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Research Article

Determination of Heavy Metals in Some Fruits and Vegetables from Selected Market's in Anambra State

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Abstract

The concentration of the heavy metals (Cu, Pb, Cd, Hg, As and Zn) in fruits and vegetables from selected markets in Anambra State were determined using Atomic Absorption Spectroscopy AAS). Fruits and vegetable from three different markets were sampled, digested using concentrated nitric acid and hydrochloric acid in 3:1 ratio. The concentrations of the heavy metals obtained for fruits and vegetables obtained from Ose Market Onitsha, Nkwo Ogbe Market, Ihiala and Nkwo Nnewi Market are showed as follows; for Ose market Onitsha Cu ranges from (1.62 - 10.37 mg/kg), Pd(1.23 - 9.11mg/kg), Cd(0.70 mg/kg), Hg(0.02 - 0.45 mg/kg) As(1.03 - 7.88 mg/kg), Zn(22.94 - 146.45 mg/kg), for Nkwo Ogbe market Ihiala, Cu ranges from (1.62 - 13.46 mg/kg), Pb(1.24 - 8.71 mg/kg), Cd(0.04 - 0.54 mg/kg), Hg(0.01 - 0.47mg/kg), As(1.03 - 5.94 mg/kg), Zn(25.11 - 135.66 mg/kg) and Nkwo Nnewi market, Cu ranges from (1.44 - 9.76mg/kg), Pb(1.33 - 10.66mg/kg), Cd(0.03 - 0.53 mg/kg), Hg (0.01 - 0.75 mg/kg), As(1.21- 9.51 mg/kg) and Zn (23.09 - 146.76 mg/ kg).The concentrations for each heavy metal in the sample gotten from each market were compared with the standard set by World Health Organization/Food and Agricultural Organization (WHO/FAO). When compared with the standards, some fruits and vegetables exceeded the permissible limit while some were found to be within the safe limit. Considering the possible health effects due to the consumption of contaminated fruits and leafy vegetables, it is required that proper action should be taken to avoid chronic exposure and consequent adverse health implications.

Keywords: Heavy Metals; Contamination; Health hazard; Fruits; Vegetable and Permissible Limit

Introduction

The last three decades have seen an increase in global concern over health diseases [1]. Most of these diseases are however not easily detected and may be acquired during childhood and manifest in adulthood [2]. Although modern technology advancement has improved the living condition of many people, one cannot totally overlook its adverse impact on the environment. Industrialization and urbanization has increased the production of hazardous waste affluent that are dangerous to human health [3]. Agricultural revolution that lead to commercial farming involving the use of chemical fertilizer, pesticides, herbicides and other synthetic chemicals for farming. These heavy chemicals long run affects human health and overall ecosystem directly [4]. One of the issues is the presence of heavy metals. Heavy metals toxicity has shown to be one of the major threats to health with several health risk associated with it [5]. Heavy metals are naturally occurring metallic elements that have high atomic weight and a density at least five times greater than that of water [6]. They are metals with metallic properties and atomic number > 20 [7]. They are elements that have a relatively high density that is toxic or poisonous at low concentration. They are released in the environment by both natural and anthropogenic sources such as industrial discharge, automobile exhaust and mining. Generally heavy metals are not biodegradable; they have long half-life with the potential for accumulation in different body organs leading to unwanted side effects [8,9]. They include Pb, Cd, Zn, Cu, Co, Ni, Ar, Hg and Cr [10]. Fruits and vegetables are edible plant products that are good for health which are widely used for culinary purpose [11]. They are

