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ASSESSMENT OF HEAVY METALS AND PHYTOREMEDIATION POTENTIALS OF CASSAVA IN CRUDE OIL IMPACTED FARMLAND SOILS IN MMAHU, IMO STATE

Mmekam C. U. and Nwawuike I. M.*

Department of Soil Science and Environment, Imo State University Owerri, Imo State.

*Corresponding Author's Email: nobleify200@gmail.com

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ABSTRACT: *The concentration of Cr, As, Fe, Ni and Cd in crude oil impacted soils and cassava plant part samples from Mmahu area in Niger Delta, Nigeria and the phytoremediation potentials of cassava were assessed. The samples were collected from three crude oil exploitation sites. In each exploitation site, five farmlands were sampled. Soil samples were collected at the beginning and end of each farmland using soil auger and bulked together to form 15 composite samples. Soil samples were air-dried and sieved to remove root debris. The cassava tubers were collected close to where the soil samples were collected from each sampled farmland. The cassava tuber was peeled and separated into tubers and peels. The plant samples were sun dried and ground using ceramic mortar. The tubers and the peels from the two points were also bulked to get a total of 15 cassava tuber samples and 15 cassava peel samples. All samples were analyzed for heavy metals using Atomic Absorption Spectroscopy (AAS). The results indicated that although Cr, As, Fe and Ni were found present in the soil, they were below the FAO/WHO soil permissible limits, while the value of Cd was far above the limit. It was also found that As, Cr and Cd concentrations were higher in cassava peels and tubers in all the three sites sampled when compared to the soil samples. The results of Contamination Factor (CF) and degree of contamination (C_d) showed Cd to be the highest heavy metal element with the highest CF and C_d value, followed by Fe which is of moderate contamination, while Cr, As and Ni had low CF and C_d. The result of the Pollution Load Index (PLI) of the cassava samples showed that the cassava peels and tubers in all three sites were polluted. The results of the bioaccumulation factors (BAF) of heavy metals in cassava peels and tubers indicated that cassava has high efficiency in bioaccumulation of these metals. The results obtained on Bio-translocation Factor (BTF) implied that cassava has in-situ phytoremediation potentials but there were variations in the elements translocated across the three sites. These variations might be attributed to the variation in cassava varieties across the three sites.*

KEYWORDS: Heavy Metals, Cassava, Phytoremediation, Bioaccumulation, Bio-translocation.

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INTRODUCTION

Soil is universally acknowledged as one of the crucial elements of the environment, following water and air. A healthy soil is essential to life on earth as it supports the production of most food eaten by humans. Therefore, conservation and protection of soil health is vital to guaranteeing human existence. Chen et al. (2009) stated that pollutants entering the soil cause alterations to soil quality pose risks to life and trigger environmental concerns. Soil pollution can be caused by either natural change in the environment of the soil or by anthropogenic activities and a combination of the two factors. Crude oil, a type of fossil fuel, is one of the leading sources of energy globally (Internal Energy Agency, 2021). However, their extensive production, transportation, consumption and disposal process contributes greatly to widespread environmental pollution (Gitypour et al., 2004). In countries like Nigeria with poorly supervised, poorly educated populace and inept leadership, with active exploration activities, structure constructions, maintenance and upgrade, refineries construction and operation, and ample oil resources, the leakage, seepage, and infiltration of petroleum pollutants and their derivatives into the soil are viewed as some of the major soil contaminants (Jaskulak et al., 2020).

Crude oil pollution causes the deterioration of arable soils in the Niger Delta region, creating adverse impact on the physical, chemical, and biological properties of the soil (Phil-Eze & Okoro, 2009). The contamination of arable soils and crops near the drilling sites with heavy metals has been viewed as a significant environmental issue (Kalil et al., 2011). Heavy metals such as chromium, arsenic, iron, nickel and cadmium in the soil disrupts the ecosystem and poses serious health risks. Assessment of heavy metal pollution in farmlands is of major significance to the control and mitigation of the rising severity of soil pollution from heavy metals (Zhao et al., 2022). Excavation and chemical treatments are conventional methods of remediating contaminated soils. However, they are often expensive, disruptive, and not always sustainable in the long term, hence the need for phytoremediation, an eco-friendly technology that is economical, efficient and environmentally friendly. Phytoremediation harnesses the inherent abilities of plants to absorb, degrade, remove or stabilize contaminants in the soil, thereby restoring the health of the contaminated soil and improving ecosystem functions. Berti and Cunningham (2000) described phytoremediation as a plant-based method that uses plants to absorb and eliminate elemental pollutants or reduce their bioavailability in soils, while Liu et al. (2020) described it as a green approach that leverages hyper-accumulator plants and their rhizospheric microorganisms to stabilize, transport or break down pollutants in soil, water and the environment.

Cassava, botanically known as *Manihot esculenta*, is a perennial woody shrub in the *Euphorbiaceae* family with an edible root grown across numerous tropical and subtropical parts of the world. It has a significant agricultural importance in developing countries like Nigeria as it is a staple crop. Aside from its importance as a food source, cassava has strong potential for phytoremediation of heavy metal polluted soils. The Niger Delta is Africa's largest delta and ranks as the third largest across the globe, with a total area of 112,106 km^2. The Niger Delta region of Nigeria is known for its wealth of natural resources. Its large oil and gas reserves are central to the country's economy. Located in the southernmost part of the country, the region is characterized by coastal barrier islands, mangroves, freshwater swamp forests and lowland rainforests. The Niger Delta is abundant in resources, yet environmental degradation is driving its inhabitants into poverty. Arable soils degradation in the Niger Delta region negatively impacts the soil ecosystem and affects food security and the health of humans and wildlife; therefore, assessing the concentrations of heavy metals in the soil and phytoremediation potentials of cassava (*Manihot esculenta*) in the contaminated soils will help restore soil health and thereby increase arable soils which in turn improves agricultural productivity. This study primarily aims to assess the concentrations of heavy metals (chromium, arsenic, iron, nickel and cadmium) in crude oil impacted farmland soils and the phytoremediation potentials of cassava (*Manihot esculenta*) in Mmahu, Imo State.

MATERIALS AND METHOD

Description of Study Area

Mmahu is a town located in Ohaji/Egbema Local Government Area which is situated in the south-western part of Imo State. The latitude of Mmahu is approximately 5.52393°N and the longitude is approximately 6.75255°E. The area is known for its rich oil and gas resources and its rich agricultural activities. The geology of the soils of Ohaji/Egbema is from the Benin Formation (Ahukaemere et al., 2016). According to Ezeigbo (1989), Ohaji/Egbema is part of a major physiographic region with undulating lowland plain which is connected to its geological features. Ohaji/Egbema is primarily drained by the Otammiri River and its tributaries. Okoli (2004) described the climate of the study area to have two distinct seasons which are dry and rainy seasons, both of which are warm. The dry season occurs between November and March and the rainy season occurs between April and October. The mean annual rainfall is about 2500 mm and the annual temperature range is about 26–30°C (NIMET 2014). Mmahu has a typical rainforest vegetation of southeastern Nigeria characterized by trees and shrubs; the soils are generally humid and suitable for the cultivation of arable crops such as cassava, yam, maize and cocoyam. The area is plagued with crude oil pollution; the menace can clearly be seen on the farmlands and the river. The degraded farmlands had very little vegetation with split oil on most of the soil surface. The river is dark and covered with split oil floating on it.

