Journal of Natural Sciences Research
ISSN 2224-3186 (Paper) ISSN 2225-0921 (Online)
Vol.14, No.8, 2023 www.iiste.org

Assessment of Heavy Metals in Designated Tropical Soils and Vegetables Using X-Ray Fluorescence Spectroscopy

Abraham Olasupo Oladebeye[1*] Mudasiru Bode Okunade[2] Aderonke Adenike Oladebeye[3]
1. Department of Science Laboratory Technology, University of Medical Sciences, Ondo, Nigeria
2. Department of Chemical Sciences, Achievers University, Owo, Nigeria
3. Department of Food Technology, Auchi Polytechnic, Auchi, Nigeria
*Corresponding author: e-mail: aooladebeye@unimed.edu.ng; ORCID: 0000-0002-5095-9311

The research is self-financed

Abstract
X-ray fluorescence (XRF) technique was used to investigate the accumulation of heavy metals in fluted pumpkin (Telfairia occidentalis), African spinach (Amaranthus hybridus) and water leaf (Talinum triangulare) harvested from two (2) farms in St. Louis and Osuma Layout in Owo Local Government Area, Ondo State. The heavy metals detected, chromium (Cr), zinc (Zn), manganese (Mn), iron (Fe), titanium (Ti), strontium (Sr) and aluminium (Al) were more available in the soil samples than the vegetable samples except Zn and Mn. Although their proportions were higher than the permissible limits of WHO/FAO for soils and plants, their bioaccumulation in the soil samples was Al > Fe > Ti > Mn > Sr > Cr > Zn and bioavailability in the vegetable samples was Al > Fe > Ti > Mn > Sr > Zn > Cr. The peak concentrations (%) of Cr (0.015±0.001) and Mn (0.39±0.03) were obtained in Talinum triangulare from Osuma Layout (TtOL), Zn (0.072±0.003) and Fe (3.00±0.01) in Talinum triangulare from St. Louis (TtSL), Ti (1.31±0.01) and Sr (0.068±0.001) in Telfairia occidentalis from Osuma Layout (ToOL) while Al (6.33±0.03) in Amaranthum hybridus from St. Louis (AhSL). Both negative and positive correlations existed between metal pairs ($p < 0.05$). Based on their bio-concentration factor (BCF) values, TtOL was Cr hyperaccumulator and ToOL was both Mn and Ti hyperaccumulators. Zn hyperaccumulation was competitive and was in the decreasing order of TtOL > TtSL > ToSL (Telfairia occidentalis from St. Louis) > AhSL. Among all the vegetable samples, TtSL was the most significant nonaccumulator for Cr. All the vegetable samples studied have potential for selective phytoextraction of heavy metals from polluted soils.

Keywords: Heavy metals, hyperaccumulator, phytoextraction, bio-concentration factor (BCF)
DOI: 10.7176/JNSR/14-8-01
Publication date: May 31st 2023

Alteration of ecosystem quality occurs when potentially toxic elements known as heavy metals find their way into it through human and natural activities (Jaishankar *et al.,* 2014). Soil is a long-term sink of heavy metals, which may be transported from ground waters or taken up by plants, thereby posing risks to the plants, and serving as a major route of heavy metals exposure to animals and humans that depend on them for sustainability (Tsafe *et al*., 2012; Ashraf *et al.,* 2014). Heavy metals include all toxic metallic chemical elements and metalloids (Briffa, *et al.,* 2020), which are either essential cofactors, such as cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), zinc (Zn) or non-essential, such as arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg), etc (Wang *et al.. 2014;* Theron *et al*., 2012).

The global health concerns, arising from environmental pollution of soil and water by heavy metals are due to their toxicity and non-biodegradability over a period of time, even at low concentrations (Briffa, *et al.,* 2020). In spite of prevalence in inadequate consumption of vegetable and fruits that resulted in about 3.9 million deaths globally in 2017 and call for their inclusion in our diet to promote good health and lower risk of non-communicable diseases (Ashton *et al.,* 2019; Mello-Rodrigues *et al.,* 2019; WHO, 2018; Nour *et al.,* 2017), there is need for safe consumption of these food items, ensuring that they meet international requirements (Sobukola *et al.*, 2010).

It is on this basis that this study was designed to investigate bioaccumulation of heavy metals in leafy vegetables from selected locally grown vegetables in Nigeria in relation to the bioavailability of the same metals in the soil on which they grow. Selected for this research work are fluted pumpkin (Telfairia occidentalis), African spinach (Amaranthus hybridus) and water leaf (Talinum trianguilare).

Fluted Pumpkin (*Telfairia occidentalis*) is a species of *cucurbitaceace* family in the tropics, largely consumed in West Africa (Uboh *et al.*, 2011), grown as a leaf vegetable with medicinal and edible seeds (Ajayi *et al.,* 2006). Its native names are *Ubong* in Ibibio and *Ugu* in Igbo. It spreads by creeping across the ground with lobed leaves and long slim twisting tendrils (Uboh *et al.*, 2011). *Telfairia occidentalis* is rich in protein and iron, hence extracts from the leaves can be used to boost blood for anaemia patients (Ajayi et al., 2004).

African spinach (Amaranthus hybridus) is a species of Amarantaceae, globally found in both tropical and temperate regions (Ogwu, 2020). The leaves are alternate petioled, 3 – 6 inches long, dull green, and rough, hairy, ovate or rhombic with wavy margins (Mepha et al., 2007).

Waterleaf (*Talinum triangulare*), a *portulacea* family, originated from tropical Africa, especially West Africa, and in Asia and South America, has high resistance to pests (Schippers, 2000) and extraordinary tolerance for temperature, water and soil stresses (Oladoye and Liu 2022). Swarna *et al.* (2013) have reported its use as a natural pigment for food colorants.

Gezahegn *et al.* (2017) have documented x-ray fluorescence (XRF) spectroscopy as a suitable technique for detection of elements such as Na, Mg, P, S, Cl, K, Ca at higher concentrations or under highly specialized conditions, and heavy metals at trace levels with the exception of lightest elements (e.g. H, B, C, N, O).

