DISTRIBUTION AND HEALTH RISK ASSESSMENT OF CHROMIUM, MANGANESE AND ARSENIC VIA INGESTION FOODS FROM INDUSTRALISED LOCATIONS IN THE SOUTH EASTERN STATES OF NIGERIA.

ABSTRACT

This study investigated the health risk associated with Cr, Mn and As through consumption of some food crops in selected industrialized areas located in the South Eastern states of Nigeria. Mean concentrations of Cr and Mn ranged from $0.01\pm0.01^{\circ}$ mg/kg to 26.32 ± 0.02^{d} mg/kg and $0.01\pm0.00b$ mg/kg to $5.53\pm0.00b$ mg/kg .They metals indicated some degree of contamination as they exceeded WHO permissible limits of 0.2 and 2 mgkg⁻¹ for Cr and Mn respectively in some samples except for As which was Below Detection Limit(BDL) (<0.01mg/kg). Values of daily intake for Cr, Mn and As for an adult was higher in Cassava than the other foods. Target Hazard Quotient(THQ) > 1 was recorded in all samples for different locations except for Star apple and Kolanut which was < 1.Cancer Risk(CR) values for fruits and nuts ranged 10^{-3} to 10^{-6} while those of vegetables and tubers ranged 10^{-2} to 10^{-5} . The CR values obtained for Cr exceeded USEPA prescriptions thus indicating a probability of contracting cancer while Values for As were not. This study suggests further consideration of the metals as chemicals of concern with respect to industrial locations in South Eastern, Nigeria.

Keywords: Health risk assessment; Bioaccumulation factors; Target Hazard Quotient; Carcinogenic Risk; Heavy metals.

INTRODUCTION

Recently, the public are becoming conscious of the presence of Heavy metals which is on exponential increase in the environment. Thus posing serious threat to human health particularly in areas with anthropogenic pressure and industrialization (Onyedikachi et al.,(2018);Suruchi and Pankay(2011). Although, some persons think these concerns are exaggerated, the awareness of the effects of these contaminants in our foods, drinking water and air is of utmost importance (Onyedikachi et al.,(2018). Ingestion of food crops contaminated with heavy metals decreases the bioavailability of some essential nutrients. This can deplete the immunological response leading to gastrointestinal cancer, intrauterine growth retardation, impaired psycho-social facilities, etc.(Tasrina et al.,(2015). Within the European community, 11 elements of highest concern are arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin and thallium (MEPPRM(2014). Some of these elements are actually necessary for humans in little quantities while others are very toxic and not needed by the body. The affect the central nervous system, kidneys, liver, skin, bones or teeth (Zevenhoven and Kilipinen.,(2001). Food crops growing in polluted farmlands with increasing impartation of heavy metals may serve as bio-indicators of Pollution Index(Dereje et al.,(2016).

Chromium is a heavy metal that can be found all around the environment especially in some industries. These includes: tanneries, textile, chromium plating, steel production and refractories etc(Peters *et al.*,(2018). The Oxidation State and Solubility of Chromium grossly indicates the

levels of Threat and consequential effects(Srivastava et al., (2005). Chromium presents in varying oxidation states in the environment ranging from Cr^{2+} to Cr^{6+} with trivalent (Cr III) and hexavalent (Cr VI) as the most common (Peters et al., (2018). The Cr (III) has the most stable form, serves as an essential nutrients beneficial to man and other animals(Peters et al.,(2018);Stepnewska and Wolinska.,(2005). Cr VI on the other hand, is the state of Chromium that has attracted environmental interest because it has been shown to be corrosive to the skin because of its acidic nature and also considered a potential carcinogen(Bini et al., 2008; Das and Mashra., 2008). Arsenic (As) is also a highly toxic and thus poses serious health threat to man and other animals(Rosas Castor et al., (2014). The increase in As concentration levels in the Soil in present times is as a result of irrigation with As containing water, improper refuse disposal use of pesticides rich in As as well as various industrial and anthropogenic activities like ore mining and smelting(Lambkin and Alloway.,(2003). Humans may consume As from contaminated foods, and also exposure to it can result in some diseases such as lesions, neurological defects, atherosclerosis and cancer (Zhongjun et al., (2016). Manganese (Mn) on the other hand is an essential metal for the normalization of normal body functions for the development of in most mammals. Mn is a co-factor which binds and regulates enzymes like arginase, Superoxide dismutase and Pyruvate carboxylase throughout the body. Exposure to this metal can lead to progressive, permanent, neurodegenerative damage, resulting in symptoms similar to idiopathic Parkinson's disease(Crossgrove et al., (2003). However, despite all the above reports, a lot of people consume or are constantly exposed to these metals directly or indirectly via various anthropogenic activities.

Human health risk assessment has been adopted by many environmental scientists to assess hazardous metals risk. It is a very effective approach to determine health risk levels posed by various contaminants(Wu *et al.*,(2009);Nkpaa *et al.*,(2016). In Nigeria, especially in urban centers where there are numerous anthropogenic activities which bioaccumulates in plants/crops leading to the toxicity of the plant by contaminants thus affecting the entire ecosystem.

The estimate of the imminent risks of trace metals to human health via the intake of food crops in this present study is divided into carcinogenic and non-carcinogenic risk (Yujun et al., (2011). It was endorsed by the US Environmental Protection Agency (USEPA) for the evaluation of the possible threat to human lives as a result of long term exposure to pollutants(USEPA .,1998a). This informative tool has been so useful and valuable to alot of researchers (Yujun et al.,(2011); Wang et al.,(2005); Avila et al.,(2016). Some studies have reported some heavy metal contamination in plants grown in Industrialized areas. However, assessment and comparison of human health risk associated with heavy metal contamination via intake of four variety of food Crops as seen in this Study in the South East States in Nigeria is still very limited. Therefore, the main objective of the present study was to assess the degree of contamination by comparing the various Heavy Metal(Cr, As and Mn) concentration with Standard Permissible Limits and also evaluate the potential health risks associated with Cr, As and Mn via the consumption of some commonly consumed Vegetables, Tubers, Fruits and Nuts in six(6) selected industrialized locations in the South East geopolitical zones of Nigeria using the Estimated Daily Intake(EDI), Bioaccumulation Factor(BCF), Target Hazard Quotient(THQ) and Incremental Lifetime Cancer Risk(ILCR).

Materials and methods

Description of the studied areas

Southeastern Nigeria also known as Igboland or Igbo speaking nation. It consist of five(5) major States: Abia, Anambra, Imo, Ebonyi and Enugu. It occupies an area of a total of 40,000km²(1600sqmi). It has highest elevation of 1000m(3300ft) and a lowest of om(0ft). It is primarily located in the lowland forest region of Nigeria(Chigere.,(2000). They industrial Study locations around selected industrial locations in this Study are as follows:

Ishiagu is a town in the Ivo local government area of Ebonyi state, Nigeria. It is located on the plains of south eastern savannah belt. It lies in the latitude of 5^0 56^1 55.72968^0 N and longitude of 7^0 34 16. 29804" E. The prevailing climate conditions are high temperature and humidity for more than half a year. Vegetation types are mangrove and fresh water swamp, and rain forest/Savannah zone. Farming activities and quarrying/mining activities dominates the region.

Osisioma town is a town in the Osisioma ngwa local government area of Abia state, Nigeria. It has covers an area of 198km^2 , and has a population of around 219,632. The postal code of the area is 451. Vegetation type is tropical rain forest it lies in on the latitude of 5^0 10'46.734"N and longitude of 7^0 19¹ 39.402" ⁰ E. The industry of present in the area include Tonimas Nigeria limited which deals with the manufacture and distribution of refined petroleum products, lubricants, foods and beverages industry and plastics industry.

Ninth mile is a part of Ngwo, a town located in udi local government area of Enugu state, Nigeria. It lies in the latitude 6^0 25' 19.56072"N and longitude 7^0 24' 24.50088" E. They are one of the major commercial nerve centers found in Enugu state. Ngwo is a hilly area with much of the land area being up to 600 meters above sea level.. Enugu is in Savannah zone of Nigeria. The temperature is 27.2° C. Most companies found at Ngwo are bottling companies which include Seven Up company, breweries, coca-cola bottling company.

Irete is a community in the owerri west local government area of Imo state. It lies in the latitide $5^0 30^1 0.606$ "N 0 N and longitude $6^0 59^0 31.062$ " E. The altitude is 60.20m. It has an area of around 5100 km². The average annual temperature above 20^oC. The vegetation type is tropical rain forest vegetation.

Akwu-uru industrial layout is located in the Nnewi south local government area of Anambra State, Nigeria. It lies in the latitude $5^0 59' 48.50088"$ N and longitude $6^0 55^1 18.43788"$ E. The city spans over 2789 km² in Anambra State. Geographically, Akwu-uru industrial layout Nnewi falls within the tropical rain forest region of Nigeria. The area is rich in agricultural produce.