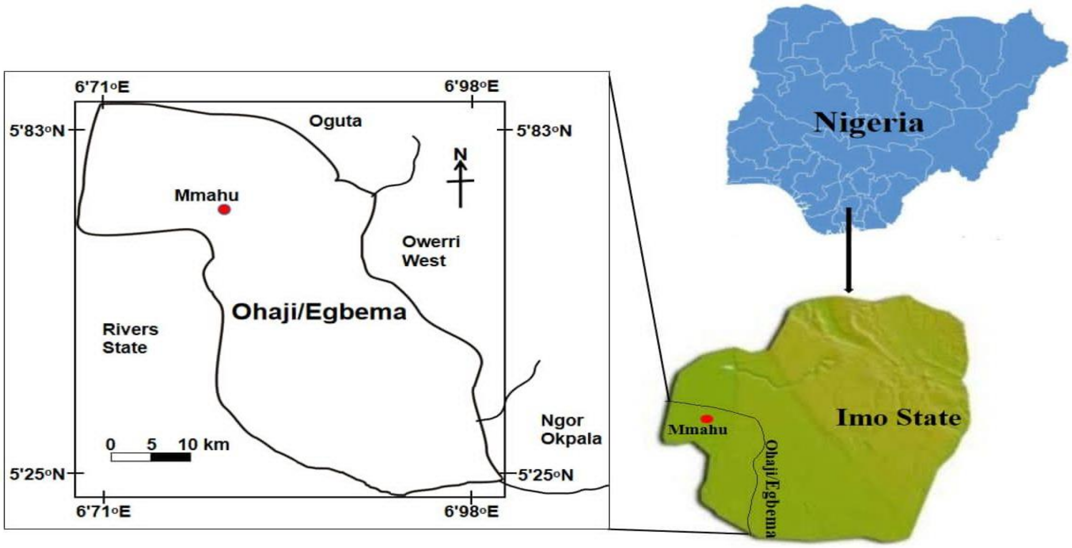

Figure 1: Map of the study area

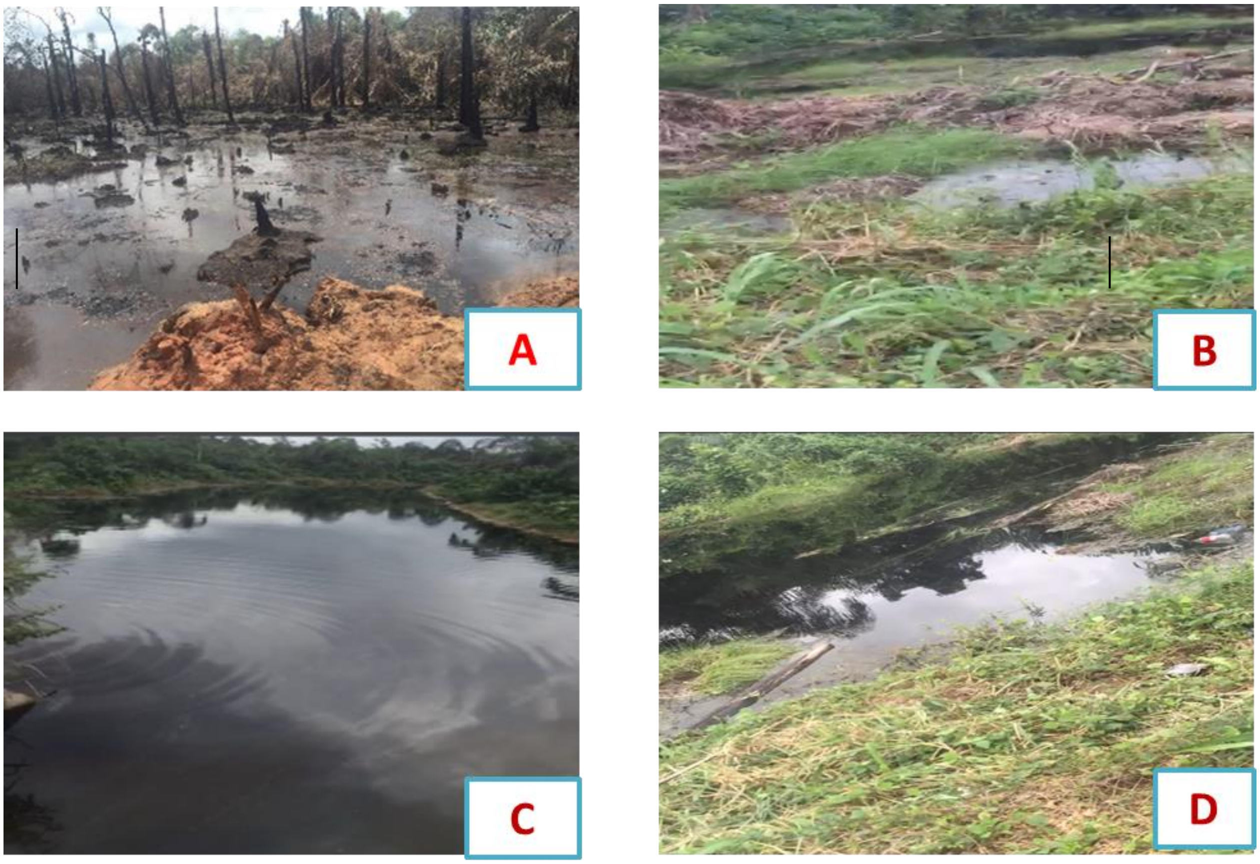

Figure 2: The images of the menace from the study area

Sample Collection and Preparation

The samples were collected from three crude oil exploitation sites. The crude oil exploitation sites were labeled A, B and C. In each site, five farmlands was sampled; soil samples were collected at the beginning and end points of each farmland using soil auger and bulked together to form 15 composite soil samples. The composites soil samples were air-dried and sieved to remove root debris. The cassava tubers were collected close to where the soil samples were collected from each sampled farmland. The cassava tuber was peeled and separated into tubers and peels. The plant samples were sun dried and ground using ceramic mortar. The tuber and the peel from the two points were also bulked to get a total of 15 cassava tuber samples and 15 cassava peel samples. The grinded plant samples were put into Ziploc bags and labeled for laboratory analysis. Ethanol was used to sterilize the mortar and pestle after each grinding to prevent contamination of the samples.

Laboratory Analysis

Five heavy metals (Cr, As, Fe, Ni and Cd) were analyzed for both the soil samples and plant samples using Atomic Absorption Spectroscopy (AAS). Particle size distribution for soil samples was analyzed using a modified Boyoucous method. The pH of the soil samples was analyzed using glass electrode pH meter method with pH meter (Hanna instruments) using soil/water ratio of 1:2.5. Organic matter and organic carbon content of the soil samples were analyzed using Walker and Black method.

Statistical Analysis

Analysis of variance (ANOVA) was used to determine the variations in the soil properties and the cassava plant samples across the farmlands near the exploitation sites. KaleidaGraph 4.0 was used to plot a graph showing variation among sampled soil, cassava tubers and cassava peels across the three exploitation sites. Correlation analysis was also used to determine the relationship between soil properties and heavy metal concentrations in the soil.

Environmental Risk Assessment (ERA)

Contamination Factor (CF)

Determination of the extent of heavy metal contamination was carried out using contamination factor. According to Tomlinson et al. (1980), contamination factor is thus:

$CF = C_{metal} / C_{background}$

where:

C_{metal} is the current metal concentration in the sample

$C_{background}$ is the background metal concentration.

The upper continental crust as proposed by Taylor and McLennan (1985) was used in this study as the background metal concentration. The CF is interpreted as follows: CF < 1 signifies low

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contamination, $1 \leq CF < 3$ signifies moderate contamination, $3 = CF \leq 6$ signifies considerable contamination, and $CF \geq 6$ signifies very high contamination (Tomlinson et al., 1980).

Degree of Contamination (C_d)

To further determine the extent soils in Mmahu have been polluted by oil production, the degree of contamination proposed by Hakanson (1980) was employed. It is a sedimentological diagnostic tool and is given as:

$$C_d = \sum CF$$

The degree of contamination of an element is computed by summing up the contamination factors of a particular element in the samples. The interpretation of C_d is given as: $C_d < 6$ shows low C_d, $6 < C_d < 12$ means moderate C_d, $12 < C_d < 24$ is considerable C_d, while $C_d > 24$ is high C_d and shows strong anthropogenic pollution.

