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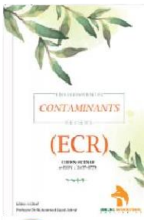

RESEARCH ARTICLE

HEALTH RISK ASSESSMENT OF HEAVY METALS CONTAMINATION OF SOILS AND *MANIHOT ESCULENTA* IN UTAEWA DUMPSITE, IKOT ABASI, NIGERIA

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ABSTRACT

Dumping of wastes from industrial facilities and domestic sources indiscriminately have led to incessant and injurious pollution of environmental components with heavy metals and other pollutants. To a far greater extent heavy metal pollution of soils is eliciting global attention and public health concern. This study was undertaken to assess the levels of heavy metal pollution in soils from Utaewa dumpsite in Ikot Abasi, Niger Delta, Nigeria , which few years ago was the site for the dumping of industrial wastes from Aluminium Smelter Company of Nigeria Limited, Ikot Abasi , but now being used for farming. Five soil samples and three *Manihot esculenta* (cassava tubers) samples were taken from the dumpsite, for heavy metal analyses (vanadium, copper, lead, cadmium, arsenic, zinc, iron, nickel , cobalt , aluminium, silver and selenium) , by inductively coupled plasma spectrometry. The results indicated the levels of cadmium and silver were below detection limits. Other metals were below the maximum permissible limits in soils. All the values of the heavy metals were lower than the permissible limits in crops, except As (0.503 mg/kg) and Se (0.594 mg/kg) as regulated. The pollution load index (PLI) of heavy metals in the soils during the rainy and dry seasons were 0.047 and 0.048 respectively, and the difference in the pollution load index for the two seasons is not significant ($p < 0.05$). Transfer factors for all the metals were less than one, except vanadium which had a value of 144.8, during the rainy season and 48.28, during the dry season, indicating enhanced transfer of vanadium and other metals from soil to the *Manihot esculenta* in both seasons, raising human health concern.

KEYWORDS

Heavy metals, dumpsite, pollution, contamination factor, transfer factor, pollution load index

1. INTRODUCTION

Indiscriminate dumping of wastes with toxic materials from industrial facilities and domestic sources have led to iinjurious pollution of environmental components such as soil, water and air with heavy metals and organic pollutants (Etesin and Ogbonna, 2023). To a far greater extent heavy metals contamination of soils, sediments and underground waters is eliciting global attention and public health concerns (Giaccio et al., 2012). Heavy metals are basically metals and metalloids that possess biological toxicity, such as cadmium, mercury, arsenic, lead, and chromium (Martínez-Graña et al., 2014). These toxic metals are ubiquitous in the environment, and they enter the ecosystem mainly as a fallout of anthropogenic activities (García Sánchez, 2008). Heavy metal contamination is a major threat to the health and well-being of organisms and human beings due to potential accumulation risk through the food chain. This constitute important factor in plants and human health concern with documented evidences of the adverse effects. (Etesin et al., 2015; Lwin et al., 2018; Ahmed et al., 2015; Ali et al., 2016).

There are major impacts of heavy metal pollution on humans and other organisms such as, alteration of the diversity, population size and overall activity of the soil microbial communities which creates toxic effects on soil microorganisms (Ashraf and Ali, 2007). There has been reported cases of enhanced lead metal concentrations in soils, mostly at dumpsites, where both industrial and domestic wastes are discharged. This enhancement likely led to decrease in soil productivity and uptake of the metal by the plants from soils which poses a great health risk to humans through the food chain (Jordao et al., 2006). Generally, uptake of soil heavy metals by plants is a potential health threat to humans that should be given serious attention by regular monitoring of the concentration levels of metals in the siol. (Nuralykyzy et al., 2021).

Soil has been classified as the critical environmental medium, which is subject to various organic and inorganic pollutants resulting from different anthropogenic activities (Al-Khashman and Shawabkeh, 2006). The crave for rapid economic boost, with the increasing demands for metals during the course of industrialization and urbanization, has put a great burden on soil, resulting to more and more heavy metal pollutants becoming widespread (Yang et al., 2011). The general effects and dire consequences of environmental pollution in Ikot Abasi LGA and across the world have been well studied and documented, and are widely known (Olujide, 2006; Enemugwem, 2009; WHO, 2010; Ukpong et al., 2017; Chijioke et al., 2018; Atting et al., 2019; Doulgeridou et al., 2020; Lavenir et al., 2020). The concerns about the integrity and pollution status of agro-ecosystems worldwide has attracted much attention.

Therefore, much attention has been focused worldwide on heavy metals pollution of environments within the past few decades due to indiscriminate dumping of wastes from anthropogenic sources. Researchers are generally of the views that it is a major global problem threatening the sustainability of agro environments, biota species and humans who ingest resources from the contaminated ecosystems (Barrera and Ariza, 2017; Naggar et al., 2018; Weissmannova et al., 2019; Alhjahdali and Alhassan, 2020; Liu et al., 2021; Hamid et al., 2022). Published

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information implicated heavy metals among the one hundred and twenty-nine (129) contaminants (including organics, pesticides etc) which are designated by the United States Environmental Protection Agency (US EPA) as priority pollutants, having been known or suspected to be the cause of carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity (Tchobonoglous et al., 2004). Therefore, heavy metal presence and release into or removal from the environment are regulated in a global scale including Nigeria (Tchobonoglous et al., 2004; WHO, 2010; Weissmannova et al., 2019; Etesin et al., 2021).

