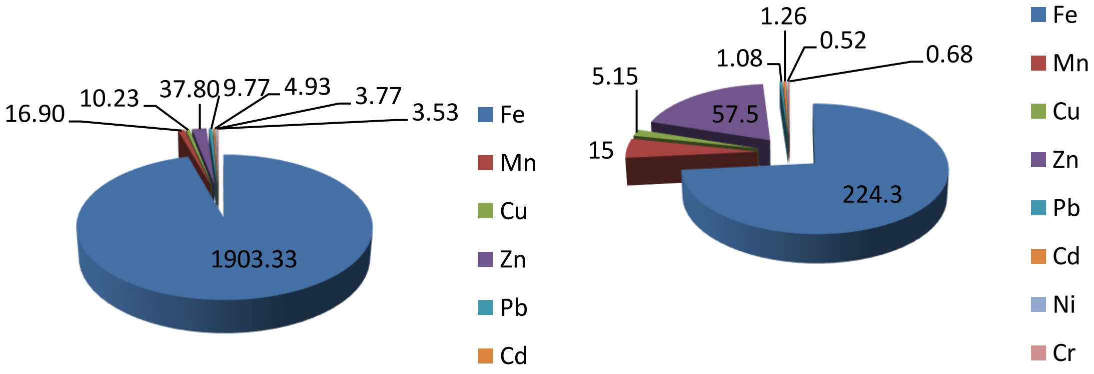
Heavy metal components of the soils

In Benin City, the average concentrations (mg kg^{-1}) of these metallic elements within the contaminated site were as follows: Fe (1, 622.50), Zn (103.25), Mn (55.00), Cu (21.13), Cr (17.38), Pb (15.25), Cd (12.50) and Ni (9.38) (Fig. 1). The control soil contained relatively lower concentrations of the HMs with a slight difference in the order of abundance: Fe (264.8) > Zn (42.7) > Mn (18.6) > Cu (6.79) > Cd (1.67) > Pb (1.43) > Cr (0.89) > Ni (0.68). The highest mean level of Fe (1,903.33) was computed in Abudu contaminated soil (Fig. 2). Concentration of this element was about 95.60 % of the other tested elements added together. The trend of heavy metal accumulation in soil was Fe > Zn > Mn > Cu > Pb > Cd > Ni > Cr. There were relatively lower levels of these metals in the control soil where Fe (176.9) was most concentrated and Ni (0.76) was least, based on the recorded order of abundance: Fe > Zn > Mn > Cu > Cd > Cr > Pb > Ni.



(a) Contaminated soil (b) Control

Figure 1: Levels of HMs in contaminated and control soils at Benin City.



(a) Contaminated soil (b) Control

Figure 2: Levels of heavy metals in contaminated and control soils at Abudu.

The study areas based on the index of geoaccumulation (Igeo) showed that they were extremely polluted (Igeo > 5) with Fe, Mn, Cu and Zn (Table 3). Classification of the pollution levels of Pb and Cd varied among the sampled areas: Benin was severely polluted (3 < Igeo ≤ 4) while Abudu was moderately to severely polluted (2 < Igeo ≤ 3) with the elements. The levels of Ni (0 < Igeo ≤ 1) were classified as slightly polluted in Abudu but between moderate to highly pollution in Benin (2 < Igeo ≤ 3). Concentrations of Cr were severe (3 < Igeo ≤ 4) in Benin and moderate (1 < Igeo ≤ 2) in Abudu.

Table 3: Geoaccumulation index, contamination factor, degree of contamination and pollution load index for heavy metals in soils at Benin and Abudu sites

Sample	Heavy metals (g kg^{-1})								C_{deg}	PLI
	Fe	Mn	Cu	Zn	Pb	Cd	Ni	Cr		
	Geoaccumulation factor									
Benin	18.13	9.41	6.58	11.52	3.86	3.80	2.09	3.37		
Abudu	17.78	8.02	5.97	10.47	2.90	2.70	0.93	1.71		
	Contamination factor									
Benin	6.13	2.96	3.11	2.42	10.66	7.49	13.79	19.5	66.07	5.23
Abudu	10.8	0.73	1.12	0.67	8.49	2.50	4.96	2.54	31.78	2.27

C_{deg} = Degree of contamination; PLI = Pollution load index

The contamination factor (Table 3) described soil in Benin City as very high ($Cf \geq 6$) in levels of Fe, Pb, Cd, Ni and Cr. In Benin, Cu was considerably high ($3 \leq Cf < 6$) while Mn and Zn were moderate ($1 \leq Cf < 3$) while in Abudu, Fe and Pb were high, with considerable levels ($3 \leq Cf < 6$) of Ni, moderate levels ($1 \leq Cf < 3$) of Cu and Cd as well as low concentrations ($Cf < 1$) of Mn and Zn. The degree of soil contamination (CD) was more in Benin City (66.07) than Abudu (31.78) and both exceeded 20 which suggested they needed to be cleaned up. Similarly, the PLI values in both Benin (5.23) and Abudu (2.27) were >1 which implied that the sites were deteriorating.

