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Analysis of Heavy Metals in Some Food Crops and Soils Impacted with Crude Oil in Southern Nigeria

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Abstract: *The contamination of food crops grown in crude oil-impacted soils by heavy metals is becoming alarming due to incessant oil spills. Some physicochemical and heavy metals (Fe, Ni, Cr, Pb, Cd, Zn, and Cu) analyses of crude oil-impacted soils from southern Nigeria and some food crops are grown on them were carried out using standard analytical procedures. The soil samples were collected from different communities (Atia, Ntafre, Ntak Ifaha, Esitikeme, Awah) and a control sample was also collected from a nearby non-oil impacted farmland in Mkpanak community, all in Ibeno Local Government Area of Akwa Ibom State, Nigeria. Some food crop samples (Manihot esculenta Crantz, Dioscorea alata, Zea mays L., Musa paradisiaca and Colocasia esculenta) were randomly collected simultaneously along with the soil samples from all sites. The results revealed that the soils' pH varied from 5.35±2.10 to 6.18±0.00 which indicated that the soils under study were acidic while that of the control was 7.94±1.52. The organic matter (OM) content in all the impacted soil samples was higher (12.95±0.35 % to 17.05±4.28 %) compared to the control soil (6.74±1.30 %) sample. The concentrations of the heavy metals in the soils in terms of abundance were in the order: Fe > Zn > Ni > Cu > Cr > Pb > Cd which showed that Fe is the most sufficient. It was observed that most of the studied crops especially Manihot esculenta C. had values of heavy metals higher than the values recorded for their respective soil samples. Also, the levels of all the studied metals exceeded the permissible limits set by WHO/FAO except for Zn and Cu. However, the soil-to-plant transfer factor (TF) showed that the highest TF recorded was in Zn, with most values above 1 followed by Cr and Cd. This is an indication that Zn, Cr and Cd were the most bio-available metals. This signified that residents could be exposed to substantial health risks associated with heavy metals via the consumption of these food crops.*

Keywords*: Heavy metal ions, crude oil, transfer, soil, food crop*

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1.0 Introduction

Southern Nigeria which forms part of the Niger Delta is greatly endowed with abundant natural resources like crude oil, and this gives rise to increased industrial activities, especially oil exploration and exploitation. The Niger Delta region is one of the world's largest wetlands which covers an area of approximately 75,000 km^2 (7.5% of Nigeria) with an estimated population of about 22 million (Useh and Dauda, 2018) and the region's oil resources account for 90 % of the nation's export earnings (Okoye and Okwute, 2014; Onakpa *et al.*, 2018; Harrison *et al.*, 2018). Nonetheless, the oil-rich region which contributes the highest percentage of national wealth is subjected to severe environmental degradation due to oil spill which has caused excessive destruction and continuous harm to the physical, social, and economic health of the people. In most of the oil bearing communities, their sources of potable water, farmlands and rivers they used for cultivation and fishing respectively have all been

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polluted by the activities of oil companies without the quantifiable effort of remediation or compensation (Raymond and Felix, 2011; Onakpa *et al.,* 2018). Accidental and deliberate crude oil spills have posed a serious environmental problem, due to the possibility of air, water and soil contamination (Raymond and Felix, 2011; Emurotu and Onianwa, 2017) Organic and inorganic substances, which include varied heavy metals, synthetic or naturally occurring organic compounds (particularly petroleum hydrocarbons), all constitute the main mix of environmental contaminants in nature (Useh and Ikokoh, 2016). The major routes by which these compounds enter the environment are via industrial, mining and agricultural activities. These chemical contaminants are found naturally, however, due to anthropogenic activities they become more intense and get released into the environment (Useh and Dauda, 2018).

Oil exploitation and crude-oil spill on land introduce petroleum-based hydrocarbons (PHCs), additives and metallic salts such as elevated concentrations of heavy metals, which negatively impact soil biological, chemical and physical characteristics such as the structure, biodiversity, microbial populations, nutrient cycles, the bioavailability of minerals, etc Chukwujindu, 2011; Nwaichi *et al.*, 2016]. Heavy metal contamination is a serious environmental health challenge and is potentially dangerous due to its bioaccumulation through the food chain (Onakpa *et al.,* 2018; Salman *et al.,* 2019). When the soils are contaminated with heavy metals, it affects the proper growth of crops and the quality yield of agricultural products, then these plants or crops grown on it take up the metals through absorption which consequently gets accumulated in their tissues (Harrison *et al.*, 2018; Ajayi and Olasukanmi, 2021). Some plants tend to accumulate contaminants in certain organs and the distribution depends on the mobility of the contaminant in the plant tissues, the type of plant, and the conditions of its growth (Nwaichi *et al.,* 2016; Onakpa *et al.,* 2018). Most plant species cannot adapt to elevated levels of heavy metal content, but some plants survive, grow, and reproduce in soils contaminated with heavy metals. A vast majority of these species tolerate heavy metal concentrations and retain most of the heavy metals in the roots with minimal translocation to the leaves (Mbong *et al.,* 2014; Harrison *et al.,* 2018; Josephat *et al.,* 2020; Štofejová *et al.,* 2021).

Soil-to-crop transfer of heavy metals is the major pathway of human exposure by consuming contaminated plants and animals and this has been known to result in various biochemical disorders (Emurotu and Onianwa, 2017; Tatah *et al.,* 2020). Several complications associated with such contamination were observed to include but are not limited to damage to the nervous system, kidney disease, heart disease and infertility (Alum *et al.,* 2014; Nesta *et al.,* 2015; Tatah *et al.,* 2020). The level of crude oil contamination continues to surge with associated socio-economic and environmental impacts and presently, the issue is gaining global recognition as it poses a significant challenge to the present and future generations. Crude oil contaminated sites in Southern Nigeria especially Akwa Ibom State, are poorly investigated to know the extent of heavy metals contamination. More so, Southern Nigeria is a region where most of the inhabitants are peasant farmers, hence it becomes imperative to determine the degree of heavy metals contamination in some food crops and soils impacted with crude oil to monitor the contaminant level. Therefore, ths study aimed to carry out an analysis of heavy metals in some food crops and soils impacted with crude oil in Southern Nigeria.