Contamination of soil by heavy metals is of a public health concern and most important apprehension throughout the industrialized world (Hinojosa et al., 2004). Heavy metal pollution not only result in adverse effects on various parameters relating to plant quality and yield but also cause changes in the size, composition and activity of the microbial community (Yao and Huang, 2003). Therefore, heavy metals are considered as one of the major sources of soil pollution. Heavy metal pollution of the soil is caused by various metals especially Cu, Ni, Cd, Zn, Cr, and Pb (Hinojosa et al., 2004). The adverse effects of heavy metals on soil biological and biochemical properties are well documented. The soil properties i.e. organic matter, clay contents and pH have major influences on the extent of the effects of metals on biological and biochemical properties (Speira et al., 1999).

A group researchers reported that the application of waste materials from fish ponds in a farm may likely results in excessive accumulation of metals in the environment (Aladesanmi et al., 2014; Onuoha, 2017). A report by the United States Environmental Protection Agency (USEPA) highlighted that the utilization of organic wastes from refuse dumps as a source manure can aggravate availability of toxic metals in soil (USEPA, 2022). According to a study, uptake of soil heavy metals by plants is a potential health threat to animals and humans through the food chain, that should be given serious consideration (Nuralykyzy et al., 2021). The consumption of heavy metal contaminated food can seriously deplete some essential nutrients in the body that are further responsible for decreasing immunological defences (Etesin and Ogbonna, 2023).

Recently researchers inn their studies, reported that cadmium (Cd) is a well-known toxicant and the target organs for Cd toxicity have been identified as liver, placenta, kidneys, lungs, brain and bones (Etesin and Ogbonna, 2023; Sobha et al., 2007). Depending on the extent of exposure, the causal effects of heavy metal toxicity include nausea, vomiting, abdominal cramps, dyspnea and muscular weakness. Severe exposure may result in pulmonary odema and death. Pulmonary effects (emphysema, bronchiolitis and alveolitis) and renal effects may occur following sub- chronic inhalation exposure to cadmium and its compounds (Hinojosa el al., 2004).

A group researcher in their study asserted that on a global scale, more than ten million soil sites are polluted, with more than fifty per cent (%) of these soil sites are contaminated with heavy metals (He et al., 2015). Pollution caused by heavy metals in soils may result from multiple sources, such as atmospheric deposition, waste disposal, waste incineration, urban effluents, traffic emission, fertilizer application, and the long-term application of wastewater in agriculture (Cachada et al., 2012; Lv et al., 2015).

In consideration of eco-toxicological studies, the following metals have been associated with the toxic effects indicated in humans through the food chain (USEPA, 2023):

- Arsenic, As breathing problems, death, decrease of intelligence, etc.
- Cadmium, Cd kidney damage, hypertension, cancer, ititi etc.
- Bismuth, Bi implicated in renal failure
- Chromium, Cr - implicated in renal failure, lung cancer, etc.
- Cobalt, Co - causes goiter
- Copper, Cu - causes shortage of blood, irritation, etc.
- Iron, Fe - causes vomiting, bleeding, heart failure, stomach ulcer and may lead to eventual death.
- Lead, Pb , high blood pressure, kidney damage, learning difficulty.
- Mercury, Hg , Blindness, death, brain damage, genetic mutation, mental retardation.
- Manganese, Mn - Parkinson-like syndrome, respiratory diseases etc
- Nickel, Ni - Dermatitis, eczema, reduced sperm, lung diseases, etc
- Silver, Ag - bone marrow depression, pulmonary diseases, blue-grey skin,nail discoloration.
- Thallium, Th - vomiting, diarrhea, pain and coma etc
- Zinc, Zn - vomiting, cholera, abdominal pain, anemia etc
- Aluminum, Al - muscular condition, alzheimer's disease Parkinson's disease, cancer, dementia, senility etc (Ansari *et al,* 2004;

Many studies have indicated bioaccumulation of heavy metals which are highly influenced by the prevailing physico-chemical condition of the environment, speciation, biota metabolism, uptake and excretion rates and the plant species concerned (Ansari et al., 2004; Maher et al., 2016; US EPA, 2023). Environmental bioindicators or biomonitors of heavy metals pollution are organisms whose bioaccumulated heavy metals concentration is used to assess the pollution status or ecological and/or health risk due to specific metal concentration (Maher et al., 2016; Simpson and Kumar, 2016; Barrera and Ariza, 2017; US EPA, 2007; 2023). Sedentary organisms are preferred to migratory organism for use as bioindicators, like plantsand animals in a given study area.

The aims of this study include:

- determination of the distribution of heavy metals namely ; cadmium, lead, zinc, copper, iron, manganese, arsenic, mercury, in the soils and *Manihot esculenta* planted and harvested in soils of Utaewa dumpsite, Ikot Abasi as to create awareness of their pollution status in the ecosystems.
- to estimate the ecological and health risks associated with heavy metals data obtained with a view to safeguarding the ecosystem and human health .

2. MATERIALS AND METHODS

2.1 The Study Area

The dumpsite is located in Ikot Abasi , which lies within the Southeast of the Niger Delta in Nigeria (Figure 1). Ikot Abasi Local Government Area is located between latitude 4.3111 ° and 4.4512 ° North and between longitude 7.5213 ° and 8.0219 ° East (Etesin and Inim, 2021). Ikot Abasi is a local government in Akwa Ibom State that hosts facilities of Exxon Mobil, Aluminium Smelter Company of Nigeria (ALSCON), SEPTA gas station, Ibom Power Company Limited, Ikot Abasi . The dumpsite has received both industrial and domestic wastes from these facilities for more than fifteen years. With the discontinuation of wastes disposal at the dumpsite, there is presently some farming activities going on within the dumpsite and the environs.