Pollution Load Index (PLI)

The magnitude of heavy metal concentrations in the soil and plant samples was determined by application of the bio-concentration factor. According to Tomlinson et al. (1980), pollution load index is given as:

$$PLI = {}^{n}\sqrt{CF_1 \times CF_2 \ldots \times CFn}$$

where:

n is the number of heavy metals and CF is the contamination factor.

PLI value < 1 is unpolluted, PLI = 1 indicates heavy metal load that approximates to the background concentration, while PLI > 1 is polluted (Cabrera et al., 1999).

Phytoremediation Potential Analyses (PPA)

Bio-accumulation Factor (BAF)

To determine the extent of heavy metal concentrations in the peels and tubers of *M. esculenta* samples, the bio-accumulation factor was employed. Yoon et al. (2006) expressed bio-concentration factor thus:

$$BAF\ (peels) = Pmc/Smc$$

$$BAF\ (tubers) = Tmc/Smc$$

where:

Pmc and Tmc are heavy metal concentrations in the peels and tubers respectively, while Smc is the soil metal concentration.

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BAF > 1 is an indication of hyperaccumulation.

Bio-translocation Factor (BTF)

The rate at which metals concentrated on the cassava peel were transferred to the tuber was determined using bio-translocation factor (BTF). According to Nwawuike and Ishiga (2019), bio-translocation factor is given as concentration in leaf divided by concentration in root. In line with this formula, this study formulated bio-translocation factor for cassava tuber as follows: To determine the rate at which metal concentrations on the soil were transferred to the tubers, bio-translocation factor (BTF) was used. Yanqun et al. (2005) expressed BTF thus:

BTF = Tmc/Pmc

where: Tmc = Tuber metal concentration;

Pmc = Peel metal concentration

BTF > 1 indicates effective translocation (Rezvani & Zaefarian, 2011)

RESULTS AND DISCUSSION

The Physicochemical Parameters of the Farmland Soils

The results of the physicochemical parameters (Particle size distribution, pH and soil organic matter) are presented in Table 1. The particle size distribution of the soils of the studied sites varied significantly ($P < 0.05$) in all the three particles. They ranged from 7.40 to 12.60% (clay), 10.60 to 20.60% (silt) and 70.40 to 80.40% (total sand). The highest were from Site A (12.60%), Site C (20.60%) and Site B (80.40%) for clay, silt and total sand respectively. Generally, the sampled soils had a low percentage of clay and silt with a high percentage of sand. The high sand percent could be related to the parent material (sedimentary rock) of the soils. According to Obi (2000), the texture is a permanent property of the soil.

The pH of the three sites evaluated varied significantly. They ranged from 4.80 to 5.66 which indicated a moderate to slight acidic soil nature. Soil pH is essential for the fertility of the soil and it also affects the nutrients availability to plants (Neina, 2019). An acidic soil encourages mobility of heavy metals while an alkaline soil decreases the mobility of heavy metals (Keshavarzi & Kumar, 2020; Tian et al., 2017). The pH of Site B is within the range of pH required for optimal plant growth (5.5–7.5) while Sites A and C are below this range. This implies that the soil pH values of Sites A and C would likely have more heavy metal mobility.

Soils collected from the farmland near the three exploitation sites showed significant differences in soil organic matter (SOM) content. The SOM ranged from 2.38 to 5.39% with the highest from Site C. Site A was statistically similar with Site C with the two being of high range, according to Esu (1991). Site B was of medium range. The high SOM found could be related to the presence of hydrocarbon content introduced into the soil from the crude oil exploratory site.

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The SOM value obtained in the study is in line with the works of Okonokhua et al. (2007), Kayode et al. (2009) and Udebuani et al. (2011) on crude oil contaminated soils.

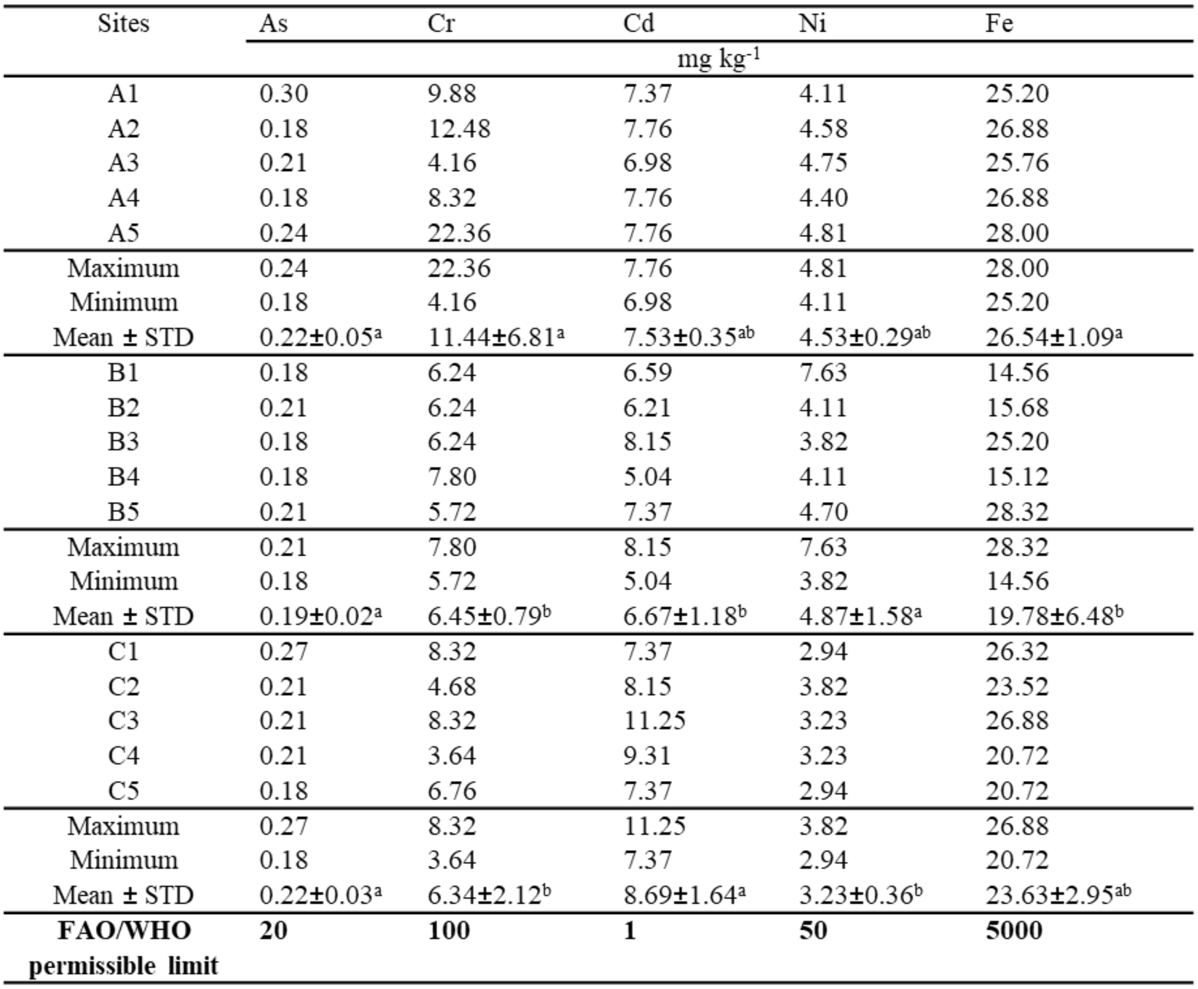
Table 1: Some selected soil parameters from the farmland soils near the exploitation sites in Mmahu