A previous work has investigated the potentials of these vegetable varieties, obtained from eastern Nigeria, to uptake heavy metals from the soils on which they grow, revealing high potential of *Talinum triangulare* and *Amaranthus hybridus* for heavy metals uptake (Oladebeye *et al.,* 2020).

This present research focuses on estimating the heavy metals present in two designated soils obtained from Owo Local Government Area, Ondo State, Nigeria, and their bioaccumulation in the tissues of fluted pumpkin (*Telfairia occidentalis*), African spinach (*Amaranthus hybridus*) and water leaf (*Talinum triangulare*) that grow on them. This will help harness the potentials of the selected vegetable samples as hyperaccumulators in phytoextraction techniques. X-ray Fluorescence (XRF) technique was used for this investigation and the data obtained were subjected to statistical analysis, using IBM SPSS 23.0 software (SPSS Inc., Chicago, IL) 2015.

2. Materials and Methods

2.1 Study Locations

Owo, situated halfway between the towns of Ile-Ife and Benin-City, is located on Latitude 7.1989° N and Longitude 5.5932° E with a population of 222,262, based on 2006 population census (Figure 1). The study locations in Owo Local Government Area were farmlands at St. Louis and Osuma Layout. The farmland at St. Louis was behind St. Louis Grammar School (**Latitude** NS: $7^{o}12^{'}17.702^{''}$; **Longitude** EW: $5^{o}34^{'}31.381^{''}$; **Altitude:** 318 meters). The farmland at Osuma Layout was located close to Adedewe Nursery School, along old Owo-Akure Road (**Latitude** NS: $7^{o}12^{'}50.719^{''}$; **Longitude** EW: $5^{o}33^{'}6.394^{''}$; **Altitude:** 324 meters).

Figure 1. Map of Ondo State showing Owo Local Government Area

2.2 Sample Collection

Random sampling technique was employed to collect the vegetable samples of fluted pumpkin leaves (*Telfairia occidentalis*), African spinach, "Green" (*Amaranthus hybridus*) and waterleaf (*Talinum triangulare*) from the two study locations to obtain composite samples. The leaves of vegetable samples were separated from the whole plants with the aid of hand gloves and a stainless steel knife and were carefully packaged in polythene bags and labelled. Similarly, random samples of soils from the study locations were taken at uniform depth of 15 cm with the aid of a hand trowel that had been pre-cleaned with concentrated nitric acid in order to prevent heavy metal contamination prior to analysis (Oladebeye *et al., 2020*). The soil samples obtained from the farmlands at St. Louis and Osuma Layout were designated SSL and SOL respectively. The vegetable samples were labelled as ToSL (*Telfairia occidentalis* from St. Louis), AhSL (*Amaranthum hybridus* from St. Louis), *Talinum triangulare* from St. Louis (TtSL), *Telfairia occidentalis* from Osuma Layout (ToOL), AhOL (*Amaranthum hybridus* from Osuma Layout) and TtOL (*Talinum triangulare* from Osuma Layout).

2.3 Preparation of Vegetable Samples
The vegetable samples were first washed with tap water and subsequently, with de-ionized water to remove air pollutants. Moisture was removed from the samples by oven-drying them at 105 ºC for 48 h. The dried samples were pulverized, using agate pestle and mortar, sieved (0.5 mm mesh size), labelled and stored in dry plastic containers that had been pre-cleaned with concentrated nitric acid to check heavy metal contamination prior to analysis (Oladebeye *et al., 2020*).

2.4 Preparation of Soil Samples
The soil samples were air dried for 48 h, ground and sieved using 0.5 mm mesh size sieve to have uniform particle size. Each sample was labelled and stored in a dry plastic container that had been pre-cleaned with concentrated nitric acid prior to analysis with X-ray fluorescence (XRF) spectrometer (Oladebeye *et al.,* 2020).

2.5 Determination of Elemental Compositions
The previous methods described by Guerra *et al.* (2014) and Oladebeye *et al.* (2020) were adopted with some modifications. The sample was oven-dried at 80 °C for 20 h, ground after cooling, sieved with 50 μm sieve-size and pellet with weight of 200 mg and diameter of 2.5 cm was made in a pellet-pressing machine under 15 ton of pressure. The pellet was irradiated with a primary radiation from a Cd-109 radioactive source for a period of 2500 s. Two irradiations were done; pure sample and sample with a molybdenum target on top. These two measurements were then used to calculate the absorption corrections. The characteristic x-rays emitted by the elements in the sample were detected by a liquid nitrogen cooled Si (Li) detector. To obtain optimum detection of elements, different filters of 0.05 mm Ti filter at applied voltage of 14-35 kV and 900 mA and 0.05 mm Fe filter at 37 kV and 45 mA current were used.

2.6 Bio-Concentration Factor (BCF)
Here, we defined bio-concentration factor as the availability of metals in the tissues of plants in comparison with their availability in the soil. This was different from the transfer (or uptake) factor that would involve fresh cultivation of the plant sample on the soil sample (Kachenko and Singh, 2006; Tsafe *et al*., 2012; Rezapour *et al.,* 2019; Keeflee *et al.,* 2020). Mathematically, BCF was deduced by dividing the concentration of metal in the plant by the elemental concentration in soil without fresh cultivation.

Mathematically,

$$\text{Bio} - \text{Concentration Factor} = \frac{\text{concentration of metal in plant}}{\text{concentration of metal in soil}}$$

3. Statistical Analysis
The statistical analysis, which included descriptive analysis, ANOVA, Pearson's Correlation of the data generated in this study was carried out with IBM SPSS 23.0 software for both soil and vegetable samples from the two study locations.

4. Results and Discussion
4.1 Heavy Metal Concentrations
The heavy metals detected in the soil and vegetable samples from two study locations in Owo Local Government Area, Ondo State are chromium (Cr), zinc (Zn), manganese (Mn), iron (Fe), titanium (Ti), strontium (Sr) and aluminium (Al) (Table 1). Generally, in terms of mean concentrations, Cr, Fe, Ti, Sr and Al are more available in the soil than in the vegetables that grow on them whereas an opposite trend is obtained for Zn and Mn (Fig. 2). The mean Al concentration in the soil samples is the highest, followed by the mean Fe concentration while the mean Cr concentration is the lowest. This implies that soil is a major reservoir of metals that are being deposited and transported in the universe.