The present study revealed the concentrations of metals in both sampled plants and the permissible limit set up for plants by WHO (Table 4). The concentrations of Fe in the plants exceeded that (20 mg kg $^{-1}$) set up for plants. The limit (mg kg $^{-1}$) set up for Mn (200) was higher than the values recorded for both test plants; 10.53 for the species in Benin and 34.30 for the one selected at Abudu.

Table 4: Heavy metal concentrations in the predominant plants and permissible limits

Heavy metal	Levels of heavy metals (mg kg^{-1}) in whole plant				Limits in plants (mg kg^{-1})
	***P. pelucida* in Benin**		***E. indica at* Abudu**		
	Range	**Mean**	**Range**	**Mean**	
Fe	483.0-630.0	603.00	513.8 - 753.3	634.17	20.0
Mn	8.0 - 13.0	10.53	22.3 - 42.8	34.03	200.0
Cu	2.5-10.0	6.25	12.9 - 18.2	16.13	10.0
Zn	54.0 - 86.0	68.88	68.7 - 118.2	97.67	50.0
Pb	Trace	trace	11.3 - 18.0	14.97	10.0
Cd	2.0 - 5.5	3.63	8.3 - 12.2	9.63	0.3
Ni	Trace	trace	0.0 -10.0	3.33	1.5
Cr	trace - 6.5	4.33	7.2 -11.7	9.77	1.5

Permissible limits for plants (WHO, 1998; WHO, 2005)

Mean values (mg kg $^{-1}$) of Cu found in *Eleucine Indica* sampled at Abudu (16.13) exceeded the limit set up for Cu (10) unlike in *Peperomia pelucida* selected from Benin (6.25). The permissible limit (mg kg^{-1}) for Zn (50) was exceeded by the concentrations recorded of both *P. pellucida* (68.88) and *E. indica* (97.67). Only the sampled plant species at Abudu (14.97 mg kg^{-1}) exceeded the limit (10.0 mg kg^{-1}) set for Pb while both plant species in Benin and Abudu with respective concentrations (mg kg $^{-1}$) of 3.63 and 9.63 for Cd exceeded the permissible limit (0.3 mg kg^{-1}) set up by WHO. Only *E. indica* accumulated higher concentrations of Ni (10 mg kg^{-1}) than the comparable limit (1.5 mg kg^{-1}) set up by WHO while trace amounts were observed in *P. pellucida*. The sampled species of *P. pellucida* and *E. indica* accumulated 4.33 and 9.77 of Cr, respectively, which were higher than the permissible limits for plants (1.5 mg kg^{-1}).

The bioaccumulation factor (BAF), the biological accumulation coefficient (BAC) and transfer factor (TF) of the sampled plant species are displayed in Table 5. While the BAC was computed for *Peperomia pellucida* in Benin City because its roots were too small for analysis, the BAF and TF were used for *E. indica*. It was observed that the BAC of *P. pellucida* for both Cu (0.95) and Zn (0.92) elements were close to 1 unlike the values for other metals which were < 0.69; while trace amounts were recorded for both Pb and Ni. *E. indica* showed BCF values > 1 for all the tested metals, besides Fe. Figures higher than 1.0 were recorded for Mn, Cu and Pb while those of Zn, Cd and Ni were even above 2. Much higher values were obtained for Cr: 4.47 and 5.59. Four metals were identified with TF > 1 for *E. indica* which included Fe (1.51), Zn (1.03), Pb (1.11) and Cd (1.07). The highest values recorded for Mn and Cu were 0.72 and 0.92, respectively; while those computed for Ni (0.33) and Cr (0.23) were quite low.