widely used to increase the quality of soups (leafy vegetables) also for their dietary purposes [12]. They are good source of fiber, selected minerals, vitamins and antioxidants. They are made up of chiefly cellulose, hemi cellulose and pectin substance that gives their texture and firmness [12]. They contain water, calcium, iron, sulphur and potash which make them to be of importance in our diets [11]. Due to the presence of these vitamin and mineral in fruits and vegetable, they play a unique role in healthy living. However, plants are known to contain both essential and toxic metals which they uptake, translate and accumulate through various transportation mechanism [7]. Although fruits and vegetables are of great health benefit, the accumulation of their contaminants in the bodies of consumer over a long period of time is of major concern as it can result to serious health conditions [13]. In addition to the soil, other sources of heavy metals for plants are rainfalls in atmospheric polluted area, traffic density, use of oil or fossil fuels for heating, atmospheric dusts, plant protection agents, irrigation water and fertilizer which could be absorbed through aerial parts such as the fruits and leaves [10,14,15]. They can leach into living systems from natural ore deposits and other sources such as waste disposal of heavy metal containing waste which accounts for higher percentage of most heavy metal in the environment [16]. Some heavy metals like iron, copper, manganese and zinc are nutritionally essential for a healthy life when present in food in small quantity. Few also are of great negative impact to human health. Heavy metals like lead and cadmium are among the most abundant heavy metals and are particularly toxic [13]. Excessive amount of these metals in food is associated with etiology of a number of diseases especially with cardiovascular, kidney, nervous as well as bone disease [14,17]. Cadmium last for a long time in the body and can cause renal damages, abnormal urinary excretion of protein and decrease in bone calcium. Although zinc is an essential mineral due to its biological and public health significance, it can be toxic when consumed in excess [18]. Arsenic is the 20th most abundant element on earth and 3rd on the periodic table. Human are exposed to arsenic via air, water and food [5]. Long exposure to arsenic can cause blood vessel destruction, gastro intestinal tissue, heart and brain dysfunction, skin pigmentation, cancer of skin, bladder, lungs, liver colon and kidney [19,20]. Mercury can be harmful at a very low concentration because it's high toxicity and ability to bio accumulate. It is one of the most toxic elements among the studied trace metals and exposure to high level could permanently damage the brain, kidney, liver, immune system, pituitary gland, developing fetus [11,21,22]. Copper and zinc are essential minerals due to their biological and public health significance; however zinc can be toxic when consumed in excess [18]. Excess zinc can cause copper deficiency, autism, nausea, vomiting, stomach pain and diarrhea [23]. Excess copper intake can cause liver, kidney and heart parenchymatous injury [24]. Despite the variations in the heavy metal contents of different fruits and vegetable, there is a permissible guideline of heavy metals in fruits and vegetables set by the Food Nutrition Board of World Health Organization. Since heavy metals is one of the most important considerations in food quality assurance, there is a need for constant test and analysis of most consumed leafy vegetable and fruits to ensure that their heavy metal content are not above international recommended permissible limit.

Aim of the Study

Hence this study aims at determining the heavy metal content of most consumed fruits and vegetable in three selected markets in Anambra State, comparing the result with recommended limits set by WHO/FAO.

Materials and Methods

Material

The Beaker, Conical flask, Funnel, Whatman no 5 Filter paper, Measuring cylinder, Weighing balance, Deionized water, AAS spectrophotometer, Mortar and pestle, Nitric acid, Hydrochloric acid, Crucible, Desiccator, Muffle furnace.

Sample collection

A total of 13 samples consisting of seven (7) fruits and six (6) vegetables were purchased separately from Ihiala market, Ose market and Nkwo nnewi market in Anambra state. Edible portions were used for the analysis. The fruits includes Paw-paw (*Carica papaya*), banana (*Musa paradisiaca*), Apple (*Malus domestica*), Water melon (*Citrulus laratus*), Cucumber (*Cucumis sativus*), Bush mango (*Irvingia gabonensis*) Guava (*Psidium guajava*) while vegetables includes Uziza leave (*Piper guineese*), Pumpkin leave (*Telfairia occidentalis*), Bitter leave (*Vernonia amygdalina*), Oha leave (*Pterocarpa mildraedil*), Scent leaf (*Ocimum gratissimum*) and water leave (*Talinum triangulare*). The samples were stored in polythene bags according to their types in refrigerator.

Sample preparation and treatment

The collected samples were washed thoroughly with water to remove dust particles and possible parasites. Vegetables were washed and cut while the fruits were peeled. Samples were dried using oven. The dried samples were then pounded with crucible to fine powder. Each sample were labeled for identification and stored in close tight bottle for further experimentation.

Digestion procedure

Samples were heated in 20 ml mixture of concentrated acids (Nitric and Hydrochloric acids in 3:1 ratio) for 3hrs in a water bath maintained at 70ºC for dissolving the content until a clear brownish solution was obtained using wet digestion method. After cooling, these solutions were re-constituted to 50ml volume with de-

ionized water. Each sample was filtered using Whatman no 5 filter paper and stored in acid-washed polythene bottles. The stored samples were further used for analysis of heavy metals using flame atomic absorption spectroscopy. Concentration of each metal was determined from the absorbance volume of the replicate and articulated in mg/kg.

Atomic absorption spectrophotometry

Heavy metal analysis was done according to AOAC 1995 using varian AA240 atomic absorption spectrophotometer in seven (7) fruits and six (6) vegetables using wet digestion method [44]. Standards for Cu, Zn, Pb, Cd, As, Hg, procured from Merck, Germany were used as reference analyte for quantitative estimation of heavy metals as well as accurate calibration and quality assurance of each analyte. The standard stock solutions (1000 mg/kg) were diluted to obtain working standard solution ranging from 5 mg/kg to 20 mg/kg and stored at 4ºC. An acidity of 0.1% nitric acid was maintained in all the solutions. A calibration curve was plotted between measured absorbance and concentration (mg/kg). All the samples were analyzed using flame atomic absorption spectrophometer [45]. Measurements were made using standard cathode lamp for Zn, Cu, Pb, Cd, As, Hg.