The study area, Ikot Abasi, being part of the Niger Delta is underlain by the sedimentary formation of the Late Tertiary and Holocene ages (Udo et al., 2013). Deposits of recent alluvium and beach ridge sands occurred along the coast and the estuaries of the Imo and flood plains of Uta Ewa creek (Magnus et al., 2012). The study area is made up of matured, coarse and moderately sorted coastal plain sands which overlies the Bende-Ameki formation and dips south westward (Enemugwem, 2009). The landscape of the study area comprises of a low-lying plain and riverine areas with no portion exceeding 175 meters above mean sea level. The physiography of the area is that of a beach ridge complex characterized by a succession of sub-parallel sand ridges (Kumer, 2013). The physical relief of the study area is flat, though with some marshy river-washed soils around the banks of the Utaewa River (Etesin et al., 2013).

Ikot Abasi Local Government Area falls within the tropical zone and her vegetation is the green foliage of trees/shrubs and the oil palm tree belt. The Local Government Area has two seasons: the wet season and the dry season. There are abundant deposits of crude oil and clay in the study area. Forest resources include mangroves, nipa palm, timber, palm produce while the area is also noted for seafood production. Farm crops range from yam, cassava, cocoyam, plantain to maize and vegetables (Akankpo and Igbokwe, 2011).

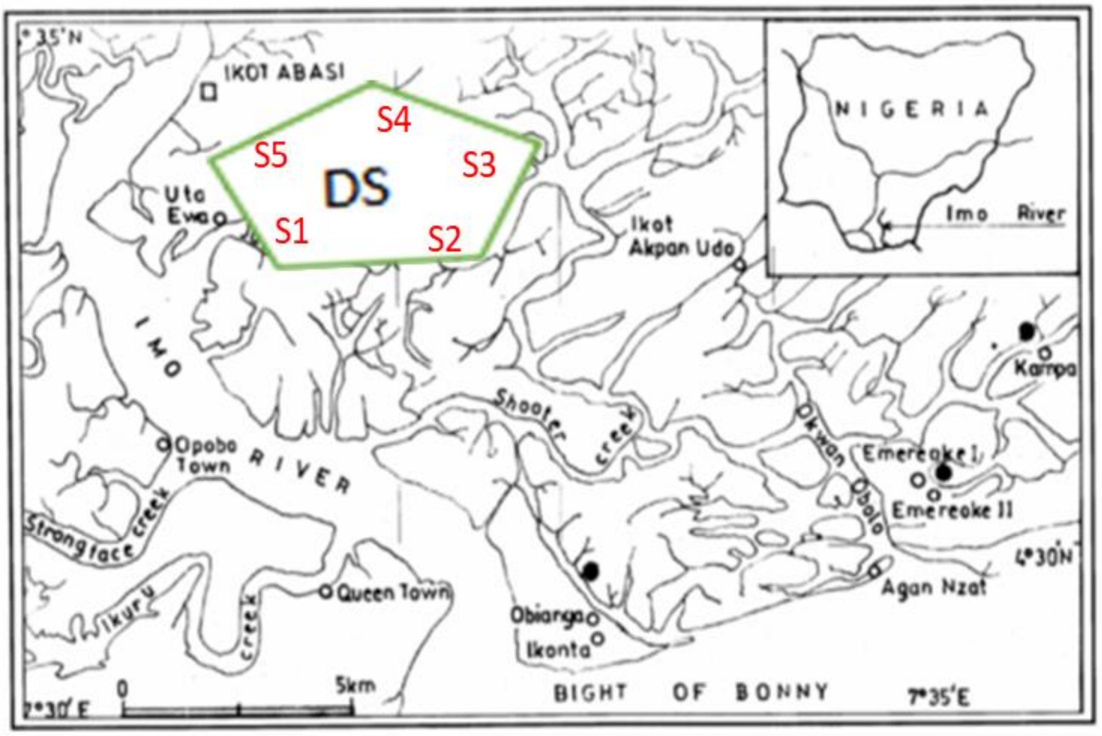

Figure 1: Map of Ikot Abasi showing the sampling locations at the dumpsite (DS)

2.2 Materials and Reagents

The materials and reagents required for the research projects were:

- Soil Auger , for sampling of soil samples
- Analar grade hydrochloric acid (37 %)
- Analar grade nitric acid (98 %)
- Analar grade perchloric acid
- Demineralised water
- Distilled water
- Polyethylene bags
- Volumetric flasks (100 mls
- Beakers (250 ml)
- Filter papers
- Sample bottles
- Erlenmeyer flask (250 ml)

2.3 Collection of soil samples and Preparations

The soil samples were collected from strategic locations around the dumpsite (S1-S5) according to the method of APHA, 2005, whereby sub-surface soil samples (10–15 cm) were sampled from five locations using soil Auger sampler and stored in black polyethylene bags. Heavy metals are more enriched, according to studies, within the surface 0 - 10.0 cm depth sediment profile (Batley and Simpson, 2016; Benson *et al.*, 2016).

The soil samples were transported to the Laboratory, air –dried and sieved to about 63 microns particle size. Soil samples were collected from the study area to cover April and May, 2023 during the rainy season, October and November, 2023 during the dry season.

2.4 Collection of samples of *Manihot esculenta* and preparation

The samples of *Manihot esculenta* roots were harvested from three locations around the dumpsite (C1-C3) and transported to the Laboratory for further processing for heavy metal analysis. The samples were harvested from the study area to cover April and June, 2023 during the rainy season, October and November, 2023 during the dry season. The root tubers of *Manihot esculenta* were processed by removing the outer cover, the tubers were grated and air-dried for few days before digestion.