2.0 Materials and Methods

2.1 Study Area

Akwa Ibom State is located in the south-south geopolitical zone and is one of the major oil–producing States in Nigeria with 31 Local Government Areas (LGAs). The study was carried out in Ibeno which is one of the LGAs in Akwa Ibom State occupying the largest Atlantic coastline of more than 129 km and the town lies on the eastern side of the Kwa Ibo River about 3 km from the river mouth (Figure 1), and it has an estimated population of more than 74, 840 people as at 2006 (NPC, 2006; Alum *et al.,* 2014; Useh and Ikokoh, 2016). Ibeno lies in the Mangrove Forest Belt of the Niger Delta region of Nigeria, bounded to the west by Eastern Obolo, to the north by Onna, Esit Eket and Eket LGA, and to the south by the Atlantic Ocean. The geographic coordinates of Ibeno lie within Latitude 4.568693° North and Longitude 7.976396° East of the Greenwich Meridian. Located in the mangrove swamp forest, the area has rain throughout the year with the peak between May and September (Useh and Ikokoh, 2016). The climatic condition in Ibeno is favorable all year round for fishing and farming which is the prime occupation of the people with such agricultural produce as yam, cassava, vegetables, corn, plantain and palm products. Ibeno Beach, the longest in West Africa, is a popular tourist attraction.

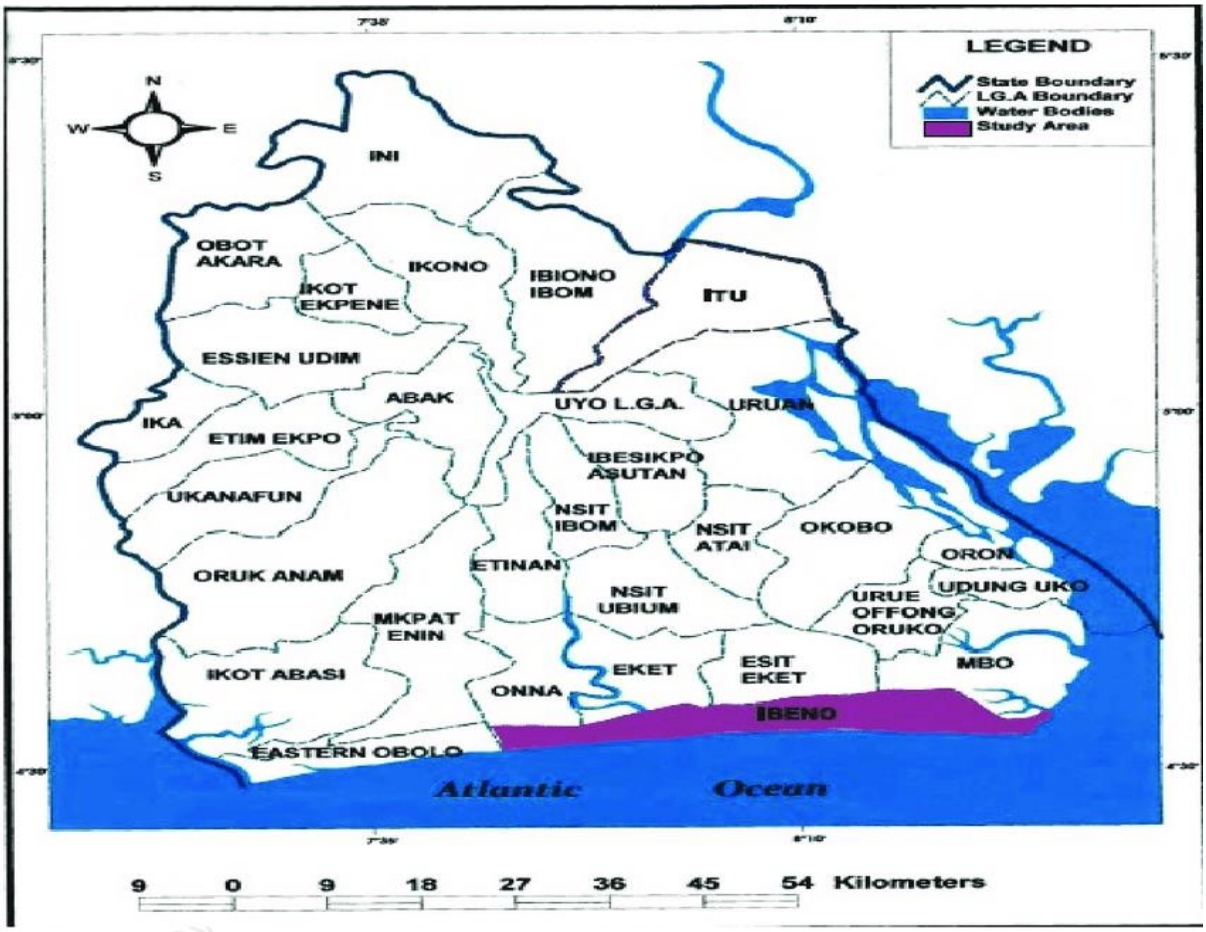

Fig. 1: Map of Akwa Ibom State showing the Study Area (Source: Ukpong, 2013)

2.2 Sample collection, handling and preservation

US EPA (SW-846) guidelines were applied, using composite sampling for collecting soil samples where sub-samples were collected from randomly selected locations in an area. Fifty (50) soil samples were randomly collected using a soil auger from the depth of 0-15 cm from five selected oil-impacted communities (Atia, Ntafre, Ntak Ifaha, Esitikeme, Awah) in Ibeno and were coded SL1, SL2, SL3, SL4 and SL5 respectively and stored (Useh *et al.,* 2022). There were ten (10) replicates for each sampling site and the sub-samples were thoroughly mixed to obtain a representative sample of each. Control samples were collected from another nearby non-oil impacted farmland in Mkpanak community. These were stored in well-labelled amber glass bottles with a Teflon-lined screw cap, held at 4°C immediately in a cooler of ice and transported to the laboratory for pre-treatment and analyses (Useh and Dauda, 2018). The soil samples were air-dried for two weeks, rolled manually, mixed and sieved with 2 mm mesh to remove stones and debris. These were properly stored in well-labelled air-tight containers until analysis. Further, a total of one hundred and fifty (150) staple food crop samples of cassava tubers (*Manihot esculenta Crantz*), yam tubers (*Dioscorea alata*), maize (*Zea mays L.*), plantain fruits (*Musa paradisiaca*) and taro (*Colocasia esculenta*) were randomly harvested simultaneously along with the soil samples from all sites based on their availability (Emurotu and Onianwa, 2017; Onwuka *et al.,* 2021). The food crop samples were thoroughly washed with potable water to remove dirt and then peeled, the edible parts were cut into smaller sizes to possibly increase their surface areas for easy drying. The samples were dried in an oven at 105°C to a constant weight after which they were pulverized, sieved and stored in air-tight containers before analysis.