Statistical analysis

Completely randomized design (CRD) by [46] was used. Mean value of all the duplicate analytical determinations were subjected to analysis of variance (ANOVA). Significant difference were determine using SPSS statistical tools version 21 at 5% ($P < 0.05$) acceptable level.

Result and Discussion

Heavy metals are considered the most important constituents of pollution from the terrestrial environment due to toxicity, portioning in the soil and accumulation in plants. Since heavy affects the nutritive values of agricultural materials and also have deteriorating effect on human beings. Therefore, there is a need for adequate control of heavy metal concentration in foods with regards to the stipulated standard set by WHO and other international regulators [25]. Table 1-3 shows the heavy metal content of some fruits and vegetables from 3 markets locations in Anambra State comparing them with WHO permissible guideline for heavy metals in fruits and Vegetables.

Sample of Fruits	Copper mg/kg	Lead mg/kg	Cadmium mg/kg	Mercury mg/kg	Arsenic mg/kg	Zinc mg/kg
Apple	$1.89^{g} \pm 0.10$	$1.45^{e} \pm 0.03$	$0.22^{a} \pm 0.01$	$0.06^{c} \pm 0.01$	$3.25^{c} \pm 0.01$	$22.94^{f} \pm 0.06$
Water Melon	$3.85^{a} \pm 0.02$	$2.43^{c} \pm 0.04$	$0.14^{b} \pm 0.02$	$0.17^{b} \pm 0.00$	$2.55^{d} \pm 0.01$	$57.56^{b} \pm 0.01$
Pawpaw	$2.05^{e} \pm 0.02$	$8.00^{a} \pm 0.00$	$0.24^{a} \pm 0.01$	$0.18^{b} \pm 0.01$	$1.13^{b} \pm 0.02$	$36.58^{d} \pm 0.04$
Banana	$3.64^{b} \pm 0.01$	$1.23^{g} \pm 0.01$	$0.00^{d} \pm 0.00$	$0.25^{a} \pm 0.01$	$4.03^{b} \pm 0.04$	$71.27^{a} \pm 0.03$
Bush Mango	$2.01^{f} \pm 0.01$	$1.78^{e} \pm 0.03$	$0.01^{d} \pm 0.00$	$0.07^{a} \pm 0.01$	$7.88^{a} \pm 0.02$	$40.13^{c} \pm 0.04$
Guava	$2.13^{d} \pm 0.04$	$3.83^{b} \pm 0.04$	$0.08^{c} \pm 0.01$	$0.25^{a} \pm 0.00$	$2.05^{e} \pm 0.06$	$31.48^{e} \pm 0.04$
Cucumber	$2.90^{c} \pm 0.05$	$2.33^{d} \pm 0.00$	$0.16^{b} \pm 0.02$	$0.17^{b} \pm 0.02$	$2.55^{d} \pm 0.01$	$57.55^{b} \pm 0.0.2$
Sample of Vegetable	**Copper mg/kg**	**Lead mg/kg**	**Cadmium mg/kg**	**Mercury mg/kg**	**Arsenic mg/kg**	**Zinc mg/kg**
Pumpkin Leave	$10.37^{a} \pm 0.03$	$2.27^{e} \pm 0.01$	$0.15^{b} \pm 0.01$	$0.02^{c} \pm 0.00$	$4.72^{b} \pm 0.03$	$136.75^{b} \pm 0.02$
Bitter Leave	$6.74^{b} \pm 0.02$	$5.13^{c} \pm 0.04$	$0.70^{a} \pm 0.00$	$0.00^{d} \pm 0.00$	$3.65^{c} \pm 0.01$	$123.94^{c} \pm 0.01$
Water Leave	$4.52^{d} \pm 0.01$	$9.11^{a} \pm 0.01$	$0.00^{e} \pm 0.00$	$0.45^{a} \pm 0.00$	$7.87^{a} \pm 0.04$	$146.45^{a} \pm 0.01$
Uziza Leave	$3.38^{e} \pm 0.02$	$1.73^{f} \pm 0.00$	$0.02^{d} \pm 0.01$	$0.10^{b} \pm 0.00$	$4.76^{b} \pm 0.01$	$60.55^{e} \pm 0.01$
Oha Leave	$6.53^{c} \pm 0.03$	$8.05^{b} \pm 0.02$	$0.04^{c} \pm 0.01$	$0.00^{d} \pm 0.00$	$1.03^{e} \pm 0.04$	$117.18^{d} \pm 0.01$
Scent leave	$1.62^{f} \pm 0.02$	$3.92^{d} \pm 0.03$	$0.05^{c} \pm 0.01$	$0.00^{d} \pm 0.00$	$0.01^{d} \pm 0.01$	$54.43^{d} \pm 0.01$

Table 1: Concentration of heavy metals in fruits and vegetables obtained from Ose market Onitsha, Anambra State.

