IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)
e-ISSN: 2319-2402,p- ISSN: 2319-2399.Volume 12, Issue 10 Ver. I (October. 2018), PP 42-47
www.iosrjournals.org

Heavy Metal Levels in Cabbage, Carrots and Tomatoes Sampled at Marian Market, Calabar, Nigeria.

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Abstract: *Zn, Cr, Ni and Pb concentrations in cabbage, carrot and tomatoes were determined using Atomic Absorption Spectrophotometer. The order of concentrations of each heavy metals were Zn; tomato (0.20 ± 0.009mg/kg) > carrot (0.197± 0.03mg/kg) > cabbage (0.174 ±0.03mg/kg), all well below WHO permissible limit of 50mg/kg. Cr; carrot (0.187 ± 0.005mg/kg) > cabbage (0.0613 ± 0.002mg/kg) > tomato (0.0517 ± 0.008mg/kg), all below WHO limit of 1.3mg/kg. Ni; Carrot (0.112± 0.005mg/kg) > cabbage (0.1023± 0.03mg/kg) tomato, below detectable limit (BDL), all less than WHO limit of 10mg/kg. Pb; cabbage (0.06±0.004 mg/kg) > tomato (0.045± 0.005 mg/kg) > carrot (BDL), all below WHO limit of 2mg/kg. Since concentrations of all the heavy metals studied in cabbage, carrot and tomatoes were below WHO permissible limits for plants, consumers in Calabar are not at risk of Zn, Cr, Ni or Pb toxicity. We recommend that; (i) Soils be tested for the presence and levels of heavy metals, if high, bioremediation carried out before cultivation of vegetables (ii) Fruits and vegetables be properly covered during transportation from farm to market, to avoid contamination with heavy metals from the exhausts of vehicles. (iii) Fruits and vegetables should be thoroughly washed before consumption.*

Keywords:_Bioaccumulation, Biodegradable, Environmental Pollution, Health Effects, and Toxicity_

Date of Submission: 12-10-2018 Date of acceptance: 27-10-2018

I. Introduction

Fruits and vegetables are rich sources of vitamins, minerals, carbohydrates, amino acids and fibres. They also have beneficial antioxidant activities, and act as buffering agents for acidic substances produced during the digestion processes [1]. However, these plants may contain both essential and toxic elements, such as heavy metals, at a wide range of concentrations [2]. Heavy metal contamination of fruits and vegetables cannot be understated as these food stuffs are important components of the human diet. The intake of heavy metal contaminated fruit and vegetables may pose a risk to human health [3].

Heavy metals are elements and metalloids that have atomic densities greater than 5g/cm^3[4]. They have an atomic number greater than 20 [5]. Examples of heavy metals include; iron (Fe), lead (Pb), nickel (Ni), cadmium (Cd), chromium (Cr), copper (Cu) and zinc (Zn) among others. Heavy metals such as iron (Fe), tin (Sn), copper (Cu), manganese (Mn) and vanadium (V) occur naturally in the environment and could serve as plant nutrients, depending on their concentrations [6]. Other heavy metals like cadmium (Cd), lead (Pb) and nickel (Ni) though not essential for plant growth, are readily taken up and accumulated by common vegetables and plants as a whole. These absorbed metals get bio-accumulated in the roots, stems, fruits, grains and leaves of plants [7].

Environmental pollution by heavy metals, even if it is at low concentrations and the long term cumulative health effects that go with it, are of major health concern all over the world. They are not biodegradable, have long biological half-lives, and have the potential that can enable them be accumulated in different body organs, leading to unwanted side effects [8, 9]. Some of these elements are important for the normal functions of the body, but when their concentrations exceed the optimum limit, they cause acute and chronic poisoning, leading to reduced quality of life, and even death]10]. Metals such as lead, chromium, cadmium and copper are cumulative poisons.

The bioaccumulation of lead (Pb) in the human body interferes with proper functioning of the mitochondria, impairing respiration, causing constipation, swelling of the brain, paralysis and can eventually lead to death [11]. It is a well-known neurotoxin; with the impairment of development in children as its most critical effect [12]. On the cellular or molecular level, lead may permit or enhance carcinogenic events involved in DNA damage, inhibit DNA repair and regulation of tumor suppressor and promoter genes [13]. It is a toxic element that can be harmful to plants, although some plants can accumulate large amounts of it without any visible changes in their appearance. The permissible limit of lead in plants, recommended by WHO is 2mg/kg [14].

Chromium (Cr) exists in 2^+, 3^+, 5^+, and 6^+, oxidation states. Chromium in 6^+, oxidation state is the most toxic. Ingestion of chromium (vi) has been linked to stomach tumors, allergic contact dermatitis, lung cancer, asthma or damage to the nasal epithelia and skin [15]. In the cell, chromium toxicity may result in chromosome abnormalities [16]. The permissible limit of chromium in plants recommended by WHO is 1.40mg/kg [14].