Umudike in Ikwuano Local Government Area in Abia State was the reference area. It is located in the humid forest zone of Nigeria and lies within latitude 050 29'N and longitude 07° 33'E with an altitude of 122m above sea level. Annual rainfall in Umudike ranges from 1990 to 2200 mm, bio modally distributed with peaks in July and September. The soil is sandy clay loam (coarse-textured) and classified as an ultisol. This study area is the control area because there is no industry in the area. The selection of the study area was based on availability of the samples.

Collection of samples

Five(5) samples each of twelve(12) different food crops which includes- Vegetables: Bitter leaf (Vernonia amygdalina), Water leaf (Talinum triangulare), Pumpkin leaf (Telfairia occidentalis); Tubers- yam (Dioscorea alata), Cocoyam (Colocasia esculenta) and cassava (Manihot esculenta), Fruits included orange (Citrus sinensis), paw paw (Carica papaya), star apple (Chrysophyllum albidum) and Nuts- kola nut (Cola acumulata), palm kernel nut (Elaeis guineensis jacq), coconut (Cocos nucifera) were harvested from farmlands close to the industries(Study sites) at Osisioma, Akwuuru, Ishiagu, Ngwo, Irete and Umudike (a university farmland devoid of industries) was the control for this study. At each study site, the diagonal length of each sampling site was marked into five equal points and soil adhering to the roots of the food crops (from depth of 16–30 cm) were collected by shaking it off. The soil samples after the manual removal of non soil debris and particles such as stones, wooden particles etc. were parkaged in an aluminium foil and then taken to the laboratory for further preparations. At the laboratory, the soil samples were air dried for three days i.e when a steady weight was achieved ground and sieved using a 2 mm stainless steel mesh. Fresh samples of different food crops collected were washed with distilled water to remove dirt particles. After the water had evaporated, The vegetables were plucked and selected and spreadout on a flat foiled surface, The skin of the tubers were also peeled and chopped in to tiny cubes for easy drying, the fruits were peeled to remove exocarp(skin) while endocarp(flesh) was collected. The flesh of the nuts were also collected and chopped into tiny cubes(the hard shells of Coconut and Palm kernel nut were removed to access the flesh although this was not needed for the Kolanut). Each sample was weighed, oven dried at 55°C for 72hours, pulverised into powder and sieved using 0.15mm sized sieve.

Samples for Analysis

Procedure for Heavy Metals In Soil: (aqua-regia digestion): 0.5g of the sieved soil was transferred into 100ml Pyrex glass beakers, a mixture of 2ml HNO3, 6ml of HCl (1:3) and 20ml distilled water was added to the soil sample. The mixture was heated up on a hot plate until the total volume was 10ml after evaporation. The soil extract was cooled and filtered to remove insoluble matter after volumn was made up to 100ml in a volumetric flask using distilled water. The soil extract was analysed using the Atomic Absorption Spectrophotometer and concentration units were reported in mg/kg for each heavy metal been determined.

Procedure for Heavy Metals in Fruit, Nuts, Tubers & Vegetables :(Dry ashing method): Samples were air-dried at room temperature and blended into powder. 0.1g of samples were transferred into clean porcelain crucibles and dry-ashed in an Oceanic SX-2 type muffle furnace at a temperature of 450°C until the samples turned greyish-ash. Samples were left to cool in a dessicator for about 30minutes. A solution of the ash was prepared by adding 5ml of 1N nitric acid (HNO3) and 10ml of 1N hydrochloric acid (HCl); ash solution was heated on a hotplate to near-dryness before sample extract was filtered into 100ml volumetric flask using distilled water. A reagent blank containing the same acid mixtures used was prepared devoid of sample. All samples and reagent were aspirated into the e GBC Avanta PM A6600 flame atomic absorption spectrophotometer (FAAS).

Quality assurance and quality control

Quality assurance regulations were applied to ensure accuracy of the results. All the reagents were of analytical grade and glassware were washed properly with Deionized water. For the purpose of accuracy in the analytical procedure, Sample analysis were carried out repeatedly and compared with internationally certified plant and soil standard reference material (SRM) of the

National Institute of Standard and Technology(Peters *et al.*,(2018). The percent recovery, relative standard deviation (RSD) of the duplicate samples, The limit of detection (LOD) and the limit of quantification (LOQ) of the analytical method for each metal were calculated as triple the standard deviation of the series of measurement taken for each solution. The values of LOD, LOQ, percent recovery, and RSD for the Samples are presented on Table 7. The standard operating conditions for the analysis of heavy metals using Atomic Absorption Spectrometry used in our experiments are given as follows: The Acetylene and air were the carrier gas(70Ψ) with a slit width of 7mm with a slit width of 7 mm.

wavelengths: $Cr(\lambda) = 357.90$ nm, $As(\lambda) = 332.1$ nm and Mn (λ) = 279.50 nm with a slit width of 0.7 nm for Cr and As while 0.2 nm for Mn[33]. The extract was puffed directly into the atomic absorption spectrophotometer machine.

ANALYSIS OF DATA

Human Health Risk Assessment

HHRA was investigated in order to understand the cancer and non cancer effects of the heavy metals on the human health. Serious effects were based on threshold limits (reference dose). To calculate the potential human health risk levels of the selected heavy metals in soil and some crops. The Daily Intake of Heavy metals(DIM) in mg/kg/day, Target hazard quotients (THQs), Cancer Risk(CR) were calculated for Cr, Mn and As to determine the doses received via the individual pathway, respectively.

Daily Intake of heavy metals

According to Khan *et al.*, 2008 and Mahmood and Malik (2014), the daily intake of metals (DIM) was determined by the following equation:

Average weight

In this Study, calculations were made based on the standard assumption for an integrate USEPA risk analysis, considering an adult body weight of 60 kg and the average daily foodcrops intake for adults is considered to be 0.9,0.355,0.445, 0.154, 0.05 and 0.345 kg person-1 day-1 for tubers(Cassava,cocoyam and yam), fruits, nuts and vegetables respectively(Peters *et al.*,2018;Avila *et al.*,2016;Zhuang *et al.*,2009).

Target Hazard Quotient

The non carcinogenic human health risks from consumption of crops in this study by the populace around the various selected industrial agricultural zones were assessed based on the target hazard quotient (THQ). THQ is defined as the ratio between exposure and reference oral dose (RfD). This is used to express the risk associated with ailments other than cancer contracted from a contaminant exposure (Yu-Jun *et al.*, 2011). If the ratio is equal to or greater than 1, an exposed population is likely to experience risk in their health but when THQ <1,the exposed population are unlikely to come up with health risks. The methods used for the estimation of THQ and target cancer risk (CR) have been provided in USEPA Region III Risk-Based Concentration Table, January–June 1996 (Zhuang *et al.*,2009;Han et al.,1998;Guerra et al.,2012;USEPA.,2011b)based on the equation below:

Where THQ is the target hazard quotient, DIM is the daily intake of heavy metals (mg/kg/day), heavy metal concentration in vegetables is expressed in mg/kg, average body weight is 60 kg, and RfD is the oral reference dose (mg/kg/day). RfD is an estimation of the daily oral intake for an expose human population, which does not cause damaging effect during a period of a lifetime; it is usually used in EPA's non-cancer health risk analysis(Han et al.,1998;Guerra et al.,2012). The RFDs are 0.003,0.0003,0.014 in mg/kg/day for Cr, As and Mn respectively.

Incremental Lifetime Cancer Risk(ILCR)

ILCR is the assessment of carcinogenic health effect as a result of exposure to heavy metals or pollutants over a period of a lifetime. The Ingestion Cancer Slope Factors is used to evaluate the probability of an individual developing cancer from ingestion of a level of contaminant over a period of a lifetime as described by USEPA(2004) and ATSDR(2010). Ingestion cancer slope factors are expressed in units of $(mg/kg/day)^{-1}$.

Lifetime probability of contracting cancer due to exposure to site-related chemicals is calculated as follows:

$$ILCR = DIM \ x \ CSF$$

Where DIM is the daily intake of each heavy metal (mg/kg/day) and CSF is the ingestion cancer slope factor (mg/kg/day) -1. According to USEPA, CR between 10^{-6} (1 in 1,000,000) and 10^{-4} (1 in 10,000) represent a range of permissible predicted lifetime risks for carcinogens[38,39]. Contaminants for which the risk factor is below 10^{-6} may be eliminated from further consideration as a chemical of concern[40]. The ingestion cancer slope factors is given for Cr and As are 0.5 and 1.5 respectively while non is given for Mn owing to its unique characteristics. The risk associated with the carcinogenic health risk of a target metal is expressed as the probability of contracting cancer over a lifetime of 70 years [39,40].

STATISTICAL ANALYSIS FOR METAL ANALYSIS

The least significant difference (LSD) was used to compare differences in each sample within treatments. Data was reported the mean concentration of heavymetal(s) \pm Standard Error of mean. One way analysis of variance (ANOVA) was used to determine significant difference between groups, considering a level of significance of less than or equal to (p \leq 0.05) by using SPSS.