Values are mean duplicate determination with ± standard deviation.

Similar superscripts on the same column are not significantly different ($P<0.05$).

Sample of Fruits	Copper mg/kg	Lead mg/kg	Cadmium mg/kg	Mercury mg/kg	Arsenic mg/kg	Zinc mg/kg
Apple	$1.62^{e} \pm 0.03$	$1.24^{f} \pm 0.01$	$0.04^{f} \pm 0.01$	$0.47^{a} \pm 0.00$	$3.02^{b} \pm 0.01$	$25.11^{g} \pm 0.01$
Water Melon	$2.84^{b} \pm 0.05$	$2.55^{d} \pm 0.01$	$0.12^{e} \pm 0.02$	$0.16^{e} \pm 0.00$	$2.33^{d} \pm 0.01$	$54.11^{a} \pm 0.02$
Pawpaw	$2.07^{b} \pm 0.01$	$7.60^{a} \pm 0.01$	$0.11^{e} \pm 0.01$	$0.20^{b} \pm 0.00$	$1.18^{e} \pm 0.01$	$35.59^{e} \pm 0.01$
Banana	$8.98^{a} \pm 0.02$	$2.09^{e} \pm 0.01$	$0.51^{b} \pm 0.01$	$0.19^{c} \pm 0.00$	$1.19^{e} \pm 0.01$	$40.61^{c} \pm 0.01$
Bush Mango	$1.94^{f} \pm 0.04$	$1.24^{f} \pm 0.01$	$0.21^{c} \pm 0.01$	$0.02^{f} \pm 0.00$	$3.48^{a} \pm 0.01$	$37.08^{d} \pm 0.02$
Guava	$1.96^{d} \pm 0.02$	$3.55^{b} \pm 0.01$	$0.54^{a} \pm 0.01$	$0.00^{g} \pm 0.00$	$3.46^{a} \pm 0.01$	$29.54^{f} \pm 0.01$
Cucumber	$2.81^{b} \pm 0.01$	$2.26^{c} \pm 0.01$	$0.18^{d} \pm 0.00$	$0.18^{d} \pm 0.01$	$2.43^{c} \pm 0.01$	$49.57^{b} \pm 0.01$

Sample of Vegetable	Copper mg/kg	Lead mg/kg	Cadmium mg/kg	Mercury mg/kg	Arsenic mg/kg	Zinc mg/kg
Pumpkin Leave	$8.92^{b} \pm 0.02$	$2.18^{e} \pm 0.01$	$0.15^{ab} \pm 0.01$	$0.18^{a} \pm 0.00$	$2.30^{d} \pm 0.00$	$120.45^{b} \pm 0.01$
Bitter Leave	$13.46^{a} \pm 0.01$	$4.92^{c} \pm 0.02$	$0.09^{c} \pm 0.01$	$0.01^{d} \pm 0.00$	$5.94^{a} \pm 0.01$	$119.88^{c} \pm 0.01$
Water Leave	$4.55^{c} \pm 0.02$	$8.71^{a} \pm 0.02$	$0.08^{c} \pm 0.01$	$0.02^{c} \pm 0.00$	$3.41^{c} \pm 0.00$	$135.66^{a} \pm 0.01$
Uziza Leave	$4.01^{e} \pm 0.01$	$1.84^{f} \pm 0.01$	$0.13^{b} \pm 0.001$	$0.00^{e} \pm 0.00$	$1.03^{f} \pm 0.01$	$53.04^{e} \pm 0.01$
Oha Leave	$4.51^{d} \pm 0.01$	$7.18^{b} \pm 0.01$	$0.16^{a} \pm 0.01$	$0.08^{b} \pm 0.00$	$5.03^{b} \pm 0.01$	$54.20^{d} \pm 0.01$
Scent Leave	$2.54^{f} \pm 0.01$	$3.19^{d} \pm 0.01$	$0.04^{d} \pm 0.01$	$0.00^{e} \pm 0.00$	$1.08^{e} \pm 0.01$	$37.24^{f} \pm 0.01$

Table 2: Concentration of heavy metals in fruits and vegetables obtained from Nkwo Ogbe Market Ihiala, Anambra State.