2.2.1 Reagents

All chemicals and reagents were of analytical grade and the highest purity possible. They were supplied by BDH Labs (UK). BDH Chemicals Limited Poole England.

2.3 Physicochemical Analysis of Soil Samples

Physicochemical properties such as pH, conductivity, soil texture, bulk density, organic matter, and cation exchange capacity (CEC) were analyzed. The pH and electrical conductivity were measured in a soil suspension (1:10 w/v dilution) by a digital pH meter (Jenway model 3015) and conductivity meter (Systronics-304), respectively. The texture of the soil was determined by using the hydrometer method while the bulk density was determined gravimetrically. Organic matter was examined by the Potassium dichromate titration method (Useh and Dauda, 2018). The cation exchange capacity (CEC) of soil was determined as per the procedure outlined by Useh *et al.,* (2015).

2.4 Heavy Metals Analysis

Digestion was carried out using the conventional aqua regia (3:1, v/v, HCl to HNO_3) digestion procedure according to the method described by Useh *et al.,* (2022) and the heavy metals (Fe, Ni, Cr, Pb, Cd, Zn, and Cu) analysis was done using atomic absorption spectrophotometer (Perkin Elmer 400 series) according to APHA method (APHA, 2009).

2.5 Transfer Factor of Metal from Soil to Plant

Metal uptake from soil to plants measured by transfer factor (TF) or Bioconcentration Factor (BCF) is an index used to assess metal mobility from soil to plants. It is one simple way to explain human exposure to metals through the food chain (Mbong *et al.,* 2014; Hammed *et al.,* 2017). For each particular metal, the TF can vary greatly from one environment to another or depending on the type of plant (Mohamad *et al.,* 2016; Devi *et al.,* 2020). The main parameters that modify TF are; the physical and chemical characteristics of soils, behaviour of trace metals in soils and plants, and environmental changes (Yeasmin *et al.,* 2013; Gabriel and Kasali, 2014). Metal concentrations in the extracts of soils and plants were calculated based on the dry weight. The Transfer factor from soil to plants was calculated as the ratio of metal concentration in plants and metal concentration in the soil as stated in equation (1) (Yeasmin *et al.,* 2013, Mohamad *et al.,* 2016; Devi *et al.,* 2020).

$$TF = \frac{C_{Plant}}{C_{Soil}} \quad (1)$$

where; TF is the Transfer factor, C plant and C soil represent the heavy metal concentration in extracts of plants and soils on a dry weight basis, respectively.

2.6 Statistical analysis

All the statistical analyses were performed using statistical software SPSS Windows version 25.0 and Analysis of Variance (ANOVA).

3.0 Results and Discussion

The results of the physicochemical properties of the soil samples from the study area: Atia, Ntafre, Ntak Ifaha, Esitikeme, Awah and Mkpana communities are recorded in Table 1. The measured pH values for the studied soils varied from 5.35±2.10 in SL4 to 6.18±0.00 in SL2 which indicated that the soils under study were acidic while that of the control was 7.94±1.52 which was to some extent alkaline in nature. This showed that soil acidity decreased in the non-oil impacted site. The effect of crude oil on the soil pH could be attributed to the change in soil biochemistry and the production of organic acids by microbial metabolism which was confirmed by Babatunde and Tosin, (2012) that oil may alter soil biochemistry parameters such as pH, oxygen and nutrient availability. In general, the soil of this pH is suitable for metal bioavailability, since most heavy metals are more mobile and available at a lower pH (Radomirovi´c *et al.*, 2020). The electrical conductivity (EC) ranged from 955±2.84 dS/cm in SL2 to 1873±6.32 dS/cm in SL1 with the control site recording 863±7.41 dS/cm. All the studied sites except SL2 (Ntafre) relatively have higher values of EC compared to the control, causing a salinity effect and limiting yield for crops (Dhanasekarapandian *et al.*, 2019).

Table 1. Physicochemical properties of the soil samples

Sampling locations	Sample Code	pH	EC (dS/cm)	Soil texture	Bulk density (g/cm3)	Organic matter (%)	CEC (cmolc/kg)
Atia	SL1	5.70±1.02	1873±6.32	Clay loam	1.85±0.00	15.61±3.64	8.38±1.10
Ntafre	SL2	6.18±0.00	955±2.84	Loam	2.14±0.01	15.29±1.37	10.14±2.21
Ntak Ifaha	SL3	5.62±0.36	1679±0.20	Clay loam	2.23±0.01	17.05±4.28	10.92±1.30
Esitikeme	SL4	5.35±2.10	1684±6.11	Clay loam	2.17±0.02	12.95±0.35	7.73±1.06
Awah	SL5	6.09±0.10	1792±5.83	Silt loam	1.94±0.10	14.87±0.51	8.67±0.10
Mkpanak	Control	7.94±1.52	863±7.41	Loam	1.32±0.10	6.74±1.30	16.22±4.13

Values are means of triplicate determinations ± standard deviation.

The soil texture was found to be generally clay loam or loamy soil in all the studied sites including the control site and metals tend to accumulate in the clay fraction of the soil because clay sized particles have a large number of ionic binding sites due to higher amount of surface area (Chukwujindu, 2011; Alina *et al.*, 2012). As expected, due to hydrocarbons from the long-term oil spill, the organic matter (OM) content in all the impacted soil samples was higher (12.95±0.35 % to 17.05±4.28 %) compared to the control soil (6.74±1.30 %) sample. This is in agreement with the previous work of Useh and Dauda, (2018) who recorded higher values of OM in the petroleum contaminated soils compared to the control site. Bulk density is an indication of soil compaction. It reflects the ability of the soil to function for structural support, water and solute movement, and soil aeration (Dhanasekarapandian *et al.*, 2019). The bulk density in all the studied sites was relatively high (1.85±0.00 g/cm3 in SL1 to 2.23±0.01 g/cm3 in SL3) compared to that of the control soil sample, 1.32±0.10 g/cm3. The high bulk density recorded here indicated low soil porosity and soil compaction which may cause restrictions to plant growth and poor movement of air and water through the soil. Cation exchange capacity (CEC) is a useful indicator of soil fertility because it shows the ability of the soil to supply important plant nutrients like Ca^{2+}, Mg^{2+} and other cations. From the results, the CEC ranged from