RESULTS AND DISCUSSION

The heavy metal concentrations (Cr, Mn, and As) in the selected food crops, i.e., Bitter leaf (*Vernonia amygdalina*), Water leaf (*Talinum triangulare*), Pumpkin leaf (*Telfairia occidentalis*); yam (*Dioscorea alata*), Cocoyam (*Colocasia esculenta*) and cassava (*Manihot esculenta*), orange (*Citrus sinensis*), paw paw (*Carica papaya*), star apple (*Chrysophyllum albidum*) and

kola nut (Cola acumulata), palm kernel nut (Elaeis guineensis), coconut (Cocos nucifera) grown in the vicinity of industrialized locations in the five(5) South Eastern States of Nigeria and also a Control site, Umudike(a University agricultural zone devoid of industry(s) with their respective Soils are presented on Table1 and 5. Results for the mean concentrations of Cr in selected crops had Concentrations ranging from 0.01±0.01c for pawpaw(Enugu) to 26.32±0.02d in pumpkin collected from Owerri (highest average concentration). This was followed by Palm kernel (Elaies guineensis) collected from Akwu-uru with concentration of (26.30±0.00b)Mg/kg dry weight(dw). The result also showed that Cr among the metals had the highest concentration in the vegetables analyzed followed by nuts, fruits and then tubers cumulatively across all the sites. There was significant (p < 0.05) difference between Cr, Mn, and As in the Food crops from the study sites when compared with their corresponding permissible limits. The average concentration of Cr for food samples exceeded the standard permissible limit of 0.2mg/kg for samples from Anambra while all samples except orange and palmkernel nut for Ebonyi and Pawpaw, Cassava, Bitter leaf and Pumpkin for Enugu exceeded the limits permissible. The highest concentration was recorded for pumpkin in Owerri while yam, Bitter leaf, Kolanut and palmkernel nut were below the limits. However those of Abia had almost all Samples below the limit except for Star apple. Whereas Kolanut, Palmkernel nut, Bitterleaf, pawpaw and yam were also below the limits for the control samples. Total mean concentrations of Cr in the industrial areas were in the order as follows: Anambra>Ebonyi >Owerri >Control>Abia > Enugu. Mn on the other hand had all samples exceeding the permissible limit of 2mg/kg except for star apple and pumpkin for Abia State. Also, Some vegetables(Bitterleaf and Waterleaf) and fruits(pawpaw and orange) from Anambra exceeded the limits In Ebonyi, Owerri and Control locations and Cassava coconut and Kolanut; pumpkin and coconut and cassava, star apple and coconut again had values above limits. However, all food samples for Enugu industrial location had average concentrations of Mn within Safe limits. Considering the average Concentrations of vegetables ranging from (0.004 -26.32),(0.022 - 23.30),(0.05 to 2.81) and (0.2-5.31), (0.05 - 3.48) and (0.48 to 4.92) for Telferia ocidentalis, Vernonia amygdalina and Talinum triangulare respectively. Tubers ranged from (0.02-5.42), (0.02-0.75), (0.02-2.98) and (0.08-4.92), (0.08-0.91) and (0.11-3.55) for Manihot esculenta, Dioscorea alata and Colocassia esculenta. Fruits ranged from (0.03 to 14.18),(0.37-1.16),(0.01-12.57) and (0.01-2.14),(0.3 to 3.17) and (0.014 to 2.85) for Citrus sinensis, Chyrysophyllum albidum and Carica papaya. Nuts ranged (0.08 -11.01, (0.05 to 3.25), (0.03 to 26.30) and (0.2-4.4), (0.18-2.96) and (0.16 to 5.53) in Cocos nucifera, Cola acuminata and *Elaies guineensis* we will notice that most values especially the highest values exceeded 0.2 and 2mg/kg for Cr and Mn respectively by USEPA and EU except for Chyrysophyllum albidum while values for As were all Below detection Limits.

Average concentration in Soil also had water leaf significantly higher(p<0.05) than other vegetables and tubers analysed with a record of 119.8±0.00a followed by B.leaf soil for Owerri(41.1±0.00e). Concentrations for Mn ranged from 0.01 to 5.53±0.00 in Palmkernelnut(Anambra). The concentrations of Mn in the soil samples had its highest in waterleaf from Abia(26.51±0.00a),followed by Cassava soil (25.51±0.01a)mg/kg respectively .All the soil concentration were below 500mg/kg given as benchmark by regulatory bodies(USEPA and EU) . Enugu had the least(0.16±0.00) for Bitter leaf soil. Generally, there was significant differences (p < 0.05) in the chromium concentration in all crops collected from the soils in the industrialized areas of the different South Eastern states in Nigeria. The concentration of heavy metals in the food crops from Anambra was significantly (p < 0.05) higher than those of other locations. For the Soils, All Samples from Anambra exceeded

permissible limits(Cr=2.3mg/kg) in Soil while Control Soil had values within safe limits. Enugu also had all samples below the limits except for waterleaf soil(> 2.3mg/kg). Other samples from the other states had variations in results as some were> 2.3 while the other were<2.3 in mg/kg. For Mn and As, all they Soil samples were within safe limits as none had concentrations > 500 and 100mg/kg permissible limits respectively as set by USEPA and EU. Total heavy metal (mg/kg) concentrations in soils presented on Table 5 indicated the variations in the concentration of heavy metals in the six sites (mg/kg) in the various soil samples from study agricultural zones showing highest levels of Cr concentration(17.69±0.01c,119.8±0.00a,32.9±0.01c,16.86±0.01b,35.36±0.01f and 2.19±0.00c in waterleaves from Abia and Anambra, then yam, waterleaf, cocoyam and cassava from Ebonyi, Enugu, Owerri and Control respectively indicating serious pollution as the permissible limits of 2.3mg/kg stipulated for Soils was grossly exceeded. However, Mn, and As values may not be of concern since it was lower than 500mg/kg guideline mark for Mn and 100 in As for Soil respectively. The highest values for Manganese were in vegetable Soils(W. leaf and B.leaf) with values as follows 26.51±0.00a,15.79±0.01b for W.leaf in Abia and Anambra States respectively and 24.84±0.00,0.91±0.00d,5.44±0.01a,3.08±0.01e Ebonyi, Enugu, Owerri and Control respectively. While for As were Below Detection Limits(0.01mg/kg).

In this Study, the observed discrepancies in the average concentrations of Heavy metals may indicate that they compounds leached by rainwater could have migrated through cracks in soil, asphalt roadways, and masonry walls, forming high-content chromium crystals on their surfaces(USEPA,2004). Cr levels in control samples (Umudike) was higher (p<0.05) in some food samples than those of Osisioma and Ngwo. This could be attributed to flooding, which mobilizes heavy metals from soils particularly when readily oxidizable organic nutrients are available(WHO., 2011)]. This is possible also as records of annual rainfall exceeded 2,000-2,500 mm/year in the area. Other anthropogenic means like industrial activities and the use of agrochemicals like fertilizers may also affect the levels of environmental contamination as the areas(Lui et al.,2007;Tiwari et al.,2009). Accumulation of water overtime from rainfalls may also contributes to the accumulation of metallic oxides, which probably have increased mineralization by strains of microbial genera. It is common knowledge that certain strains of microbes could increase the concentrations of Pollutants in the soil(Avila et al., 2016). This may also make the area more vulnerable to biodegradation(Nkpaa et al., 2017). The use of organic manure possibly by farmers in the area may also have attenuated those farm lands overtime. The intake of food crops contaminated with heavy metals may also reduce the bioavailability of some essential nutrients in Soil. Thus can affect these immune system/ response resulting in Cancer of the gastrointestinal tract, intrauterine growth reduction, impaired psycho-social facilities etc(Tasrina et al., (2015).

There was significant variation in the various food groups analysed in this Study and this could be attributed to differences in the rate by which different plants absorb and accumulate Metals (Tiwari *et al.*,(1996). The differences in concentrations for foods recorded in this study is attributable to the type of Crop, properties of the medium and characteristics of the root(root structure and lenght), organic matter content and the pH(Tanganu *et al.*,2011). The larger surface areas of vegetables which is in constant contact with air laden with dust and pollutants could also be a reason(Lu *et al.*,2014). The duration of cultivation takes shorter timeframe as they are due for consumption in about 2-3 months(vegetables) and therefore the organic matter content of the soil may be easily distorted thus exposing plant to more contaminants, tubers can be harvested annually or biennielly while the fruits and nuts that are perennial these may be considered

because variations in soil organic matter in cultivated lands precipitously may result in their degradation(Ratnayake *et al.*,(2011) thus increase in bioaccumulation through active transport of minerals from soil-plants this is attributable to their different uptake and accumulations based on concentrations and availability heavy metals(Idodo-Umeh and OObeibu.,(2010).