Table 1. Heavy metal concentrations of soil and vegetable samples

Sample		Mineral (%)						
		Cr	**Zn**	**Mn**	**Fe**	**Ti**	**Sr**	**Al**
Soil	SSL	0.019 ± 0.001^{a}	0.018 ± 0.001^{a}	0.16 ± 0.02^{ab}	6.43 ± 0.02^{a}	1.67 ± 0.01^{a}	0.052 ± 0.001^{b}	7.51 ± 0.02^{a}
	SOL	0.011 ± 0.001^{b}	0.008 ± 0.000^{b}	0.14 ± 0.01^{a}	3.57 ± 0.01^{b}	1.10 ± 0.02^{b}	0.073 ± 0.001^{a}	6.44 ± 0.01^{b}
Mean (Soil)		**0.015±0.005**	**0.013±0.006**	**0.15±0.02**	**5.00±1.57**	**1.38±0.31**	**0.062±0.012**	**6.97±0.58**
Vegetable	ToSL	0.009 ± 0.000^{b}	0.058 ± 0.001^{b}	0.08 ± 0.01^{c}	1.03 ± 0.01^{e}	0.31 ± 0.00^{e}	0.014 ± 0.001^{f}	5.44 ± 0.02^{c}
	AhSL	0.014 ± 0.001^{a}	0.039 ± 0.001^{c}	0.09 ± 0.01^{c}	2.74 ± 0.01^{b}	0.41 ± 0.01^{d}	0.032 ± 0.001^{e}	6.33 ± 0.03^{a}
	TtSL	BDL	0.072 ± 0.003^{a}	0.14 ± 0.01^{b}	3.00 ± 0.01^{a}	0.71 ± 0.01^{c}	0.049 ± 0.001^{d}	6.15 ± 0.02^{b}
	ToOL	0.005 ± 0.000^{c}	0.004 ± 0.000^{e}	0.16 ± 0.01^{b}	2.58 ± 0.01^{c}	1.31 ± 0.01^{a}	0.068 ± 0.001^{a}	4.64 ± 0.02^{e}
	AhOL	0.003 ± 0.000^{d}	0.007 ± 0.000^{d}	0.08 ± 0.00^{c}	2.18 ± 0.02^{d}	0.90 ± 0.01^{b}	0.052 ± 0.001^{c}	5.05 ± 0.01^{d}
	TtOL	0.015 ± 0.001^{a}	0.038 ± 0.001^{c}	0.39 ± 0.03^{a}	0.84 ± 0.01^{f}	0.27 ± 0.00^{f}	0.060 ± 0.001^{b}	3.83 ± 0.02^{f}
Mean (Vegetable)		**0.008±0.006**	**0.036±0.025**	**0.16±0.11**	**2.06±0.86**	**0.65±0.38**	**0.046±0.018**	**5.24±0.89**

SSL = soil sample from St. Louis; ToSL = *Telfairia occidentalis* from St. Louis; AhSL = *Amaranthum hybridus* from St. Louis; TtSL = *Talinum triangulare* from St. Louis; SOL = soil sample from Osuma Layout; ToOL = *Telfairia occidentalis* from Osuma Layout; AhOL = *Amaranthum hybridus* from Osuma Layout; TtOL = *Talinum triangulare* from Osuma Layout. *Mean ±SD along the column with different superscript are significantly different at 5% level with* a > b > c > d > e > f. *Mean separation done by Duncan Multiple Range Test. BDL = Below Detection Limit*

Amaranthum hybridus from St. Louis (AhSL) and *Talinum triangulare* from Osuma Layout (TtOL) exhibit the same peak concentration of Cr ($p < 0.05$). The least concentration of Cr (0.003±0.000%) is obtained in *Amaranthum hybridus* from Osuma Layout (AhOL) while it is below detection limit in *Talinum triangulare* from St. Louis (TtSL). Chromium persists in the environment as either Cr (III) or Cr (VI). Cr (VI), being a strong oxidizing agent, corrosive, is soluble in alkaline and mildly acidic water, toxic and potential carcinogen to plants and animals as a result of its tendency to diffuse through cell membranes and oxidize biological molecules (Jaishankar *et al.,* 2014). However, the Cr concentrations in both vegetable and soil samples are higher than the recommended limits of 1.3 mg/kg for vegetables and 0.10 mg/kg for soil by WHO (Chiroma *et al.,* 2014; WHO, 2011).