Sites	Clay	Silt	Total Sand	pH	Organic Matter
		%			%
A1	13.00	17.00	70.00	5.20	4.13
A2	17.00	11.00	72.00	4.90	5.85
A3	11.00	11.00	70.00	5.30	4.75
A4	11.00	19.00	70.00	4.90	4.68
A5	11.00	19.00	70.00	4.80	5.71
Maximum	17.00	19.00	72.00	5.30	5.85
Minimum	11.00	11.00	70.00	4.80	4.13
Mean ± STD	12.60 ± 2.61^{a}	15.40 ± 4.10^{ab}	70.40 ± 0.89^{b}	5.02 ± 0.22^{b}	5.02 ± 0.73^{a}
B1	9.00	5.00	86.00	6.20	2.06
B2	9.00	3.00	88.00	5.70	2.06
B3	9.00	3.00	88.00	6.20	2.00
B4	9.00	21.00	70.00	5.10	1.93
B5	9.00	21.00	70.00	5.10	3.85
Maximum	9.00	21.00	88.00	6.20	3.85
Minimum	9.00	3.00	70.00	5.10	1.93
Mean ± STD	9.0 ± 0.00^{b}	10.60 ± 9.53^{b}	80.40 ± 9.53^{a}	5.66 ± 0.55^{a}	2.38 ± 0.82^{b}
C1	7.00	27.00	66.00	4.80	5.09
C2	7.00	21.00	72.00	4.80	5.71
C3	7.00	19.00	74.00	4.70	5.30
C4	7.00	19.00	74.00	4.70	5.57
C5	9.00	17.00	74.00	5.00	5.30
Maximum	9.00	27.00	74.00	5.00	5.71
Minimum	7.00	17.00	66.00	4.70	5.09
Mean ± STD	7.40 ± 0.89^{b}	20.60 ± 3.85^{a}	72.00 ± 3.46^{b}	4.80 ± 0.12^{b}	5.39 ± 0.25^{a}

Heavy Metal Concentration in the Farmland Soils

A Single Factor ANOVA of the heavy metal data revealed that studied heavy metal levels were noted to be significantly ($P < 0.05$) in Cr, Cd, Ni and Fe, with As showing no significant across the farmland soils from the three exploratory sites. The mean and ranges of heavy metals in the farmland soils across the three exploratory sites (A, B and C) are shown in Table 2. Across the study area, the mean concentrations of heavy metals (mg/kg dry weight) in soil samples were found in the following ranges: As (0.19–0.22); Cr (6.34–11.44); Cd (6.67–8.68); Ni (3.23–4.87) and Fe (19.78–26.54). The highest mean concentration of the heavy metals for As (0.22 mg/kg), Cr (11.44 mg/kg), Cd (8.69 mg/kg), Ni (4.87 mg/kg) and Fe (26.54 mg/kg) were from Site A, Site A, Site C, Site B and Site A respectively. Based on the mean values, the heavy metal concentrations decreased in the following order: Fe > Cr > Cd > Ni > As. Despite the trend of the result showed, Cd was the only heavy metal among the evaluated heavy metals that had its values higher than the FAO/WHO soil permissible limits. The results obtained showed that all the evaluated heavy metals were detected in the farmland soils but Cd value is far above the maximum FAO/WHO permissible limit (3 mg/kg). This suggests that crude oil bearing heavy metals from the exploitation sites find their way to the farmland soils. Thus, further supporting the earlier reports that heavy metals were builds up in soils polluted by crude oil and its various products (Chen et al., 2000; Agbogidi, 2010; Chukwuma et al., 2010). The high Fe value obtained may be attributed to the fact that most soils are Fe-rich in nature (Osuji & Onojake, 2004). The standard deviation (SD) value reflects the heterogeneous distribution of heavy metals. High SD values showed high heterogeneous distribution. The SD results obtained in this study exhibited low heterogeneous distribution except those found on Cr in Site A and on Fe in Site B.

Table 2: Heavy metal concentration of the farmland soils near the exploitation sites in Mmahu



Sites	As	Cr	Cd	Ni	Fe
	mg kg^{-1}				
A1	0.30	9.88	7.37	4.11	25.20
A2	0.18	12.48	7.76	4.58	26.88
A3	0.21	4.16	6.98	4.75	25.76
A4	0.18	8.32	7.76	4.40	26.88
A5	0.24	22.36	7.76	4.81	28.00
Maximum	0.24	22.36	7.76	4.81	28.00
Minimum	0.18	4.16	6.98	4.11	25.20
Mean ± STD	0.22±0.05^{a}	11.44±6.81^{a}	7.53±0.35^{ab}	4.53±0.29^{ab}	26.54±1.09^{a}
B1	0.18	6.24	6.59	7.63	14.56
B2	0.21	6.24	6.21	4.11	15.68
B3	0.18	6.24	8.15	3.82	25.20
B4	0.18	7.80	5.04	4.11	15.12
B5	0.21	5.72	7.37	4.70	28.32
Maximum	0.21	7.80	8.15	7.63	28.32
Minimum	0.18	5.72	5.04	3.82	14.56
Mean ± STD	0.19±0.02^{a}	6.45±0.79^{b}	6.67±1.18^{b}	4.87±1.58^{a}	19.78±6.48^{b}
C1	0.27	8.32	7.37	2.94	26.32
C2	0.21	4.68	8.15	3.82	23.52
C3	0.21	8.32	11.25	3.23	26.88
C4	0.21	3.64	9.31	3.23	20.72
C5	0.18	6.76	7.37	2.94	20.72
Maximum	0.27	8.32	11.25	3.82	26.88
Minimum	0.18	3.64	7.37	2.94	20.72
Mean ± STD	0.22±0.03^{a}	6.34±2.12^{b}	8.69±1.64^{a}	3.23±0.36^{b}	23.63±2.95^{ab}
FAO/WHO permissible limit	**20**	**100**	**1**	**50**	**5000**

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The Interrelationship Between Soil Properties and Heavy Metal Concentrations in Both the Soil and in the Cassava Plant Parts in the Exploitation Sites A, B and C

Table 3 shows the interrelationship among the selected heavy metals and soil properties in the three sites (A, B and C) sampled. Clay showed no significant correlation with any of the heavy metals determined but correlated positively and significantly with only Ni (0.98**) in Site B. In Site C, clay showed a negative but weak significant correlation with As (-0.61*) and Fe (-0.56*). Silt – TS was the only association found in Site A which is weak but significant. Silt in Site B correlated negatively and strongly with TS (-1.00**) and pH (-0.92**) but weakly and positively with OM (0.56*). In Site C, silt also showed a strong negative association with TS (-0.98**) while maintaining a positive correlation with As (0.97**) and Fe (0.60*). TS showed negative association with pH (-0.31) though not significant, and positive significant correlation with OM (0.63*) in Site A while in Site B, positive significant association was found with pH (0.91**) and negative with OM (-0.56*). In Site C, only TS – OM (0.56*) association was obtained but no significant correlation with pH. A significant correlation was also obtained between TS – Cd (0.51*) and TS – Fe (-0.56*) in Site C.

pH in Sites A and C showed negative association with almost all the selected heavy metals while in Site B, only As and Fe were negative though not significant. In Site A, OM showed positive significant correlation with all the analyzed heavy metals from the farmland soils except with As (-0.50*) which is of weak negative association. Sites B and C have a combination of both negative and positive association. In Site B, As (0.64*) and Fe (0.73**) were positive with Cr (-0.98**) showing negative association. In Site C, OM – Cr was (-0.95**) and OM – Ni was (0.85**). The result obtained from the correlation matrix with regards to soil properties implies that variations exist among the three sites evaluated in this study. Also, there is every likelihood that some of the analyzed heavy metals are geogenic and not anthropogenic.