The Arsenic concentration as shown on Table 1 for all the sample gave similar concentrations (0.01mg/kg dw) and were lower than the permissible standard limit (0.2mg/kg)stated by WHO(2010). However, high concentration exposure overtime can possibly reach toxic concentration at low levels[52]. Similar to the result in this study was the findings of Chimezie *et al.*, (2013) reported that there were no Arsenic detection in soil samples from highly industrialized Lagos environment. Also Oti *et al.*, (2012) reported very low arsenic concentration on vegetables from Enyigba lead mine in Ebonyi state, Nigeria. The low and similar As concentration obtained from soils and crops collected from the contaminated soil in industrialized areas of South Eastern states could be due to changes in the pH of the soils where the samples were collected as As is more mobile in neutral and alkaline than in acidic environment(Straskraba and Morgan.,2006).Also Goldberg and Glaubig.,(1998) reported that soils demonstrate their maximum arsenic retention at a P^{H} near 10.5.It could also be that high iron availablity in the soil immobilized As dispersion(Chowdhury et al.,(2000).

Soil pollution with heavy metals due to discharge of untreated industrial wastes is a insistently major threat to ecological integrity and human well being. Cr has often and still been described as an essential trace element in humans and some animals(Akan *et al.*,2009), in higher concentration, Cr is highly toxic and carcinogenic in nature(Martins and Griswood.,2009). Exposure to higher amounts of chromium compounds in humans can lead to the inhibition of erythrocyte glutathione reductase, which in turn lowers the capacity to reduce methermo globin to hemoglobin(Monisha *et al.*,2014). Also exposure to chromium compounds can result in the formation of ulcers which will persist for months and heal very slowly(Monisha *et al.*,2014).In addition, Cr exposure in toxic levels to workers in industries enhances the oxidative stress (reactive oxygen species (ROS) and hydroxyl (OH) radical generation) which may result in damages to the cells and organs such as genotoxicity, chromosomal malformations, and carcinogenicity. Cr contamination mechanisms are associated with other health implications in different occupational settings around the globe(Junaid *et al.*,2016).

Mn is classified as Not classifiable as to Human carcinogenicity although several epidemiology studies have reported Mn as a well established neurotoxin following inhalation by humans in occupational environs and also low IQ and memory effects in children exposed to Mn . Bone malfunction, Skin lesions are associated with low levels Mn. It is one of the essential minerals although high levels that exceeds the permissible limits in food if ingested could accumulate and result in damage to dopaminergic systems. Also, Mn accumulation in the brain results in neurotoxicity that may develop into a parkinsonian syndrome/manganism(Crossgrove et al.,2003). For Mn, its primary target is the Central Nervous System(CNS) and the brain regions mostly affected are the globus pallidus and striatum of the basal ganglia, whereas the neurodegeneration in Idiopsthic Parkinson's Disease(IPD) occurs mainly in the substantia /nigra(Walter et al., (2003). There have also been reports on the reproductive system where reduced testicular weight in male rats and post implantation loss in female rats was reported(ATSDR.,2010). However, information about these effects is limited(ATSDR.,2010). As, a known Human carcinogen based on guideline for carcinogenic assessment by USEPA(2004) has shown increased lung cancer mortality in multiple human populations exposed basically through inhalation other effects includes skin cancer and internal vital organ

cancers(liver, kidney, lung and bladder). Exposure to As is toxic and can cause nausea, vomiting , reduced production of erythrocyte and leukocyte, tingling sensation in hands and legs(Chowdhury *et al.*,2000) .It can result in cancers of the lungs, liver and skin(Smith *et al.*,2000)

Health Risk Assessments

Values of daily intake of Cr, Mn and As calculated for average adult are presented on Table 2 revealed that the total values of daily intake of metals were high for Cassava(0.08.0.03,0.03,0.009)mg/kg/day grown in Anambra above 0.003 Mg/Kg/body weight reference Oral Dose. This is expected as Cassava and its products makeup the overall Staple food for the South Eastern States in Nigeria and the entire nation(Dereje et al.,(2016).

The daily intake of chromium was highest in Pumpkin (0.15) followed by Bitter leaf(0.13) from Owerri and Anambra in Mg/Kg/body weight. These were above the established reference dose of 0.003 Mg/Kg/body weight/ day recommended by(USEPA.,(2004);USDOE.,(2001;WHO.,(2011). The total daily intake of Mn were within tolerable Oral reference Dose for consumption of selected crops while As values for all the studied areas for vegetables, fruits and nuts and for tubers were similar as the average concentrations were BDL(<0.01). The daily intake of arsenic below established tolerable daily intake in this study was the of 0.003 Mg/Kg/day(USEPA.,2004;USDOE.,2001).

Assessment of the risk involved via the consumption of heavymetals is paramount(Zhuang *et al.*,2009) in other to avert impending danger to human health. EDI is calculated as the mean concentration multiplied by the daily intake of a particular food specie divided by the average weight(Avila *et al.*,2016). Interestingly, in this Study EDI values for Cr were above the established reference dose of 0.003 Mg/Kg/body weight/ day recommended by (USEPA.,(2004);USDOE.,(2001;WHO.,(2011)...While the total daily intake of Mn and As were within tolerable Oral reference Dose for consumption of selected crops. Values for As values for all the studied areas for vegetables, fruits and nuts and for tubers were similar as the average concentrations were BDL(<0.01) .However, bioaccumulation overtime may result in harmful effects(cancer and non cancer effects) on humans especially the exposed populace.

The Target Hazard Quotient of selected food crops from Industrialized and Non-Industrialized areas presented on Table 3 showed the highest THQ values for crops grown at Owerri(50.45in Pumpkin)followed by Anambra (44.66 and 27.1 in Bitterleaf and Cassava). THQ indicates a level of concern. The interpretation of the THQ value is binary; THQ is either > 1 or <1, Where THQ >1 indicates a reason for human health risk concern[]. Most samples collected from all study sites gave values (THQ <1) for Mn but for 5.27 for *Manihot esculenta* in Control followed by *Telferia occidentalis* (2.18) and (2.02) for Abia and Owerri respectively.THQ of <1 may imply that consumers of these food crops (fruits, nuts tubers& vegetables) from the study areas may experience significant health risk(Tiwari *et al.*,2009). On the other hand, the total hazard quotient of As from the studied areas were less than 1. This observation signifies that the consumers of food crops (fruits nuts vegetables and tubers) from the study areas may not experience significant health risk from intake of As through food crop consumption. However, its bioaccumulation overtime may pose serious risk. THQ has been an important tool used to evaluate non cancer effects of heavy metals in health risk assessment(Onyedikachi *et al.*,2018). THQ values of > 1 indicates a concern for non cancer human health risk while THQ <1

versa. In this Study, Cr had values above 1 for most of the samples like the vegetables, Tubers, fruits and nuts(although not in all locations under study) except for Star apple and Kolanut which was all through the locations < 1. THQ values were highest in Pumpkin, waterleaf and Cassava suggesting high levels of concern due to their large values. However, it is pertinent to know that some of the ingested heavy metals are seemly not absorbed in the body due to metabolism and excretion although some quantity bioaccumulate overtime in the body resulting in serious health concerns (Dereje *et al.*,2016;Zhuang.,2009).

Incremental Lifetime Cancer Risk(ILCR) as presented on Table 4 is estimated as a lifetime probability of contracting cancer over a lifetime of 70 years. ILCR results for Cr for vegetables and tubers for then ranged from 10^{-2} to 10^{-5} , while the Fruits and nuts ranged from 10^{-3} to 10^{-6} . Cancer Slope Factors(CSF) are used to measure the potential risk to cancer in connection with exposure to a carcinogenic or potential carcinogenic substances. It is an upper bound approximating a 95% confidence limit for cancer risk from a lifetime exposure to carcinogens via ingestion or inhalation.

There was no results for ILCR for Mn because there is no available Cancer Slope Factor based on the stipulated guideline values by USEPA. As on the other from table 1 presented values below detectable limits(BDL) but then It has a characteristics CSF value of 1.5mg/kg indicating high levels of cancer risk potency. However, for this study values were below the range of concern.

In this Study, fruits and nuts ranged from 10^{-3} to 10^{-6} while those of vegetables and nut ranged 10^{-2} to 10^{-5} . Considering the above result as collated for all the study areas, the ILCR obtained for Cr, indicated the probability of contracting cancer in a 70year lifetime. Although, the average carcinogenic risk from the crop samples may be unsafe for consumption based on the established guideline values of 10^{-6} (1 in 1,000000) to 10^{-4} (1 in 10000) set by USEPA(Peter *et al.*,2018). Just as stated above, some contaminants taking in by exposed individuals are stored in vivo thus indicating that persons within the study areas may contract cancer due to Cr exposure over a lifetime period of 70 years especially in Anambra, whose values were consistently higher than other areas assessed. Also, As had values below the range owing to their very low concentration(BDL). Irrespective of their low ILCR values, prolong exposure to this toxic metal endogenously could result in serious health risk like Cancer.

CONCLUSION

This study concludes that there is significant health risks associated with the consumption of food crops from the industrialized areas of Akwu- uru, Ishiagu, irete, umudike, Osisioma, and Ngwo analysed for the southeastern states in Nigeria. Based on human health perspective and prevention of disease, consumption of vegetables, tubers, fruits and nuts may not be safe due to Cr and As accumulation in the areas. Thus suggesting that they be placed for further consideration as a matter of urgency as people living people living in the assessed area may suffer serious cancer as well as non cancer risk. With respect to this study, government, regulatory bodies, policy makers and other concerned stakeholders should help in making recommendations that would fuel efficient mitigating measures.