Table 5: Remediation potential of the predominant plants

Sample	**Heavy metals (g kg^{-1})**							
	Fe	**Mn**	**Cu**	**Zn**	**Pb**	**Cd**	**Ni**	**Cr**
			BAC of *P. pellucida* in Benin City					
SP 1	0.26	0.21	0.44	0.65	trace	0.25	trace	Trace
SP 2	0.34	0.12	0.17	0.61	trace	0.44	trace	0.21
SP 3	0.69	0.38	***0.95***	***0.92***	trace	0.27	trace	0.37
			BAF of *E. indica* in Abudu					
SP 1	0.32	**1.91**	**1.08**	**1.42**	**1.49**	0.71	**2.27**	**4.47**
SP 2	0.24	0.59	0.67	**1.26**	0.57	**2.89**	0.00	**5.59**
SP 3	0.12	**1.87**	**1.00**	**2.5**	0.85	0.89	0.00	0.89
			TF of *E. indica* Abudu					
SP 1	0.31	0.48	0.92	0.67	0.64	0.87	0.33	0.22
SP 2	0.18	0.72	0.61	0.21	0.51	0.51	0.00	0.23
SP 3	**1.51**	0.46	0.73	**1.03**	**1.11**	**1.07**	0.00	0.16

SP = Sampling point

Table 6: Correlation between soil properties and heavy metals at Benin and Abudu sites

Region	Soil Property	Heavy metals in plants							
		Fe	Mn	Cu	Zn	Pb	Cd	Ni	Cr
Benin	Clay	$.992^{**}$	0.87	0.938	0.672	0.939	$.966^{*}$	$.996^{**}$	0.846
	pH	-0.476	-0.892	-0.792	-0.886	-0.272	-0.346	-0.506	-0.059
	EC	$.981^{*}$	0.859	0.897	0.697	0.957^{*}	0.973^{*}	0.987^{*}	0.872
	Org. C	-0.158	0.188	0.235	0.105	-0.411	-0.321	-0.148	-0.546
	N	0.580	0.941	0.785	$.995^{**}$	0.455	0.501	0.613	0.264
	P	0.065	0.646	0.43	0.811	-0.108	-0.05	0.104	-0.311
	ECEC	0.842	0.554	0.575	0.454	0.948	0.916	0.84	$.955^{*}$
Abudu	Clay	-0.046	-0.094	0.821	-0.551	-0.206	-0.127	0.111	-0.201
	pH	0.67	-0.786	-0.094	-0.241	0.771	0.325	0.786	0.500
	Org. C	0.638	-0.22	-0.201	0.409	0.206	0.895^{*}	-0.044	-0.333
	N	0.16	0.104	0.126	0.173	0.131	0.351	-0.262	-0.811
	P	$-.903^{*}$	$.991^{**}$	-0.272	0.446	-0.786	-0.55	$-.926^{*}$	-0.393
	ECEC	0.566	-0.241	-0.187	0.293	0.652	0.657	0.034	-0.709

***$p < 0.05$; **$p < 0.01$**

Correlation coefficient between soil properties and HMs (Table 6) showed very significant ($p < 0.01$) positive correlation of clay with both Fe and Ni, N and Zn as well as significant ($p < 0.05$) positive correlation between clay and Cd in Benin. Significant positive correlation was recorded between EC with Fe, Pb, Cd and Ni as well as between ECEC and Cr in Benin. Positive significant correlation was recorded between organic C and Cd, while the significant relationship was negative between P and Fe, Mn and Ni at Abudu.

There were significant relationships between HMs in soils and those in plants at both sites (Table 7). While negative significant ($p < 0.05$) correlations were found for Fe in soil and Cd in plant ($r = -0.95$), as well as for Zn in soil and Cu in plant ($r = -0.98$), positive significant correlations were detected between Cd in soil and Cd in plant ($r = 0.98$), Cr in soil and Cd in plant ($r = 0.99$), and very significant ($p < 0.01$) relationship were found between Pb in soil and Cd in plant (1.00) in Benin City. Assessment of Abudu site revealed positive very significant correlations for Cu in soil and Mn in plant ($r = 1.00$), Cu in soil and Ni in plant ($r = 0.97$) and negative very significant relationship for Zn in soil and Ni in plant (-0.98) in addition to significant positive relationship for Cu in soil and Cd in plant ($r = 0.88$) and significant negative correlation between Zn in soil and Mn in plant ($r = -0.92$).