Values are mean duplicate determination with ± standard deviation.

Similar superscripts on the same column are not significantly different ($P < 0.05$).

Sample of Fruits	Copper mg/kg	Lead mg/kg	Cadmium mg/kg	Mercury mg/kg	Arsenic mg/kg	Zinc mg/kg
Apple	$2.00^{e} \pm 0.01$	$1.33^{f} \pm 0.01$	$0.21^{e} \pm 0.01$	$0.07^{d} \pm 0.00$	$3.28^{c} \pm 0.00$	$23.09^{g} \pm 0.01$
Water Melon	$3.68^{b} \pm 0.01$	$2.38^{d} \pm 0.01$	$0.08^{f} \pm 0.01$	$0.16^{bc} \pm 0.00$	$2.53^{d} \pm 0.00$	$56.09^{b} \pm 0.01$
Pawpaw	$9.76^{a} \pm 0.01$	$44.56^{a} \pm 0.02$	0.53 ± 0.00	$0.15^{bcd} \pm 0.00$	$1.21^{f} \pm 0.01$	$27.57^{f} \pm 0.01$
Banana	$2.68^{d} \pm 0.01$	$10.66^{b} \pm 0.01$	$0.48^{b} \pm 0.01$	$0.22^{b} \pm 0.00$	$4.86^{b} \pm 0.01$	$57.97^{a} \pm 0.01$
Bush Mango	$2.02^{e} \pm 0.01$	$1.36^{f} \pm 0.01$	$0.33^{c} \pm 0.01$	$0.75^{a} \pm 0.00$	$9.51^{a} \pm 0.01$	$33.48^{e} \pm 0.01$
Guava	$1.44^{f} \pm 0.01$	$1.64^{e} \pm 0.01$	$0.28^{d} \pm 0.01$	$0.14^{bcd} \pm 0.11$	$2.31^{e} \pm 0.01$	$40.66^{d} \pm 0.01$
Cucumber	$2.84^{c} \pm 0.01$	$2.88^{c} \pm 0.02$	$0.50^{a} \pm 0.01$	$0.08^{bc} \pm 0.10$	$2.51^{d} \pm 0.01$	$53.24^{c} \pm 0.01$
Sample of Vegetable	**Copper mg/kg**	**Lead mg/kg**	**Cadmium mg/kg**	**Mercury mg/kg**	**Arsenic mg/kg**	**Zinc mg/kg**
Pumpkin Leave	$2.11^{e} \pm 0.01$	$2.01^{d} \pm 0.01$	$0.10^{c} \pm 0.00$	$0.25^{b} \pm 0.00$	$5.91^{a} \pm 0.01$	$130.00^{b} \pm 0.00$
Bitter Leave	$6.72^{a} \pm 0.02$	$2.01^{d} \pm 0.01$	$0.22^{a} \pm 0.01$	$0.03^{d} \pm 0.00$	$3.76^{e} \pm 0.01$	$113.28^{c} \pm 0.01$
Water Leave	$3.48^{d} \pm 0.01$	$8.71^{a} \pm 0.01$	$0.21^{a} \pm 0.02$	$0.01^{f} \pm 0.00$	$4.12^{d} \pm 0.01$	$146.76^{a} \pm 0.01$
Uziza Leave	$3.70^{c} \pm 0.01$	$1.76^{e} \pm 0.00$	$0.20^{a} \pm 0.01$	$0.39^{a} \pm 0.00$	$4.60^{b} \pm 0.00$	$60.12^{d} \pm 0.01$
Oha Leave	$4.38^{b} \pm 0.01$	$7.25^{b} \pm 0.01$	$0.16^{b} \pm 0.01$	$0.09^{c} \pm 0.00$	$3.71^{b} \pm 0.00$	$51.64^{e} \pm 0.01$
Scent Leaves	$1.64^{f} \pm 0.01$	$3.52^{c} \pm 0.02$	$0.03^{d} \pm 0.00$	$0.03^{e} \pm 0.00$	$4.28^{c} \pm 0.01$	$28.08^{f} \pm 0.01$

Table 3: Concentration of heavy metals in fruits and vegetables obtained from Nkwo Market Nnewi, Anambra State.

Values are mean duplicate determination with ± standard deviation.

Similar superscripts on the same column are not significantly different ($P<0.05$).