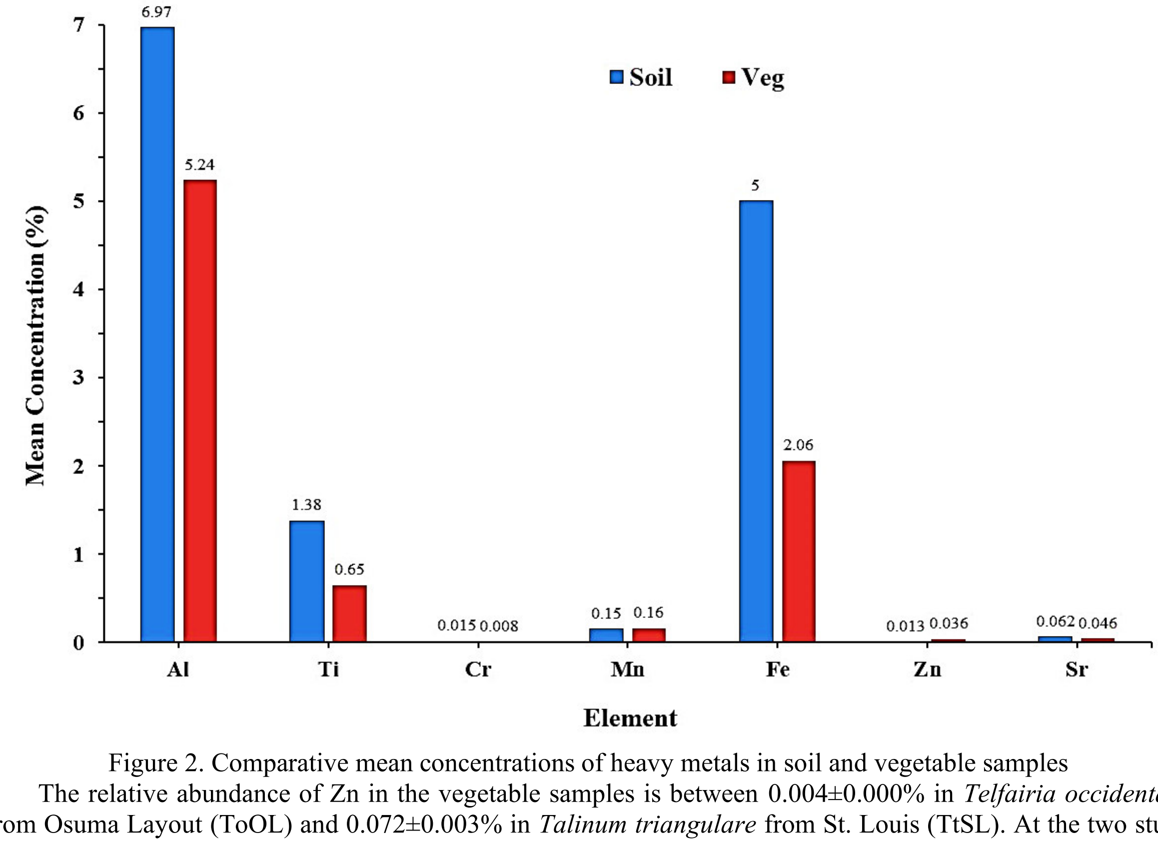

Figure 2. Comparative mean concentrations of heavy metals in soil and vegetable samples

The relative abundance of Zn in the vegetable samples is between 0.004±0.000% in *Telfairia occidentalis* from Osuma Layout (ToOL) and 0.072±0.003% in *Talinum triangulare* from St. Louis (TtSL). At the two study locations, the concentration of Zn in *Talinum triangulare* appears the highest, when compared to other vegetable samples. Mean zinc concentrations of 0.100±0.000 mg/kg and 0.070±0.0010 mg/kg have been reported for fluted pumpkin plants and water leaves respectively (Sobukola *et al.,* 2010). Prolonged bioaccumulation of Zn, via a common zinc-calcium transport carrier, is liable for damage of reactive oxygen species in plant, animal and human tissues (De Schamphelaere *et al.,* 2004; Loro *et al.,* 2012; Delahaut *et al.,* 2020). However, zinc deficiency has been designated by the World Health Organization as a major disease contributing factor for growth impairment, sexual dysfunction, inflammation, gastrointestinal symptoms, or cutaneous involvement (Narváez-Caicedo *et al.,* 2018). The concentrations of zinc in both the soil and vegetable samples are quite above the recommended limits of 0.033 mg/kg for soil and 50 mg/kg for plants by WHO (Shah *et al* 2011; Nazir *et al.,* 2015).

Talinum triangulare obtained from the two study locations is the richest in Mn concentration among all the vegetable samples studied with TtOL higher in Mn concentration than TtSL. This variation as a result of difference in bioavailability of Mn in the soil samples. *Amaranthum hybridus* appears as the poorest in Mn concentration, which is less a quarter of the same heavy metal found in *Talinum triangulare*. The exceptional higher concentration of Mn in *Talinum triangulare* species than the soils on which they grow may be due to high adsorption capacity of their tissues, which then account for the low concentrations available for other vegetable studied with low adsorption capacities. Manganese (Mn) exists in soil in three oxidation states as Mn^{2+} (phytoavailable form), Mn^{3+} and Mn^{4+} (insoluble, yet reducible forms), and their bioavailability is largely influence by the soil Mn concentration, pH and electron activities (Fernando and Lynch, 2015). Both lack and excess manganese have negative impacts on human health with the brain being the main target organ for its accumulation and toxicity such as manganese poisoning (manganism) and Parkinson's disease (Aschner and Aschner, 2005; Zaitsev *et al.,* 2020).

Iron (Fe) concentration ranges from 3.57±0.01 to 6.43±0.02% in the soil samples and 0.84±0.01 to 3.00±0.01% in the vegetable samples. Among the vegetable samples studied, *Talinum triangulare* species at St. Louis is the richest in Fe concentration while the poorest is the *Talinum triangulare* species obtained from Osuma Layout. However, the data obtained are higher than the recommended limit of WHO of 20 mg/kg in plants (Shah *et al*., 2011) and 300 mg/kg in soils (Chiroma *et al.,* 2014; Iyama *et al.,* 2022). However, Fe concentration of more than 10 mg/kg can cause rapid increase in pulse rate and coagulation of blood in blood vessels, hypertension and drowsiness (Shah *et al*., 2011).

Titanium (Ti) concentration ranges from 0.27±0.00 to 1.31±0.01% in the vegetable samples. Among the vegetable samples studied, *Telfairia occidentalis* species at Osuma Layout (ToOL) is the richest in Ti concentration while the poorest is the *Talinum triangulare* species obtained from Osuma Layout. *Talinum triangulare* species studied, thus, behave differently in different soils and locations. Increase in crop yield, in terms of crop quality and quantity, has been attributed to Ti-enhanced chlorophyll biosynthesis and enzymatic activities, increased photosynthesis and nutrient uptake, such as increased concentrations of chlorophyll a and b, and total chlorophyll (Cigler *et al.,* 2010; Kovacik *et al.,* 2014; Lyn *et al.,* 2017). As a beneficial element to plants, Ti plays synergetic role, at low concentration, and antagonistic role, at a very high concentration, with Fe. While Fe is considered an essential elements to plants, Ti is considered as a complementary element (Lyn *et al.,* 2017). This study shows lower concentrations of Ti in both soils and vegetable samples than the concentrations of Fe. This implies that Ti is expected to play synergetic role with Fe in all the vegetable samples. The concentrations of Ti obtained in this study has no guideline for comparison in WHO permissible limit (Chiroma *et al.,* 2014; WHO, 2011). However, Ti concentrations of 0.15 mg/kg and 0.065 mg/kg have been reported for *Solanum* sp. and *Aramanthus* sp. respectively (Rono and Wakhungu, 2021). The major sources of high Ti contamination are soils around the industrial area of the steel-making plants (Wang *et al.,* 2021).