2.5 Digestion of soil samples

Digestion of the soil samples were carried out according to the methods adopted, whereby, one gram of < 63 micron soil samples were extracted in a 250 ml borosilicate beaker using 3: 1 ratio, HCl : HNO3 mixed acid solution and heated to near dryness on a hot plate (Etesin et al., 2015; Etesin and ogbonna, 2023).The digest was removed from heat and 20 ml deionised water added and allowed to cool. The digests were filtered through Whatman Grade A filter paper into 100 ml volumetric flask and made up to the mark with deionized water. The coloured digests were decolourised by adding some grams of activated charcoal and filtered through Whatman Grade A filter paper (APHA, 2021)

2.6 Digestion of roots tubers of Manihot esculenta

Digestion of the prepared root tubers of Manihot esculenta samples was carried out according to the methods adopted by (Shiraishi et al., 1990; Etesin and ogbonna, 2023). Five (5) grams of the prepared samples were digested in a 250 ml borosilicate beaker using 4: 1 ratio, HNO3 : $HClO_4$ mixed acid solution and heated to near dryness on a hot plate, with formation of white fumes. 20 ml of 0. 5 M HNO_3 solution was added and filtered through grade A Whatman filter paper. The filtrate was transferred to 100 ml volumetric flask and make up to the mark with 0.5 M HNO_3.

2.7 Determination of heavy metals in soil digests

Inductively coupled plasma-optical emission spectrophotometer (Model: Agilent 720 ICP-OES) was used to analyze the total metal content in each 100 ml soil digests. Prior to the ICP-OES analysis, the samples of the soil matrix had been prepared as described in the proceeding sections (Simpson et al., 2016; Tuo et al., 2019; US EPA, 2023). The instrumental procedure used for the ICP-OES analysis is presented in detail in Appendix A. The ICP-OES method was chosen because of its very low detection limits (ppb), simultaneous multielement analysis and high linear dynamic range (Morais et al., 2014; US EPA, 2023).

2.8 Determination of heavy metals in *Manihot esculenta* digests

Inductively coupled plasma-optical emission spectrophotometer (Model: Agilent 720 ICP-OES) was used to analyze the total metal content in each 100 ml digest of *Manihot esculenta.* Prior to the ICP-OES analysis, the samples of the *Manihot esculenta* matrix had been prepared as described in the proceeding section (Simpson et al., 2016; Tuo et al., 2019; US EPA, 2023). The instrumental procedure used for the ICP-OES analysis is presented in detail in Appendix A. The ICP-OES method was chosen because of its very low detection limits (ppb), simultaneous multielement analysis and high linear dynamic range (Morais et al., 2014; US EPA, 2023).

2.9 Determination of contamination factor (CF) and pollution load index (PLI)

The contamination factor (CF) is an index method for calculating the degree of contamination by heavy metals relative to the average continental or crustal background composition of the metal concerned (Pandey et al., 2015). The reference composition could otherwise be a measured local or regional background concentration from a geologically similar, but uncontaminated area (Benson et al., 2016; Onjefu et al., 2020).

The equation for contamination factor (CF) is:

$$CF = C_M / C_B \tag{1}$$

Where,

C_M is the measured concentration of a given heavy metal in a soil sample,

C_B is the standard preindustrial (uncontaminated) reference level of the metal in mg/kg.

The contamination factor categorizes soil / sediment quality into four classes namely:

C F < 1; indicates low contamination status:

1 < CF <3; moderate contamination status;

3 < CF <5; considerable contamination status; and

6 < CF; very high contamination status (Benson et al., 2016; Onjefu et al., 2016, 2020).

Pollution load index (PLI) is calculated by the modified formula. (Islam et al., 2015b; Ali et al., 2016):

$$PLI = (CF_1 \times CF_2 \times CF_3 \text{------} CFn)^{1/n} \tag{2}$$

PLI = 0 ; soil or sediment is excellent ,

PLI = 1; no pollution of the soil

PLI > 1 ; baseline pollution of the soil level, which indicates progressive deterioration of soil quality.

3.0 Data analysis

All data obtained in the study were subjected to analysis of variance (ANOVA) for spatial and seasonal variations, with the level of significance set at $p < 0.05$. The statistical analysis of the data was performed using SPSS, Version 25 software, including determinations of mean, standard deviation and other calculations for the data acquired.

3. RESULTS AND DISCUSSION

3.1 Results of Heavy metals determination in Soils

The results of heavy metal analyses in soils from Utaewa dumpsite during rainy season are presented in Table 1. The mean results (mg/kg) obtained were as follows : V (0.005 ± 0.008); Cr (3.713 ± 0.638) ; Mn (6.546 ± 1.442) ; Fe (3517 ± 374) ; Co (0.01 ±0.001) ; Ni (1.853 ± 0.377) ; Cu (3.169 ± 0.726) ; Ag (< 0.001) ; Zn (16.93 ± 1.147) ; Cd (< 0.001) ; Al (4394 ± 758); Pb (3.355 ± 0.58) As (1.638 ± 0.414). The values of the heavy metals were below their background values, except Arsenic (1.638 mg/kg) with a background value of 1.5 mg/kg . The results of the heavy metals were in the following order during the rainy season; Al > Fe > Zn > Mn > Cu > Cr > Pb > Ni > As > Co > V > Ag , Cd.