Zinc is one of the important heavy metals that plays a vital role in the physiological and metabolic processes of many organisms. Ingestion of a high amount of zinc results in nausea, vomiting, pain, cramps and diarrhoea[17]. The permissible limit of zinc in plants is 50mg/kg [14].

Nickel (Ni), although a micronutrient to most organisms, is known to be carcinogenic when consumed in high quantities [18]. It can cause respiratory disorder, lung cancer, dermatitis and inhibition of enzymatic activities in the body. It also inhibits photosynthesis and respiration in plants [19]. The recommended limit for nickel in plants is 10 mg/kg [14].

Though heavy metals are natural constituents of the soil, their concentrations and other pollutants are increased through discharges into the environment by industrial activities, automobile exhausts, heavy-duty electric power generators; waste burning and the use of pesticides in agriculture. Man, animals and plants take up these metals from the environment through the air, water and food[20]

Plants including vegetables and fruits take up heavy metals and accumulate them in their edible and non-edible parts at quantities high enough to cause clinical problems to both animals and human beings [21]. [22], reported that vegetables contaminated with lead (Pb) and cadmium(Cd) in Romania, significantly contributed to decreased human life expectancy (9-10 years) within the affected areas.

Cadmium and lead are the most toxic elements for man [23]. In terms of environmental concentration, lead is the heavy metal closest to the level in which toxic signs manifest than any other substance [24]. Other elements such as Cr, Co and Ni, although essential for man, but at concentrations higher than those recommended, they may cause metabolic disorders. Moreover, an increasing awareness in terms of the importance of vegetables and fruit to human diet suggests that the monitoring of heavy metals in food crops should be carried out frequently.

Vegetables and fruits are important components of healthy diets, and the varieties are as important as the quantity. No single fruits or vegetable provides all of the nutrients needed to be healthy. A diet rich in vegetables and fruit can lower blood pressure, reduce risk of heart disease and stroke, prevent some types of cancer, lower risk of eye and digestive problems, and have a positive effect upon blood sugar which can help keep appetite and/or diabetes in check. Although, all fruits and vegetables likely contribute to this benefit, green leafy vegetables (such as lettuce, spinach), cruciferous vegetables (such as cabbage, broccoli) and citrus fruits (such as oranges, lemons) make important contributions [25].

The main sources of heavy metals in crops are their growth media (soil, air, and nutrient solutions) from which these heavy metals are taken up by the roots or foliage [26].

Tomato is an edible often red fruit of the plant *Solanum lycopersicum*, commonly known as the tomato plant. The plant belongs to the Nightshade family, *solanaceae* [27]. Tomato is consumed in diverse ways, including raw or as ingredient in many dishes, sauces, salads and drinks. While tomatoes are botanically berry-type fruit, they are considered culinary vegetables as an ingredient or side dish for savory meals. It also contains lycopene a known antioxidant that fights cancer [28]. Tomatoes are acidic, making them especially easy to preserve in home canning whole, in pieces, as tomato sauce or paste. A tomato is 95% water, contains 4% carbohydrates and less than 1% each of fat and protein. A 100 grams of raw tomatoes supplies 18 calories of energy and are a moderate source of vitamin C [29]. Tomato also contains lycopene which is a very powerful antioxidant that helps prevent the development of cancer. [30], reported that heavy metal levels reported in tomatoes were higher in the skin than in pulp. The pulp contamination of fruits and vegetables may be related to pollutants in farm soil, while the skin contamination may depend on air pollution from highway traffic [31]. Tomato tends to accumulate more of Fe, Zn and Cu than any other heavy metal since it is essential for its growth.

Cabbage is a leafy green annual vegetable crop grown for its dense-leaved heads. It descends from the wild cabbage *Brassicaoleracea*. It is a multi-layered vegetable. As a vegetable, cabbage can be prepared in many different ways for eating. It can be pickled, fermented for dishes or eaten raw. Cabbage is a good source of vitamin K, it also contains dietary fibre. Cabbage is also a moderate source of vitamin B6. [32]. It can be consumed as a laxative [33] and cabbage juice could be used as an antidote for mushroom poisoning [34]. Cabbage also contains the heavy metals Fe, Zn and Cu in small quantities. [32].

Carrot is a root vegetable, usually orange in color, though purple, black, red and yellow cultivars exist. Carrots are a domesticated form of the wild carrot, *Daucuscarote*. It belongs to the family *apiaceae*. The roots and the greens are commonly eaten. The roots contain high quantities of alpha and beta-carotene, vitamins B and K. Carrots are widely used in many cuisines, especially in the preparation of salads [35]. Carrot contains the heavy metals Fe, Zn, and Cu in small quantities [36].

The aim of this work was to determine the presence and concentration of the heavy metals Pb, Cr, Zn, Ni in carrots, cabbage and tomatoes sampled from Marian Market, Calabar**.**

II. Materials and Methods

2.1 Study Area

The study area Calabar metropolis lies between latitudes 4°54' and 4°58' N and longitude 8°15' and 8°25' E. Marian Market is located in the heart of Calabar Municipality. The average annual temperature is 26.1ºC, while the average annual rainfall is 2750mm. This site was chosen for the collection of these samples because, it is the gateway or entry point through which fruits and vegetables from the northern part of the country are brought into Calabar for sales within the metropolis and adjoining local government areas.

2.2 Sample Collection

Fresh and whole carrots, cabbages and tomatoes were randomly bought from different traders at Marian Market on arrival of the fruits and vegetables from the north. The different samples were pooled into separate and labelled polyethylene bags and stored in the refrigerator in the laboratory.

2.3 Pretreatment and digestion of the samples

Samples were taken to the Chemistry Research Laboratory, University of Calabar (Unical) and spread on paper to dry at room temperature. The samples were washed with deionized water and pulverized using a mortar and pestle separately. To one gram (1g) of ground sample in a digestion flask, 20ml of nitric acid and 5ml of perchloric acid were added to form a mixture. This mixture was then heated to a clear solution. The digest was diluted to 100ml with deionised water in a standard volumetric flask for analysis.

2.4 Determination of nickel by Heptoxime method

To 5ml of each sample in a beaker was added 2ml of sodium tartrate, followed by 2 drops of methyl orange indicator and enough 6N sodium hydroxide to make the solution alkaline. One (1) ml of acetic acid, 2ml of Cupterron reagent, 5ml of chloroform were added and the mixture shook for 5minutes in a separator funnel forming a yellow coloured complex. The complex was then added to 1ml of hydroxylaminehydrochloride and allowed to stand for 10min. Thereafter, 5ml of heptoxime reagent, 10ml of chloroform were added to extract nickel from the mixture. Finally, 5ml of 1N hydrochloric acid was added to the extract and the concentration was determined at a wavelength of 445nm using Spectrophotometer Model: Varian.

2.5 Determination of chromium (Cr) using colorimetric method

To 10 ml of each sample in a test-tube was added1ml of phenylcarbazide solution and shaken to mix well. The mixture was allowed to stand for 10min for full color development. Three (3) ml was measured into a cuvette and the concentration was determined at a wave length of 540nm using Spectrophotometer Model: Varian.

2.6 Determination of lead (Pb)

To 5 ml of the diluted sample in a separating funnel was added 2ml of dithizone reagent. The chloroform layer was decanted and the lower one retained. Three (3) ml of the extract was measured into a cuvette and used to determine the concentration of lead at the wavelength of 510nm using Spectrophotometer Model: Varian.

2.7 Determination of zinc (Zn) using Zincon Method

To 5 ml of the sample in a small beaker; 0.1g of sodium absorbate, 3ml of borate-sodium buffer of pH 9.0, 1ml of potassium cyanide and 1ml of Zincon reagent were added and shaken thoroughly for 2minutes. The mixture was allowed to settle. One (1) ml of cyclohexanone was added to the mixture and allowed to stand for 2 minutes, the concentration was then determined at the wavelength of 620nm using Spectrophotometer Model: Varian.

III. Results and Discussion

Metals are known to be present in the soil and water, consequently crops planted on contaminated soil or/and irrigated with polluted water tend to absorb them. In effect these metals become stored in parts of plants including the fruits, leaves and roots.

On analysis of tomatoes, carrots and cabbage bought from Marian Market, Calabar, it was found that tomatoes contained the highest amount of Zn 0.207±0.00090 mg/kg, followed by carrot 0.197±0.00030mg/kg and cabbage 0.174 ±0.000031mg/kg,(see Table 1).

Carrot had the highest quantity of Cr 0.187±0.00046mg/kg, followed by cabbage 0.0613 ±0.00017 mg/kg, and tomato the least 0.0517 ± 0.000082 mg/kg, (see Table 1).Cabbage had the highest amount of Pb 0.06 ± 0.0003924 mg/kg, followed by tomato 0.045 ± 0.000050 mg/kg while the amount in carrot was below detectable level (see Table 1).Carrot had the highest amount of Ni 0.112 ± 0005 mg/kg, followed by cabbage 0.1023 ± 0.00025 mg/kg, while the amount in tomato was below detectable level, (see Table 1).

Table 1.0: Mean Concentration (mg/kg) of Heavy Metals in Fruits and Vegetables bought from Marian Market, Calabar.

Fruits and Vegetables	Zn	Pb	Cr	Ni
Cabbage	0.174 ± 0.03	0.06 ± 0.004	0.0613 ± 0.002	0.1023 ± 0.003
Carrot	0.197 ± 0.030	BDL	0.187 ± 0.005	0.112 ± 0.005
Tomato	0.20 ± 0.009	0.045 ± 0.005	0.0517 ± 0.008	BDL
WHO/FAO permissible limit of metals	50mg/kg	2mg/kg	1.3mg/kg	10mg/kg

Means of triplicates ± standard deviation.

This study was to determine the presence and concentration of the heavy metals; Pb, Cr, Ni and Zn in carrot, cabbage and tomatoes bought from Marian Market Calabar. Though heavy metals are natural constituents of the soil, their concentrations and other pollutants are increased through discharged into the environment by industrial activities, automobile exhausts, heavy-duty electric power generators; waste burning and the use of pesticides in agriculture, as well as irrigation of plants using contaminated sources. Man, animals and plants take up these metals from the environment through the air, water and food [20]

Most of these heavy metals though essential for growth and development, have limits beyond which they can harm plants and human beings, on the consumption of these plants.

Heavy metals are not biodegradable and have long biological half-lives and have potentials that can enable them permeate and be residual in different body organs [7, 9] including roots, leaves, stems, fruits and other parts of plants. They are then transferred to humans when such contaminated plants are eaten.

Interactions with the traders on fruits and vegetables in Marian Market revealed that these fruits and vegetables are not always thoroughly washed because of their perishable nature. The traders stated that thorough washing hastens decay of fruits and vegetables that are perishable. So they only tend to clean the fruits by removing sand and other visible dirt. This implies that metals from soil, highway traffic or preservatives are not thoroughly removed from the fruits and vegetables through washing before being sold in the market.

Some of these metals are known to be harmful to human beings. Some diseases caused by these metals include the following; allergic contact dermatitis caused by chromium [15]. In this study the concentration of chromium ranged between 0.0517 mg/kg and 0.187 mg/kg. These values are well below the permissible limit for the element [14]. This may suggest that consumers of carrots, cabbage and tomatoes in Calabar are not at risk of developing allergic contact dermatitis.

Nickel is carcinogenic when consumed in high quantities [18]. In this study the concentration of nickel ranged between 0.1023 mg/kg and 0.112 mg/kg in cabbage and carrot, but it was not detected in tomatoes. The WHO permissible limit of nickel in plants is 10 mg/kg. It follows that consumers of cabbage and carrots in Calabar may likely not develop cancer. Also tomato contains ~~lycopenea~~lycopene a known antioxidant that fights cancer [28].

Zinc though required by the body in small quantities, can cause serious health problems including diarrhoea when ingested in high quantities [18]. In this study the concentration of zinc ranged between0.174 mg/kg and 0.20 mg/kg. The permissible limit for zinc is 50 mg/kg. The values obtained in this study are within the range allowed and therefore may pose no danger to consumers [14].

Lead can cause constipation, swelling of the brain and/or paralysis leading to death [11].It is a well-known neurotoxin; with the impairment of development in children as its most critical effect [12]. In this study the average concentration of lead was 0.06 mg/kg in cabbage and 0.045 mg/kg in tomato. It was not detected in carrots. These values are well below the permissible limit in plants, 2 mg/kg, so their consumption may not pose any danger [14].

Because of the health and nutritional benefits of fruits and vegetables to man, taking into account the need to prevent the consumption of high amounts of these heavy metals through fruits and vegetables, the World Health Organization [14] established permissible limits of these metals in fruits and vegetables. Concentrations above these limits in plants including fruits and vegetables, are deemed poisonous and unfit for human consumption. However, in this study, none of heavy metals investigated in cabbage, carrot and tomatoes was above the WHO permissible limit.

IV. Conclusion and Recommendations

In this study, the concentration of Zn, Pb, Cr and Ni in carrot, cabbage and tomatoes; sampled from Marian Market Calabar, were all below the permissible limits [14].

Although the concentrations of the heavy metals evaluated were not of injurious levels, it is advised that the populace be sensitized on the dangers inherent in consuming fruits and vegetables that contain high amounts of heavy metals.

The following are recommended:

i) Soils should be tested for the presence of heavy metals; if high levels are found, bioremediation should be carried out before the cultivation of fruits and vegetables.
ii) Fruits and vegetables should be properly covered before transportation from the farm to the market, to avoid contamination with heavy metals from the exhaust of vehicles.
iii) Fruits and vegetables should be thoroughly washed before consumption.

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Ndibukke, E. E. O. "Heavy Metal Levels in Cabbage, Carrots and Tomatoes Sampled at Marian Market, Calabar, Nigeria.." IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT) 12.10(2018): 42-47.