The range of Sr in the vegetable samples is from 0.014±0.001% in *Telfairia occidentalis* from St. Louis (ToSL) to 0.068±0.001% in *Telfairia occidentalis* from Osuma Layout (ToOL). The uptake and distribution of Sr in plants have been likened to those of calcium (Kabata-Pendias and Mukherjee 2007; Dresler *et al.,* 2018). Although the physiological role of strontium in plants has remained unidentified, its physical and chemical similarities with calcium can make it interfere with calcium being taken up (Kabata-Pendias and Mukherjee 2007; Gupta *et al.,* 2018). The concentrations of Sr obtained in this study has no guideline for comparison in WHO permissible limit (Chiroma *et al.,* 2014; WHO, 2011),

Al mean concentrations in both soil and vegetable samples in this study are the highest among all the heavy metals detected. The least concentration of Al among the vegetable samples is 3.83±0.02% in *Talinum triangulare* from Osuma Layout (TtOL) while the highest concentration is 6.33±0.03 mg/kg in *Amaranthum hybridus* from St. Louis (AhSL). The least concentration of Al (3.83±0.02%) is higher than the peak concentration of Fe (3.00±0.01%) obtained in the vegetable samples studied. The soil pH and the chemical environment of the soil solution determine the total Al concentration in the soil and the forms of Al species (Kisnieriene and Lepeikaite, 2015). The toxic effect of different Al species on plant growth is in the order $_{13}Al > Al^{3+} > Al(OH)_2^+ > Al(OH)_3 > Al(OH)_4^-$ (Neenu and Karthika, 2019). Aluminium has no biological role and is a toxic non-essential metal to microorganisms, enzymes, nervous, osseous and hemopoietic cells (Olaniran *et al*., 2013; Barabasz *et al*., 2002). In humans and animals, the lungs, central nervous system and bone are the target of aluminium poisoning (Jessica *et al.,* 2020). Specifically, in humans, the cause of many disorders associated with intercellular communication, cellular growth and secretory functions are as a result of ability of Al^{3+} replacing Mg^{2+} and Fe^{3+} (Jaishankar *et al.,* 2014). The concentrations of Al obtained in this study has no guideline for comparison in WHO permissible limit (Chiroma *et al.,* 2014; Kinuthia *et al.,* 2020). However, range of Al concentration of 11.00 – 27.00 mg/kg has been reported for soils obtained around transformer in Akoko-Edo community (Ogunlana *et al.,* 2020).

4.2 Inter-Elements Correlation

Inter-elements correlation of the heavy metals detected in the soil and vegetable samples studied is depicted in Table 2.

Table 2. Pearson correlation of heavy metals bioaccumulation in vegetable samples

Mineral	Mineral						
	Cr	Zn	Mn	Fe	Ti	Sr	Al
Cr	1.000	0.013	0.478	-0.558	-0.672	-0.202	-0.273
Zn		1.000	0.100	-0.074	-0.635	-0.557	0.490
Mn			1.000	-0.507	-0.271	0.548	-0.743
Fe				1.000	0.586	0.207	0.645
Ti					1.000	0.613	-0.096
Sr						1.000	-0.594
Al							1.000

Correlation is significant at the 0.05 level (2-tailed); N = 6

The negative r values imply no correlation while the positive values imply correlation between the elements ($p<0.05$). Positive correlation implies that an increase in one metal corresponds to the increase in the other metal found in the same soil and vegetable samples. From Table 2, positive correlations of Cr-Zn (r = 0.013), Cr-Mn (r= 0.478), Zn-Mn (r= 0.100), Zn-Al (r = 0.490), Mn-Sr (r = 0.548), Fe-Ti (r = 0.586), Fe-Sr (r = 0.507), Fe-Al (r = 0.645), and Ti-Sr (r = 0.613) are obtained. Similarly, negative correlations of Cr-Fe (r = -0.558), Cr-Ti (r = -0.672), Cr-Sr (r = -0.202), Cr-Al (r = -0.273), Zn-Fe (-0.074), Zn-Ti (r = -0.557), Mn-Fe (r = -0.507), Mn-Ti (r = -0.271), Mn-Al (r = -0.743), Ti-Al (r = -0.096) and Sr-Al (r = -0.594) are obtained.

4.3 Bio-Concentration Factor (BCF)

The uptake, accumulation and distribution of metals in plants depend, among other things, on the nutrient source. Soil is the major source of metals that are bioaccumulated in plants due to its deposition on the earth surface, mechanism of transfer of metals and ability to retain metals for a long period of time. Hyperaccumulator plants, that is, plants that grow in serpentine soils with high concentrations of metals, having potential in the management of polluted soils through the mechanism called phytoextraction have been reported (Shallari *et al.,* 1998; Brady *et al.,* 2005; Osmani *et al.,* 2015). A vegetable plant with BCF ≥ 1 has the tendency of being a hyperaccumulator plant. Table 3 depicts the BCF values of the vegetable samples studied. With BCF value of 1.36, TtOL is Cr hyperaccumulator. There is competition among the ToSL, AhSl, TtSL and TtOL as Zn hyperaccumulator, possessing BCF values of 3.22, 2.17, 4.00 and 4.75 respectively. In other words, their decreasing order of hyperaccumulation ability TtOL > TtSL > ToSL > AhSL.