The results of heavy metal analyses in soils from Utaewa dumpsite during dry season are presented in Table 2 . The mean results (mg/kg) obtained were as follows : V (0.015 ± 0.007); Cr (3.296 ± 0.99) ; Mn (4.666 ± 1.26) ; Fe (3029 ± 260) ; Co (0.02 ±0.001) ; Ni (1.486 ± 0.38) ; Cu (3.499 ± 1.06) ; Ag (< 0.001) ; Zn (14.03 ± 1.06) ; Cd (< 0.001) ; Al (3803 ± 590); Pb (2.012 ± 0.31) As (1.243 ± 0.32). The values of the heavy metals were below their background values.

Table 1: Results of heavy metals in soils during rainy season

Sample	V	Cr	Mn	Fe	Co	Ni	Cu	Ag	Zn	Cd	Al	Pb	As
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Soil 1	0.02	3.662	6.722	3554	< 0.001	1.614	3.558	< 0.001	16.36	< 0.001	4888	3.866	1.824
Soil 2	< 0.001	2.986	5.186	3712	< 0.001	2.054	3.337	< 0.001	18.9	< 0.001	5108	2.896	1.534
Soil 3	0.001	4.613	8.221	4015	0.01	1.901	4.901	< 0.001	16.86	< 0.001	4612	3.175	0.975
Soil 4	0.003	3.277	4.975	3218	0.02	2.332	2.995	< 0.001	15.98	< 0.001	3189	4.065	2.065
Soil 5	0.02	4.026	7.624	3088	< 0.001	1.864	3.553	< 0.001	16.54	< 0.001	4175	2.775	1.772
Mean	0.005 ± 008	3.713 ± 0.638	6.546 ± 1.442	3517± 374	0.01 ± 0.001	1.853 ± 0.377	3.669 ± 0.726	< 0.001	16.93 ± 1.147	< 0.001	4394 ± 758	3.355 ± 0.58	1.634 ± 0.414

3.2 Results of Heavy metals determination in Manihot esculenta.

The results of heavy metal analyses in Manihot esculenta from Utaewa dumpsite are presented in Table 3. The mean results (mg/kg) obtained were as follows : V (0.724 ± 0.033); Cr (0.012 ± 0.002) ; Mn (0.025 ± 0.004) ; Fe (38.71 ± 0.41) ; Co (< 0.001) ; Ni (0.029 ± 0.005) ; Cu (2.88 ± 0.035) ; Ag (< 0.001) ; Zn (7.469 ± 0.022) ; Cd (< 0.001) ; Al (51.10 ± 0.45); Pb (0.19 ± 0.02); As (0.503 ± 0.01); Se (0.594 ± 0.025). All the values of the heavy metals were lower than the permissible limits in crops , except As (0.503 mg/kg) and Se (0.594 mg/kg) , as regulated (FAO/WHO, 2011; SEPA, 2005) .

3.3 Contamination factors of heavy metals in soils

The contamination factors of heavy metals in the soils of Utaewa dumpsite during the rainy season are presented in Table 4. The contamination factors obtained were V (0.000057), Cr (0.169) , Mn (0.012) , Fe (0.248) , Co (0.001), Ni (0.124), Cu (0.122), Zn (0.282) , Al (0.061), Pb (0.224), As (1. 089). The lowest CF was in V metal while As had the highest value of 1.089. All the metals except As had CF of less than one, which indicates uncontaminated status, while the CF value for As was greater than one, which indicates moderate contamination status of the soil, which is also depicted in Figure 2.

The contamination factors of heavy metals in the soils of Utaewa dumpsite during the dry season are presented in Table 5. The contamination factors obtained were V (0.00017), Cr (0.150) , Mn (0.009) , Fe (0.213) , Co (0.003), Ni (0.099), Cu (0.117), Zn (0.234) , Al (0.053), Pb (0.134), As (0.829). The lowest CF was in V metal while as had the highest value of 0.829. All the metals had CF of less than one, which indicates uncontaminated status, which is also depicted in Figure 3. The difference in the contamination factors of the metals in the soil from the dumpsite during the rainy and the wet seasons was not significant ($p < 0.05$).

3.4 Pollution load index (PLI) of heavy metals in soils

The pollution load index (PLI) of heavy metals in the soils during the rainy and dry seasons calculated were 0.047 and 0.048 respectively (Table 4 and Table 5). The difference in the pollution load index for the rainy and dry seasons is not significant ($p < 0.05$)

Table 2: Results of heavy metals in soils during rainy season

Sample	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Ag**	**Zn**	**Cd**	**Al**	**Pb**	**As**
	(mg/kg)	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**
Soil 1	0.04	3.826	5.962	3419	< 0.001	1.275	4.905	< 0.001	14.99	< 0.001	4174	1.854	1.574
Soil 2	< 0.001	1.875	3.781	2894	< 0.001	1.934	2.075	< 0.001	16.22	< 0.001	3877	2.066	1.117
Soil 3	0.004	4.171	4.964	3119	0.03	0.971	4.055	< 0.001	12.54	< 0.001	4186	1.721	0.762
Soil 4	0.001	2.641	2.972	2977	0.01	1.704	3.145	< 0.001	11.96	< 0.001	2763	2.515	1.442
Soil 5	0.03	3.966	5.653	2739	< 0.001	1.544	3.315	< 0.001	14.42	< 0.001	4016	1.903	1.322
Mean	0.015 ± 0.007	3.296 ± 0.99	4.666 ± 1.26	3029 ± 260	0.02 ± 0.001	1.486 ± 0.38	3.499 ± 1.06	< 0.001	14.03 ± 1.76	< 0.001	3803 ± 59	2.012 ± 0.31	1.243 ± 0.32