Metals	Values in mg/kg	Source
Lead	0.1	FAO/WHO (JECFA, 2015)
Mecury	0.1	FAO/WHO (JECFA, 2015)
Cadmium	0.2	FAO/WHO (JECFA, 2015)
Arsenic	0.1	FAO/WHO (JECFA, 2015)
Copper	4.0	FAO/WHO 1999
Zinc	60	FAO/WHO 1999

Table 4: Permissible Guideline for Heavy Metals in Fruits and Vegetables.

Copper (Cu) mg/kg

Copper is an essential mineral for human health. It functions as biocatalysts, required for pigmentation in addition to iron, maintains a healthy central nervous system, prevents anemia and interrelated with the function of Zn and Fe in the body [26]. Copper is currently used as in many technical field of (transportation, manufacturing, electricity transmission), but also in agriculture (fungicides, herbicides and fertilizer [27]. Despite the health benefit of copper to human body, deficiency of copper in human body can cause adverse health effects. Deficiency of copper can lead anemia, low number of white blood cells, osteoporosis in infant and children, defects in connective tissue leading to skeletal problems [28]. The copper content of all the fruits and vegetable from the three market locations ranges from 1. 44 ± 0.01 mg/kg to 13.46 ± 0.01 mg/kg which is higher compared to the report of [29], but lower compared to the report of [30]. All the figures reported in all the samples differs significantly from each other ($P<0.05$) in all the three market locations except for apple/bush mango in table 3 (Nkwo Nnewi Market). Some of the fruits and vegetable samples had copper content within the standard permissible limit of (4.00 mg/kg) set by [43] except for Pumpkin leave, Water leaves and Oha leave in table 1 (Onitsha market), Banana, Pumpkin leave, Water

leave, Uziza Leave and Oha leave in table 2 (Ihiala Market) and Pawpaw, Bitter leaves and Oha in table 3 (Nkwo Nnewi Market). The high content of copper in some fruits and Vegetable from these locations may be from the use of chemical fertilizer and herbicides in Ihiala which is an agrarian area. The high population density of Onitsha generates high amount of biosolids (sewage sludge) which are used as fertilizer for farming [32]. Presence of industrial clusters in Nnewi generates industrial waste especially copper which is highly used in cable and wire production. Excess copper intake over time can cause anemia, liver and kidney damages and stomach and intestinal irritation [32].

Lead (Pb) mg/kg

Lead is slightly bluish bright silvery metals in a dry atmosphere. Lead is a highly toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world [5]. Lead exists in many forms in the natural sources throughout the world and is now one of the most widely and evenly distributed trace metals [7]. Lead is found in the earth crust and has been reported to emit from anthropogenic activities such as combustion of fossil fuel, mining, paint and battery products [33]. Lead can be absorbed and stored in human bones blood and tissues. Lead in human body has been reported to increase blood pressure in adults [14]. The result from the table 1-3 showed that the lead content of all the fruits and vegetables ranges from 1.23 ± 0.01 mg/kg to 10.66 ± 0.01 mg/kg. The range is slightly lower than the report of [11] and [14] but agreed with the range reported by [34]. All the fruits and vegetable from the three market locations had high lead content which is above the 0.1 mg/kg safe limit set by [31]. The high presence of Lead in these fruits and vegetables from the three locations in consideration may be from the high level of absorbing of lead from the soil. Nnewi and Onitsha are highly populated towns with various level of industrial and domestic waste production which finds their way to various farmland and irrigation waters. High level of traffic and emission of carbon from automobile and waste batteries may be responsible for the high content of lead in fruits and vegetable from Ihiala due to the location of the town near a major high way connecting two states in Nigeria [13]. All the samples had lead content that differs significantly from each other ($P<0.05$) except for pumpkin and bitter leaves from Nkwo Nnewi. The high level of lead in this research finding represents a significant health risk for the consumers of these fruits and vegetable. Acute lead poisoning causes liver disorder in livestock, kidney, liver and immune system damages in human [35].

Cadmium (Cd) mg/kg

Cadmium is one of the toxic heavy metals to human tissue even at low concentration and does not have any biological function [33]. Cadmium is a naturally occurring metal which exist in the earth crust at about 0.1 ppm. It is the seventh most toxic heavy metal, a bye product of zinc production which humans or animal may get exposed to at work [5]. Applications of agricultural inputs such as fertilizers, pesticides and biosolids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in the soil [32]. Cadmium is very biopersistent but has few toxicological properties and once absorbed by an organism, remains resident for many years. Cadmium is highly toxic metal which can affect the human body through both acute and chronic actions [36]. Cadmium content of fruit and vegetable are represented in table 1 3 representing the three locations, the cadmium ranges from 0.03 ± 0.00 mg/kg to 0.70 ± 0.00 mg/kg. The range was slightly lower compared to the report of [9]. Most of the fruits and vegetable from the three locations had cadmium content that falls within the 0.2 mg/kg safe limit set by [31] except for Paw paw, Apple and Bitter leaf in table 1, Bush mango and Guava in table 2, Apple, Cucumber, Paw paw, Banana, Bush mango, Guava, Bitter leave and Water leave in table 3. Nnewi market had more fruits and vegetables with higher cadmium content above the [31] safe limit compared to other locations; this may be from the large volume of industrial waste from various industrial clusters in Nnewi. All the fruits and vegetables from the three locations differs significantly ($P<0.05$) except for Apple/Paw paw, Banana/Bush mango, Oha/Scent leaves in table 1. Water melon/Paw paw, Uziza leave/Pumpkin leave, Bitter leave/Water leave in table 2. Cucumber/Paw paw, Bitter leave/Water leave/Uziza leave in table 3. Cadmium is predominantly found in fruits and vegetables due to its high rate of soil to plant transfer [37]. Again, the use of phosphoric fertilizer in vegetable and fruit garden can be a factor contributing to the high content of cadmium in all the locations [13]. Prolong accumulation of cadmium in human body can lead to some health issues such as kidney damages, renal disorder and human carcinogen [38]. Prolong consumption of some of these fruits and vegetable may lead to health system hazard due to accumulation of cadmium in body [11].

Mercury (Cu) mg/kg

Mercury is considered a global pollutant that comes from industrial location sources such as smelters or coal fired power plant [11]. Mercury belongs to same group of the periodic table with Zn and Cd. It is a liquid in standard ambient temperature ion, it is a naturally occurring metal which is shiny-white, odourless liquid and becomes colourless, odourless gas when heated. Mercury is very toxic and exceedingly bio accumulative [5]. It is a major non essential trace metal but not needed in food. It's presence in food suggests contamination [33]. It exist in three forms; metallic elements, inorganic salt and organic compounds, each of which possess different toxicity and bioavailable. Although mercury is a naturally found in soil, mercury can also find their way

to the soil through fossil fuel combustion, industrial processes, pesticides, herbicides and industrial liquid waste. Environmental contaminations of mercury can both be from natural sources and from anthropogenic emissions such as industrial activities and mining. Excessive exposure to mercury through contaminated foods and water has been associated with a wide spectrum of adverse health effects including damages to immune system and pituitary gland causing untold damages that may sometimes result into death [11]. The mercury content of fruits and vegetable arising from this study presented in table 1 3 from the three market locations ranges from 0.01 ± 0.00 mg/kg to 0.75 ± 0.00 mg/kg. In some cases, mercury was not detected in Oha leave and Scent leave in table 1, Uziza and Scent leave in table 2. The ranges are slightly higher than the range reported by [39] but agreed with the range [40] reported on pumpkin leaves. The mercury content of both fruits and vegetables from the three locations differs significantly at ($P<0.05$) except for Water melon/Paw paw/Cucumber, Banana / Bush mango and Bitter leave/Oha leave/Scent leave in table 1, Uziza leave/Scent leave in table 2, Water melon/Cucumber/Paw paw/ Guava in table 3. Some of the fruits and vegetable contains mercury limit that falls within the safe limit of 0.10 mg/kg set by [31] except for Water melon, Paw paw, Banana, Guava, Guava, Cucumber and Water leave in table 1, Apple, Water melon, Cucumber, Paw paw, Banana and Pumpkin table 2 and Water melon, Paw paw, Banana, Bush Mango, Guava, Pumpkin and Uziza leave in table 3, all are above the save limit set by [31]. Continuous consumption of these fruits can lead to potential health risk associated with mercury. Bush mango from Nkwo Nnewi had the highest mercury content of 0.75 mg/kg, this may be from industrial waste generated in Nnewi industrial clusters which finds their way to most farm lands. Mercury is associated with kidney damage, rheumatoid arthritis and disease of circulatory system [32,38].

Arsenic (As) mg/kg

Arsenic is a naturally occurring element that is widely distributed in the earth crust. Arsenic is one of the non essential heavy metals found in the environment. Arsenic exist both in organic and inorganic forms also in found in nature and in man made products, including some pesticides. Low levels of arsenic are found in soil, water and air [11]. Arsenic is taken up by plants as they grow, meaning that metals makes its way into our food. Humans may encounter arsenic by natural means, industrial sources, or from unintended sources. Human being are exposed to arsenic through natural activities such as volcanic activities, dissolution of mineral (particularly into ground water) exudates from vegetation and wind-blown dust, human activities such as mining, metal smelting, combustion of fossil fuels, agricultural pesticides production and use in timber with preservatives [31]. Exposure to Arsenic can cause health danger which could be acute or chronic basis, on acute basis the symptoms includes nausea, vomiting, diarrhea, cyanosis, confusion and hallucinations. On chronic basis, it could cause kerotosis, pigmentation/hypo pigmentation of feet hands and fingers, lung cancer, chronic bronchitis, chronic obstructive pulmonary disease, kidney and liver cancer [41]. The arsenic content of both fruit and vegetables from the three locations 1-3 ranges from 1.03 ± 0.01 mg/kg to 9.51 ± 001 mg/kg. The entire sample from the three market locations differs significantly ($P<0.05$) from each other except for Water melon/ Cucumber, Pumpkin leave/Uziza leave in table1, Paw paw/Banana, Bush mango/Guava in table 2 and Water melon/Cucumber in table 3. The range of arsenic in vegetable and fruits from the three locations agreed with range reported by [34] but lower compared to the range reported by [40]. The high content of arsenic in fruits and vegetables from these three locations may be from human activities such as combustion of fossil fuels, agricultural pesticide production and use in timber treatment which in directly enter the soil and are absorbed by plants [42]. All the fruits and vegetable had arsenic level above the safe limit of 0.1 mg/kg set by [31]. This means that consuming of these fruits and vegetable would certainly result in dangerous health consequences including kidney and liver damage, gastrointestinal effects and damages DNA [34].

Zinc (Zn) mg/kg

Zinc is the 23rd most abundant element in the earth's crust, its concentrations are rising unnaturally due to addition of zinc through human activities [38]. It is an essential mineral due to it exceptional biological and public health significance. Zinc is a transition metal with atomic number 30, atomic mass 65.4. It is naturally in soil but concentrations are rising unnaturally due to anthropogenic additions. Most zinc is added during industrial activities, such as mining coal, waste combustion and steel processing [32]. It is an essential element for normal growth and development in the body. It is widely used in industries such as galvanization, paint, batteries, smelting, fertilizer and pesticides, fossil fuel combustion, pigment, polymer stabilizer [38]. Waste water from these industries finds their way to the oceans and farmlands where crops normally absorb them. When zinc is present in large quantity in human body, it affects considerably human's health [38], although human health can handle large extent of zinc too much of it can still cause health problems [47]. Zinc content of both fruits and vegetables from the three market locations 1, 2 and 3 ranges from 22.94 ± 0.06 mg/kg to 146.76 ± 001 mg/kg. The entire sample from the three market locations differs significantly ($P<0.05$) except Water melon/ Cucumber, Oha leave/Scent leave in table 1. The range of zinc in vegetables and fruits from the three locations are high compared to the range reported by [11-13]. All the fruits from the three market locations had a zinc content within the 60 mg/kg permissible limit set by [43] except for Banana in table 1 which may be from solid

waste which are normally dumped around the root of banana which might contain zinc effluents. Some of the vegetables from the three market locations fall within the safe limit except for Pumpkin leave, Bitter leave, Water melon, Oha leave and Uziza leave in table 1, Pumpkin leave, Bitter leave and Water melon in table 2, Pumpkin leave, Bitter leave, Water melon and Uziza leave in table 3. The high content of zinc in some of these vegetables may be from fertilizer applied on the soil during cultivation or the water used for irrigation purpose. Prolong consumption of these vegetables may cause some health implications. Excess zinc in human body system can lead to depression, lethargy, neurological

Conclusion

From the investigation carried out so far in the determination of the concentration of heavy metals in fruits and vegetables obtained from three selected markets in Anambra State, it was observed that some of the fruits and vegetables showed low levels of heavy metals while some showed high levels of heavy metals in them. When compared with the standard permissible limit set by the FAO/WHO (Food and Agricultural Organization and World Health Organization), the levels of heavy metals were observed to be higher than the safe limit set by the FAO/WHO. This may be from the high level of pollution in the area under investigation. The levels of heavy metals obtained in some of the fruits and vegetables are not within the acceptable range and can pose a health hazard to the human life. Health authorities in collaborations with Agricultural ministries in these areas should work out models to ensure reduction in the heavy metal content of soil samples in areas that are used for cultivation so as to reduce the potential health hazard.

Authors Contribution

This is our Original collaborative work. Author CAE designed the study, conducted literature searches, managed analysis of the study and wrote the manuscript. Author SIO coordinated the entire study read and supervised the analyses and approved the final manuscript for publication. Author CCO assisted in writing the manuscript, discussion and literature search. Author ACL did the statistical analysis and result interpretation while author NEU assisted in discussing the work.

Conflict of Interest

The authors declare that they have no conflict interest.

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