7.73±1.06 cmolc/kg in site SL4 to 10.92±1.30 cmolc/kg in site SL3 which were lower than that of the control, 16.22±4.13 cmolc/kg. The apparent decrease in CEC of the impacted soils could be attributed to the long-term effect of crude oil on the soil chemical properties which causes a fraction of the charged sites to be neutralized by the charged components stemming from crude oil. Soils with low CEC tends to become more acidic and would need liming more frequently than soils with high CEC (Useh and Dauda, 2018). The results of the heavy metal contents in soils collected from the five study sites and control sites are presented in Table 2. The concentrations of the studied heavy metals were in the range of Fe (3952 mg/kg to 5726 mg/kg), Ni (17.46 mg/kg to 29.18 mg/kg), Cr (8.38 mg/kg to 13.10 mg/kg), Pb (1.55 mg/kg to 3.90 mg/kg), Cd (1.38 mg/kg to 3.57 mg/kg), Zn (22.48 mg/kg to 30.25 mg/kg) and Cu (12.71 mg/kg to 18.13 mg/kg) compared to the control site (2417 mg/kg, 10.41 mg/kg, 2.73 mg/kg, 1.07 mg/kg, 0.12 mg/kg, 20.62 mg/kg and 7.94 mg/kg) respectively.

Table 2: Concentration of heavy metals in the soil samples (mg/kg)

Sampling Locations	Fe	Ni	Cr	Pb	Cd	Zn	Cu
SL1	5382	20.17	8.38	3.90	3.57	27.61	12.71
SL2	5726	17.46	11.27	1.55	1.64	22.48	17.63
SL3	3954	25.53	10.62	2.74	1.38	30.25	12.84
SL4	4792	29.18	13.10	1.92	2.82	26.07	15.61
SL5	5168	21.60	8.61	3.58	1.73	24.37	18.13
Control	2417	10.41	2.73	1.07	0.12	20.62	7.94

The concentrations of the heavy metals in terms of abundance were in the order: Fe > Zn > Ni > Cu > Cr > Pb > Cd in the soils which indicated that Fe is the most sufficient. This is in agreement with the reports of other researchers (Shigeo *et al.*, 2007; Alum *et al.*, 2014; Nwaichi *et al.*, 2016). Nigerian crude oil contains heavy metals which are not completely removed during refining processes and the higher metal contents recorded might be due to the presence of crude oil pollution (Babatunde and Tosin, 2012). The study of these heavy metals are important since they are capable of reducing crop production due to the risk of bioaccumulation and biomagnification in the food chain (Onakpa *et al.*, 2018; Harrison *et al.*, 2018). Although heavy metals at extreme concentrations are toxic to microorganisms, plants, animals and humans, a substantial proportion of minerals (metals at acceptable concentrations) are beneficial (Useh and Dauda, 2018). The fate and transport of heavy metal in soil depend significantly on the chemical form and speciation of the metal. Once in the soil, heavy metals are adsorbed by initial fast reactions which being followed by slow adsorption. They are then redistributed into different chemical forms with varying bioavailability, mobility, and toxicity which is controlled by ion exchange, adsorption, and desorption, biological immobilization and mobilization, mineral precipitation, dissolution and plant uptake (Raymond and Felix, 2011; Harrison *et al.*, 2018; Devi *et al.*, 2020).

Generally, the concentrations of the studied heavy metals were higher in the examined soil samples than that in the control. The difference in metal concentrations could simply be attributed to the nature of the soil and the level of anthropogenic activities such as crude oil exploration and exploitation going on in these areas which brought about the increased levels of metals (Onwuka *et al.*, 2021). These chemical contaminants (organic and inorganic substances including varied heavy metals) are found naturally, however, due to anthropogenic activities, they become more intense and get released into the environment causing adverse effects (Useh and Dauda, 2018). For instance, lead has been reported as neurotoxic and can accumulate in the bone marrow (Hammed *et al.,* 2017; Salman *et al.,* 2019; Radomirovi´c *et al.,* 2020). The two routes of exposure to Pb are inhalation and ingestion and Pb accumulates in the brain, gastrointestinal tract, kidneys, and central nervous system which may lead to poisoning or even death. Children exposed to lead are at risk for impaired development, lower IQ, hyperactivity, and mental deterioration, with children under the age of six being at more substantial risk (Raymond and Felix, 2011; Alina *et al.,* 2012). The toxicity of Cr strongly depends on its concentration in the soil and its uptake mechanism. The sources of Cr in the environment are both natural and anthropogenic. Anthropogenic activities like crude oil spills may lead to widespread contamination of the environment. A high concentration of Cr was found to be harmful to plant life, reducing the protein contents, inhibiting the enzyme activity and causing chlorosis and necrosis (Vinod and Chopra, 2015). Chromium is associated with allergic dermatitis in humans (Josephat *et al.,* 2020; Useh *et al.,* 2022).

The concentrations of heavy metals in food crop samples from the crude oil impacted sites and control farmland are presented in Table 3. In SL1, Fe ranged from 2792 mg/kg in *Zea mays L.* to 4121 mg/kg in *Colocasia esculenta,* Ni ranged from 14.72 mg/kg in *Zea mays L.* to 32.00 mg/kg in *Manihot esculenta C.*, Cr ranged from 16.94 mg/kg in *Colocasia esculenta* to 25.33 mg/kg *Musa paradisiaca,* Pb ranged from 1.69 mg/kg in *Zea mays L.* to 3.61 mg/kg in *Manihot esculenta C.,* Cd ranged from 1.53 mg/kg in *Musa paradisiaca* to 3.88 mg/kg in *Manihot esculenta C.,* Zn ranged from 47.93 mg/kg in *Manihot esculenta C.* to 61.43 mg/kg in *Musa paradisiaca,* and Cu ranged from 8.94 mg/kg in *Zea mays L.* to 13.52 mg/kg in *Dioscorea alata.* In SL2, Fe was between 2536 mg/kg in *Manihot esculenta C.* to 3644 mg/kg in *Musa paradisiaca,* Ni was between 16.48 mg/kg in *Dioscorea alata* to 30.17 mg/kg in *Zea mays L.,* Cr ranged from 13.76 mg/kg in *Manihot esculenta C.* to 22.31 mg/kg in *Musa paradisiaca,* Pb was between 1.46 mg/kg in *Colocasia esculenta* to 2.55 mg/kg in *Musa paradisiaca,* Cd ranged from 1.37 mg/kg in *Musa paradisiaca* to 3.46 mg/kg in *Colocasia esculenta,* Zn was between 42.49 mg/kg in *Dioscorea alata* to 64.83 mg/kg in *Musa paradisiaca,* and Cu was between 8.90 mg/kg in *Zea mays L.* to 14.82 mg/kg in *Manihot esculenta C.* In SL3, Fe ranged from 2537 mg/kg in *Colocasia esculenta* to 4173 mg/kg in *Manihot esculenta C.,* Ni ranged from 22.61 mg/kg in *Manihot esculenta C.* to 35.11 mg/kg in *Musa paradisiaca,* Cr was between 15.37 mg/kg in *Musa paradisiaca* to 23.26 mg/kg in *Manihot esculenta C.,* Pb ranged from 0.74 mg/kg in *Zea mays L.* to 3.02 mg/kg in *Dioscorea alata,* Cd was between 1.57 mg/kg in *Musa paradisiaca* to 3.16 mg/kg in *Dioscorea alata,* Zn was between 54.88 mg/kg in *Dioscorea alata* to 63.12 mg/kg in *Musa paradisiaca* and Cu ranged from 8.37 mg/kg in *Colocasia esculenta* to 14.38 mg/kg in *Musa paradisiaca.*

In SL4, Fe was between 3249 mg/kg in *Zea mays L.* to 4402 mg/kg in *Colocasia esculenta,* Ni ranged from 15.57 mg/kg in *Colocasia esculenta* to 21.73 mg/kg in *Musa paradisiaca,* Cr ranged from 9.46 mg/kg in *Musa paradisiaca* to 23.16 mg/kg in *Dioscorea alata,* Pb was between 0.66 mg/kg in *Musa paradisiaca* to 2.45 mg/kg in *Colocasia esculenta,* Cd ranged from 1.36 mg/kg in *Zea mays L.* to 3.52 mg/kg in *Colocasia esculenta,* Zn ranged from 46.49 mg/kg in *Dioscorea alata* to 61.47 mg/kg in *Musa paradisiaca,* Cu was between 8.85 mg/kg in *Musa paradisiaca* to 15.01 mg/kg in *Zea mays L.* In SL5, Fe was between 2695 mg/kg in *Colocasia esculenta* to 3763 mg/kg in *Zea mays L.,* Ni ranged from 21.48 mg/kg in *Zea mays L.* to 32.05 mg/kg in *Dioscorea alata,* Cr ranged from 10.92 mg/kg in *Musa paradisiaca* to 18.79 mg/kg in *Dioscorea alata,* Pb was between 0.48 mg/kg in *Zea mays L.* to 2.41 mg/kg in *Colocasia esculenta,*

Cd was between 2.74 mg/kg in *Manihot esculenta C.* to 3.38 mg/kg in *Musa paradisiaca,* Zn was between 46.39 mg/kg in

Musa paradisiaca to 65.31 mg/kg in *Manihot esculenta C.* and Cu ranged from 10.38 mg/kg in *Zea mays L.* to 14.63 mg/kg in *Dioscorea alata*. In the control sample,
Fe ranged from 870 mg/kg in *Zea mays L.* to 1748 mg/kg in *Manihot esculenta C.*, Ni was between 14.75 mg/kg in *Zea mays L.* to 26.33 mg/kg in *Dioscorea alata*, Cr ranged from 2.46 mg/kg in *Colocasia esculenta* to 5.48 mg/kg in *Musa paradisiaca,* Pb ranged from 0.16 mg/kg in *Manihot esculenta C.* to 0.72 mg/kg in *Dioscorea alata* but was not detected in *Zea mays L.* and *Musa paradisiaca,* Cd was between 0.13 mg/kg in *Colocasia esculenta* to 0.17 mg/kg in *Musa paradisiaca* but was not detected in *Zea mays L.*, Zn ranged from 34.15 mg/kg in *Zea mays L.* to 43.28 mg/kg in *Dioscorea alata* and Cu was between 4.39 mg/kg in *Zea mays L.* to 6.84 mg/kg in *Manihot esculenta C.*

Table 3: Concentration of heavy metals in the food crop samples (mg/kg)

Sampling Locations	Crop Samples	Heavy Metals						
		Fe	Ni	Cr	Pb	Cd	Zn	Cu
SL1	*Manihot esculenta C.*	3117	32.00	23.17	3.61	3.88	47.93	10.67
	Dioscorea alata	3845	27.36	18.65	1.84	2.94	53.18	13.52
	Zea mays L.	2792	14.72	20.72	1.69	3.27	55.37	8.94
	Musa paradisiaca	3047	17.38	25.33	2.32	1.53	61.43	10.48
	Colocasia esculenta	4121	24.81	16.94	2.47	3.54	49.25	12.63
SL2	*Manihot esculenta C.*	2536	27.39	13.76	1.48	2.57	57.38	14.82
	Dioscorea alata	3294	16.48	15.48	1.97	2.42	42.49	12.41
	Zea mays L.	3173	30.17	15.77	1.63	1.48	45.38	8.90
	Musa paradisiaca	3218	26.83	22.31	2.55	1.37	64.83	9.45
	Colocasia esculenta	3644	17.94	20.46	1.46	3.46	59.34	9.75
SL3	*Manihot esculenta C.*	4173	22.61	23.26	1.51	2.79	62.43	13.26
	Dioscorea alata	3481	25.03	16.72	3.02	3.16	54.88	10.73
	Zea mays L.	2816	28.73	18.14	0.74	3.11	57.61	12.54
	Musa paradisiaca	2692	35.11	15.37	0.91	1.57	63.12	14.38
	Colocasia esculenta	2537	25.82	16.43	1.36	1.78	60.15	8.37
SL4	*Manihot esculenta C.*	4082	20.64	19.45	2.27	2.88	57.38	11.36
	Dioscorea alata	3387	18.85	23.16	1.83	3.33	46.49	13.42
	Zea mays L.	3249	15.92	15.38	1.14	1.36	46.85	15.01
	Musa paradisiaca	4215	21.73	9.46	0.66	2.48	61.47	8.85
	Colocasia esculenta	4402	15.57	12.49	2.45	3.52	52.64	9.33
SL5	*Manihot esculenta C.*	3625	30.44	16.21	0.59	2.74	65.31	13.26
	Dioscorea alata	3458	32.05	18.79	1.64	3.26	63.15	14.63
	Zea mays L.	3763	21.48	15.56	0.48	3.21	52.00	10.38
	Musa paradisiaca	2842	25.39	10.92	2.05	3.38	46.39	10.45
	Colocasia esculenta	2695	25.27	14.85	2.41	3.22	59.41	13.47
Control	*Manihot esculenta C.*	1748	14.97	5.26	0.16	0.16	34.36	6.84
	Dioscorea alata	1593	26.33	3.74	0.72	0.15	43.28	4.57
	Zea mays L.	870	14.75	2.94	ND	ND	34.15	4.39
	Musa paradisiaca	895	17.58	5.48	ND	0.17	35.00	8.44
	Colocasia esculenta	1576	18.46	2.46	0.51	0.13	37.03	5.12
FAO/WHO Standards		425.5	10	1.3	0.1	0.1	100	20

****ND = not detected**

It was observed that most of the studied plants had values of heavy metals higher than the values recorded for their respective soil samples. This could be attributed to the high metal contents of the impacted soils which are eventually accumulated by the crop samples grown on them.

Also, the proliferation of heavy metal contents in the food crops could be attributed to the increased availability of such cations in soil due to an anaerobic reducing environment caused by crude oil in the studied soil (Mbong *et al.*, 2014; Alum *et al.*, 2014; Hammed *et al.*, 2017). Further, the concentrations of heavy metals in *Manihot esculenta Crantz*, *Dioscorea alata*, *Zea mays L.*, *Musa paradisiaca* and *Colocasia esculenta* from the impacted sites were above those of the control counterparts and this is in agreement with the findings of other researchers (Shigeo *et al.*, 2007; Essiett *et al.*, 2010; Yeasmin *et al.*, 2013; Gabriel *et al.*, 2014; Hammed *et al.*, 2017; Harrison *et al.*, 2018). Also, the levels of all the studied metals exceeded the permissible limits set by WHO/FAO except for Zn and Cu which were within the normal range of metals in plant samples and were also below the levels recommended by WHO/FAO for metals in foods and vegetables. These findings call for greater concern, particularly as heavy metals tend to bioaccumulate in food crops and pose a serious health risk to humans and animals. These studies are indicative of potential health hazards faced by the indigenous populace who feed on these crops continually. Okoye and Okwute, (2014) noted that some components of crude oil are highly lipophilic, even small amounts entering the environment accumulate in organisms due to gradual and steady build-up.

The soil-to-plant transfer factor (TF) is one of the key components used to measure the level of human exposure to metals in the food chain Shigeo *et al.*, 2007; Yeasmin *et al.*, 2013). It entails the extent to which heavy metals in the soil accumulate in the plants and shows the amount of risk or hazard associated with the ingestion of food crops from the study area. From the results obtained, the highest transfer factor recorded was in Zn, with most values above 1 (one) followed by Cr and Cd (Table 4). This is in agreement with the works of Amusan *et al.*, (2005) and Mbong *et al.*, (2014) who reported higher transfer factors greater than 1 for Zn and Fe but in variance with the works of Mohamad *et al.*, (2016) and Devi *et al.*, (2020). This is an indication that Zn, Cr and Cd were the most bio-available metals and this could be due to their weak adsorption onto the soil organic matter which rendered them more bio-available to plants (Dhanasekarapandian *et al.*, 2019). Zn is essential to plants and animals in very low concentrations by serving as components of enzymes, structural proteins, and pigments and also helping to maintain the ionic balance of cells (Gabriel and Kasali, 2014; Hammed *et al.*, 2017).

Zn and other trace metals are important for the proper functioning of biological systems and their deficiency or excess could lead to several disorders. The heavy metals transfer factor recorded in this study is considered very high because TF values close to or above 1 are considered high values (Yeasmin *et al.*, 2013; Hammed *et al.*, 2017) These results confirmed that the food crops were highly enriched with Zn and then with Cr and Cd probably from anthropogenic sources like the oil spill, and this is based on the suggestion that the greater the transfer coefficient value, the greater the chances of plant-metal contamination (Ajayi and Olasukanmi, 2021). The high level of transfer factors (TF) as recorded here is an indication of a possible transfer of heavy metals accumulated in the crude oil impacted soils into the human system through the consumption of food products obtained from this environment. According to Mohamad *et al.*, (2016),

Transfer factor (TF) is an essential tool for investigating the human health risk index and according to Alina *et al.*, (2012), the physicochemical properties of soil and the type of plants grown on them could influence the mobility of metals from soil to the different plants. However, these properties are affected by industrial activities such as oil exploration. Therefore, it implies that the transfer factor of heavy metals from soil to plants was a determinant of the level of heavy metal pollution of the food crops cultivated in the study area.