Table 3: Results of heavy metals in Manihot esculenta (Cassava)

Cassava	V	Cr	Mn	Fe	Co	Ni	Cu	Ag	Zn	Cd	Al	Pb	As	Se
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
C 1	0.701 ± 0.02	< 0.001	0.003 ± 0.001	35.81 ± 0.056	< 0.001	0.02 ± 0.005	1.63 ± 0.05	< 0.001	6.466 ± 0.025	<0.001	55.21 ± 1.077	0.164 ± 0.031	0.615 ± 0.011	0.848 ± 0.024
C 2	0.518 ± 0.012	0.02 ± 0.002	0.052 ± 0.005	41.09 ± 0.042	< 0.001	0.05 ± 0.002	3.99 ± 0.021	< 0.001	9.011 ± 0.025	< 0.001	46.09 ± 0.051	0.315 ± 0.017	0.523 ± 0.006	0.619 ± 0.032
C 3	0.954 ± 0.051	0.016 ± 0.042	0.019 ± 0.006	39.87 ± 0.019	< 0.001	0.018 ± 0.007	3.01 ± 0.03	< 0.001	7.011 ± 0.016	< 0.001	51.99 ± 0.215	0.092 ± 0.008	0.37 1 ± 0.009	0.314 ± 0.015
Mean	0.724 ± 0.033	0.012 ± 0.002	0.025 ± 0.004	38.71 ± 0.04	< 0.001	0.029 ± 0.005	2.88 ± 0.035	< 0.001	7.469 ± 0.022	< 0.001	51.10 ± 0.45	0.19 ± 0.02	0.503 ± 0.01	0.594 ± 0.025
Permissible														
Limits in crops	5.0	5.0	10.0	100.0	0.01	10.0	20.0	NA	100.0	< 0.1	10.0	9.0	< 0.1	< 0.1
(SEPA, 2005														
FAO/WHO, 2011)														
	NA = not available													

The results of the heavy metals were in the following order during the dry season ; Al > Fe > Zn > Mn > Cu > Cr > Pb > Ni > As > Co > V > Ag , Cd .

Table 4: Contamination Factor of Soils (CF) during rainy season

	V	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Al**	**Pb**	**As**
CF	0.000057	0.169	0.012	0.248	0.001	0.124	0.122	0.282	0.061	0.224	1.089
PLI					**0.047**						

Table 5: Contamination Factor of Soils (CF) during dry season

	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Al	Pb	As
CF	0.00017	0.150	0.009	0.213	0.003	0.099	0.117	0.234	0.053	0.134	0.829
PLI					**0.048**						