Table 3. Bio-Concentration factor of heavy metals in the vegetable samples relative to their soil sources

Heavy Metal	Bio-Concentration Factor *					
	ToSL	AhSL	TtSL	ToOL	AhOL	TtOL
Cr	0.47	0.74	0.00	0.45	0.27	1.36
Zn	3.22	2.17	4.00	0.50	0.88	4.75
Mn	0.50	0.56	0.88	1.14	0.57	2.79
Fe	0.16	0.43	0.47	0.72	0.61	0.24
Ti	0.19	0.25	0.43	1.20	0.83	0.25
Sr	0.29	0.62	0.92	0.93	0.71	0.84
Al	0.72	0.84	0.82	0.72	0.78	0.59

$$*\text{Bio} - \text{Concentration Factor} = \frac{\text{concentration of metal in plant}}{\text{concentration of metal in soil}}$$

This difference implies that the mechanism of phytoextraction is not the same for different plants that grow on the same soil and under identical environmental conditions. ToOL is both Mn hyperaccumulator and Ti hyperaccumulator with BCF values of 1.14 and 1.20 respectively. However, TtOL exhibits higher potential as Mn hyperaccumulator than ToOL due to higher BCF value of 2.79. It is worthy of note that TtSL is the most significant nonaccumulator for Cr. *Brassicaceae*, *Fabaceae*, *Euphorbiaceae*, *Asterraceae*, *Lamiaceae*, and *Scrophulariaceae* are parts of the approximately 400 hyperaccumulators that have been reported (Lasat, 2000; Ghosh and Singh, 2005; Salt *et al.,* 1998; Dushenkov, 2003). Insoluble metals are capable of forming oxides of carbon, sulphur and phosphorus in the vascular system of plants (Raskin and Ensley, 2000; Wuana and Okieimen, 2011).

5. Conclusion

Fluted pumpkin (*Telfairia occidentali*s)*,* African spinach (*Amaranthus hybridus*) and water leaf (*Talinum* triangulare) randomly selected from designated farms in Owo Local Government Area, Ondo State, Nigeria are found to contain Cr, Zn, Mn, Fe, Ti, Sr and Al at concentrations higher than the permissible limits of WHO/FAO for soils and plants. The soil samples are richer in these heavy metals more than the vegetable samples. In the vegetable samples, the most available heavy metal detected is Al, followed by Fe while the least is Cr. Hyperaccumulators, among the vegetable samples, exhibit BCF values greater than 1. This study reveals that there is no suitable hyperaccumulator for Al, Sr and Fe among all the vegetable samples. However, AhSL, ToSL,TtSL and TtOL are competitive Zn hyperaccumulators. It is worthy of note that the most efficient hyperaccumulators are *Talinum triangulare* species from the two study location. For phytoextraction technologies, the vegetable samples studied have potentials that can be harnessed.

6. References

Ajayi, S.A., Berjak, P., Kioko, J.I., Dulloo, M.E. & Vodouhe, R.S. (2006), "Responses of fluted pumpkin (*Telfairia occidentalis*) seeds to desiccation, chilling and hydrated storage". *Journal of Botany*, **72**(4), 544-550.

Ajayi, S.A., Dulloo, M.E., Vodouhe, R.S., Berjak, P. & Kioko, J.I. (2004), "Conservation status of *Telfairia spp* in sub-Saharan Africa". Paper presented at the Regional workshop on Plant Genetic Resources and food security in West and Central Africa, held at IITA, Ibadan,

Aschner, J.L., & Aschner, M. (2005), "Nutritional aspects of manganese homeostasis. *Molecular Aspect of Medicine,* **26**(4–5), 353–362.

Ashraf, M.A., Maah, M.J. & Yusoff, I. (2014), "Soil Contamination, Risk Assessment and Remediation. In (Ed.), Environmental Risk Assessment of Soil Contamination". I*ntechOpen*. https://doi.org/10.5772/57287

Ashton, L.M., Sharkey, T., Whatnall, M.C., Williams, R.L., Bezzina, A., Aguiar, E.J., Collins, C.E. & Hutchesson, M.J. (2019), Effectiveness of interventions and behaviour change techniques for improving dietary intake in young adults: A systematic review and meta-analysis of RCTs. *Nutrients*, **11**, 825.

Barabasz, W., Albinska, D., Jaskowska, M. & Lipiec, J. (2002), "Ecotoxicology of Aluminium". *Polish Journal of Environmental Studies,* **11**(3), 199–203.

Brady, K.U., Kruckeberg, A.R. & Bradshaw, H.D. (2005), "Evolutionary ecology of plant adaption to serpentine soils". *Annuual Review of Ecology, Evolution, and Systematics,* **36**, 243-266.

Briffa, J., Sinagra, E. & Blundell, R. (2020), "Heavy metal pollution in the environment and their toxicological effects on humans". *Heliyon,* **6** e04691.

Chiroma, T.M., Ebewele, R.O. & Hymore, F.K. (2014), "Comparative Assessment of heavy metal levels in soil, vegetables and urban grey water used for irrigation in Yola and Kano". *International Refereed Journal of Engineering and Science,* **3**(2), 1–9.

Cigler, P., Olejnickova, J., Hruby, M., Csefalvay, L., Peterka, J., and Kuzel, S. (2010), "Interaction between iron and titanium metabolism in spinach: a chlorophyll fluorescence study in hydropony". *Journal of Plant Physiology,* **167**, 1592-1597.

De Schamphelaere, K.A.C. & Janssen, C.R. (2004), "Bioavailability and Chronic Toxicity of Zinc to Juvenile Rainbow Trout (*Oncorhynchus mykiss*): Comparison with Other Fish Species and Development of a Biotic Ligand Model". *Environmental Science and Technology,* **38**, 6201–6209.

Delahaut, V., Rašković, B., Salvado, M.S., Bervoets, L., Blust, R. & De Boeck, G. (2020), "Toxicity and bioaccumulation of Cadmium, Copper and Zinc in a direct comparison at equitoxic concentrations in common carp (*Cyprinus carpio*) juveniles". *PloS one,* **15**(4), e0220485. https://doi.org/10.1371/journal.pone.0220485.

Dresler, S., Wojciak-Kosior, M., Sowa, I., Strzemski, M., Sawicki, J., Kovacik, J. & Blicharski, T. (2018), "Effect of Long-Term Strontium Exposure on the Content of Phytoestrogens and Allantoin in Soybean". *International Journal of Molecular Science,* **19**, 3864. doi:10.3390/ijms19123864.

Dushenkov, S. (2003), "Trends in phytoremediation of radionuclides". *Plant Soil,* **249**(1), 167–175.

Fernando, D.R. & Lynch, J.P. (2015), "Manganese phytotoxicity: new light on an old problem". *Annals of Botany,* **116**(3), 313–319.