Table 4: Transfer factor of heavy metals from soil to crops

Station	Crop Samples	Heavy Metals						
		Fe	**Ni**	**Cr**	**Pb**	**Cd**	**Zn**	**Cu**
SL1	*Manihot esculenta C.*	0.5792	0.5865	0.4155	0.9256	1.0868	1.7360	0.8395
	Dioscorea alata	0.7144	1.3565	2.2255	0.4718	0.8235	1.9261	1.0637
	Zea mays L.	0.5188	0.7298	2.4726	0.4333	0.9160	2.0054	0.7034
	Musa paradisiaca	0.5661	0.8617	1.0227	0.5949	0.4286	2.2249	0.8245
	Colocasia esculenta	0.7657	1.2300	2.0215	0.6333	0.9916	1.7838	0.9937
SL2	*Manihot esculenta C.*	0.4429	1.5687	1.2209	0.9548	1.5671	2.5525	0.8406
	Dioscorea alata	0.5753	0.9439	1.3736	1.2710	1.4756	1.8901	0.7039
	Zea mays L.	0.5541	1.7279	1.3993	1.0516	0.9024	2.0187	0.5048
	Musa paradisiaca	0.5620	1.5367	1.9796	1.6452	0.8354	2.8839	0.5360
	Colocasia esculenta	0.6364	1.0275	1.8154	0.9419	2.1098	2.6397	0.5530
SL3	*Manihot esculenta C.*	1.0554	0.8856	2.1902	0.5511	2.0217	2.0638	1.0327
	Dioscorea alata	0.8804	0.9804	1.5744	1.1022	2.2899	1.8142	0.8357
	Zea mays L.	0.7122	1.1253	1.7081	0.2701	2.2536	1.9045	0.9766
	Musa paradisiaca	0.6808	1.3752	1.4473	0.3321	1.1377	2.0866	1.1199
	Colocasia esculenta	0.6416	1.0114	1.5471	0.4964	1.2899	1.9884	0.6519
SL4	*Manihot esculenta C.*	0.8518	0.7073	1.4847	1.1823	1.0213	2.2010	0.7277
	Dioscorea alata	0.7068	0.6460	1.7679	0.9531	1.1809	1.7833	0.8597
	Zea mays L.	0.6780	0.5456	1.1740	0.5938	0.4823	1.7971	0.9616
	Musa paradisiaca	0.8796	0.7447	0.7221	0.3438	0.8794	2.3579	0.5669
	Colocasia esculenta	0.9186	0.5336	0.9534	1.2760	1.2482	2.0192	0.5977
SL5	*Manihot esculenta C.*	0.7014	1.4093	1.8827	0.4158	1.5838	2.6799	0.7314
	Dioscorea alata	0.6691	1.4838	2.1823	0.4581	1.8844	2.5913	0.8069
	Zea mays L.	0.7281	0.9944	1.8072	0.1341	1.8555	2.1338	0.5725
	Musa paradisiaca	0.5499	1.1755	1.2683	0.5726	1.9538	1.9036	0.5764
	Colocasia esculenta	0.5215	1.1699	1.7247	0.6732	1.8613	2.4378	0.7430
Control	*Manihot esculenta C.*	0.7232	1.4380	1.9267	0.1495	1.3333	1.6663	0.8615
	Dioscorea alata	0.6591	2.5293	1.3699	0.6729	1.2500	2.0989	0.5756
	Zea mays L.	0.3599	1.4169	1.0769	-	-	1.6562	0.5529
	Musa paradisiaca	0.3703	1.6888	2.0073	-	1.4167	1.6974	1.0630
	Colocasia esculenta	0.6520	1.7733	0.9011	0.4766	1.0833	1.7958	0.6448

4.0 Conclusion

Continuous consumption of food crops contaminated with heavy metals may contribute to the development of various disorders. Results obtained from this work indicated that crude oil spill increased the heavy metals concentration of the soil and accumulation in food crops grown on them which suggest that the peasant farmers on this impacted sites are at greater risk. So it is necessary to monitor the levels of these metals in soil and food crops. Soil-to-plant transfer of heavy metal is a key factor used to assess human exposure risk via the food chain. The computed transfer factors revealed that the food crops were highly enriched with heavy metals especially Zn, Cr and Cd. Therefore, it could be concluded that Zn, Cr and Cd were the most bio-available metals.

6.0 References

Ajayi, A. A. & Olasukanmi, A. A. (2021). Heavy Metal in Cassava Roots (Manihot esculenta) Harvested from Farm Land along Ilaro-Ibese Road, Ogun State Nigeria. *International Journal of Progressive Sciences and Technologies*. 29, 2, pp.302-306.

Alina, L. I., Adinaberbecea, K. & Laţo, F. C. (2012). The Transfer Factor of Metals in Soil-Plant System. *Research Journal of Agricultural Science*, 44, 3, pp. 20 - 32.

Alum, E.U, Essien, E.B & Abbey, B.W. (2014). Heavy Metals Content of Food Crops Grown in Oil Exploration Areas of Rivers State. *International Journal of Science and Nature*. 5, 3, pp. 486-493.

American Public Health Association. Standard methods for the examination of water and wastewater. APHA, AWWA, WEF/2009, APHA Publication. 20th ed. Washington DC; 2009.

Babatunde, S. B. & Tosin, A. O. (2012). Characteristics of Soils and Heavy Metal Content of Vegetation in Oil Spill Impacted Land in Nigeria. *Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy*: Vol. 17, Article 2. Available at: https://scholarworks.umass.edu/soilsproceedings/vol17/iss1/2

Chukwujindu M. A. (2011). Assessment of heavy metal speciation in soils impacted with crude oil in the Niger Delta, Nigeria, Chemical Speciation & Bioavailability, 23, 1, 7-15, DOI: 10.3184/095422911X12964002282100

Devi, S. P., Sukirno1, Sri, M. & Kharistya, R. (2020). Transfer factor as indicator of heavy metal content in plants around Adipala steam power plant. Conf. Series: *Journal of Physics*: IOP Conf. Series 1436. IOP Publishing doi:10.1088/1742-6596/1436/1/012133

Dhanasekarapandian, M., Chandran, S., Kumar, V. & Surendran, U. (2019), Assessment of heavy metals in soil, paddy straw and SEM analysis of the soil for the impact of wastewater irrigation in Girudhumal sub basin of Tamil Nadu, India, *Global NEST Journal*, 21, 3, pp. 310-319.

Emurotu, J. E. & Onianwa, P. C. Bioaccumulation of heavy metals in soil and selected food crops cultivated in Kogi State, north central Nigeria. *Environmental System Research*. 6, pp. 21 – 30. DOI 10.1186/s40068-017-0098-1

Essiett, U. A., Effiong, G. S., Ogbemudia, F. O. & Bruno, E. J. (2010). Heavy metal concentrations in plants growing in crude oil contaminated soil in Akwa Ibom State, South-Eastern Nigeria. *African Journal of Pharmacy and Pharmacology*. 4, 7, pp. 465-470.

Gabriel, O. A. & Kasali, A. A. (2014). Effect of crude oil pollution on heavy metal contents, microbial population in soil, and maize and cowpea growth. *Agricultural Sciences*. 5, 1, pp. 43-50. http://dx.doi.org/10.4236/as.2014.51004.

Hammed, A. O., Lukuman, A., Gbola, K. A., Mohammed, O. A. (2017). Heavy Metal Contents in Soil and Plants at Dumpsites: A Case Study of Awotan and Ajakanga Dumpsite Ibadan, Oyo State, Nigeria. *Journal of Environment and Earth Science*. 7, 4, pp.36 – 45.

Harrison, U. E., 1osu, S. R. & Ekanem, J. O. (2018). Heavy Metals Accumulation in Leaves and Tubers of Cassava (Manihot Esculenta Crantz) Grown in Crude Oil Contaminated Soil at Ikot Ada Udo, Nigeria. J. Appl. Sci. Environ. Manage. 22, 6, pp. 845 –851. DOI: https://dx.doi.org/10.4314/jasem.v22i6.1

Josephat, N. O., Judith, N. N., Ukaoma, A. A. & Odangowei, I. O. (2020). Heavy Metals in Cassava (Manihot esculenta Crantz) Harvested from Farmlands along Highways in Owerri, Nigeria. *Turkish Journal of Agriculture - Food Science and Technology*, 8, 4, pp. 800-806. DOI: https://doi.org/10.24925/turjaf.v8i4.800-806.2737

Mbong, E. O., Akpan, E. E. & Osu, S. R. (2014). Soil-plant heavy metal relations and transfer factor index of habitats densely distributed with Citrus reticulata (tangerine). *J. Res. Environ. Sci. Toxicology*. 3, 4, pp. 61 - 65

Mohamad, S., Rouhollah, M. & Hadi, G. (2016). Accumulation and Soil-to-Plant Transfer Factor of Lead and Manganese in some Plant Species in Semnan Province, Central Iran. *Iranian Journal of Toxicology*. 10, 3, pp. 29-33.

National Population Commission (NPC). (2006). Population and Housing Census of the Federal Republic of Nigeria: National and State Population and Housing Tables, Federal Republic of Nigeria - Abuja: 2009.

Nesta, B. S., Shouta, M. M., Nakayama, O. A., Yoshinori, I., Julius, N. F., Elvis, B., Hazuki, M. & Mayumi I. (2015). Accumulation of Heavy Metals and Metalloid in Foodstuffs from Agricultural Soils around Tarkwa Area in Ghana, and Associated Human Health Risks. *Int. J. Environ. Res. Public Health*. 1, 2, pp. 8811-8827; doi:10.3390/ijerph120808811

Nwaichi, E.O., Chuku, L.C. & Ighoavwogan, E. (2016). Polycyclic Aromatic Hydrocarbons and Selected Heavy Metals in Some Oil Polluted Sites in Delta State Nigeria. *Journal of Environmental Protection* , 7, 1389-1410. http://dx.doi.org/10.4236/jep.2016.710120

Okoye, C. O., & Okwute, G. A. (2014). Heavy Metal Concentrations in Food Crops Grown in Crude Oil Impacted Soils in Olomoro, Delta State-Nigeria and Their Health Implications. *International Journal of Engineering Science Invention*. 3, 3, pp. 15 – 21.

Onakpa, M. M, Njan, A. A. & Kalu, O. C. (2018). A Review of Heavy Metal Contamination of Food Crops in Nigeria. *Annals of Global Health*. 84, 3, pp. 488–494. DOI: https://doi.org/10.29024/aogh.2314

Onwuka, C., Eboatu, A.N., Ajiwe, V. I. and Morah, E. J. (2021). Pollution Studies on Soils from Crude Oil Producing Areas of Rivers State, Niger Delta Region, Nigeria. *Open Access Library Journal*, 8, 4, 75 - 83. https://doi.org/10.4236/oalib.1107583

Radomirovi´c, M., ´Cirovi´c, Ž., Maksin, D., Baki´c, T., Luki´c, J., Stankovi´c, S. & Onjia, A. (2020). Ecological Risk Assessment of Heavy Metals in the Soil at a Former Painting Industry Facility. *Front. Environ. Sci*. 8:560415. doi: 10.3389/fenvs.2020.560415

Raymond, A. W. and Felix, E. O. (2011). Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. *International Scholarly Research Network.* Vol. 2011, doi:10.5402/2011/402647

Salman, A. S., Salah, A. M., El-Montser, M. S. & Mahmoud, A. A. (2019). Soil characterization and heavy metal pollution assessment in Orabi farms, El Obour, Egypt. *Bulletin of the National Research Centre*. 43:42. https://doi.org/10.1186/s42269-019-0082-1

Shigeo, U., Keiko, T. & Ikuko, H. (2007). Soil-to-Plant Transfer Factors of Stable Elements and Naturally Occurring Radionuclides (1) Upland Field Crops Collected in Japan, *Journal of Nuclear*

Science and Technology, 44, 4, pp. 628-640, DOI: 10.1080/18811248.2007.9711851.

Štofejová, L. Fazekaš, J. & Fazekašová, D. (2021). Analysis of Heavy Metal Content in Soil and Plants in the Dumping Ground of Magnesite Mining Factory Jelšava-Lubeník (Slovakia). *Sustainability*. 13, 2, 4508. https://doi.org/ 10.3390/su13084508

Tatah, V. S., Yakubu, E. O., Ayantse, L. M., Dearsley, F. U. & Uba S. A, (2020). Determination of Heavy Metals in Soil and Water Samples from Mambilla Artisanal Mining Site and Its Environs. *Trends Applied Sci. Res.*, 15, 2, pp. 125-132. DOI: 10.3923/tasr.2020.125.132

Ukpong, E. C. (2013). Performance evaluation of activated sludge wastewater treatment plant (ASWTP) at QIT, Ibeno Local Government Area of Akwa Ibom state, Niger. *The International Journal of Engineering and Science*. 2, 7, pp. 1-13.

Useh, M. U. & Dauda, M. S. (2018). Heavy Metals Contamination and their Potential Toxicity in Petroleum Sludge Impacted Soils from Itsekiri Communities, Delta State, Nigeria. *Chemical Science International Journal*. 24, 1, pp. 1-15.

Useh, M. U. & Ikokoh, P. P. (2016). Assessment of Heavy Metals Concentration of Crude Oil Polluted Soil and Water in Some Coastal Communities of Akwa Ibom State, Nigeria. *International Journal of Environmental Chemistry*, 1, 1, pp. 9-13.

Useh, M. U., Etuk-Udo, G. A. & Dauda, M. S. (2015). Evaluating the physico-chemical properties and heavy metals in soils of municipal waste dumpsites at Kubwa, Abuja, Nigeria. *Journal of Chemistry and Chemical Sciences*. 5, 1, pp. 654-662.

Useh, M. U., Uzama, D. & Obigwa, P. (2022). Effects of Abattoir Activities in the Surrounding Soils within Abuja, Nigeria. *Communication in Physical Sciences*, 8, 1, pp. 58-74.

Vinod, K. & Chopra, A. K. (2015). Toxicity of Chromium in Agricultural Crops with Respect to its Chemical Speciation-A Review. *World Applied Sciences Journal*. 33, 6, pp. 944-969. doi: 10.5829/idosi.wasj.2015.33.06.9533

Yeasmin, N. J., Ashraful, I. I. & Shawkat, A. (2013). Transfer of metals from soil to vegetables and possible health risk assessment. *Springer Plus*. 2:385. doi:10.1186/2193-1801-2-385.

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