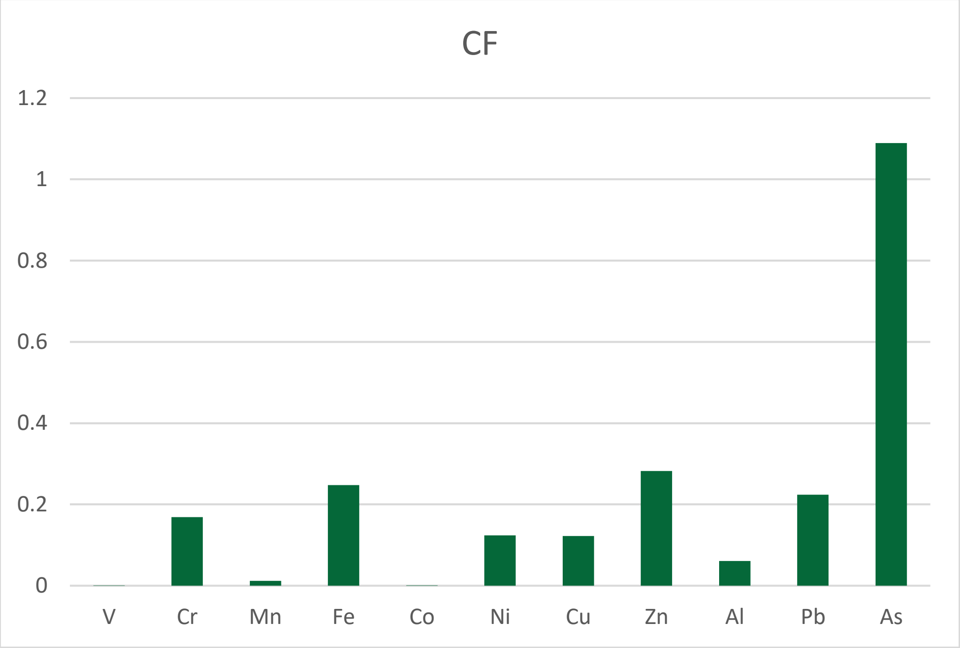

Figure 2: Contamination Factor of Soils in Utaewa Dumpsite during rainy season

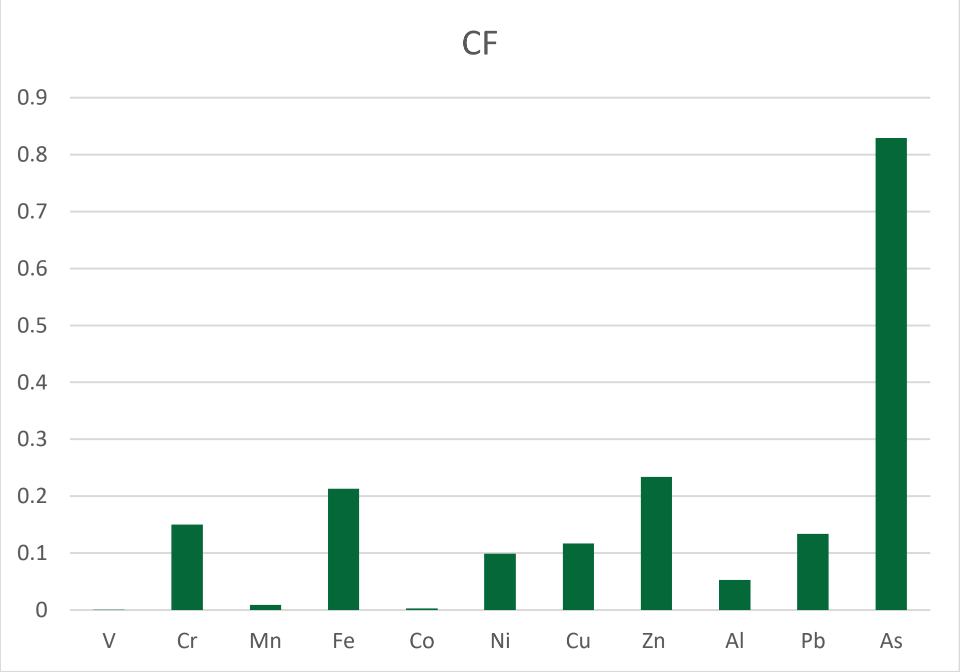

Figure 3: Contamination Factor of Soils in Utaewa Dumpsite during dry season

3.5 Transfer Factor (TF) of heavy metals in Manihot esculenta

The transfer factor (TF) of heavy metals in Manihot esculenta from Utaewa dumpsite is presented in Table 6. Transfer factors for all the metals were less than one, except vanadium which had a value of 144.8, during the rainy season. Comparatively, the transfer factors of heavy metals during the dry season were less than one, except vanadium which had a value of 48.28, indicating the enhanced transfer of vanadium from soil to the Manihot esculenta in both seasons (Figure 4)

Table 6: Transfer Factor (Accumulation Factor) of heavy metals in Manihot esculenta

	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Al	Pb	As
TF (R)	144.8	0.003	0.004	0.011	0.1	0.016	0.78	0.44	0.012	0.057	0.308
TF (D)	48.28	0.004	0.005	0.013	0.05	0.02	0.82	0.53	0.013	0.094	0.405

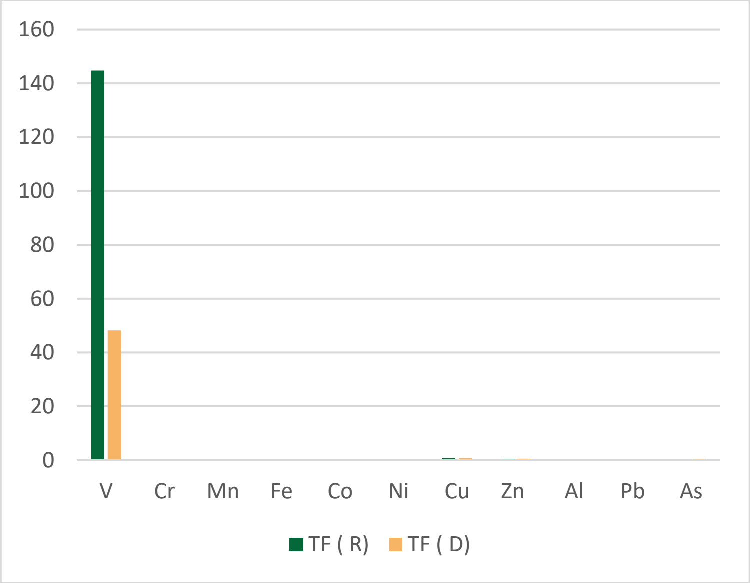

Figure 4: Transfer factor of heavy metals in *Manihot esculenta*

4. DISCUSSION

In the soils of the Utaewa dumpsite sampled during the rainy season, heavy metals, such as As, Pb , Al, Fe exceeded their respective maximum permissible limits in soils (WHO, 2016). The same trend was observed during the dry season, with these metals, As, Pb, Al, and Fe, exceeding their respective maximum permissible limits in soils. However, in the same soils in both the rainy and dry seasons, Co, Ag and Cd were below the detection limits of less than 0.001mg/kg. All other heavy metals namely, V, Cr , Mn, Ni, Cu, and Zn , in both rainy and dry seasons were below their maximum permissible limits in soils.

In a similar study of metal contaminations in Luoyang, Booji, and Spain Urban soils that receive industrial wastes , contaminations with Pb, As, was reported as a serious health concern, due to enhanced concentrations that exceeded the maximum permissible limits in soils, which is comparable to the contaminations of Pb and As in this study (Chao et al., 2014; Zang et al., 2011).

Heavy metals concentrations determined in Manihot esculenta tubers harvested from Utaewa dumpsite had As, Se and Al values (Table 3), which exceeded the permissible limits in crops according to the FAO/WHO regulations (SEPA, 2005; FAO/WHO, 2011). Other metals, Vanadium, chromium, manganese, iron, nickel, copper and zinc determined in the crop were below their respective permissible limits in crops (Emurotu and Onianwa, 2017). However, cadmium, cobalt and silver were below the detection limits and seem to pose no health concern to humans through the food chain. In a similar study of metal contaminations of some crops, including cassava, in Kogi , Nigeria, all the heavy metals studied, such as lead, cadmium , arsenic , iron, copper, zinc, nickel and manganese were below the permissible limits in crops , except in cassava and maize , in which nickel metal had a significant higher value (Emurotu and Onianwa, 2017).