Table 1: Mean concentration of heavy metals (mg/kg dry weight) in crops and selected vegetables. The results are expressed as triplicate mean \pm S.E.

		Abia	Anambra	Ebonyi	Enugu	Owerri	Control
0	D 1.	2.04+0.01	0.02.0.001	0.0.00	0.004+0.00		0.20 + 0.01
Cr	Pumpkin	3.94±0.01	0.03±0.00b	0.2±0.00c	0.004±0.00	26.32±0.02 d	0.38±0.01e
	Bitter	a 0.06±0.02	23.30±0.00	2.02 ± 0.00	b 0.03±0.00a	a 0.19±0.00d	0.022±0.00
	leaf	а	b	c			а
	Waterlea f	0.05±0.01 b	2.81±0.02a	2.4±0.01c	0.19±0.01c	0.9±0.01c	1.11±0.01d
	Cassava	0.05±0.01 a	5.42±0.00b	2.32±0.00	0.07±0.00a	0.65±0.02d	2.32±0.02c
	Yam	0.02±0.00	0.24±0.00b	0.75±0.00	0.69±0.01b	0.034±0.00	0.17±0.00d
	Cocoya	a 0.02±0.00 b	0.22±0.01b	b 2.98±0.01 d	1.18±0.00c	c 2.28±0.00d	0.43±0.01b
	m Orange	0.03±0.01	14.18±0.00	0.09±0.00	0.91±0.01d	3.39±0.00c	0.21±0.00c
	Star	a 0.72±0.00	b 0.98±0.02a	c 0.37±0.00	1.05±0.00c	0.67±0.00d	1.16±0.00d
	Apple Pawpaw	a 0.02±0.01	12.57±0.00	c 0.44±0.01	0.01±0.01c	1.83±0.00d	0.01±0.00c
	Coconut	a 0.08±0.00	b 11.01±0.00	a 0.79±0.00	0.45±0.00c	2.82±0.00b	1.63±0.01c
	Kola nut	c 0.88±0.00	b 1.14±0.01a	b 3.25±0.02	0.28±0.01d	с 0.05±0.00a	0.14±0.00d
	Palm Kernel	b 0.03±0.02	26.3±0.02b	d 0.09±0.00 d	0.44±0.00d	0.07±0.01c	0.11±0.01c
M	Pumpkin	a 5.31±0.00	0.45±0.01b	d 0.2±0.01c	0.25±0.00d	4.92±0.00a	0.8±0.00b
n	Bitter leaf	a 1.12±0.02 a	3.48±0.00b	1.93±0.00 d	0.16±0.01c	0.05±0.00c	0.23±0.00b

	Waterlea f	0.63±0.00	3.18±0.01b	0.81±0.00 e	0.48±0.00c	1.08±0.00d	1.72±0.01d
	Cassava	a 0.08±0.01	0.47±0.00b	e 2.37±0.02 d	0.46±0.02d	0.18±0.01d	4.92±0.02d
	Yam	a 0.71±0.00 a	0.21±0.01c	u 0.68±0.01 c	0.91±0.00c	0.08±0.00c	0.17±0.00b
	Cocoya m	a 0.15±0.00	0.11±0.00d	3.55±0.00 c	1.22±0.00d	0.51±0.00c	0.71±0.01d
	Orange	0.01±0.01 b	2.14±0.00c	0.21±0.00 c	1.32±0.02d	0.42±0.0oc	0.22±0.02d
	Star Apple	3.17±0.00 a	0.98±0.00b	0.23±0.00 c	1.31±0.01b	1.15±0.02b	4.1±0.01e
	Pawpaw	0.01±0.00 c	2.85±0.01c	0.7±0.01d a	0.05±0.00b	0.34±0.01a	0.004±0.00
	Coconut	0.2±0.01b	1.59±0.00a	1.07±0.00 d	0.49±0.00d	4.4±0.00c	3.69±0.00b
	Kola nut	0.7±0.00b	0.32±0.00a	2.96±0.01 d	0.32±0.00d	1.35±0.00c	0.18±0.01c
	Palm Kernel	0.3±0.00a	5.53±0.00b	0.5±0.00e	0.64±0.01d	0.17±0.00a	0.16±0.01d
As	Pumpkin	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Bitter leaf	< 0.01	< 0.01	<0.01	<0.01	< 0.01	< 0.01
	Waterlea f	< 0.01	<0.01	<0.01	< 0.01	< 0.01	< 0.01
	Cassava	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Yam	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
		< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Cocoya						
	m						
	Orange	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Star	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Apple	0.01	0.01	0.01	0.01	0.01	0.01
	Pawpaw	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Coconut	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Kolanut	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	Palm Kernel	<0.01	<0.01	< 0.01	<0.01	<0.01	<0.01

Values in different superscript letters in the same column are significantly different at 0.05 level ($P \le 0.05$) while same superscript letters (b) in the same column are not significantly different at greater than 0.05 (P > 0.05). <0.01 mg/kg indicates BDL- Below detection limit.

South	Lastern State a	Abia	Anambra	Ebonyi	Enugu	Owerri	<u>Control</u>
Cr	Pumpkin	2.27E-02	1.73E-04	1.15E-03	2.30E-05	1.51E-01	2.19E-03
	Bitter leaf	3.45E-04	1.34E-01	1.16E-02	1.73E-04	1.09E-03	1.27E-04
	Waterleaf	2.88E-04	1.62E-02	1.38E-02	1.09E-03	5.18E-03	6.38E-03
	Cassava	7.50E-04	8.13E-02	3.48E-02	1.05E-03	9.75E-03	3.48E-02
	Yam	1.48E-04	1.78E-03	5.56E-03	5.12E-03	2.52E-04	1.26E-03
	Cocoyam	1.18E-04	1.30E-03	1.76E-02	6.98E-03	1.35E-02	2.54E-03
	Orange	7.70E-05	3.64E-02	2.31E-04	2.34E-03	8.70E-03	5.39E-04
	Star Apple	1.85E-03	2.52E-03	9.50E-04	2.70E-03	1.72E-03	2.98E-03
	Pawpaw	5.13E-05	3.23E-02	1.13E-03	2.57E-05	4.70E-03	3.08E-05

Table 2: Daily Intake (mg kg⁻¹ day⁻¹) of Heavy Metals in selected Food Crops From six South Eastern State and control site.

	Coconut	6.67E-05	9.18E-03	6.58E-04	3.75E-04	2.35E-03	1.36E-03
	Kola nut	7.33E-04	9.50E-04	2.71E-03	2.33E-04	4.17E-05	1.17E-04
	Palm Kernel	2.50E-05	2.19E-02	7.50E-05	3.67E-04	5.83E-05	9.17E-05
Mn	Pumpkin	3.05E-02	2.59E-03	1.15E-03	1.44E-03	2.83E-02	4.60E-03
	Bitter leaf	6.44E-03	2.00E-02	1.11E-02	9.20E-04	2.88E-04	1.32E-03
	Waterleaf	3.62E-03	1.83E-02	4.66E-03	2.76E-03	6.21E-03	9.89E-03
	Cassava	1.20E-03	7.05E-03	3.56E-02	6.90E-03	2.70E-03	7.38E-02
	Yam	5.27E-03	1.56E-03	5.04E-03	6.75E-03	5.93E-04	1.26E-03
	Cocoyam	8.88E-04	6.51E-04	2.10E-02	7.22E-03	3.02E-03	4.20E-03
	Orange	2.57E-05	5.49E-03	5.39E-04	3.39E-03	1.08E-03	5.65E-04
	Star Apple	8.14E-03	2.52E-03	5.90E-04	3.36E-03	2.95E-03	1.05E-02
	Pawpaw	2.57E-05	7.32E-03	1.80E-03	1.28E-04	8.73E-04	1.03E-05
	Coconut	1.67E-04	1.33E-03	8.92E-04	4.08E-04	3.67E-03	3.08E-03
	Kola nut	5.83E-04	2.67E-04	2.47E-03	2.67E-04	1.13E-03	1.50E-04
	Palm Kernel	2.50E-04	4.61E-03	4.17E-04	5.33E-04	1.42E-04	1.33E-04
As	Pumpkin	5.75E-05	5.75E-05	5.75E-05	5.75E-05	5.75E-05	5.75E-05

Bitter leaf	5.75E-05	5.75E-05	5.75E-05	5.75E-05	5.75E-05	5.75E-05
Waterleaf	5.75E-05	5.75E-05	5.75E-05	5.75E-05	5.75E-05	5.75E-05
Cassava	1.50E-04	1.50E-04	1.50E-04	1.50E-04	1.50E-04	1.50E-04
Yam	7.42E-05	7.42E-05	7.42E-05	7.42E-05	7.42E-05	7.42E-05
Cocoyam	5.92E-05	5.92E-05	5.92E-05	5.92E-05	5.92E-05	5.92E-05
Orange	2.57E-05	2.57E-05	2.57E-05	2.57E-05	2.57E-05	2.57E-05
Orange	2.3712-03	2.5712-05	2.571-03	2.3712-03	2.5712-05	2.5712-05
Star Apple	2.57E-05	2.57E-05	2.57E-05	2.57E-05	2.57E-05	2.57E-05
Pawpaw	2.57E-05	2.57E-05	2.57E-05	2.57E-05	2.57E-05	2.57E-05
Coconut	8.33E-06	8.33E-06	8.33E-06	8.33E-06	8.33E-06	8.33E-06
Kolanut	8.33E-06	8.33E-06	8.33E-06	8.33E-06	8.33E-06	8.33E-06
Palm Kernel	8.33E-06	8.33E-06	8.33E-06	8.33E-06	8.33E-06	8.33E-06

Heavy	food	ABIA	ANAMBRA	EBONYI	ENUGU	0WERRI	CONTRO
Metals	samples						
Cr	Pumpkin	7.55E+00	5.75E-02	3.83E-01	7.67E-03	5.04E+01	7.28E-0
	Bitter leaf	1.15E-01	4.47E+01	3.87E+00	5.75E-02	3.64E-01	4.22E-0
	Waterleaf	9.58E-02	5.39E+00	4.60E+00	3.64E-01	1.73E+00	2.13E+
	Cassava	2.50E-01	2.71E+01	1.16E+01	0.35 0000	3.25 0000	1.16E+0
	Yam	4.94E-02	5.93E-01	1.85E+00	1.71E+00	8.41E-02	4.20E-0
	Cocoyam	3.94E-02	4.34E-01	5.88E+00	2.33E+00	4.50E+00	8.48E-0
	Orange	2.57E-02	1.21E+01	7.70E-02	7.79E-01	2.90E+00	1.80E-
	Star Apple	6.16E-01	8.38E-01	3.17E-01	8.98E-01	5.73E-01	9.92E-
	Pawpaw	1.71E-02	1.08E+01	3.76E-01	8.56E-03	1.57E+00	1.03E-
	Coconut	2.22E-02	3.06E+00	2.19E-01	1.25E-01	7.83E-01	4.53E-
	Kola nut	2.44E-01	3.17E-01	9.03E-01	7.78E-02	1.39E-02	3.89E-
	Palm						
	Kernel	8.33E-03	7.31E+00	2.50E-02	1.22E-01	1.94E-02	3.06E-
Mn	Pumpkin	2.18E+00	1.85E-01	8.21E-02	1.03E-01	2.02E+00	3.29E-
	Bitter leaf	4.60E-01	1.43E+00	7.93E-01	6.57E-02	2.05E-02	9.45E-
	Waterleaf	2.59E-01	1.31E+00	3.33E-01	1.97E-01	4.44E-01	7.06E-
	Cassava	8.57E-02	5.04E-01	2.54E+00	4.93E-01	1.93E-01	5.27E+
	Yam	3.76E-01	1.11E-01	3.60E-01	4.82E-01	4.24E-02	9.01E-
	Cocoyam	6.34E-02	4.65E-02	1.50E+00	5.16E-01	2.16E-01	3.00E-
	Orange	1.83E-03	3.92E-01	3.85E-02	2.42E-01	7.70E-02	4.03E-
	Star Apple	5.81E-01	1.80E-01	4.22E-02	2.40E-01	2.11E-01	7.52E-
	Pawpaw	1.83E-03	5.23E-01	1.28E-01	9.17E-03	6.23E-02	7.33E-
	Coconut	1.19E-02	9.46E-02	6.37E-02	2.92E-02	2.62E-01	2.20E-
	Kola nut	4.17E-02	1.90E-02	1.76E-01	1.90E-02	8.04E-02	1.07E-
	Palm						
	Kernel	1.79E-02	3.29E-01	2.98E-02	3.81E-02	1.01E-02	9.52E-
As	Pumpkin	7.55E+00	5.75E-02	3.83E-01	7.67E-03	5.04E+01	7.28E-
	Bitter leaf	1.29E-02	1.29E-02	1.29E-02	1.29E-02	1.29E-02	1.29E-
	Waterleaf	1.29E-02	1.29E-02	1.29E-02	1.29E-02	1.29E-02	1.29E-
	Cassava	4.03E-02	4.03E-02	4.03E-02	4.03E-02	4.03E-02	4.03E-
	Yam	1.72E-02	1.72E-02	1.72E-02	1.72E-02	1.72E-02	1.72E-
	Cocoyam	1.26E-02	1.26E-02	1.26E-02	1.26E-02	1.26E-02	1.26E-
	Orange	3.89E-03	3.89E-03	3.89E-03	3.89E-03	3.89E-03	3.89E-
	Star Apple	3.89E-03	3.89E-03	3.89E-03	3.89E-03	3.89E-03	3.89E-
	Pawpaw	3.89E-03	3.89E-03	3.89E-03	3.89E-03	3.89E-03	3.89E-
	Coconut	1.11E-03	1.11E-03	1.11E-03	1.11E-03	1.11E-03	1.11E-
	Kolanut	1.11E-03	1.11E-03	1.11E-03	1.11E-03	1.11E-03	1.11E-

TABLE 3: TARGET HARZARD QUOTIENT FOR FOOD SAMPLES COLLECTED FROM THE INDUSTRALISED LOCATIONS.

Palm						
Kernel	1.11E-03	1.11E-03	1.11E-03	1.11E-03	1.11E-03	1.11E-03

TABLE 4: INCREMENTAL LIFE TIME CANCER RISK ASSOCIATED WITH INGESTION

						OF CRO	<u>OPS</u>
Heavy	food	ABIA	ANAMBRA	EBONYI	ENUGU	0WERRI	CONTROL
Metals	samples						
Cr	Pumpkin	7.55E+00	5.75E-02	3.83E-01	7.67E-03	5.04E+01	7.28E-01
	Bitter leaf	1.15E-01	4.47E+01	3.87E+00	5.75E-02	3.64E-01	4.22E-02
	Waterleaf	9.58E-02	5.39E+00	4.60E+00	3.64E-01	1.73E+00	2.13E+00
	Cassava	2.50E-01	2.71E+01	1.16E+01	0.35 0000	3.25 0000	1.16E+01
	Yam	4.94E-02	5.93E-01	1.85E+00	1.71E+00	8.41E-02	4.20E-01
	Cocoyam	3.94E-02	4.34E-01	5.88E+00	2.33E+00	4.50E+00	8.48E-01
	Orange	2.57E-02	1.21E+01	7.70E-02	7.79E-01	2.90E+00	1.80E-01
	Star Apple	6.16E-01	8.38E-01	3.17E-01	8.98E-01	5.73E-01	9.92E-01
	Pawpaw	1.71E-02	1.08E+01	3.76E-01	8.56E-03	1.57E+00	1.03E-02
	Coconut	2.22E-02	3.06E+00	2.19E-01	1.25E-01	7.83E-01	4.53E-01
	Kola nut	2.44E-01	3.17E-01	9.03E-01	7.78E-02	1.39E-02	3.89E-02
	Palm						
	Kernel	8.33E-03	7.31E+00	2.50E-02	1.22E-01	1.94E-02	3.06E-02
Mn	Pumpkin	2.18E+00	1.85E-01	8.21E-02	1.03E-01	2.02E+00	3.29E-01
	Bitter leaf	4.60E-01	1.43E+00	7.93E-01	6.57E-02	2.05E-02	9.45E-02
	Waterleaf	2.59E-01	1.31E+00	3.33E-01	1.97E-01	4.44E-01	7.06E-01
	Cassava	8.57E-02	5.04E-01	2.54E+00	4.93E-01	1.93E-01	5.27E+00
	Yam	3.76E-01	1.11E-01	3.60E-01	4.82E-01	4.24E-02	9.01E-02
	Cocoyam	6.34E-02	4.65E-02	1.50E+00	5.16E-01	2.16E-01	3.00E-01
	Orange	1.83E-03	3.92E-01	3.85E-02	2.42E-01	7.70E-02	4.03E-02
	Star Apple	5.81E-01	1.80E-01	4.22E-02	2.40E-01	2.11E-01	7.52E-01
	Pawpaw	1.83E-03	5.23E-01	1.28E-01	9.17E-03	6.23E-02	7.33E-04
	Coconut	1.19E-02	9.46E-02	6.37E-02	2.92E-02	2.62E-01	2.20E-01
	Kola nut	4.17E-02	1.90E-02	1.76E-01	1.90E-02	8.04E-02	1.07E-02
	Palm						
	Kernel	1.79E-02	3.29E-01	2.98E-02	3.81E-02	1.01E-02	9.52E-03
As	Pumpkin	7.55E+00	5.75E-02	3.83E-01	7.67E-03	5.04E+01	7.28E-01
	Bitter leaf	1.29E-02	1.29E-02	1.29E-02	1.29E-02	1.29E-02	1.29E-02
	Waterleaf	1.29E-02	1.29E-02	1.29E-02	1.29E-02	1.29E-02	1.29E-02
	Cassava	4.03E-02	4.03E-02	4.03E-02	4.03E-02	4.03E-02	4.03E-02
	Yam	1.72E-02	1.72E-02	1.72E-02	1.72E-02	1.72E-02	1.72E-02
	Cocoyam	1.26E-02	1.26E-02	1.26E-02	1.26E-02	1.26E-02	1.26E-02
	Orange	3.89E-03	3.89E-03	3.89E-03	3.89E-03	3.89E-03	3.89E-03
	Star Apple	3.89E-03	3.89E-03	3.89E-03	3.89E-03	3.89E-03	3.89E-03
	Pawpaw	3.89E-03	3.89E-03	3.89E-03	3.89E-03	3.89E-03	3.89E-03
	Coconut	1.11E-03	1.11E-03	1.11E-03	1.11E-03	1.11E-03	1.11E-03
	Kolanut	1.11E-03	1.11E-03	1.11E-03	1.11E-03	1.11E-03	1.11E-03
	Palm	1.11E-03	1.11E-03	1.11E-03	1.11E-03	1.11E-03	1.11E-03

SOIL	· · ·	Abia	Anambra	Ebonyi	Enugu	Owerri	Control
Cr	Pumpkin	4.93±0.01a	4.5(0.00	5.43±0.01b	0.34±0.01c	1.16±0.00d	0.52±0.00c
	Bitter leaf	0.76±0.01c	4.56±0.00a	13.25±0.01b	0.2±0.01d	41.1±0.00e	1.93±0.00f
	Waterleaf	17.69±0.01c	105.7±0.00a	0.26±0.01d	16.86±0.01b	0.32±0.00d	1.11±0.00e
	Cassava	10.88±0.01a	119.8±0.00a	1.51±0.01c	0.07±0.01d	2.05±0.01e	2.19±0.00e
	Yam	0.24±0.01a	6.99±0.00b	32.9±0.01c	0.69±0.01e	0.55±0.01e	0.17±0.00e
	Cocoyam	4.97±0.00a	4.57±0.00b	1.12±0.00c	1.18±0.01d	35.36±0.01f	0.43±0.00d
Mn	Pumpkin	13.9±0.01a	4.13±0.00b 0.28±0.01d	9.17±0.00b	0.25±0.00d	1.27±0.01c	0.63±0.01d
	Bitter leaf	2.16±0.01a	10.66±0.01b	24.84±0.00c	0.16±0.00d	5.44±0.010a	308±0.01e
	Waterleaf	26.51±0.00a	15.79±0.01b	17.94±0.00c	0.48±0.00d	0.99±0.00e	1.72±0.01d
	Cassava	25.51±0.01a	7.82±0.01b	6.55±0.01c	0.46±0.00d	0.85±0.00	2.65±0.00
	Yam	1.71±0.01a	6.47±0.01b	1950 ±012c	0.91±0.00d	0.9±0.00a	0.17±0.01a
	Cocoyam	19.77±0.01a	5.77±0.01b	18.31±0.00c	1.22±0.00d	3.49±0.00b	0.71±0.01e
As	Pumpkin	<0.01	< 0.01	<0.01	<0.01	<0.01	<0.01
	Bitter leaf	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Waterleaf	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Cassava	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Yam	< 0.01	< 0.01	< 0.01	< 0.01	<0.01	< 0.01

Table 5: Mean concentration of heavy metals (mg/kg dry weight) in soil .The results are expressed as triplicate mean \pm S.E.

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Cocoyam	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
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Values in different letters (a, b) in the same column are significantly different at 0.05 level (P \leq 0.05) while same superscript letters (b) in the same column are not significantly different at greater than 0.05 (P > 0.05). <0.01 mg/kg indicates BDL- Below detection limit .

REFERENCE

1. Adeel, M; Riffact, NM .(2014) Human health risk assessment of heavy metals via consumption of contaminated vegetables collected from different irrigation sources in Lahore, Pakistan. *Arab J Chem.* 7:91–99.

2. Aigberua, A; Tarawou, T. (2017). Assessment of Heavy Metals in Muscle of Tilapia zilli from some Nun River Estuaries in the Niger Delta Region of Nigeria. *Academic Journal of Chemistry* .2(9), 96-101).

- 3. Akan, JC; Abdulrahman, FIA; Ogugbuaja, VO; Ayodele, JT. (2009). Heavy Metals and Anion Levels in Some Samples of Vegetable Grown Within the Vicinity of Challawa Industrial Area, Kano State, Nigeria . *Ame J App Sci* .6(3): 534-542.
- 4. Amirah, MN; Afiza, AS; Faizal, WIW; Nurliyana, MH. (2013). Human health risk assessment of metal contamination through consumption of fish. *Journal of Environment Pollution and Human Health*. 1. 1-5.
- 5. ATSDR (2010) .Agency for toxic substance and disease registry, public health assessment and health consultation. CENEX supply and marketing, Incorporated, Quicy, Grant County, Washington.
- 6. Avila, P; Eduardo Ferreira da Silva, and Carla Candeias. (2016) Health risk assessment through consumption of vegetables rich in heavy metals: the case study of the surrounding villages from Panasqueira mine, Central Portugal. *Environ Geochem and Health.* 39(3).
- 7. Bini, C; Maleci, L; Romanin, A. (2008) The chromium issue in soils of the leather tannery district in Italy. J Geochem Explor. 96: 194–202.
- 8. Chigere, Nkem Hyginus .(2000). Foreign Missionary Background and Indigenous Evangelization in Igboland: Igboland and The Igbo People of Nigeria. Transaction Publishers, USA. p. 17. ISBN 3-8258-4964-3. Retrieved January 04,2019.
- 9. Chimezie, A; Teddy, E; Oghenetega, U. (2013) Heavy metal levels in soil samples from highly industrialized Lagos environment. *African J of Environ Sci and Tech* .7(9):917-924.
- Chowdhury, UK; Biswas, BK; Chowdhury, TR; Samanta, G; Mandal, BK; Basu, GC; Chakraborti, D.(2000). Groundwater arsenic contamination in Bangladesh and West Bengal. *India Environ Heal Persp.* 108(5):393–397.
- 11. Crossgrove, JS; Allen, DD; Bukaveckas, BL; Rhineheimer, SS; Yokel, RA.(2003) Manganese distribution across the blood-brain barrier I: evidence for carrier-mediated influx of manganese citrate as well as manganese and manganese transferrin. *NeuroToxicology*. 24:3–13.
- 12. Das, AP; Mishra, S. (2008). Hexavalent chromium (VI): environment pollutant and health hazard. *J of Environ Res and Dev.* 2(3): 386–392.
- 13. Dereje, H; Ermias, H; Alemayehu, PW. (2016) Spectrophotometric Method for the Determination of Atmospheric Cr Pollution as a Factor to Accelerated Corrosion. International Journal of Analytical Chemistry. Article ID 7214932, 7 pages.
- 14. Goldberg, S; Glaubig, RA. (1998) Anion sorption on a calcareous, montmorillonitic soil arsenic. *J Soil Sci.* 52:1154–1157.
- 15. Guerra, F; Trevizam, AR; Muraoka, T; Marcante, NC.(2012) Heavy metals in vegetables and potential risk for human health. *Sci and Agric*.69(1), 54–60.
- 16. Han, B; Jen, WL; Chen, RY; Fang, GT; Hung, TC. (1998) Estimation of target hazard quotients and potential health risks for metals by consumption of seafood in Taiwan. *Arch Environ Contam Toxi*. 35(4): 711–720.
- 17. Harmanescu, M; Alda, LM; Bordean, DM; Gogoasa, I; Gergen. (2011). Heavy metals health risk assessment for population via consumption of vegetables grown in old mining area; a case study: Banat County, Romania. *Chem Cent J*. 5:64
- 18. Homa, D; Haile, E; Washe, AP. (2016). Determination of spatial chromium contamination of the environment around industrial zones. *Inter Journal of Analytical Chemistry*, vol. 2016,Article ID 7214932.

- 19. Idodo-Umeh, G; Ogbeibu, AE. (2010) Bioaccumulation of Heavy Metal in cassava tubers and plantain fruits grown in soil impacted with petroleum and non petroleum activities. *Res J Environ Sci.* 4:33-41.
- 20. Junaid, M; Hamid, M,Z.; Malik, RN; Peis, DS.(2016). Toxicity and Oxidative stress induced by Chromium in workers exposed from different occupational settings around the globe: A review. *Environmental Science Pollution Research*..23(20):20151-20167.
- 21. Kumar, B; Mukherjee, DP. (2011). Assessment of human health risk for arsenic, copper, nickel, mercury and zinc in fish collected from tropical wetlands in India. *Advances in Life Sciences and Technology*. 2, 13–24.
- 22. Lambkin DC, Alloway BJ. (2003). Arsenate-induced phosphate release from soils and its effect on plant phosphorus. *Water Air Soil Poll*. 144: 41–56.
- 23. Liu, CW; Liang, CP; Huang FM.(2007) Assessing the human health risks from exposure of inorganicarsenic through oyster (Crassostrea gigas) consumption in Taiwan. *Science of the Total Environment*. 361: 57–66.
- 24. Lu, S; Xiaoyong, L; Xiulan, Y; Ganghui, Z; Dong, M. (2014). Evaluation of heavy metal and polycyclic aromatic hydrocarbons accumulation in plants from typical industrial sites: potential candidate in phytoremediation for co-contamination. *Environ Sci Pollut Res*
- 25. Mahmoud, MAM; Abdel-Mohsein, HS. (2015). Health risk assessment of heavy metals for Egyptian population via consumption of poultry edibles. *Adv in Ani and Vet Sci.* 3(1), 58–70.
- 26. Martin, S; Griswold, W (2009) Human health effects of heavy metals. *Environmental Science and Technology Briefs for Citizens*.(15):1–6.
- MEPPRM (2014). Ministry of environment and physical planning Republic of Macedonia. http://airquality.moepp.gov.mk/?page_id=3234 & lang=en. Retrieved 1st Janaury 2014.
- 28. Nkpaa KW, Amadi BA, and Wegwu MO. (2017). Hazardous metals levels in groundwater from Gokana, Rivers State, Nigeria: Non-cancer and cancer health risk assessment. *Hum and Ecol Risk Assess*. 24(1): 214–224.
- 29. Nkpaa, KW; Iwuanyanwu, KCP; Wegwu, MO; Essien, EB. (2016). Health risk assessment of hazardous metals for population via consumption of seafood from Ogoniland, Rivers State, Nigeria; a case study of Kaa, B-Dere, and Bodo City. *Spring Inter Pub Switzerland*. 188(9),1-10.
- Nwaichi, EO; Wegwu, M.O; Nwosu, UL (2014) Distribution of selected carcinogenic hydrocarbon and heavy metals in an oil-polluted agriculture zone. *Spring Intern Pub Swit* 186:8697–8706.
- 31. Onyedikachi, UB; Belonwu, DC; and Mattew OW (2018). Human health risk assessment of heavy metals in soils and commonly consumed food crops from quarry sites located at Isiagwu, Ebonyi State. *Ovidius University Annals of Chemistry*. 29: 8 24.
- Oti, JO; Wilberforce ,FI; Nwabue. (2012) Heavy Metals Effect due to Contamination of Vegetables from Enyigba Lead Mine in Ebonyi State, Nigeria., DOI: <u>10.5539/ep.v2n1p19</u>.
- 33. Peters, DE; Eebu1, C; Nkpaa, KW.(2018). Potential Human Health Risk Assessment of Heavy Metals via Consumption of Root Tubers from Ogoniland, Rivers State, Nigeria. *Biological Trace Element Research*. https://doi.org/10.1007/s12011-018-1330-1

- 34. Ratnayake, RR; Seneviratne, G; Kulasooriya, SA. 2011. The Effect of Cultivation on Organic Carbon Content in the Clay Mineral Fraction of Soils. International Journal of Soil Science, 6: 217-223. DOI: 10.3923/ijss.2011.217.223
- Rosas-Castor, JM; Guzmán-Mar, JL; Hernández-Ramírez, A; Garza-González, MT; Hinojosa-Reyes, L. (2014) Arsenic accumulation in maize crop (*Zea mays L.*): A review. *Sci Total Environ* .488(489)-:176–187.
- Smith, AH; Lingas, EO; Rahman, M.(2000). Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. Bull World Health Organization.78(9):1093– 1103.
- 37. Srivastava, M; Ma, LQ; Singh, N; Singh, S. (2005). Antioxidant responses of hyperaccumulator and sensitive fern species to arsenic. *J Bot*. 56:1335–1342.
- 38. Stępniewska, Z; Wolińska, A. (2005). Soil dehydrogenase activity in the presence of chromium (III) and (VI). *Int Agro.* 19:79–83.
- 39. Straskraba, V; Moran, RE.(2006). Environmental occurrence and impact of arsenic at the gold mining siyes in the western united states *J inter wat Asso.* 9:181-191.
- 40. SuruchI, Pankaj, K. (2011). Assessment of heavy metal contamination in different vegetables grown in and around urban areas. *Res J of Environ Toxicol* 5:162-179.
- 41. Tanganu, B.V., Abdullah, S.R.S., Basri, H., Idris, M., Anuar, N. and Muklisin, M. (2011). A review on Heavy Metals (As, Pb and Hg) Uptake by plants through phytoremediation. *International Journal of Chemical Engineering*. Article ID 939161. http://dx.doi.org/10.1155/2011/939161
- 42. Tasrina, RC; Rowshon, A; Mustafzur, AMR; Rafqul, I; Ali, MP(2015). Heavy Metals Contamination in Vegetables and its Growing Soil. *J Envir Analyt Chem.* 2(3):2-6.
- 43. Tiwari, VM; Wahr, J; Swenson, S.(2009). Dwindling groundwater resources in northern India, from satellite gravity observations. *Geophys. Res. Lett.* 36: L18401.
- 44. USDOE. The risk assessment information system (RAIS) (2001) U.S. Department of energyork ridge operations office (ORO).
- 45. USEPA (2004). Risk assessment guidance for superfund volume I: human health evaluation manual (part E). http://www.epa.gov/ oswer/risk assessment/ragse/pdf/introduction.pdf.
- 46. USEPA (2011a). USEPA Regional Screening Level (RSL) Summary Table: November 2011. Available at: http://www.epa.gov/regshwmd/risk/human/Index.htm , last update: 6th December.
- 47. USEPA (2011b). Screening level (RSL) for chemical contaminant at superfound sites, U.S. Environmental Protection Agency.
- 48. USEPA(1998a). Hubson River PCBs reassessment RI/FS Phase 2 Human Health Risk Assessment, scope of work, Region II, U.S. Environmental Protection Agency, Washington, D.C. 290. Broadway New York. N.Y. 10007.
- 49. Valberg, PA; Drivas, PJ; McCarthy, S. (1996) Evaluating the health impacts of incinerator emissions. *J of Haz Mat.* 4: 205–227.
- 50. Walter, U; Niehaus, L; Probst, T; Benecke, R; Meyer, BU; Dressler, D. (2003). Brain parenchyma sonography discriminates Parkinson's disease and atypical parkinsonian syndromes. Neurology. 60(1):74–77.

- 51. Wang, X; Sato, T; Xing, B; Tao, S. (2005) Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish. *The Sci of the Total Environ.* 350: 28–37.
- 52. Wegwu, MO; Uwakwe, AA; Anabi, MA.(2010). Efficacy of Enhanced Natural Attenuaution (Land Farming) Technique In The Remediation of Crude Oil Polluted Agricultural Land. *Arch of Appl Sci Res* .2(2): 431-442.
- 53. WHO (2011). Evaluation of certain contaminants in food: seventy-second report of the joint FAO/WHO expert committee on food additives. WHO Techn Rep Series <u>959</u>
- 54. Wu, B; Zhao, DY; Jia, HY; Zhang, Y; Zhang, XX; Cheng, SP. (2009) Preliminary risk assessment of trace metal pollution in surface water from Yangtze River in Nanjing section, China. *Bull Environ Contam Toxicol.* 82:405–409.
- 55. Yu-jun, Y; Zhifeng, Y; Shanghong, Z. (2011)Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River Basin. *Journal of Environ Pollu* .159: 2575–2585.
- 56. Zevenhoven, R; Kilpinen, P (2001) Control of pollutants in flue gases and fuel gases. Report TKK—ENY—4. June 2001, 1st Ed. Espoo.
- 57. Zhongjun Fu, Weihua Li, Xiaolong Xing, Mengmeng Xu, Xiaoyang Liu, Haochuan Li, Yadong Xue, Zonghua Liu, and Jihua Tang (2016). Genetic analysis of arsenic accumulation in maize using QTL mapping. *Sci Rep, Nat pub grp.* 6: 21292.
- 58. Zhuang, P; Zou, B; Lm, NY; Li, ZA. (2009). Heavy metal contamination in soils and food crops around Dabaoshan mine in Guangdong, China: Implication for human health. *Environ. Geochem. Health.* 31:707-715.

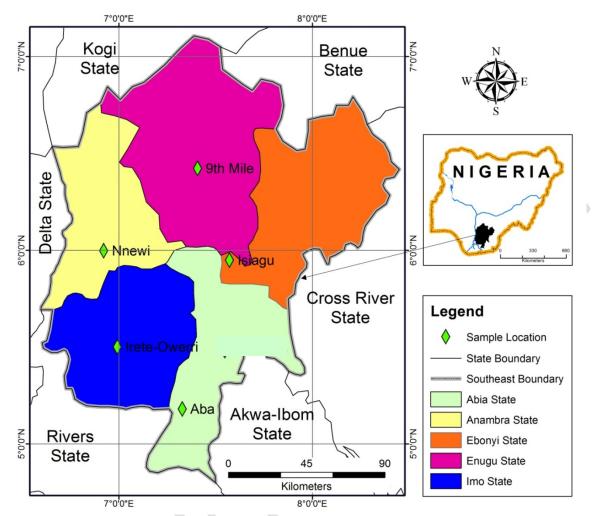


Figure 1: Map of the South Eastern States of Nigeria showing some industrial areas of study.