Ishiga et al. (1999) and Roser (2000) reported that Fe_2O_2 and TiO_2 contents are used as proxies to define elemental sources in their research. Elements that showed correlation with Fe reflect that those elements are geogenic. However, if there is a negative relationship between Fe and other heavy metals evaluated, it suggests that they are anthropogenic or additional natural processes have contributed to its elemental enrichment (Dalai & Ishiga, 2013). In Site A, there is strong Fe – Cd and Fe – Cr with weak Fe – Ni associations. This implies that in Site A, Fe has a strong influence in the distribution of Cd and Cr within the farmland soils of Site A but plays a little role in Ni distribution. Though negative but not significant with Fe, the As found in Site A is more anthropogenic and not geogenic. In Site B, Fe correlated positively with Cd (0.75**) and As (0.31), and negatively with Cr (-0.77**) and Ni (-0.37), despite the fact that only Cd and Cr were significant. The results imply that Cd and As are geogenic while Cr and Ni are anthropogenic. In Site C, Fe correlated positively with all the heavy metal elements, although some are moderately significant (As = 0.65* and Cr = 0.56*) with Cd (0.36) and Ni (0.01) weakly correlated. In Site C, the results from the correlation matrix implies that all the evaluated heavy metal elements are geogenic.

Table 3: The relationship between soil properties and heavy metal concentrations in the soils of the exploitation Sites A, B and C

	Clay	*Silt*	*TS*	*pH*	*OM*	*As*	*Cd*	*Cr*	*Ni*	*Fe*
Clay	1									
Silt	**-0.54***	1								
TS	**0.94****	**-0.60***	1							
pH	-0.16	-0.46	-0.31	1						
OM	0.41	-0.22	**0.63***	**-0.70***	1					
As	-0.19	0.34	-0.47	0.38	**-0.50***	1				
Cd	0.30	0.49	0.38	**-0.95****	**0.55***	-0.30	1			
Cr	0.04	0.48	0.09	**-0.76****	**0.64***	0.19	**0.66***	1		
Ni	-0.19	-0.28	0.09	-0.27	**0.71****	-0.47	-0.02	0.33	1	
Fe	-0.06	0.35	0.17	**-0.91****	**0.81****	-0.44	**0.75****	**0.77****	**0.62***	1

	Clay	*Silt*	*TS*	*pH*	*OM*	*As*	*Cd*	*Cr*	*Ni*	*Fe*
Clay	1									
Silt	-0.37	1								
TS	0.33	**-1.00****	1							
pH	**0.55***	**-0.92****	**0.91****	1						
OM	-0.21	**0.56***	**-0.56***	**-0.53***	1					
As	-0.41	0.15	-0.13	-0.43	**0.64***	1				
Cd	-0.04	-0.37	0.38	0.49	0.35	0.09	1			
Cr	0.17	-0.40	0.40	0.38	**-0.98****	**-0.66***	-0.49	1		
Ni	**0.98****	-0.23	0.19	0.41	-0.03	-0.27	-0.04	-0.01	1	
Fe	-0.45	0.26	-0.24	-0.16	**0.73****	0.31	**0.78****	**-0.77****	-0.37	1

	Clay	*Silt*	*TS*	*pH*	*OM*	*As*	*Cd*	*Cr*	*Ni*	*Fe*
Clay	1									
Silt	**-0.52***	1								
TS	0.32	**-0.98****	1							
pH	**0.83****	-0.11	-0.10	1						
OM	-0.22	-0.42	**0.53***	-0.12	1					
As	**-0.61***	**0.97****	**-0.92****	-0.28	-0.47	1				
Cd	-0.45	-0.36	**0.51***	**-0.86****	0.14	-0.18	1			
Cr	0.18	0.24	-0.32	-0.06	**-0.95****	0.33	0.14	1		
Ni	-0.46	-0.11	0.24	-0.27	**0.86****	-0.19	0.19	**-0.79***	1	
Fe	**-0.56***	**0.60***	**-0.52***	**-0.55***	-0.48	**0.65***	0.36	**0.56***	0.01	1

****. Correlation is significant at the 0.01 level (2-tailed). *. Correlation is significant at the 0.05 level (2-tailed)**

Heavy Metal Concentration in the Cassava Plant Parts

The concentration of five (5) heavy metals in different parts of *Manihot esculenta* sampled (peels and tubers) from five farmland soils each from the three exploitation sites in Mmahu Ohaji-Egbema are summarized in Tables 4 and 5respectively. The results indicate that heavy metal concentrations differed significantly (P<0.05) among the different parts of *Manihot esculenta* analyzed in this study except As concentrations. The highest mean values of As (2.32, 2.10 mg/kg), Cr (33.80, 27.56 mg/kg), Cd (45.47, 49.65 mg/kg), Ni (4.11, 4.28 mg/kg) and Fe (14.00, 9.52 mg/kg) were recorded in Sites C and B for As, Site C and Site C for Cr, Site A and Site A for Cd, Site B and Site B for Ni, and Site B and Site C for Fe in cassava peels and tubers respectively. The lowest mean values of As (1.65, 1.65 mg/kg), Cr (16.48, 15.08 mg/kg), Cd (31.42, 32.19 mg/kg), Ni (3.58, 3.52 mg/kg) and Fe (7.28, 2.80 mg/kg) were recorded in Site B and Site A for As, Site B and Site B for Cr, Site B and Site C for Cd, Site C and Site A for Ni and Site C, Site A and Site B for Fe in cassava peel and tuber respectively. The highest mean values of As, Cr and Cd in *M. esculenta* collected from all the cassava part samples from the farmland soils exceeded the international permissible limit of As (0.2 mg/kg), Cr (2.0 mg/kg) and Cd (0.2 mg/kg) in food (Tables 3 and 4). The results of heavy metal in the cassava plant parts reveals crude oil contamination on the farmland soil due to near proximity from the exploitation sites which increasingly raises the levels of heavy metals in the soils of the farmland soils, and these metals are being taken up by the cassava plant. The result corroborates with the findings of Harrison et al. (2018) who reported the concentration of heavy metals in cassava root plants in crude oil polluted soil. This is expected since areas near petroleum activities have higher level of pollutants, including heavy metals (Nkwocha & Duru, 2010).

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Table 4: Heavy metal concentration in the cassava peel from cassava harvested in the farmland soils near the exploitation sites in Mmahu

Sites	As	Cr	Cd	Ni	Fe
	mg kg^{-1}				
A1	1.87	20.80	42.38	3.82	8.40
A2	1.50	15.20	43.38	3.23	5.60
A3	2.25	28.60	48.49	3.82	5.60
A4	1.12	15.20	50.42	3.52	8.40
A5	1.87	17.80	42.67	3.82	8.40
Maximum	2.25	**28.60**	50.42	3.82	8.40
Minimum	1.12	**15.20**	42.38	3.23	5.60
Mean ± STD	1.72±0.43^{a}	**19.52±5.58^{b}**	45.47±3.72^{a}	3.64±0.26^{a}	7.28±1.53^{b}
B1	1.87	15.60	17.46	3.82	14.00
B2	1.87	18.20	38.79	4.70	8.40
B3	1.50	12.60	32.97	4.70	11.20
B4	1.50	17.80	42.67	4.40	19.60
B5	1.50	18.20	25.21	2.94	16.80
Maximum	1.87	18.20	**42.67**	4.70	**19.60**
Minimum	1.50	12.60	**17.46**	2.94	**8.40**
Mean ± STD	1.65±0.20^{a}	16.48±2.42^{b}	**31.42±10.20^{b}**	4.11±0.75^{a}	**14.00±4.43^{a}**
C1	1.87	15.60	38.79	4.99	11.20
C2	3.75	33.80	40.73	3.82	5.60
C3	2.25	31.20	42.67	3.23	5.60
C4	1.87	41.60	38.79	3.23	8.40
C5	1.87	46.80	46.55	2.64	5.60
Maximum	3.75	**46.80**	46.55	4.99	11.20
Minimum	1.87	**15.60**	38.79	2.64	5.60
Mean ± STD	2.32±0.81^{a}	**33.80±11.91^{a}**	41.50±3.25^{a}	3.58±0.89^{a}	7.28±2.50^{b}
FAO/WHO permissible limit	0.2	2.0	0.2	67.5	48

Table 5: Heavy metal concentration in the cassava tuber from cassava harvested in the farmland soils near the exploitation sites in Mmahu

Sites	As	Cr	Cd	Ni	Fe
	mg kg^{-1}				
A1	1.87	15.60	46.55	3.52	8.40
A2	1.87	10.40	36.85	3.82	5.60
A3	1.50	26.00	42.67	2.94	8.40
A4	1.50	23.40	62.06	3.82	5.60
A5	1.50	28.60	60.12	3.52	2.80
Maximum	1.87	28.60	62.06	3.82	8.40
Minimum	1.50	10.40	36.85	2.94	2.80
Mean ± STD	1.65±0.20^{a}	20.80±7.58^{ab}	49.65±11.02^{a}	3.52±0.36^{b}	6.16±2.34^{b}
B1	1.50	13.00	40.73	4.40	2.80
B2	1.50	31.20	46.55	4.40	2.80
B3	1.87	13.00	38.79	3.23	2.80
B4	1.87	10.40	32.97	4.70	2.80
B5	3.75	7.80	46.55	4.70	2.80
Maximum	3.75	31.20	46.55	4.70	2.80
Minimum	1.50	7.80	32.97	3.23	2.80
Mean ± STD	2.10±0.94^{a}	15.08±9.27^{b}	41.12±5.72^{ab}	4.28±0.61^{a}	2.80±0.00^{c}
C1	1.50	23.40	23.27	3.52	14.00
C2	1.87	28.60	40.73	3.82	11.20
C3	1.50	18.20	27.15	3.52	5.60
C4	1.87	36.40	31.03	4.11	8.40
C5	1.87	31.20	38.79	4.70	8.40
Maximum	1.87	36.40	40.73	4.70	14.00
Minimum	1.50	18.20	23.27	3.52	5.60
Mean ± STD	1.72±0.20^{a}	27.56±7.02^{a}	32.19±7.46^{b}	3.93±0.49^{ab}	9.52±3.19^{a}
FAO/WHO permissible limit	0.2	2.0	0.2	67.5	48

Comparison Between Heavy Metal Concentration in Farmland Soils and Cassava Plant Parts (Peels and Tubers)

The comparison of the soil heavy metal concentration mean values in Table 2 and cassava plant parts heavy metal concentration mean values in Tables 3 and 4 show variations in concentrations. It was found that As, Cr and Cd concentrations were higher in cassava peel and cassava tuber in all the three sites sampled. Fe concentrations in the soil were higher than that found on the cassava peel and tuber in all the three sites sampled. Ni concentrations in the soil, despite not being below permissible limits, were higher than that found in the cassava peels and tubers in Site A and Site B but lower in Site C. The graphical comparison of heavy metal concentration in the soil to concentration in cassava peel and tuber for the sampled sites are shown in Figure 3 for Site A, Site B and Site C respectively.

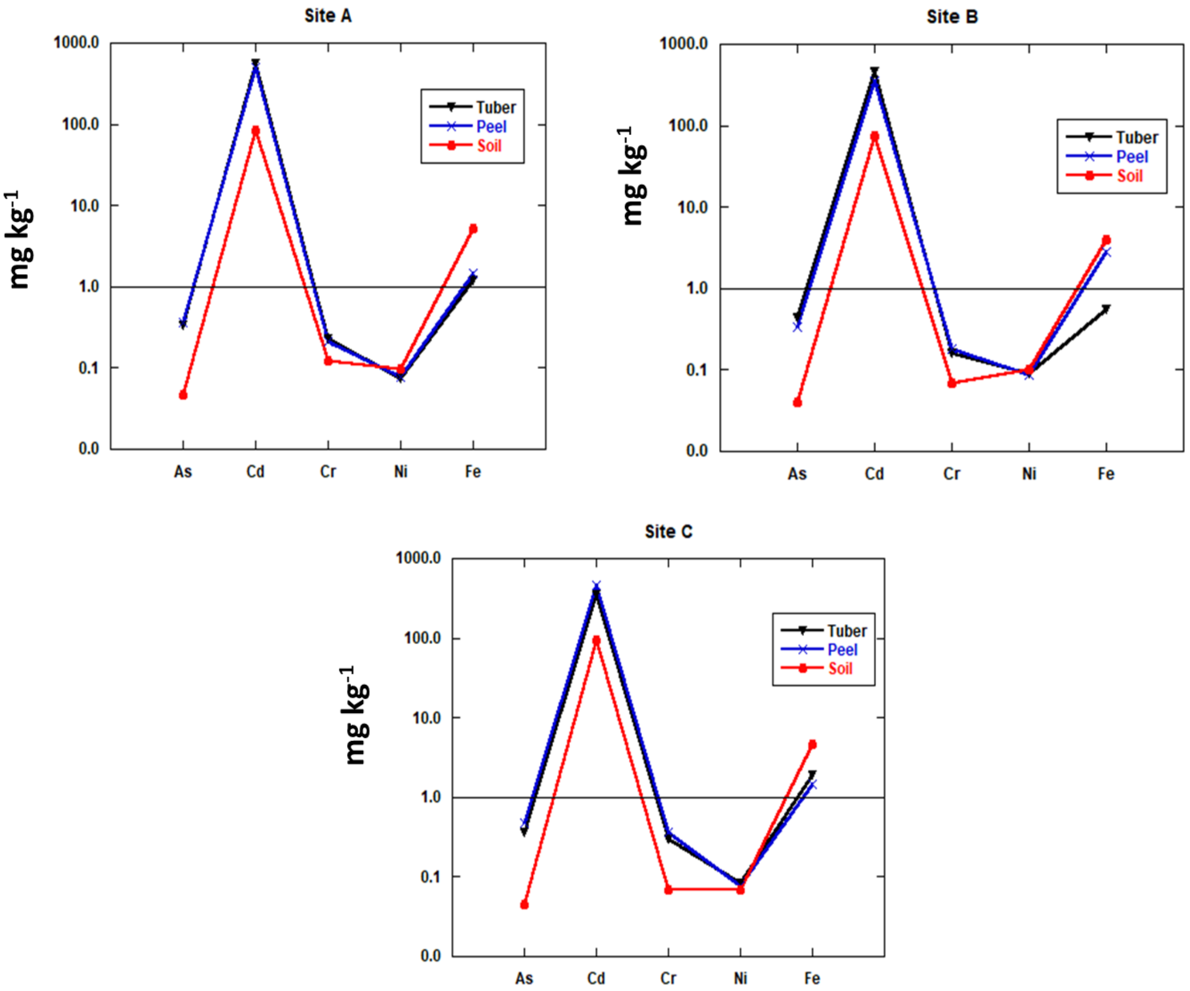

Fig. 3: Concentrations of metals in soils in comparison with concentrations in the cassava peels and cassava tubers in farmland soils near the exploitation sites in Mmahu

Contamination Factor (CF) and Degree of Contamination (C_d) for the Soil and the Cassava Plant Parts (Peels and Tubers)

Contamination Factor (CF) is used to assess the extent of high metal contamination in the soil and in the cassava plant parts (peel and tuber). The calculated CF values for heavy metals are given in Table 6. Variations were found in the values of CF in sampled soils across the three sites. CF values of the studied metals in the three sites were found in the order of Cd > Fe > Cr > Ni > As for Site A, Cd > Fe > Ni > Cr > As for Site B, and Cd > Fe > Cr = Ni > As for Site C, indicating that Cd has the highest CF value in all the three sites while As has the lowest value. The cassava peel and tuber followed the same trend in CF (Cd > Fe > Cr > Ni > As) for all the three sampled sites. As, Cr and Ni showed CF < 1.0 in soil, cassava peels and cassava tubers, indicating low contamination of the studied samples. The CF of Fe in the soil is seen to have considerable contamination while that found in cassava peels is moderately contaminated in the three sites. CF of Fe in the cassava tuber ranges from low to moderate contamination with the highest value (1.89) in Site C and the lowest (0.56) in Site B. CF of the Cd in all the evaluated samples (soil, cassava peels and cassava tubers) are of very high contamination. The very high contamination found in Cd spells serious danger to the soil ecology and humans at large because they are very toxic even at low concentrations, causing nutrient imbalance in the soil and kidney disorders, as well as itai itai disease to humans over time (WHO, 2007).

Degree of Contamination (C_d) of heavy metals depicted in Table 6 for each sampled site (A, B and C) showed Cd to have the highest degree of contamination in the sampled materials (soil, cassava peels and cassava tubers). The C_d of Fe in the soil was more (moderate degree of contamination) compared to that found in cassava plant parts which is of low degree of contamination. Cr, As and Ni showed low C_d in the soils, cassava peels and cassava tubers in the three sampled sites.

The ecological implications of the unacceptable levels of Cd have already been previously demonstrated in Ohaji/Egbema (Bawa-Allah, 2023). Though Fe, Cr, Ni and As made insignificant contributions to the ecological imbalance of the soil, they have the capacity to biomagnify and become toxic over time, while also making the soil ecologically unstable (Tietenberg, 2006). This could affect the crop productivity within the study sites over time.

Table 6: Contamination factor and degree of contamination of farmland soils near the exploitation sites in Mmahu

Sites	CF_{As}			CF_{Cr}			CF_{Cd}			CF_{Ni}			CF_{Fe}		
	Soil	Peel	Tuber	Soil	Peel	Tuber	Soil	Peel	Tuber	Soil	Peel	Tuber	Soil	Peel	Tuber
A	0.046	0.35	0.34	0.124	0.212	0.226	83.61*	505.20*	551.65*	0.096	0.077	0.075	5.27*	1.44*	1.22*
B	0.040	0.34	0.44	0.070	0.179	0.164	74.13*	349.09*	456.83*	0.103	0.087	0.091	3.92*	2.78*	0.56
C	0.045	0.48	0.36	0.069	0.367	0.300	96.54*	461.14*	357.71*	0.069	0.076	0.083	4.69*	1.44*	1.89*
C_d	0.131	1.17	1.14	0.263	0.758	0.69	**254.28***	**1315.48***	**1366.19***	0.268	0.24	0.249	**13.88**	5.66	3.67

Pollution Load Index (PLI) of Cassava Peels and Cassava Tubers

The pollution load index (PLI) was used to bring to light the pollution severity of metal concentrations in cassava peels and cassava tubers. Normally, it is used to indicate the number of times by which the metal concentrations in soils are more than the background concentrations (Nweke & Ukpai, 2016). However, in this research, it was applied to indicate the extent to which metal concentrations in cassava peel and cassava tuber are higher than the background metal concentrations in the soils. The calculated PLI values are presented in Table 7 and Figure 4. The results show that cassava peel has PLI of 10.38 (Site A), 11.42 (Site B) and 15.02 (Site C) while cassava tuber has PLI of 9.90 (Site A), 6.44 (Site B) and 12.33 (Site C). According to Cabrera et al. (1999), $PLI < 1$ is unpolluted, $PLI = 1$ indicates metal load that approximates to the background concentrations, while $PLI > 1$ is polluted. Thus, the PLI status of the cassava peel and tuber harvested from the farmland soils near the three exploratory sites are polluted. The pollution of these sites is evidently from the exploration activities. According to Nwadiogbu et al. (2024), petroleum hydrocarbon contamination and anthropogenic activities have a significant effect of increasing the concentrations of heavy metals around the crude oil mining sites.

Table 7: Pollution Load Index (PLI) of cassava peels and cassava tubers from the farmland soils near the three exploitation sites in Mmahu

Sites	PLI		Status
	Cassava Peel	Cassava Tuber	
A	10.38	9.90	Polluted
B	11.42	6.44	Polluted
C	15.02	12.33	Polluted

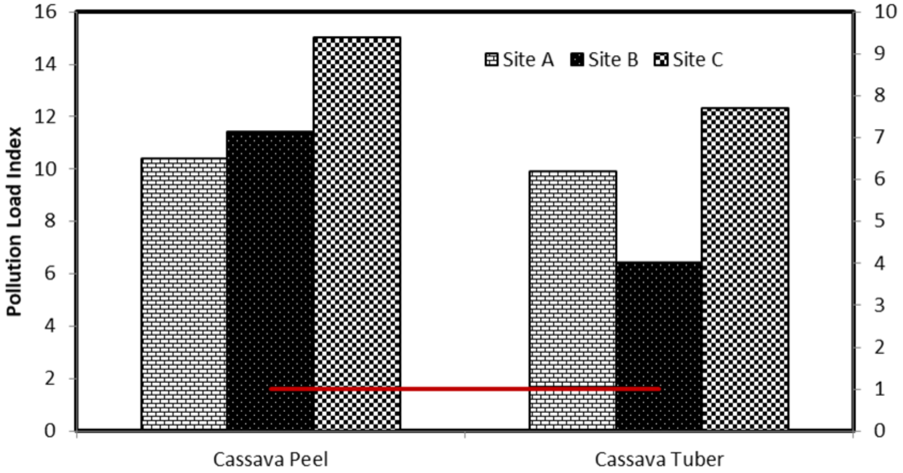

Fig. 4: Pollution load in cassava peels and cassava tubers

Bio-accumulations Factor of Cassava Peels and Cassava Tubers in the Three Crude Oil Exploitation Sites in Mmahu

The results of the bioaccumulation factors (BAF) of heavy metals in cassava peels and on the tubers of cassava are shown in Figures 5 and 6 respectively. It was found that the BAF of As, Cr and Cd were greater than 1 in the three studied sites in both the peels and the tubers. This indicates that cassava has high efficiency in bioaccumulation of these metals. However, Ni and Fe in cassava peels and cassava tubers have BAF less than 1 indicating inefficiency in the bioaccumulation of these elements. The accumulation of heavy metal found in the peel as well as in the tuber of cassava is in support of the work of Baker et al. (1994) that certain plants not only accumulate metals in the plant roots but also translocate the accumulated metals from the root to the leaf or shoot.

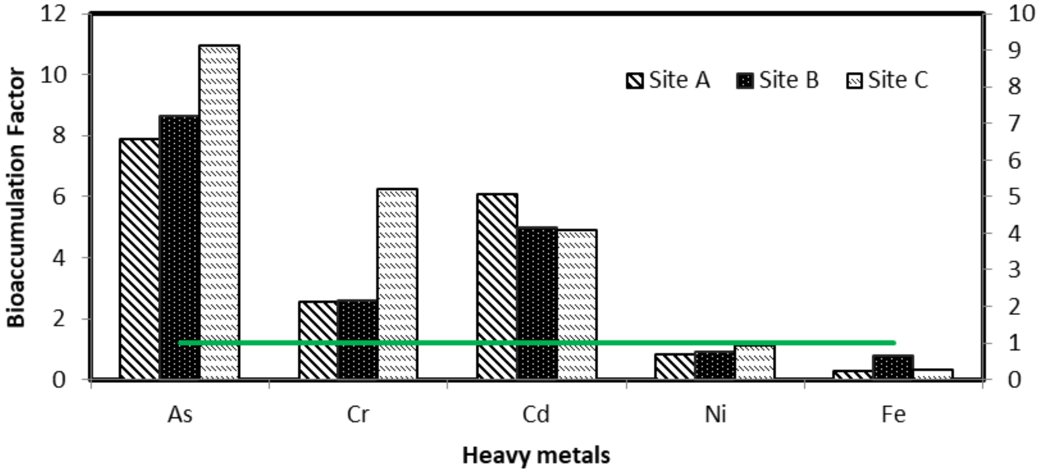

Fig. 5: Bio-accumulations factor of cassava peels in the three crude oil exploitation sites in Mmahu

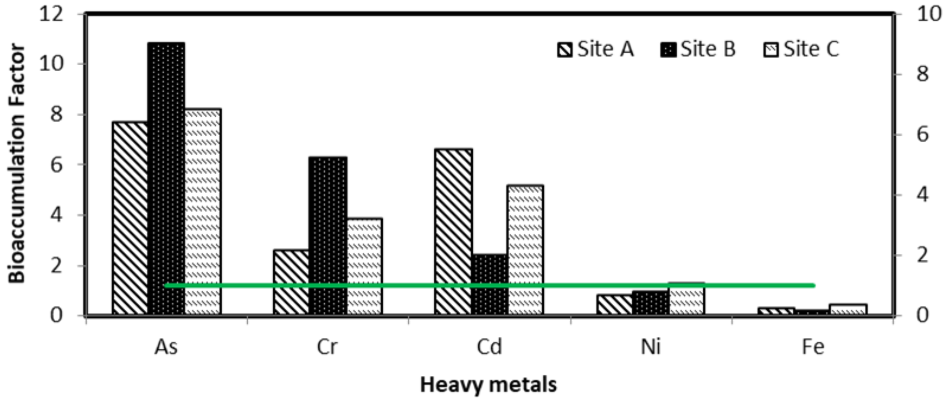

Fig. 6: Bio-accumulations factor of cassava tubers in the three crude oil exploitation sites in Mmahu

Bio-translocation Factor of Cassava Tubers in the Three Crude Oil Exploitation Sites in Mmahu

The bio-translocation factor (BTF) of cassava tubers in the cassava harvested from the farmland soils near the three oil exploitation sites in Mmahu are presented in Figure 7. The results indicate that As, Cr and Cd have BTF > 1 in Site A; As, Cr and Ni have BTF > 1 in Site B; with Site C having only Ni and Fe as the elements with BTF > 1. This is an indication that there is effective phytoextraction translocation of these metals from the peels to the tubers of the cassava.

However, Ni and Fe for Site A; Cd and Fe for Site B; and As, Cr and Cd for Site C have BTF less than 1 in their tubers, and this indicates ineffective translocation of these metals. This result obtained implies that cassava is capable of in-situ phytoremediation of heavy metal elements but there were variations in the elements' translocation across the three sites. These variations might be attributed to the variation in cassava varieties across the three sites. Notably, from Figures 5 and 6, it was observed that Site C has more of the carcinogenic elements in the peels than those found on the tubers, indicating that cassava varieties planted in Site C are different, which is reflected in the BTF values.

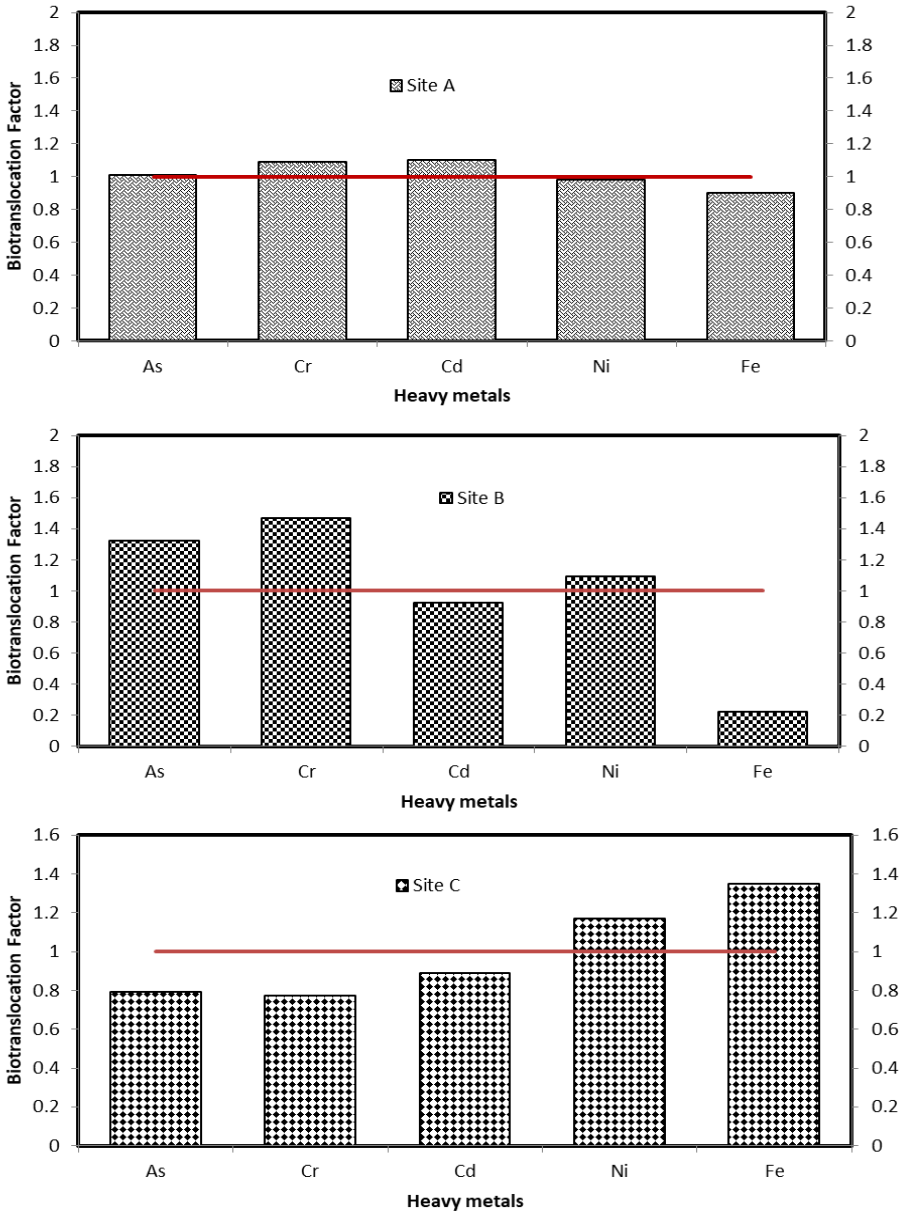

Fig. 7: Bio-translocation factor of cassava tuber in the three crude oil exploitation sites in Mmahu

CONCLUSION

In conclusion, the study revealed that the crude oil impacted farmland soils are enriched with As, Cr, Cd, Ni and Fe. Cassava plants grown on these soils accumulate reasonable amounts of these heavy metals, although some are low and some are of high value, especially Cd, a function strongly controlled by variation in soil properties and cassava varieties across the three exploitation sites. However, it is important to advise farmers against cultivating in crude oil contaminated soils for the risk of accumulation of heavy metals in plant tissues. Additionally, the practice of adding ash to the soil as a soil reclaiming agent should be encouraged. Farmers should also be advised by the extension workers to carefully select crop types or varieties with low bio-translocation factor (BTF) so as to reduce the heavy metal concentration to health risk level.

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