The transfer factors (TF) of metals into crops are shown in Table 6. Transfer factor observed for determined metals were V (48.28 – 144.8), Co (0.05– 0.1), Cu (0.78– 0.82), Ni (0.016 –0.021), Pb (0.057–0.094), Zn (0.44– 0.53), Cr (0.003 – 0.004), Mn (0.004 – 0.005), Fe (0.011 – 0.013), Al (0.012 - 0.013) and As (0.308 – 0.405). The sequence of TF for these metals in Manihot esculenta food crop determined is V > Cu > Zn > As > Pb > Ni > Co > Al > Fe > Mn > Cr. The order of transfer factors indicates that vanadium was the most bio-available and chromium was the least of the bio-available.

A group researcher have reported that organic carbon content and pH are soil parameters having infuence on transfer factor of metals from soil to crop, with the net influence of decreasing or increasing metal mobility (Xu et al., 2013). Their study further reported of significant correlation between TF of Cd and clay content. According to the study, positive correlations were observed among soil Ni, Cd, Co and Cu., in which significant negative correlation was established between Pb and pH, whereas with organic carbon it was positive. A group researcher also reported similar correlation result, whereby total organic carbon showed positive correlation with Ni, Cd and Cu and negative correlation with Pb and Co (Ying et al., 2014). Metal -soil parameters relationship has been reported to indicate binding nature of metal ions to organic substances and its absorption to soil particles (Mayuri et al., 2016). Numerous researches have revealed the exposure of humans to heavy metals via the food chain and has been well documented (Hu et al., 2013; Huang et al., 2014; Oliver, 1997).

The pollution load index (PLI) calculated (Table 4) was 0.047 during the rainy season and 0.048 during the dry season (Table 5), which indicated no pollution to baseline pollutant level in the soils of the study area and falls within the category of PLI of zero, which is excellence with no metal pollutant contamination. Thus, the seasonal variation was not significant ($P < 0.05$). The PLI calculated in this study are comparatively higher than the values reported in agro soils of Ikot Abasi, Nigeria (Etesin et al., 2023). The higher PLI values in this study could be attributed to metal enrichments from industrial wastes and urban wastes from the study area, play host to many industrial facilities.

5. CONCLUSION

Heavy metals (Cr, Fe, V, Ni, Cu, Zn, As, Al, Mn, Cd, Pb) were determined in the surface (0 – 15 cm) and sub-surface soils (15 – 30 cm) from Utaewa dumpsite in Ikot Abasi LGA of Akwa Ibom State, Nigeria, during the dry and wet seasons. The mean concentrations of heavy metals during the dry and rainy seasons were in the order: Al > Fe > Zn > Mn > Cu > Cr > Pb > Ni > As > Co > V > Ag , Cd. There was no significant variation of metal concentrations in the dry and rainy seasons ($P < 0.05$) in the study area . However, there was significant ($P < 0.05$) spatial variations of heavy metal concentrations in the study area with different metals and locations.

To investigate the contamination degree, ecological risk, and human health risk of heavy metals in the soil of the study area, contamination factor (*CF*), pollution load index (*PLI*) and transfer factor (TF) were determined based on the data obtained from the soil and crop analyses. The results of heavy metals in the soils from Utaewa dumpsite showed that the degree of heavy metals contamination decreased in the following order of contamination factor during the rainy season : As > Zn > Fe > Pb > Cr > Ni > Cu > Al > Mn > Co > V . Comparatively, the results of heavy metals in the soils from Utaewa dumpsite showed that the degree of heavy metals contamination decreased in the following order of contamination factor during the dry season : As > Zn > Fe > Cr > Pb > Cu > Ni > Al > Mn > Co > V. There was an enhanced concentration of Cu durng the dry season. In both seasons arsenic had the highest contamination factor (0.829 – 1.089), with the possibility of its toxicity to humans, thus raising a serious health concern in the study area.

Transfer factor of heavy metals from soil to food crop studied indicated vanadium as having the highest values (44.48 – 144.8), followed by copper (0.78 – 0.82) and arsenic (0.308 – 0.405), with the high rate of passing the metals through the food chain to humans due to bioavailability of the metals.

RECOMMENDATIONS

The physicochemical characteristics of the soils in the study area were not tested in this study, as such there is a strong recommendation for the physicochemical properties of the dumpsite to be studied, due to a strong influence of soil types, porosity, density, conductivity, total organic carbon on the bioavalability of heavy metals. Though, the study indicated that most metals determined like Cr, Cd, Mn Fe , Co, and Ni were below the maximum permissible limits, there is gradual build up of Cu, Pb , As and Zn , which requires close monitoring.

Therefore, there is a strong recommendation for constant monitoring of the levels of these heavy metals, in order to have a red alert once the toxic level is reached. Average concentration of determined metals (Pb, Cu, Zn , V , Ni, Fe , Mn, Cr and Cd) in food crop (*Manihot esculenta*) did not exceed permissible limits except the mean concentration of Arsenic . In this study only one food crop was studied, which does not give a general picture of heavy metal contamination, therefore, there is a strong recommendation for other food crops like pumkin, cucumber, maize and okra prevalent in the study area to be determined in subsequent study.

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AUTHOR CONTRIBUTIONS

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Etesin, Usoro Monday and Benson, Emediong Abasiama. The first draft of the manuscript was written by Etesin, Usoro Monday and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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