EVALUATION OF HEAVY METALS CONTENT IN VEGETABLES OBTAINED FROM AZARA COMMUNITY OF NASARAWA STATE

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A PROJECT SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, NASARAWA STATE UNIVERSITY, IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF DEGREE OF PGD IN BIOCHEMISTRY AND MOLECULAR BIOLOGY

DEPARTMENT OF BIOCHEMISTRY AND MOLECULAR BIOLOGY

FACULTY OF NATURAL AND APPLIED SCIENCES

NASARAWA STATE UNIVERSITY, KEFFI

NIGERIA

DECLARATION

I hereby declare that this project Title "Presence of Heavy Metals in Vegetables Consumed by Azara Community of Nasarawa State" has been written by me and it is a report of my research work. It has not been presented in any previous application for state diploma or degree. All quotations are indicated and sources of information specifically acknowledged by means of references.

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CERTIFICATION

This project "Presence of Heavy Metals in Vegetables Consumed by Azara Community of Nasarawa State" meets the regulations governing the award of postgraduate diploma, of the school of Postgraduate studies, Nasarawa State University, Keffi, and is approved for its contribution to knowledge.

-- 22/01/2020 ------------------------------

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DEDICATION

This work is dedicated to God Almighty, my heavenly father and my parents Mr. And Mrs. James Otubu.

ACKNOWLEDGEMENT

I am highly indebted to God Almighty for seeing me through my project research and to all those who in one way or the other contributed to the success of this research project.

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ABSTRACT

Heavy metals refer to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentration. Heavy metals are dangerous because they tend to bio accumulate in biological system.Vegetables constitute an important part of human diet since it contains carbohydrates, proteins, vitamins as well as trace elements. Contamination of vegetables with heavy metals from soil and atmosphere poses threat to its quality and safety.The levels of heavy metals (Zn, Barium, Cd, Cu, and Pb) in soils and some edible vegetables in Azara community were determined using spectrophotometer method.Soils and vegetable samples were collected at random in Azara community. The concentration of heavy metals in soil samples in mg/kg were determined $BaSO_4$ (0.13), Zn (0.22), Cd (0.02), Cu (0.63) and Pb (0.62) and in vegetables $BaSO_4$ (1.05), Zn (0.22), Cd (0.01), Pb (0.63), and Cu (0.9).The concentration of heavy metals in soil and vegetables from Azara community showed low levels of all heavy metals except for Barite which levels were high in both vegetables and soils. There is need for continuous monitoring of contamination level of heavy metals since they can bio-accumulate to toxic levels. Further research should be carried out and the frequency of the sampling should be taken into consideration the types of heavy metals and the seasonal flow of crop cultivation to show which season heavy metals accumulates the more.

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentration. Heavy metals are natural components of the earth's crust, they cannot be degraded or destroyed to small extent they enter the human or animal body via food, drinking water and air. As trace elements some heavy metals e.g copper, zinc, selenium are essential to maintain the metabolism of the human body. However at higher concentration they can lead to poisoning. Heavy metals are dangerous because they tend to bio accumulate.

Bioaccumulation means an increase in the concentration of chemical in a biological organism over time, compared to the chemical's concentration in the environment.

Compounds accumulated in living things anytime they are taken up and stored faster than they are broken down or metabolized.

Heavy metals occur in the soil in soluble form and in combine state. However, only soluble exchangeable and chelated metal species in soils are mobile and hence available to plants (Hector *et al.,* 2011). The accumulations of heavy metals in edible parts of vegetables absorb heavy metals from soil, air and water. Vegetables are important part of human diet, in addition to this it also serves as a source of components proteins, vitamins, iron, and calcium which have marked health effects.

Food safety is a major public concern worldwide. During the last decades the increasing demand of food safety has stimulated research regarding the risk associated with consumption of foodstuffs contaminated by pesticides, heavy metals and or toxins (D'Mello *et al.*, 2003).

Heavy metals are a general collective term which applies to the group of metals and metalloids with an atomic density greater than $4 g/cm^3$. Although it is a loosely defined term (Duffus, *et al.*, 2002) it is widely recognized and usually applies to the widespread contaminants of terrestrial and fresh water ecosystems.

1.2 Statement of Problem

Due to the presence of mineral deposit and mining activities in Azara town there is a likelihood that heavy metals could be present in large or small quantities as impurities to the desired metals that are mined. Their presence could lead to adverse effects on the health and life span of the people

1.3 Aim and Objective

- Investigate the presence of heavy metals in major vegetables consumed in Azara community.
- Ascertain the percentage of heavy metals present in the edible vegetables grown in Azara.

1.4 Significance of the Study

A comparison will be made between data collected and WHO standards and compared to tolerable limits.

This will give an insight into the health status of Azara community and also aid in making predictions for the future, should mining activities continue without structures put in place to check excesses.

1.5 Scope of the Study

The research covers only the major vegetables consumed by Azara community which may be seasonal or perennial.

CHAPTER TWO

LITERATURE REVIEW

2.1 Theoretical Review

Vegetables constitute an important part of human diet since they contain carbohydrates, proteins, vitamins, minerals as well as trace element. The contamination of vegetables with heavy metals due to soil and atmosphere poses threat to its quality and safety. Dietary intake of heavy metals also poses risk to animals and human health. High concentration of heavy metals (Cu, Cd, and Pb) in fruits and vegetables were linked to high prevalence of upper gastrointestinal cancer (Turkdogan *et al.,*2003)

Vegetables also act as buffering agents for acidic substances obtained during the digestion process.

However, these plants may contain both essential and toxic elements, such as heavy metals, at a wide range of concentrations (Bahemuka *et al.*, 1999). Metals such as lead, chromium, copper, cadmium, zinc etc are cumulative poisons. These metals cause environmental hazards and are reported to be exceptional toxic (Ellen *et al.,*1990). Contamination of vegetables with heavy metal may be due to irrigation with contaminated water, the addition of fertilizers and metal based pesticides, industrial emissions, transportation, the harvesting process, storage or at point of sale. It is well known that plants take up metals by absorbing them from contaminated soil as well as from deposit on parts of the plants exposed to the air from polluted environments (Khairiah *et al.,*2004) Lead and cadmium are among the most abundant heavy metals and are particularly toxic (WHO 1992). Excessive content of these metals in food is associated with a number of diseases, especially of the cardiovascular, renal, nervous and skeletal systems (WHO 1995). These metals are also implicated in carcinogenesis, mutagenesis, and teratogenesis (Radwan and Salama 2006)

Other metals such as copper and zinc are essential for important biochemical and physiological functions and necessary for maintaining health throughout life (Linder *et al.*, 1996)

Thirty five metals pose a threat to human health, 23 of which are heavy metals (Chojnacka *et al.*, 2005). Studies report various effects of heavy metals in drinking water (Duffus *et al.*, 2002) According to the International Agency for Research on Cancer (IARC), inorganic As and Cd are classified as human carcinogens (WHO 1992). As is related to cancer risk and skin damage, Cd is linked to kidney damage and cancer. Other effects such as heart diseases and blood cholesterol from Sb, Anaemia from Pb, kidney and liver damage from Hg, and gastrointestinal disorder from Cu are also reported (Radwan and Salama. 2006)

2.1.1 Barite Toxicity (BaSO4)

Barite mining plays a significant role in income generation, employment among artisan miners in Nasarawa State of Nigeria (Oelofse *et. al.*, 2008). Barite is the chief constituent of lithopone paint. It is extensively used as an inert volume and weight filer in drilling mud, rubber, glass, paper. It is also widely used in several chemical industries (Abubakar *et al.,* 2015). Veins of barite up to 1.8m wide and more than a kilometre long are associated with lead zinc lodes· in many parts of Nasarawa State. The principal known occurrences are at Azara, Aloshi, Akiri, Wuse and Keana. Reserves of about 100,000 tons of good quality barite have been proved more recently in the Azara area by the Nigerian Mining Corporation.

Indeed, at the time of writing this article, about 18 veins measuring about 2m x 1000m were being mined under the supervision of the Nigerian Mining Corporation (Oelofse *et al.,* 2008). Barite was first detected in Azara in the early 1960s (Courtesy of the Geological Survey of Nigeria, 1965).

The Nigeria Barite Mining and Processing Company (NBMPC) Ltd., incorporated in 1988 was charged with the exploration and exploitation of barite in Azara and in any other part of Nigeria where this mineral was found. The NBMPC Ltd is wholly owned by the Nigeria Mining Corporation with its Headquarters in Jos. Initial reconnaissance revealed eighteen (18) veins at areas like Azara, Aloshi, Akiri, Wuse and Keana in Awe Local Government Area. Of these eighteen (18) veins, detailed exploration works were carried out in fie (5), and these revealed a total reserve of seven hundred and thirty thousand (730,000) metric tons of barite (Oelofse, *et al.,* 2008). The mining of barite at Azara, provides a good source of income to the inhabitants, supplementing their income from farming. What is more, almost 80% of the total national supply of barite comes from Azara (Obaje, *et. al*., 2006). Yet barite mining poses threats and hazards that can jeopardize the environment by disrupting the ecological balance, water quality, wildlife, natural landscapes, agricultural lands, vegetation and economic trees (Aigbedion and Iyayi, 2007; Adegboye, 2012). Contaminants and toxic compounds from barite mining activities jeopardize the quality of surface and underground water, making it unsafe for drinking and industrial usage and disturbing the hydrology of the area where barite mining takes place (Roy *et al.*,2003). In Africa (Nigeria inclusive), poverty coupled with poor policy frameworks to address mining activities is a major threat to environmental sustainability (Oelofse, and Turton, 2008). With the increasing number of artisan miners in Africa, water quality has been polluted due to contamination (Oelofse and Turton, 2008).

The contamination by barite mining can result in profound irreversible destruction of the environment. In many cases the polluted sites may never be fully restored, because pollution is so persistent that there is no available remedy (EEB, 2000). Due to improper planning and negligence of barite mining regulations, an appreciable amount of environmental degradation and ecological damage to water occurs in almost every barite site in Azara-Awe.

The key questions are whether surface and groundwater supplies will remain fit for human consumption, and whether the quality of water in barite mining sites will remain adequate to support humans and wildlife (Anirudha, 2005). Barite can dissolve in water, and when it does, it can cause environmental and health hazards (Nirmal, *et al.,* 2011). Generally, mining of solid minerals has been identified as a major source of heavy metals in the environment because such minerals generally contain both heavy and essential metals.

Barium is a dense alkaline earth metal that occurs in nature as a divalent cation in combination with other elements. In addition to its natural presence in the Earth's crust, and therefore its natural occurrence in most surface waters, barium is also released to the environment via industrial emissions. The residence time of barium in the atmosphere may be up to several days. Barium sulfate exists as a white orthorhombic powder or crystals. Barite, the mineral from which barium sulfate is produced, is a moderately soft crystalline white opaque to transparent mineral. The most important impurities are iron (III) oxide, aluminium oxide, silica, and strontium sulfate.

Barite is used primarily as a constituent in drilling muds in the oil industry. It is also used as filler in a range of industrial coatings, as dense filler in some plastics and rubber products, in brake linings, and in some sealants and adhesives. The use dictates the particle size to which barite is milled. For example, drilling muds are ground to an average particle diameter of 44 µm, with a maximum of 30% of particles less than 6 µm in diameter. There is no evidence that barium undergoes biotransformation other than as a divalent cation. The toxic kinetics of barium ions would be expected to be the same as the toxic kinetics of soluble barium salts (ATSDR 1992).

Studies in rats using a soluble salt (barium chloride) have indicated that the absorbed barium ions are distributed via the blood and deposited primarily in the skeleton. The principal route of elimination for barium following oral, inhalation, or intratracheal administration is in the faeces. Following introduction into the respiratory tract, the appearance of barium sulfate in the faeces represents mucociliary clearance from the lungs and subsequent ingestion.

In humans, ingestion of high levels of soluble barium compounds may cause gastroenteritis (vomiting, diarrhoea, and abdominal pain), hypopotassaemia, hypertension, cardiac arrhythmias, and skeletal muscle paralysis. Insoluble barium sulfate has been extensively used at large doses (450 g) as an oral radiocontrast medium, and no adverse systemic effects have been reported. No experimental data are available on barium sulfate; however, due to the limited absorption of barium sulfate from the gastrointestinal tract or skin, it is unlikely that any significant systemic effects would occur.

The acute oral toxicity of barium compounds in experimental animals is slight to moderate. Intravenous infusion of barium chloride results in increased blood pressure and cardiac arrhythmias (Borzelleca *et al.*,1988)

Barium hydroxide is strongly alkaline and therefore corrosive. Barium nitrate caused mild skin irritation and severe eye irritation in rabbits. The lack of reports of skin or eye irritation in humans, despite its widespread use, suggests that barium sulfate, often used as a contrast medium, is not a strong irritant. Useful information on the sensitization potential of barium compounds was not identified (Hamilton *et al.*, 1972)

2.1.2 Zinc Toxicity

Zinc is an essential trace element that can cause symptoms of deficiency and can be toxic when exposures exceed physiological needs. The relationship between intake and health is affected by physiological factors (homeostasis) and by extrinsic factors that affect the availability of zinc for absorption and utilization or that interfere with the metabolism of zinc and biochemical processes that require zinc, in nature these relationships are not necessarily symmetrical.(WHO 1992)

The homeostatic model defines the principle of an acceptable range of exposures for an essential trace element like zinc. In the acceptable range, zinc, which is necessary for various metabolic processes, embryonic development, cellular differentiation and cell proliferation, provides the substrates for expression of the genetic potential of the individual, i.e., optimum growth, health, reproduction and development. Environmental levels of zinc providing exposures or intakes within the acceptable range do not produce adverse effects among the general human population or the environment. Nutritional zinc deficiency in humans has been reported in a number of countries (Chen *et al.*, 1985).

Acute toxicity arises from the ingestion of excessive amounts of zinc salts, either accidentally or deliberately as an emetic or dietary supplement. Vomiting usually occurs after the consumption of more than 500 mg of zinc sulfate. Mass poisoning has been reported following the drinking of acidic beverages kept in galvanized containers; fever, nausea, vomiting, stomach cramps, and diarrhoea occurred 3–12 hours after ingestion. Food poisoning attributable to the use of galvanized zinc containers in food preparation has also been reported; symptoms occurred within 24 hours and included nausea, vomiting, and diarrhoea, sometimes accompanied by bleeding and abdominal cramps (Elinder *et al*., 1986) Manifest copper deficiency, which is the major consequence of the chronic ingestion of zinc (Cousins *et al*.,1990), has been caused by zinc therapy (150–405 mg/day) for coeliac disease, sickle cell anaemia, and acrodermatitis enteropathica (Porter *et al*.,1977, Prasad *et al*., 1987). Impairment of the copper status of volunteers by dietary intake of 18.5 mg of zinc per day has been reported (Festa et al.,1985). Zinc supplementation of healthy adults with 20 times the recommended dietary allowance for 6 weeks resulted in the impairment of various immune responses (Chandra et al.,1984). Gastric erosion is another reported complication of a daily dosage of 440 mg of zinc sulfate (Elinder *et al*., 1986) Daily supplements of 80–150 mg of zinc caused a decline in high-density lipoprotein cholesterol levels in serum after several weeks (Elinder *et al*., 1986) but this effect was not found in some other studies. In an Australian study, no detrimental effect of 150 mg of zinc per day on plasma copper levels was seen in healthy volunteers over a period of 6 weeks (Samman et al., 1988). Acute toxic effects of inhaled zinc have been reported in industrial workers exposed to zinc fumes (Elinder *et al*.,1986); the symptoms include pulmonary distress, fever, chills, and gastroenteritis. In a small-scale study on zinc-refinery workers, no evidence was found of increased mortality from any type of cancer (Elinder *et al*., 1986). In subjects with low baseline levels of serum zinc, no significant difference in the risk of death from cancer or cardiovascular diseases, as compared with those with high baseline levels, was observed (Koop et al., 1968)

2.1.3 Exposure of General Population.

According to WHO the estimated average daily dietary zinc intakes range from 5.6 to 13 mg/day in infants and children from 2 months up to 19 years and from 8.8 to 14.4 mg/day in adults aged 20–50 years. Flesh foods (i.e., meat, poultry, fish and other seafood) are rich sources of readily available zinc, while fruits and vegetables contain relatively low zinc concentrations. For omnivorous adults, more than one-third of dietary zinc can be provided by flesh foods, whereas for vegetarians, plant-based foods are the major dietary source. Mean daily intake of zinc from drinking-water is estimated to be < 0.2 mg/day.

2.1.4 Lead Toxicity

Lead is a bluish or silvery grey soft metal with atomic number 82, atomic weight 207.19, specific gravity 11.34, melting point 327.5°c and boiling point 17400°C. It is the most common industrial metal that has become widespread in air, water, soil and food.

Lead is slightly soluble in water and s transported mainly through the atmosphere. It behaves like calcium in the body and accumulates in bone, liver, kidney and other tissues.

Lead is a toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world. Human exposure to lead is estimated to account for 143000 deaths every year and 0.6% of the global burden of disease (WHO 1995). Lead is a cumulative toxicant that affects multiple body systems, including the neurological, haematological, gastrointestinal, cardiovascular and renal systems. Chronic exposure commonly causes haematological effects, such as anaemia, or neurological disturbances, including headache, irritability, lethargy, convulsions, muscle weakness, ataxia, tremors and paralysis. Acute exposures may cause gastrointestinal disturbances (anorexia, nausea, and vomiting, abdominal pain), hepatic and renal damage, hypertension and neurological effects (malaise, drowsiness, and encephalopathy) that may lead to convulsions and death. (WHO 1995)

Children are particularly vulnerable to the neurotoxic effects of lead, and even low levels of exposure can cause serious and, in some cases, irreversible neurological damage. Childhood lead exposure is estimated to contribute to about 600 000 new cases of children with intellectual disabilities every year (WHO 1995).

The clinical diagnosis of lead poisoning can be difficult when there is no clear history of exposure, because poisoned individuals can be asymptomatic, and signs and symptoms, when they are present, are relatively nonspecific.

Today, laboratories primarily assess lead exposure with whole blood lead measurements. Although a number of other human tissues and fluids, such as hair, teeth, bone and urine, also reflect lead exposure, the concentration of lead in whole blood has gained wide acceptance as the most useful tool for screening and diagnostic testing (Parsons *et al.,*2001*)*.

In very young children, the lead level in whole blood is an indicator mainly of recent exposure, although there can be variable (but not dominant) input to total blood lead concentration from past accumulation of lead in the body. In adults, particularly in lead workers, the past accumulation can be a more prominent contributor to total blood lead concentrations.

Lead toxicity is a particularly insidious hazard with the potential to cause irreversible health effects. In evaluation of its toxicity in humans, it was found that bone to blood mobilization increases during pregnancy, lactation, physiological stress, chronic disease, along with advanced age (Gulson *et.al.,2003*). Its release back into the bloodstream, particularly during times of calcium stress in pregnancy period, makes the developing foetus more prone to its toxicity through mobilization as part of the blood supply and after birth through lactation (breastfeeding) of the infant. Elevated levels in pregnant women often lead to preterm labour, miscarriages, spontaneous abortion or still births and low birth weight children.

2.1.5 Copper Toxicity

Copper (Cu) is an essential trace minerals that is vitally important for physical and mental health. But due to wide spread occurrence of copper in our food, hot water pipe, nutritional deficiencies tablet and birth control pills increases chances of copper toxicity. Copper is not poisonous in its metallic state but some of its salts are poisonous. Copper is a powerful inhibitor of enzymes. It is needed by the body for a number of functions, predominantly as a cofactor for a number of enzymes such as ceruloplasmin, cytochrome oxidase, dopamine β-hydroxylase, superoxide dismutase and tyrosinase. It is present in several haematinics and its salts are also used therapeutically because of their astringent and antiseptic properties but sometimes copper salts are poisonous for human organ system (Defoe *et al.,*2007).

It is a condition in which an increase in the copper retention in the kidney occurs. Copper first start depositing in the liver and disrupts the liver's ability to detoxify elevated copper level in the body thus adversely affect nervous system, reproductive system, adrenal function, connective tissue, learning ability of new born baby, etc. When acidic foods are cooked in unlined copper cookware or in lined cookware where the lining has worn through, toxic amounts of copper can leech into the foods being cooked. This effect is exacerbated if the copper has corroded, creating reactive salts. The compounds of copper, often acting poisonously are blue vitriol (bluestone), the sulphate; and verdigris.

In large amount taken at once, either of these will cause severe vomiting, pain in the abdomen, and purging; afterwards headache, and in fatal cases, convulsions or paralysis before death. Slow poisoning will result from taking small amounts of copper daily, as in cooked or pickled articles, for a length of time.

Copper uptake occurs in a tightly regulated process through specific high affinity plasma membrane copper transporters or low affinity permeases (DeFeo *et al.,* 2007)

Binding to chaperone proteins results in the transfer of copper to its final destination or any intermediate location from which its transport to other cell compartments or efflux out of cells can occur in cases in which concentration excess the optimum level. Acting as a cofactor for a wide range of metal binding enzymes, it fluctuates between the oxidized Cu (II) and reduced Cu (I) forms.

In humans, its average intake ranges between 260 and 700μg/day although adequate intake of copper provides protection against lead, higher intake has been associated with increased lead absorption (Flora *et al.*, 1982) Its presence in excess amounts led to its involvement in the generation of highly reactive oxidative species (such as hydroxyl radicals) well known for their devastating effects in cells, particularly DNA damage and oxidation of proteins and lipids (Halliwell *et al.*, 1990) Cu (I) and Cu(II) that hold high affinity for protein sites having cysteine, methionine, and histidine side chains act as potential ligands that led to displacement of essential metal ions from their active sites, thereby resulting in the misfolding of proteins. As such, its uptake, followed by distribution and utilization, and finally excretion from the body needs to be tightly regulated (O'Halloran *et al.,* 2000).

2.1.6 Cadmium toxicity

Cadmium is an environmental contaminant unique among metals of its diverse toxic effects, extremely protracted biological half-life, low rate of excretion from the body and predominant storage in soft tissue (Benova *et al.*, 2007). Tissue cadmium concentrations in animals are closely related to cadmium in feedstuffs and the duration of cadmium load (Bokori *et al.*, 1995). Absorption and accumulation of cadmium in tissue seems to be determined by a wide range of factors nutritional and vitamin status such as iron status, age, and sex (Torra *et al* 1995; Flanagan *et al.*, 1978). Cadmium food is the most important source of cadmium exposure in the general non-smoking population in most countries (WHO, 1992). Cadmium exposure may cause kidney damage including a tubular dysfunction, evidenced by an increased excretion of low molecular weight proteins or enzymes. Animal experiments have suggested that cadmium may be risk factor for cardiovascular disease (Jarup *et al.*, 1998; