HEALTH RISK ASSESSMENT OF CHROMIUM, MANGANESE AND ARSENIC THROUGH THE CONSUMPTION OF FOOD FROM INDUSTRIAL AREAS IN SOUTH EASTERN STATES OF NIGERIA.

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ABSTRACT

Aim: This study investigated the health risk associated with chromium(Cr), manganese(Mn) and arsenic(As) through consumption of some food crops in selected industrialized areas located in the south eastern states of Nigeria using the estimated daily intake(EDI), bioaccumulation factor(BCF), target hazard quotient(THQ) and incremental lifetime cancer risk(ILCR).

Study design: Atomic absorption spectrophotometer was used to assess the concentrations of Cr, Mn and As in the different food crops and soils at the industrialized areas.

Place and Duration: Samples were collected around industrial layouts in south east states of Nigeria. Duration was between February 2018 to September 2018.

Methodology: Twelve (12) different food crops which included 3 each of vegetables, tubers fruits and nuts and their rhizophere soils were collected from farmlands close to the industries at Osisioma, Akwuuru, Ishiagu, Ngwo, Irete while Umudike was the control site for this study.

Results: Mean concentrations of Cr and Mn ranged from 0.01 ± 0.01c to 26.32 ± 0.02dmg/kg and 0.01 ± 0.00 to 5.53 ± 0.00mg/kg while As which was Below Detection Limit(<0.01)mg/kg. 60 and 11 0ut of 72 samples exceeded the WHO permissible limits of 0.2 and 2mg/kg for Cr and Mn respectively. The BAF of >1 was recorded in 26 Samples out of 108 with its highest values in Pumpkin and Waterleaf suggesting it could be tried as bioindicators .THQ > 1 was recorded in all samples for different locations except for Star apple and Kolanut. ILCR values for Cr in all the samples ranged 10^{-2} to 10^{-5} exceeding the permissible range of 10^{-4} to 10^{-6}.

Conclusion: The exposed population has the probability of contracting cancer and other ailments due to exposure to the heavy metals in this study. Therefore, this study suggests further consideration of the metals as chemicals of concern with respect to industrial locations in South Eastern, Nigeria.

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

INTRODUCTION

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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[1,2]. The awareness of the effects of these contaminants in our foods, drinking water and air is of utmost importance [1].This is because the ingestion of food crops contaminated with heavy metals decreases the bioavailability of some essential nutrients. It can also deplete the immunological response leading to cancer e.g. gastro-intestinal cancer, intrauterine growth retardation, impaired psycho-social facilities, etc. [3]. Within the European community, 11 elements of highest concern are arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin and thallium [4]. Some of these elements are actually necessary for humans in little quantities while others are very toxic and not needed by the body. They effect the central nervous system, kidneys, liver, skin, bones or teeth[5,6]. Food crops growing in polluted farmlands with increasing impartation of heavy metals may serve as bio-indicators of Pollution Index[7].

Food Crops such as 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*), coconut (*Cocos nucifera)* are cultivated in farmlands in Nigeria, especially in the South East Regions of Nigeria, and are commonly consumed food products in most households. The Igbo race/Communities make up the natives of the South East geopolitical zones of Nigeria, making up to about 70% of the populace around the Study Area. Most of the food crops evaluated in this Study generally thrive well in their Soil and forms the major staple foods consumed by the people around the selected Industrial Locations.

Chromium(Cr) can be found all around the environment. It is used by some industries like: tanneries, textile, chromium plating, steel production and refractories etc[8]. The oxidation state and solubility of Cr grossly indicates the levels of threat and consequential effects[9]. Cr 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 [8]. The Cr (III) has the most stable form and serves as an essential nutrients beneficial to man and other animals[8],[10]. 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[11] [12]. Cr (VI) is hydrophilic, has a P^h of above 6.0 and being a strong Oxidizing agent exhibits high stability in Oxidizing environment [8]. Intake of Cr (VI) above the permissible limit can result in renal and dermal injuries[13].

Arsenic (As) is also a highly toxic and thus poses serious health threat to man and other animals[14]. The increase in As concentration levels in the Soil maybe as a result of irrigation with As containing water, improper refuse disposal, use of pesticides rich in As and various industrial and anthropogenic activities like ore mining and smelting [15]. Excess As can reduce/hamper plant growth as it distorts plant metabolism and germination of seeds in soil [16] and eventual plant death[17]. Humans exposure to As through consumption of contaminated foods can result in some diseases such as lesions, neurological defects, atherosclerosis and cancer[17].

Manganese (Mn) on the other hand is an essential metal needed by most mammals. Mn is a co-factor which binds and regulates enzymes like arginase, Superoxide dismutase and Pyruvate carboxylase throughout the body. Mn deficiency has been implicated in some diseases associated with Skin lesions and bone malformation e. g Osteoporosis etc. Exposure to this metal can lead

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to progressive, permanent, neurodegenerative damage, resulting in symptoms similar to idiopathic Parkinson's disease[18]. However, despite all the above reports, a lot of people consume or are constantly exposed to these metals directly or indirectly 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[19,20]. In Nigeria, especially in urban centers where there are numerous anthropogenic activities, there is seemingly rare implementation of laws guiding the use of heavy metals in industrial processes. Toxic substances e.g. heavy metals be absorbed and bioaccumulated in plants/crops and thus may affect the entire ecosystem.

Health Risk Assessment in this study seeks to evaluate the results and outcome of human activities by calculating the adverse effects to man and the entire environment. It is one of the popular methods used to evaluate the impact of the heavy metal toxicity and its containment in vivo. 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 [21]. 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 [22,23]. This informative tool has been so useful and valuable to many researchers [21,24,25,26,27,28]. Some studies have reported some heavy metal contamination at various industralised areas. However, not so much has been done on heavy metal contamination in foods grown on agricultural soils located around industrial areas in southeastern Nigeria. 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) concentrations 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).

Description of the areas of study

The south eastern area of Nigeria consist of five(5) major States: Abia, Anambra, Imo, Ebonyi and Enugu. It occupies an area of a total of 40,000km^2(1600sqmi). It has highest elevation of 1000m(3300ft). It is primarily located in the lowland forest region of Nigeria[33]. The selection of the study area was based on availability of the samples. The study area in each state are as follows:

Osisioma is a town located in Osisioma ngwa local government of Abia state, Nigeria. It has an area of 198km^2 and also a population of around 219,632. The postal code of the area is 451. Vegetation type is tropical rain forest and lies in the latitude of 5^0 10'46.734"N and longitude of 7^0 19^1 39.402" ^{0} E . The industry located in this area is Tonimas Nigeria limited,a manufacturing and distributor of refined petroleum products, lubricants, food, beverage and plastic.

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 km^2 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. Companies found in the area include Chikason Company, Ibeto group of companies, Innoson Vehicle Manufacturing Company, Cento group of companies, Tummy Tummy Company.

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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 km^2. The average annual temperature above 20^0C. The vegetation type is tropical rain forest vegetation. Companies found here include vegetable oil processing company (camela vegetable oil Company), Roofing sheets company (Vinal Aluminium), Rhas Construction Company and other cottage company's eg portable water, bread bakers etc.

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 condition are high temperature and humidity for more than half a year. . Stone mining and quarrying companies found in the area include crushed rocks, Setraco Company and individual miners. The effluents of the quarrying companies are discharged directly on the soil/ farmlands.

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^{0}C. Most companies found at Ngwo are bottling companies which include Seven Up company, breweries, coca-cola bottling company.

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^o 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.

Materials and methods

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. After the manual removal of non soil particles like stone and wooden particles, soil samples were parkaged in aluminum foil and then transported to the laboratory for further analysis. 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, selected and spreadout on a flat foiled surface, The tubers were also peeled and chopped into tiny cubes to enable them dry faster. They fruits were peeled to remove exocarp(skin) while endocarp(flesh) were 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

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the flesh although this was not needed for the Kolanut). Each sample was weighed, oven dried at 55°C for 72hours, pulverized into powder and sieved using 0.15mm sized sieve.

Samples for Analysis

Procedure for Heavy Metals In Soil: aqua-regia digestion[1,6,8]: 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 volume was made up to 100ml in a volumetric flask using distilled water. The soil extract was analyzed 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[1,6,8]: 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 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 a GBC Avanta PM A6600 flame atomic absorption spectrophotometer (FAAS).

Quality assurance and quality control

All the reagents were of analytical grade and glassware were washed properly with Deionized water. 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[8]. The percent recovery, relative standard deviation (RSD) of the 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 Acetylene and air were the carrier gas(70Ψ).The wavelengths: Cr(λ) = 357.90 nm, As(λ)= 332.1nm 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

Bio-accumulation Factor

Bio-accumulation factor (BAF) of heavy metal for both food crops and soils were calculated with their dryweights(dw). BAF is usually used as a measure to know the potency of the food crops to bio-accumulate heavy metal as well as other elements compared to its concentrations in their respective soil[34], when the value > 1 is used bioindicator of the plants ability to remediate or extract[7]. It was calculated as follows:

$$BAF = Concentration\ in\ plants / Concentration\ in\ Soil \quad \text{.....(1)}$$

where is the Concentration of heavy metals in Food crops and soils(mg/kg).

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Human Health Risk AssessmentC(HHRA)

HHRA was investigated in order to understand the cancer and non cancer effects of the heavy metals on the human health. 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.

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Daily Intake of heavy metals

According to Khan *et al.*,[32] and Mahmood and Abdel-mohsein[37], the daily intake of metals (DIM) was determined by the following equation:

$$DIM = \frac{Concentration\ of\ heavy\ metal\ x\ Daily\ food\ intake}{Average\ weight} \quad \ldots\ldots\ldots\ldots (2)$$

In this Study, calculations were made based on the standard assumption for an integrate USEPA risk analysis, considering an average body weight of 60 kg and the average daily foodcrops intake for adults is considered to be, 0.154g/person/day for the fruits, 0.05 g/person/day for the nuts, 0.345 g/person/day for the vegetables and then 0.9,0.355,0.445 in g/person/day for cassava, cocoyam and yam respectively [7,24,35].

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Target Hazard Quotient

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THQ is defined as the ratio between exposure and reference oral dose (RfD). This is used to express the risk other than cancer [21]. 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 populace are unlikely to come up with health risks. The methods used for the estimation of THQ and CR have been provided in USEPA Region III Risk-Based Concentration Table, January–June 1996[25,35,36,39] based on the equation below:

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$$THQ = \frac{Concentration\ of\ heavy\ metal\ *\ Daily\ food\ intake}{Rf\ D\ *\ Average\ weight} \quad \ldots\ldots\ldots\ldots (3)$$

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−1, 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[36,37]. The RFDs are 0.003,0.0003,0.014 in mg/kg/day for Cr, As and Mn respectively.

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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(mg/kg/day) are 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[41] and ATSDR [43]. Lifetime probability of contracting cancer due to exposure to site-related chemicals is calculated as follows:

$$ILCR = DIM \; x \; CSF \; \ldots\ldots\ldots\ldots\ldots (4)$$

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].

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STATISTICAL ANALYSIS FOR METAL ANALYSIS

The least significant difference (LSD) was used to compare differences in each sample within treatments. Data was reported as mean ± S.E. 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 ($p < 0.05$) by using SPSS.

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RESULTS

The heavy metal concentrations (Cr, Mn, and As) in the selected food crops, i.e., Bitter Leaf, Waterleaf, Pumpkinleaf, Yam, Cocoyam, Cassava, Orange, Pawpaw, Star Apple, Kola Nut, Palm Kernel Nut, Coconut 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 Tables 1 and 2. Results for the mean concentrations of Cr in selected crops ranged from 0.01±0.01c for pawpaw(Enugu) to 26.32±0.02d for pumpkin leaf(Owerri).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 heavy metals in this study 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 from Anambra, all samples except orange and palmkernel nut for Ebonyi and then Pawpaw, Cassava, Bitter leaf and Pumpkin for Enugu exceeded the limits permissible of 0.2mg/kg for sample. 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 from Abia state exceeding the permissible limit of 2mg/kg except for star apple and pumpkin. Also, Some vegetables(Bitterleaf and Waterleaf) and fruits(pawpaw and orange) from Anambra exceeded the Mn permissible limit. Cassava, Coconut and Kolanut; Pumpkin, Coconut and Cassava, Star apple and Coconut had concentrations that exceeded Mn permissible limit in food for Ebonyi, Owerri and Control respectively. However, all food samples for Enugu industrial location had average concentrations of Mn within Safe limits.

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Considering the average Concentrations of vegetables in mg/kg 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 pumpkinleaf, bitterleaf and waterleaf respectively. Tubers in mg/kg ranging 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 cassava, yam and cocoyam respectively. Fruits in mg/kg ranging 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 orange, star apple and pawpaw and nuts in mg/kg ranging from (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) for coconut, kolanut and palm kernel nut respectively. We will notice that most values especially the highest values exceeded 0.2 and 2mg/kg for Cr and Mn respectively as given by USEPA and EU except for *Chyrysophyllum albidum* while values for As were all Below detection Limits indicating that consumption of this foods may expose people living in the study areas to serious risk.

HEAVY METALS IN THE SOIL

The mean concentration in mg/kg of Cr in waterleaf soil(119.8±0.00a) was significantly higher (*P<0.05*) than that other soil samples analyzed while that of Mn in the soil samples had its highest in waterleaf from Abia(26.51±0.00a).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. 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 6 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 As were Below Detection Limits(0.01mg/kg).

The Bioaccumulation Factor(BAF) on Table 3 for Cr, all the samples were < l except for Pumpkin from Owerri, Waterleaf from both Ebonyi and Owerri, Cassava in Ebonyi, Enugu and Control and yam and cocoyam from Enugu and control were >1 suggesting hyper accumulation of Cr in those areas. The highest bioaccumulation index was recorded in Pumpkin and Waterleaf(22.7, 9.2 and 1.5 for Owerri and Ebonyi respectively). Also, BAF values for Mn had values>1 for Pumpkin in Anambra, Enugu, Owerri and Control. Also, BAF for Waterleaf was >1 for Enugu, Owerri and Control. BCF for Cassava indicated bioaccumulation ability in samples for Enugu and Control just like the above vegetables. Bioaccumulation index of As for all food Samples from the various sites could not be assessed due to the peculiar properties of As as seen in this Study.

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DISCUSSION

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[43]. Ironically, 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[46]. 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 [40,46]. 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[24]. This may also make the area more vulnerable to biodegradation [33] .The use of organic manure possibly by farmers in the area may also have attenuated those farm lands overtime.

The observed result for Enugu may be attributable to weathering of the top soil during rainfall .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[3].

There was significant variation in the various food groups analyzed in this Study and this could be attributed to differences in the rate by which different plants absorb and accumulate Metals[47]. 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[48].The larger surface areas of vegetables which is in constant contact with air laden with dust and pollutants[49] could also be a reason. The duration of cultivation of various plant species like vegetables, tubers, fruits and nuts can affect their uptake from soil[50]. Thus, bioaccumulation of contaminants through active transport of minerals from soil-plants is attributable to their different uptake pattern, accumulations and soil availability [51].

The As concentration as shown on Table 1 for all the sample gave similar concentrations(0.01Mg/Kg dw) below the standard permissible 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*., [53] which stated that there were low As detection in soil samples from highly industrialized Lagos environment. Also Oti *et al*., [54]reported very low arsenic concentration on vegetables from Enyigba lead mine in Ebonyi state, Nigeria. Also, 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(4.2-5.6) of the soils where the samples were collected as As is more mobile in neutral and alkaline than in acidic environment[55]. It could also be that high iron availablity in the soil immobilized As dispersion[57].

Soil pollution with heavy metals due to discharge of untreated industrial wastes is a insistently major threat to ecological integrity and human well being. Exposure to higher amounts of Cr compounds in humans can lead to the inhibition of erythrocyte glutathione reductase, which in turn lowers the capacity to reduce methermoglobin to hemoglobin[58]. In addition, exposure to

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chromium compounds can result in the formation of ulcers which will persist for months and heal very slowly[58]. 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 [59].

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[18]. 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[60]. 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[43]. As, a known Human carcinogen based on guideline for carcinogenic assessment by USEPA[22,39] 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[57] .It can result in cancers of the lungs, liver and skin[61].

It has been established that translocation of materials from Soil across to plant then to humans or other animals is the major avenue for the exposure of humans and other animals to soil contamination. In this Study, the BAF values were > 1 for Cr in Pumpkin(Imo), Yam(Enugu) and others i.e Water leaf, Cocoyam and Cassava from Ebonyithus indicating higher bioaccumulation for these plants in those areas. This suggests that these plants could be tried out as possible bio indicators owing to their pattern of uptake. Peter et al. [7] reported that high BAF is an indicator for higher bioaccumulation and concentration of trace elements from Soil to Plants than Crops with lower BAF. Also, the high BAF value for Cr may be an indicator of potential in humans from the sampling areas via food consumption especially in the above vegetables. This result shows that the heavy metal transfer from soil to foodcrops is responsible for their concentration levels.

HEALTH RISK ASSESSMENT**:** EDI is calculated as the mean concentration multiplied by the daily intake of a particular food specie divided by the average weight[24]. Interestingly, in this Study EDI values(table 4) for Cr were above the established reference dose of 0.003 Mg/Kg/body weight/ day recommended by[41,42,44].While the total daily intake of Mn and As were within tolerable Oral reference Dose for consumption of selected crops. Values for As in the study 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.

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THQ is useful in evaluating non cancer effects of heavy metals in health risk assessment[1,20]. THQ values > 1 indicates a concern for non cancer human health risk while THQ <1 is vice versa. In this Study(table 5), THQ values for Cr > 1 for most of the samples like the vegetables, tubers, fruits and nuts(although not in all the study locations) 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 note 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[7,34].

In this Study, CR values for Cr on table 6 for all the samples ranged from 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, some contaminants ingested through foods by exposed individuals are bioaccumulated indicating that persons within the study areas stand the risk of contracting cancer due to Cr exposure over a lifetime period of 70 years especially in Anambra, whose values were consistently higher than other areas assessed[8]. 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.

Also, As had values below the range owing to their very low concentration. Irrespective of their low CR values, prolong exposure to this toxic metal endogenously could result in serious health risk. The percent recovery, relative standard deviation (RSD) of the samples, the limit of detection (LOD) and the limit of quantification (LOQ) of the analytical method for each metal in this study is presented table 7.

CONCLUSION AND RECOMMENDATION

This study concludes that there is significant health risks associated with the consumption of food crops from the industrialized study areas analyzed for the southeastern states in Nigeria. Cr and Mn showed a significant degree of contamination as they exceeded safe limits stipulated by World Health Organization of 0.2 and 2 $mgkg^{-1}$ in foods .They vegetables and tubers could be tried as bioindicators based on the BCF values given in this study. THQ > 1 was recorded in all samples for different locations except for Star apple and Kola nut which was < 1 indicating a health concern. Cancer Risk(CR) values for the food crops ranged from 10^{-2} to 10^{-5} above the predicted permissible risk for cancer. Based on the above results, with respect to human health perspective and prevention of disease. The consumption of vegetables, tubers, fruits and nuts may not be safe due to Cr and Mn concentrations in the areas. Thus suggesting that they be placed for further consideration as a matter of urgency as people living in the study areas may suffer serious cancer as well as non cancer risk. The government, regulatory bodies, policy makers and other concerned stakeholders should help in making recommendations that would fuel efficient mitigating measures like bioremediation, treatment of industrial waste before disposal and proper channeling of industrial effluents. In addition, industrial acts should adhere strictly to regulatory policies as regards food safety and human health.

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Conflict of interest: They Authors declare that they have no conflict of interest.

Authors contributions: Wegwu, MO' designed the study and wrote protocol, Belonwu, DC' performed statistical analysis and made some literature searches. Onyedikachi, UB' wrote the first draft of manuscript and managed the analyses of the study. All authors read, contributed and approved the final version of the manuscript.

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

	Abia	Anambra	Ebonyi	Enugu	Owerri	Control

Cr	Pumpkin	3.94±0.01a	0.03±0.00b	0.2±0.00c	0.004±0.00b	26.32±0.02d	0.38±0.01e
	Bitter leaf	0.06±0.02a	23.30±0.00b	2.02±0.00c	0.03±0.00a	0.19±0.00d	0.022±0.00a
	Waterleaf	0.05±0.01b	2.81±0.02a	2.4±0.01c	0.19±0.01c	0.9±0.01c	1.11±0.01d
	Cassava	0.05±0.01a	5.42±0.00b	2.32±0.00c	0.07±0.00a	0.65±0.02d	2.32±0.02c
	Yam	0.02±0.00a	0.24±0.00b	0.75±0.00b	0.69±0.01b	0.034±0.00c	0.17±0.00d
	Cocoyam	0.02±0.00b	0.22±0.01b	2.98±0.01d	1.18±0.00c	2.28±0.00d	0.43±0.01b
	Orange	0.03±0.01a	14.18±0.00b	0.09±0.00c	0.91±0.01d	3.39±0.00c	0.21±0.00c
	Star Apple	0.72±0.00a	0.98±0.02a	0.37±0.00c	1.05±0.00c	0.67±0.00d	1.16±0.00d
	Pawpaw	0.02±0.01a	12.57±0.00b	0.44±0.01a	0.01±0.01c	1.83±0.00d	0.01±0.00c
	Coconut	0.08±0.00c	11.01±0.00b	0.79±0.00b	0.45±0.00c	2.82±0.00bc	1.63±0.01c
	Kola nut	0.88±0.00b	1.14±0.01a	3.25±0.02d	0.28±0.01d	0.05±0.00a	0.14±0.00d
	Palm Kernel	0.03±0.02a	26.3±0.02b	0.09±0.00d	0.44±0.00d	0.07±0.01c	0.11±0.01c
Mn	Pumpkin	5.31±0.00a	0.45±0.01b	0.2±0.01c	0.25±0.00d	4.92±0.00a	0.8±0.00b
	Bitter leaf	1.12±0.02a	3.48±0.00b	1.93±0.00d	0.16±0.01c	0.05±0.00c	0.23±0.00b
	Waterleaf	0.63±0.00a	3.18±0.01b	0.81±0.00e	0.48±0.00c	1.08±0.00d	1.72±0.01d
	Cassava	0.08±0.01a	0.47±0.00b	2.37±0.02d	0.46±0.02d	0.18±0.01d	4.92±0.02d
	Yam	0.71±0.00a	0.21±0.01c	0.68±0.01c	0.91±0.00c	0.08±0.00c	0.17±0.00b
	Cocoyam	0.15±0.00	0.11±0.00d	3.55±0.00c	1.22±0.00d	0.51±0.00c	0.71±0.01d
	Orange	0.01±0.01b	2.14±0.00c	0.21±0.00c	1.32±0.02d	0.42±0.0oc	0.22±0.02d
	Star Apple	3.17±0.00a	0.98±0.00b	0.23±0.00c	1.31±0.01b	1.15±0.02b	4.1±0.01e
	Pawpaw	0.01±0.00c	2.85±0.01c	0.7±0.01da	0.05±0.00b	0.34±0.01a	0.004±0.00
	Coconut	0.2±0.01b	1.59±0.00a	1.07±0.00d	0.49±0.00d	4.4±0.00c	3.69±0.00b
	Kola nut	0.7±0.00b	0.32±0.00a	2.96±0.01d	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
	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
	Cocoyam	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Orange	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Star 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 ($P < 0.05$) while same superscript letters (b) in the same column are not significantly different at

Table 2: Mean concentration of heavy metals (mg/kg dry weight) in soil .The results ar expressed as triplicate mean ± S.E.

SOIL		Abia	Anambra	Ebonyi	Enugu	Owerri	Control
Cr	Pumpkin	4.93±0.01a	4.56±0.00a	5.43±0.01b	0.34±0.01c	1.16±0.00d	0.52±0.00c
	Bitter leaf	0.76±0.01c	105.7±0.00a	13.25±0.01b	0.2±0.01d	41.1±0.00e	1.93±0.00f
	Waterleaf	17.69±0.01c	119.8±0.00a	0.26±0.01d	16.86±0.01b	0.32±0.00d	1.11±0.00e
	Cassava	10.88±0.01a	6.99±0.00b	1.51±0.01c	0.07±0.01d	2.05±0.01e	2.19±0.00e
	Yam	0.24±0.01a	4.57±0.00b	32.9±0.01c	0.69±0.01e	0.55±0.01e	0.17±0.00e
	Cocoyam	4.97±0.00a	4.13±0.00b	1.12±0.00c	1.18±0.01d	35.36±0.01f	0.43±0.00d
Mn	Pumpkin	13.9±0.01a	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
	Cocoyam	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

<0.01 mg/kg indicates BDL- Below detection limit.

TABLE 3: Bioaccumulation of Heavy Metals in selected locations in industrial Areas in South East States of Nigeria.

	Plants	**Abia**	**Anambra**	**Ebonyi**	**Enugu**	**Imo**	**control**
Cr	Pumpkin	0.80	0.01	0.04	0.01	22.69	0.73

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	Bitter leaf	0.08	0.22	0.15	0.15	0.00	0.01
	Waterleaf	0.00	0.02	9.23	0.01	2.81	2.71
	Cassava	0.00	0.78	1.54	0.01	0.32	1.06
	Yam	0.08	0.05	0.02	2.88	0.06	0.02
	Cocoyam	0.00	0.05	2.66	0.20	0.06	0.00
Mn	Pumpkin	0.00	50.64	0.01	1.38	2.67	0.33
	Bitter leaf	0.33	0.09	0.01	2.56	0.12	0.00
	Waterleaf	0.00	0.80	0.02	0.00	1.85	0.01
	Cassava	0.00	1.41	0.12	0.06	3.32	0.62
	Yam	0.51	0.18	0.27	0.31	0.06	0.01
	Cocoyam	0.00	4.56	0.00	0.07	0.02	0.00
As	Pumpkin	BDL	BDL	BDL	BDL	BDL	BDL
	Bitter leaf	BDL	BDL	BDL	BDL	BDL	BDL
	Waterleaf	BDL	BDL	BDL	BDL	BDL	BDL
	Cassava	BDL	BDL	BDL	BDL	BDL	BDL
	Yam	BDL	BDL	BDL	BDL	BDL	BDL
	Cocoyam	BDL	BDL	BDL	BDL	BDL	BDL

Table 4: Daily Intake (mg /kg/ day) of Heavy Metals in selected Food Crops From six South Eastern State and control site.

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Heavy Metals	Plants	Abia	Anambra	Ebonyi	Enugu	Owerri	Control
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
	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
	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

TABLE 5:TARGET HARZARD QUOTIENT FOR FOOD SAMPLES COLLECTED FROM THE INDUSTRALISED LOCATIONS.

Comment [i145]: Why are here the capital letters?

Heavy Metals	Food samples	ABIA	ANAMBRA	EBONYI	ENUGU	0WERRI	CONTROL
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 Kernel	1.11E-03	1.11E-03	1.11E-03	1.11E-03	1.11E-03	1.11E-03

TABLE 6:INCREMENTAL LIFE TIME CANCER RISK ASSOCIATED WITH INGESTION OF CROPS(mg/kg/day)

Comment [i146]: Why are here the capital letters?

Heavy Metals	food samples	ABIA	ANAMBRA	EBONYI	ENUGU	0WERRI	CONTROL
Cr	Pumpkin	0.011328	0.00008625	0.000575	0.0000115	0.07567	0.001093
	Bitter leaf	0.000173	0.0669875	0.005808	8.625E-05	0.000546	6.33E-05
	Waterleaf	0.000144	0.00807875	0.0069	0.0005463	0.002588	0.003191
	Cassava	0.000375	0.04065	0.0174	0.000525	0.004875	0.0174
	Yam	7.42E-05	0.00089	0.002781	0.0025588	0.000126	0.00063
	Cocoyam	5.92E-05	0.00065083	0.008816	0.0034908	0.006745	0.001272
	Orange	3.85E-05	0.01819767	0.000116	0.0011678	0.004351	0.00027
	Star Apple	0.000924	0.00125767	0.000475	0.0013475	0.00086	0.001489
	Pawpaw	2.57E-05	0.0161315	0.000565	1.283E-05	0.002349	1.54E-05
	Coconut	3.33E-05	0.0045875	0.000329	0.0001875	0.001175	0.000679
	Kola nut	0.000367	0.000475	0.001354	0.0001167	2.08E-05	5.83E-05
	Palm Kernel	1.25E-05	0.01095833	3.75E-05	0.0001833	2.92E-05	4.58E-05
Mn	Pumpkin						
	Bitter leaf						
	Waterleaf						
	Cassava						
	Yam						
	Cocoyam						
	Orange						
	Star Apple						
	Pawpaw						
	Coconut						

As	Kola nut	–	–	–	–	–	–
	Palm Kernel	–	–	–	–	–	–
	Pumpkin	–	–	–	–	–	–
	Bitter leaf	–	–	–	–	–	–
	Waterleaf	–	–	–	–	–	–
	Cassava	–	–	–	–	–	–
	Yam	–	–	–	–	–	–
	Cocoyam	–	–	–	–	–	–
	Orange	–	–	–	–	–	–
	Star Apple	–	–	–	–	–	–
	Pawpaw	–	–	–	–	–	–
	Coconut	–	–	–	–	–	–
	Kolanut	–	–	–	–	–	–
	Palm Kernel	–	–	–	–	–	–

Comment [i147]: The font face is different than in the rest of the text.

Table 7:The Limit of detection and quantification obtained for each element in this Study as well as other quality control measures used.

..	RSD(%)	LOD(mg/kg)	LOQ(mg/kg)	Quantity of Std added (mg/kg)	Quantity Determined (mg/kg)	Sample Concentrations (mg/kg)	Percentage Recovery(%)
Cr							
Mn							
As	4.49	0.02	0.04	1.00	2.80	2.25	92.80

Comment [i148]: Something is wrong with this table, it should be rewritten.

REFERENCES

1. Onyedikachi UB, Belonwu DC, and Mattew OW. 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.2018; 29: 8 - 24.

2. Suruchi J, Pankaj K. Assessment of heavy metal contamination in different vegetables grown in and around urban areas. Res J of Environ Toxicol. 2011; 5:162-179.

3. Tasrina RC, Rowshon A, Mustafzur AMR, Rafqul I, Ali MP(2015). Heavy Metals Contamination in Vegetables and its Growing Soil. J Envir Analyt Chem .2015;*2*(3):2-6.

4. MEPPRM. Ministry of environment and physical planning Republic of Macedonia. http://airquality.moepp.gov.mk/?page_id = 3234 & lang = en. Retrieved 1st Janaury 2014.

5. Zevenhoven R, Kilpinen P. Control of pollutants in flue gases and fuel gases. Report TKK—ENY—4. June 2001, 1st Ed. Espoo.

6. Nwaichi EO, Wegwu M.O, Nwosu UL. Distribution of selected carcinogenic hydrocarbon and heavy metals in an oil-polluted agriculture zone. Spring Intern Pub Swit.2014; 186:8697–8706.

7. Dereje H, Ermias H, Alemayehu PW. Spectrophotometric Method for the Determination of Atmospheric Cr Pollution as a Factor to Accelerated Corrosion. International Journal of Analytical Chemistry. volume 2016, Article ID 7214932, 7 pages.

8. Peters Dikioye E, Eebu1 Charity, Nkpaa Kpobari W. Potential Human Health Risk Assessment of Heavy Metals via Consumption of Root Tubers from Ogoniland, Rivers State, Nigeria. Biological Trace Element.2018. Research. https://doi.org/10.1007/s12011-018-1330-1

9. Srivastava M, Ma LQ, Singh N, and Singh S. Antioxidant responses of hyper-accumulator andsensitive fern species to arsenic. J Bot .2005; 56:1335–1342.

10. Stępniewska Z and Wolińska A.Soil dehydrogenase activity in the presence of chromium (III) and (VI).Int Agro. 2005;19:79–83.

11. Bini C, Maleci L, and Romanin A. The chromium issue in soils of the leather tannery district in Italy. J Geochem Explor.2008; 96: 194–202.

12. Das AP, and Mishra S. Hexavalent chromium (VI): environment pollutant and health hazard. J of Environ Res and Dev.2008; 2(3):386–392.

13. Homa D, Haile E, Washe, AP Determination of spatial chromium contamination of the environment around industrial zones. Inter Journal of Analytical Chemistry.vol. 2016,Article ID 7214932.

14. Rosas-Castor JM, Guzmán-Mar JL, Hernández-Ramírez A, Garza-González MT, and Hinojosa-Reyes L. Arsenic accumulation in maize crop (*Zea mays* L.): A review. Sci Total Environ.2014; 488–489, 176–187.

15. Lambkin DC, Alloway BJ .Arsenate-induced phosphate release from soils and its effect on plant phosphorus. Water Air Soil Poll. 2003; 144: 41–56.
16. Fazal Ur, Rehman Shah, Nasir Ahmad, Khan Rass Masood, Firozud Din Ahmad. Heavy Metal Toxicity in Plants. Plant Adaptation and Phytoremediation. Chapter · July 2010 (pp.71-97).

17. Zhongjun F, Weihua L, Xiaolong X, Mengmeng X, Xiaoyang L, Haochuan L, Yadong X, Zonghua L,' Jihua T. Genetic analysis of arsenic accumulation in maize using QTL mapping.Sci Rep, Nat pub grp. 2016: 6: 21292.

18. Crossgrove JS, Allen DD, Bukaveckas BL, Rhineheimer SS, Yokel RA. Manganese distribution across the blood–brain barrier I: evidence for carrier-mediated influx of manganese citrate as well as manganese and manganese transferrin. NeuroToxicology. 2003;24:3–13.

19. Wu B, Zhao DY, Jia HY, Zhang Y, Zhang XX, and Cheng SP.Preliminary risk assessment of trace metal pollution in surface water from Yangtze River in Nanjing section, China. Bull Environ Contam Toxicol.2009; 82:405–409.

20. Nkpaa KW, Iwuanyanwu KCP, Wegwu MO, Essien EB. (2016). Health risk assessment of hazardous metals for population via consumption of seafood from Ogoni land, Rivers State, Nigeria; a case study of Kaa, B-Dere, and Bodo City. Spring Inter Pub Switzerland. 2016;*188*(9),1-10.

21. Yu-jun Y, Zhifeng Y, and 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. 2011; 159: 2575–2585.

22. USEPA. 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. 10007.1998a

23. Harmanescu M, Alda LM, Bordean DM, Gogoasa I, Gergen. 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.2011; 5:64

24. Avila P, Eduardo F, Carla C. 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.2016; 39(3) ·

25. Chien LC, Hung Choang KY, and Yeh CY Daily intake of TBT, Cu, Zn, Cd and As for fisherman in Taiwan. The Sci Tot Environ.2002; 285: 177–185.

26. Wang X, Sato T, Xing B, and 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.

27. Kumar, B., & Mukherjee, D. P. (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.

28. Amirah, M.N. Afiza, A.S. Faizal, W.I.W. Nurliyana, M.H. Human health risk assessment of metal contamination through consumption of fish. Journal of Environment Pollution and Human Health .2013;1. 1-5.

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

30. Chigere, NH. Foreign Missionary Background and Indigenous Evangelization in Igboland: Igboland and The Igbo People of Nigeria. Transaction Publishers, USA. 2000; p. 17. ISBN 3-8258-4964-3. Retrieved January 04,2019.

31. USEPA Regional Screening Level (RSL) Summary Table: November 2011. Available at: http://www.epa.gov/regshwmd/risk/human/Index.htm , last update: 6th December 2011a.

32. Khan S, Cao Q, Zheng YM, Huang YZ, Zhu YG. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environmental Pollution. 2007;152:686–692. doi: 10.1016/j.envpol..06.056.

33. Nkpaa KW, Amadi BA, Wegwu MO. Hazardous metals levels in groundwater from Gokana, Rivers State, Nigeria: Non-cancer and cancer health risk assessment. Hum and ecol risk ASsess. 2017; 24(1): 214–224.

34. Zhuang P, Zou B, Lm NY and Li ZA. Heavy metal contamination in soils and food crops around Dabaoshan mine in Guangdong, China: Implication for human health. Environ. Geochem. Health.2009; 31:707-715.

35. Han B, Jen WL, Chen R.Y, 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.

36. Guerra F, Trevizam AR, Muraoka T, and Marcante NC.(2012) Heavy metals in vegetables and potential risk for human health. Sci and Agric 69(1), 54–60.

37. Mahmoud MAM, and Abdel-Mohsein HS (2015). Health risk assessment of heavy metals for Egyptian population via consumption of poultry edibles. Adv in Ani and Vet Sci. 2015; 3(1): 58–70.

38. Valberg PA, Drivas PJ, and McCarthy S. Evaluating the health impacts of incinerator emissions. J of Haz Mat.1996; 4: 205–227.

39. USEPA (2011b). Screening level (RSL) for chemical contaminant at superfound sites, U.S. Environmental Protection Agency.

40. Liu CW, Liang CP, Huang FM. Assessing the human health risks from exposure of inorganicarsenic through oyster (Crassostrea gigas) consumption in Taiwan. Science of the Total Environment. 2007; 361: 57–66.

41. 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.

42. USDOE. The risk assessment information system (RAIS) .U.S. Department of energyork ridge operations office (ORO). 2001.

43. ATSDR. Agency for toxic substance and disease registry, public health assessment and health consultation. CENEX supply and marketing, Incorporated, Quicy, Grant County, Washington. 2010.

44. WHO. Evaluation of certain contaminants in food: seventy-second report of the joint FAO/WHO expert committee on food additives. WHO Techn Rep Series. 2011; 959.

45. Martin S, Griswold W. Human health effects of heavy metals. Environmental Science and Technology Briefs for Citizens. 2009;(15):1–6..

46. Wegwu MO, Uwakwe AA, and Anabi MA. Efficacy of Enhanced Natural Attenuaution (Land Farming) Technique In The Remediation of Crude Oil Polluted Agricultural Land. Arch of Appl Sci Res 2010; 2(2): 431-442.

47. Tiwari V M, Wahr J and Swenson S. Dwindling groundwater resources in northern India, from satellite gravity observations, Geophys. Res. Lett. 2009; 36: L18401.

48. Tanganu BV, Abdullah SRS, Basri H, Idris M, Anuar N, Muklisin M. A review on Heavy Metals(As,Pb and Hg) Uptake by plants through phytoremediation. International Journal of Chemical Engineering. 2011; Article ID 939161.http://dx.doi.org/10.1155/2011/939161

49. Lu S, Xiaoyong L, Xiulan Y, Ganghui Z, Dong M. 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. 2014;

50. Ratnayake, R.R, Seneviratne G. and Kulasooriya, S.A. The Effect of Cultivation on Organic Carbon Content in the Clay Mineral Fraction of Soils. International Journal of

Soil Science. 2011; 6: 217-223. DOI: 10.3923/ijss.2011.217.223

51. Idodo-Umeh G, and Ogbeibu AE. Bioaccumulation of Heavy Metal in cassava tubers and plantain fruits grown in soil impacted with petroleum and non petroleum activities. Res J Environ Sci. 2010; 4:33-41.

52. Akan JC, Abdulrahman FIA, Ogugbuaja V O, and Ayodele J T. 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. 2009; 6(3): 534-542.

53. Chimezie A, Teddy E, and Oghenetega U. Heavy metal levels in soil samples from highly industrialized Lagos environment. African J of Environ Sci and Tech. 2013; 7(9):917-924.

54. Oti JO, and Wilberforce FI, and Nwabue. Heavy Metals Effect due to Contamination of Vegetables from Enyigba Lead Mine in Ebonyi State, Nigeria., 2012 .DOI: 10.5539/ep.v2n1p19 .

55. Straskraba V, Moran RE. Environmental occurrence and impact of arsenic at the gold mining siyes in the western united states .J inter wat Asso. 2006; 9:181-191.

56. Goldberg S, and Glaubig RA. Anion sorption on a calcareous, montmorillonitic soil – arsenic. J Soil Sci. 1998; 52:1154–1157.

57. Chowdhury UK, Biswas, BK, Chowdhury TR Samanta G, Mandal BK, Basu GC, and Chakraborti D. Groundwater arsenic contamination in Bangladesh and West Bengal, India Environ Heal Persp, 2000; 108(5):393–397.
58. Monisha J, Tenzin T, Naresh A, Blessy BM, Krishnamurthy N, and Beeregowda. Toxicity, mechanism and health effects of some heavy metals. Interdiscip Toxicol.2014; 7(2): 60–72.

59. Junaid, M, Hamid MZ, Malik RN, Peis DS. Toxicity and Oxidative stress induced by Chromium in workers exposed from different occupational settings around the globe:A review. Environmental Science Pollution Research. 2016; 23(20): 20151-20167.

60. Walter U, Niehaus L, Probst T, Benecke R, Meyer BU, Dressler D. Brain parenchyma sonography discriminates Parkinson's disease and atypical parkinsonian syndromes. Neurology.2003; 60(1):74–77.

61. Smith AH, Lingas EO, Rahman M. Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. Bull World Health Organization. 2000;78(9):1093–1103.

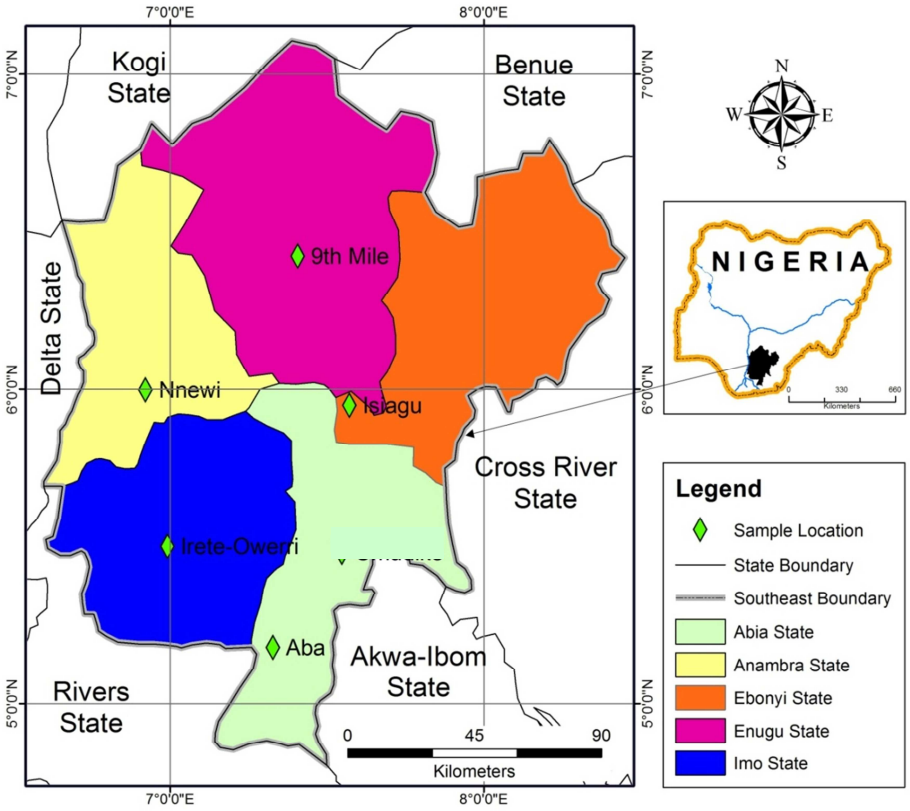

Figure 1: Map of the South Eastern States of Nigeria showing some industrial areas of study.