Table 7: Correlation between heavy metals concentrations in soils and plants at the sites

Region	Heavy metals in soil	Heavy metals in plants							
		Fe	Mn	Cu	Zn	Pb	Cd	Ni	Cr
Benin	Fe	-0.494	-0.796	-0.669	-0.721	-0.467	.951*	-0.156	0.229
	Mn	-0.334	-0.459	-0.91	-0.342	-0.435	0.611	-0.372	-0.301
	Cu	-0.219	-0.492	-0.75	-0.379	-0.268	0.725	-0.101	-0.212
	Zn	-0.424	-0.358	-.974*	-0.252	-0.572	0.393	-0.641	-0.363
	Pb	-0.669	-0.926	-0.619	-0.878	-0.611	.996**	-0.261	0.468
	Cd	-0.608	-0.885	-0.639	-0.828	-0.56	.988*	-0.22	0.386
	Ni	-0.502	-0.791	-0.699	-0.713	-0.483	0.942	-0.185	0.205
	Cr	-0.698	-.956*	-0.468	-0.935	-0.601	.989*	-0.211	0.640
Abudu	Fe	0.338	0.034	0.177	0.609	-0.176	-0.048	-0.022	-0.251
	Mn	-0.414	-0.421	-0.422	-0.409	-0.228	-0.21	-0.442	-0.045
	Cu	0.737	.997**	0.878	0.055	0.811	.881*	.973**	0.835
	Zn	-0.537	-.922*	-0.731	0.025	-0.783	-0.694	-.984**	-0.663
	Pb	0.241	-0.07	-0.211	0.737	-0.444	-0.395	-0.013	-0.563
	Cd	0.176	-0.307	-0.025	0.563	-0.431	-0.197	-0.439	-0.375
	Ni	0.367	0.543	0.465	0.245	0.391	0.282	-0.439	0.160
	Cr	-0.273	0.306	0.384	-0.612	0.667	0.307	-0.439	0.362

***p < 0.05; **p < 0.01**

Discussion

This study revealed that anthropogenic activities at the contaminated sites have caused changes in soil physicochemical properties. The loamy sand texture of the polluted Abudu soil with relatively lowest clay content had the lowest nutrient status based on the ECEC. Relative higher organic carbon in the polluted soil may have caused increase in pH. Such increase in soil pH, essential nutrients (organic C, total N, P, Ca, Mg) and heavy metals in soil due to the accumulation of spent engine oil and the eventual translocation in plant tissues have been reported (Tanimu *et al.* 2019; Okonokhua *et al.*, 2006; Vwioko *et al.*, 2006). Higher pH values of the polluted soil present in the studied area implied contamination by basic cations which would have been contained in waste deposited or spilled on such sites over the past years. These cations tend to lime the soil by increasing its pH and detoxify soil by eliminating free Al and Mn ions from the solution (Deenik and McClellan, 2007).

Determination of a higher value of degree of contamination from the sandy loam texture of Benin may be due to the more clay content compared to Abudu soil which is loamy sand. Similar to this present study, a very close association has been reported between soil texture and HM concentrations by Hong *et al.* (2022). Texture is one of the physiochemical properties of soil which have a very strong influence on HMs bioavailability. Thus, generally grasses grown on sandy soil are more metal deficient than those grown on loamy soil due to relatively low metal retention capacity.

Relatively higher pH of the polluted soils as observed in this study can be explained by Ye *et al.* (2022) who reported that lower pH has been associated with more mobility and bioavailability of metals in soils. However, such transportation can be influenced by the type and species of plant, as well as other factors such as age of plant, climatic regime and nature of soil (Pandey, 2012; Twing *et al.*, 2004). Thus, clay was assessed to be the dominant factor which influenced some HMs (Fe, Ni and Cr) in Benin while on the contrary, P was most dominant in affecting the accumulation of metals (Fe, Mn and Ni) in the soil of Abudu.

The binding ability of HMs have been described by Dube *et al.* (2001) to be collectively determined partly by their physical and chemical properties as well as mainly by the physicochemical properties of soil which include clay fraction, organic matter content, mineral composition and pH. While the clay fraction of soil is perhaps most crucial in this regard due to its mineral content, soils composed of silt and dust in addition, along with those with high organic matter, have a high sorption capacity to bind metals (Sheoran, 2009). On the contrary, sandy soils, renowned for their low sorption capacity and acidity, weakly absorb such metals which cause their movement to groundwater and surface water.

Accumulation of higher concentration of Pb in the polluted soil of Benin compared to Cd can be attributed to the relative higher organic matter content. Organic matter can influence metal behavior by binding with toxic metals and thereby alleviate metal toxicity in soils. Soils with higher OM contents have shown higher Pb contents than Cd in the control environment which implies the higher affinity and stability of Pb towards OM than Cd (Chandra and Kumar, 2017).

Higher numbers of BAF recoded especially for *E. indica* compared to BAC and TF implied concentrations of Mn, Cu, Zn, and Cr in plant roots than in shoots. This indicates high plant availability of the substrate metals as well as their limited mobility once inside the plant, a result which is in agreement with the findings of Outridge and Noller (1991).

Reduced root growth and associated decrease in yield of acid soils, as observed for *P. pellucida* of about 30 cm long in this present study can be caused by the synergistic property of Al, H and Mn toxicity, together with deficit of Ca, Mg, and Mo as stated by Lal (2007). Since the species which is a common tropical herb can grow up to 45 cm (Majumder, 2012), it may be possible to apply agronomic measures and/or chelating agents to the plant so that its BAC (0.95 and 0.92 for Cu and Zn, respectively) can be increased beyond 1. Besides, grasses can also be used for phytoextraction because of their short life cycle, high growth rate, more biomass production, and high tolerance to abiotic stresses (Malik *et al*., 2010).

Speculation of the plant species assessed in this present study has been suggested to have remediation potential by Anoliefo *et al*. (2008). These plants, *eleusine indica* and *Peperomia pellucida,* were also among the species identified along a road side in India were they were tested to have accumulated Zn and reported to have the potential for remediation (Ray and Jojo, 2010). Also, in a study carried out in Bauchi State, Nigeria, the plant analysis for mean Cu content revealed that *Eleusine indica* was reported to accumulate the highest Cu concentrations in shoot and root than in soil. Similar to the observations from this present study, Abdallah *et al*. (2012) while investigating the bioaccumulation of HMs by *Eleusine indica* sampled from dump sites at Kaduna, reported BCF > 1 for Pb, Zn, Mn and Cu. The BCF and TF were above unity in most of the treatments that involved Cu, Zn, Cr, Pb and Cd which made Chinmayee *et al*. (2012) to suggest *A. spinosus* as a potential agent for accumulation of HMs.

However, metal uptakes by plants are usually not directly correlated to increase in concentration of the external source as observed in this study due to the complex nature of soils. This weak or lack of correlations have been reported by many studies (Keller *et al*., 1998; Greger, 1999). Such relationships in most cases either between soil properties and concentrations of HMs in soils or between HMs in soils and plants imply that none of the single factor was dominant in influencing the uptake of these metals by plants. Thus, Nouri *et al*. (2001) ascribed such phenomena to be probably caused by the interaction of the various relevant soil factors and different HMs.

Positive significant correlation of clay with Fe, Ni and Cd in Benin City implies that clay will be useful towards remediating the soil from such metals; a practice that have been applied for years (Otunola and Ololade, 2020). Similarly, phosphorus-rich materials have been reported by Peiris *et al*. (2023) to be widely used as soil remediation agents mainly due to their high affinity for these metals in soil. An application which would favour the remediation of Abudu site from Mn since P correlated positively with the metal.

In addition to plant selection for remediation purpose, measures to increase bioavailability of these metals are a major strategy towards improving the efficiency of phytoextraction and chelating agents such as ethylene diamine tetraeacetic acid (EDTA) have been used effectively in such regard (*Gupta et al*., 2013; Sarwar *et al*., 2017). Consequently, the remediation potential of the two plants identified in this study can be improved upon with a view to determining their use as hyperaccumulators.

Conclusions

The study revealed that both sites were extremely polluted with Fe, Zn, Mn and Cu; Benin City was severely polluted with Pb, Cd and Cr; between moderately to highly polluted with Ni while Abudu soil was between severely to moderately polluted with Pb and Cd; moderately polluted with Cr and slightly polluted with Ni based on the geoaccumulation index (Igeo) method of assessment. *Perperomia pellucida and Eleucine indicia were* identified as the predominant plants at the contaminated sites in Benin and Abudu, respectively; both contained low levels of Mn and high concentrations of Fe, Zn, Cd and Cr which exceeded the limit set by WHO, only *E. indica* was found to exceed the limit set for Cu, Pb and Ni. Although none of the species proved to be a hyperaccumulator but *E. indica* discerned such potential for Zn, Pb and Cd as well as the ability to stabilize Mn, Cu, Ni and Cr at Abudu soil while there was implication that *P. pellucida* could be used to stabilize Cu and Zn metals in Benin. Predominant indigenous plant species can be used to clean up heavy metal polluted sites.

Authors contribution statement

Author E. R. Orhue designed the study while B. O. Okonokhua carried out the work, collected and analyzed the data and wrote the first draft of the manuscript. The final manuscript was reviewed and approved by both authors.

Conflict of interest statement

The authors declare no conflict of interest.

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