Gezahegn, W.W., Srinivasulu, A., Aruna, B., Banerjee, S., Sudarshan, M., Narayana, P.V.L. & Rao, A.D.P. (2017), "Study of Heavy Metals Accumulation in Leafy Vegetables of Ethiopia". *Journal of Environmental Science, Toxicology and Food Technology,* **11**(5), 57-68.

Ghosh, M. & Singh, S.P. (2005), "A review on phytoremediation of heavy metals and utilization of its by-products". *Applied Ecology and Environmental Research,* **3**(1), 1–18.

Guerra, M.B.B., Almeida, E., Carvalho, G.G.A., Souza, P.F., Nunes, L.C., Santos Jr., D. & Krug, F.J. (2014). "Comparison of analytical performance of benchtop and handheld energy dispersive X-ray fluorescence systems for the direct analysis of plant materials". *Journal of Analytical Atomic Spectrometry,* **29**, 667.

Gupta, D.K., Schulz, W., Steinhauser, G. & Walther, C. (2018), "Radiostrontium transport in plants and phytoremediation". *Environmental Science and Pollution Research,* **25**, 29996–30008.

Iyama, W.A., Okpara, K. & Techato, K. (2022), "Assessment of Heavy Metals in Agricultural Soils and Plant (*Vernonia amygdalina Delile*) in Port Harcourt Metropolis, Nigeria". *Agriculture,* **12***,* 27. https://doi.org/10.3390/agriculture12010027.

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B. & Beeregowda, K.N. (2014), "Toxicity, mechanism and health effects of some heavy metals". *Interdisciplinary Toxicology,* **7**(2), 60–72. https://doi.org/10.2478/intox-2014-0009.

Jessica, J., Sinagra, E. & Blundell, R. (2020), "Heavy metal pollution in the environment and their toxicological effects on humans". *Heliyon*, **6***:*e04691.

Kabata-Pendias A. & Mukherjee, A.B. (2007), "Trace Elements from Soil to Human"; Springer-Verlag: Berlin Heidelberg.

Kachenko, A.G. & Singh, B. (2006), "Heavy metals Contamination in Vegetables Grown in Urban and Metal smelter Contaminated Sites in Australia". *Water, Air and Soil Pollution*, **169**, 101-123.

Keeflee, S.N.K.M.N., Zain, W.N.A.M.D., Nor, M.N.M., Jamion, N.A. & Yong, S.K. (2020). Growth and metal uptake of spinach with application of co-compost of cat manure and spent coffee ground. *Heliyon* **6**:e05086. doi.org/10.1016/j.

Kinuthia, G.K., Ngure, V., Beti, D., Lugalia, R., Wangila, A. & Kamau, L. (2020), "Levels of heavy metals in wastewater and soil samples from open drainage channels in Nairobi, Kenya: community health implication". *Scientific Reports,* **10**, 8434. doi.org/10.1038/s41598-020-65359-5.

Kisnieriene, V. & Lapeikaite, I. (2015). When chemistry meets biology: the case of aluminium- a review. *Chemija*, **26**, 148–158.

Kovacik, P., Hudec, J., Ondrisik, P. & Poliakova, N. (2014), "The effect of liquid Mg-Titanit on creation of winter wheat phytomass". *Research Journal of Agricultural Science,* **46**, 125-131.

Lasat, M.M. (2000), "Phytoextraction of metals from contaminated soil: a review of plant/soil/metal interaction and assessment of pertinent agronomic issues". *Journal of Hazardous Substances Research,* **2**, 1–25.

Loro, V.L., Jorge, M.B., Rios, K., Silva, D. & Wood, C.M. (2012), "Oxidative stress parameters and antioxidant response to sublethal waterborne zinc in a euryhaline teleost *Fundulus heteroclitus*: Protective effects of salinity". *Aquatic Toxicology,* **110**, 187–193.

Lyn, S., Wei, X., Chen, J., Wang, C., Wang, X. & Pan, D. (2017), "Titanium as a beneficial element for crop production". *Frontiers in Plant Science*, **8**, 597. doi:10.3389/fp;ls.2017.00597

Mello-Rodrigues, V., Bray, J., Fernandes, A.C., Luci Bernardo, G., Hartwell, H., Secchi Martinelli, S., Lazzarin Uggioni, P., Barletto Cavalli, S. & Proença, R.P. (2019), "Vegetable consumption and factors associated with increased intake among college students: A scoping review of the last 10 years." *Nutrients*, **11**, 1634.

Mepha, H.D., Eboh, L. & Banigbo, D.E.B. (2007), "Effects of processing treatments on the Nutritive Composition and consumer acceptance of some Nigerian edible leafy vegetables". *African Journal of Food, Agriculture, Nutrition and Development,* **7**(1), 1-18.

Narváez-Caicedo, C., Moreano, G., Sandoval, B.A. & Jara-Palacios, M.Á. (2018), "Zinc Deficiency among Lactating Mothers from a Peri-Urban Community of the Ecuadorian Andean Region: An Initial Approach to the Need of Zinc Supplementation". *Nutrients*, **10**(7), 869. doi: 10.3390/nu10070869

Nazir, R., Khan, M., Masab, M., Ur Rehman, H., Ur Rauf, N., Shahab, S., Ameer, N., Sajed, M., Ullah, M., Rafeeq, M. & Shaheen, Z. (2015), "Accumulation of Heavy Metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) in the soil, water and plants and analysis of physicochemical parameters of soil and water Collected from Tanda Dam kohat". *Journal of Pharmaceutical Sciences and Research,* **7**(3), 89-97.

Neenu, S. & Karthika, K.S. (2019), "Aluminium toxicity in soil and plants". *Harit Dhara* **2**(1), 15-19.

Nour, M., Sui, Z., Grech, A., Rangan, A., McGeechan, K. & Allman-Farinelli, M. (2017), "The fruit and vegetable intake of young Australian adults: A population perspective". *Public Health and Nutrition,* **20**, 2499–2512.

Ogunlana, R., Korode, A.I. & Ajibade, Z.F. (2020), "Assessing the Level of Heavy Metals Concentration in Soil around Transformer at Akoko Community of Ondo State, Nigeria". *Journal of Applied Sciences and Environmental Management,* **24**(12), 2183-2189.

Ogwu, M.C. (2020), "Value of *Amaranthus L*. species in Nigeria. In (Ed.), Nutritional Value of Amaranth". *IntechOpen.* https://doi.org/10.5772/intechopen.86990

Oladebeye, A.O., Okunade, M.B. & Oladebeye, A.A. (2020), "Elemental Compositions of Tropical Vegetables and Soils in Edo State, Nigeria Using X-ray Fluorescence Technique". *Journal of Scientific Research and Reports,* **26**(2), 27-37.

Oladoye, C.T. & Liu, G. (2022), "Waterleaf, a potential leafy vegetable for Florida". doi.org/10.32473/edis-HS1434-2022

Olaniran, A.O., Balgobind, A., & Pillay, B. (2013), "Bioavailability of heavy metals in soil: impact on microbial biodegradation of organic compounds and possible improvement strategies". *International Journal of Molecular Sciences,* **14**(5), 10197–10228.

Osmani, M., Bani, A. & Hoxha, B. (2015). "Heavy Metals and Ni Phytoextractionin in the Metallurgical Area Soils in Elbasan". *Albanian Journal of Agricultural Sciences,* **14**(4), 414-419.

Raskin, I. & Ensley, B.D. (2000), "Phytoremediation of Toxic Metals: Using Plants to Clean Up the Environment", John Wiley & Sons:New York.

Rezapour, S., Atashpaz, B., Moghaddam, S.S., Kalavrouriotis, I.K. & Damalas, C.A. (2019), "Cadmium accumulation, translocation factor and health risk potential in wastewater irrigated soil wheat (*Triticum aestivum L.*) system". *Chemosphere,* **231**, 579-587.

Rono, D.K. & Wakhungu, J.W. (2021), "Titanium, zinc, lead, chromium, cadmium, cobalt and copper concentrations in vegetables produced using wastewater in urban and peri-urban areas of Nairobi-City County, Kenya". *Current Journal of Applied Science and Technology,* **49**(1), 102-118.

Salt, D.E., Smith, R.D. & Raskin, I. (1998), "Phytoremediation". *Annual Review of Plant Physiology and Plant Molecular Biology,* **49**, 643–668.

Schippers, R.R. (2000), "African Indigenous Vegetables: An overview of the cultivated species", NRI/ACP, EU, Chatten:UK

Shah, A., Niaz, A., Ullah, N., Rehman, A., Akhlaq, M., Zakir, M. & Khan, M.S. (2013), "Comparative Study of Heavy Metals in Soil and Selected Medicinal Plants". *Journal of Chemistry.* https://doi.org/10.1155/2013/621265.

Shallari, S., Schwartz, C., Hasko, A. & Morel, J.L. (1998), "Heavy metals in soils and plants of serpentine and industrial sites of Albania". *Science of the Total Environment,* **209**, 133-142.

Sobukola, P.O., Adeniran, O.M., Odedairo, A.A. & Kajihausa, O.E. (2010), "Heavy metal levels of some fruits and leafy vegetables from selected markets in Lagos, Nigeria". *African Journal of Food Science,* **4**(2), 389-393.

Swarna, J., Lokeswari, T.S., Smita, M. & Ravindhran, R. (2013), "Characterization and determination of in vitro antioxidant potential of betalains from *talinum triangulare* (JACQ) wild". *Food Chemistry,* **141** (4), 4382–4390. https://doi.org/10.1016/j.foodchem.2013.06.108

Theron, A.J., Tintinger, G.R. & Anderson, R. (2012), "Harmful interactions of non-essential heavy metals with cells of the innate immune system". *Journal of Clinical Toxicology,* **S3**, 005.

Tsafe, A.I., Hassan, L.G., Sahabi, D.M., Alhassan, Y. & Bala, B.M. (2012), "Evaluation of Heavy Metals Uptake and Risk Assessment of Vegetables Grown in Yargadama of Northern Nigeria". *Journal of Basic and Applied Scientific Research,* **2**(7), 6708-6714.

Uboh, E., Akpanabiatu, M.I., Edet, E.E. & Okon, I.E. (2011), "Distribution of heavy metals in fluted pumpkin (*Telfeiria occidentalis*) leaves planted at traffic congested highway". *International Journal of Advanced Biotechnology and Research,* **2**(2), 250.

Wang, J., Wang, L., Wang, Y., Tsang, D.C.W., Yang, X., Beiyuan, J., Yin, M., Xiao, T., Jiang, Y, Lin, W., Zhou, Y. & Liu, J. (2021), "Emerging risks of toxic metao(loid)s in soil-vegetables influenced by steel-making activities and isotopic source apportionment". *Environment International,* **146**, 106207.

Wang, Y., Yang, X., Zhang, X., Dong, L., Zhang, J., Wei, Y., Feng, Y. & Lu, L. (2014), "Improved plant growth and Zn accumulation in grains of rice (*Oryza sativa L.*) by inoculation of endophytic microbes isolated from a Zn Hyperaccumulator, Sedum alfredii H". *Journal of Agricultural and Food Chemistry,* **62**(8), 1783-1791. doi: 10.1021/jf404152u

WHO (World Health Organization) (2011), "Guidelines for Drinking Water Quality" (4th ed). WHO Press, Geneva, Switzerland (2011). 58. Joint FAO/WHO. Codex Alimentarious Commission on Food Standards Programme. Codex committee on contaminants in foods, 5th session, Te Hague, Netherlands; CF 5 INF/1.

WHO (World Health Organization) (2018), "Increasing Fruit and Vegetable Consumption to Reduce the Risk of Non-Communicable Diseases". In World Health Organization, E-Library of Evidence for Nutrition Actions (eLENA); World Health Organization: Geneva, Switzerland.

Wuana, R.A. & Okieimen, F.E. (2011), "Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation". *Communications in Soil Science and Plant Analysis,* **42**, 111-122. doi.org/10.5402/2011/402647.

Zaitsev, G.A., Dubrovina, O.A. & Shainurov, R.I. (2020), "Iron and manganese migration in "soil-plant" system in Scots pine stands in conditions of contamination by the steel plant's emissions". *Scientific Reports,* **10**(1), 11025. https://doi.org/10.1038/s41598-020-68114-y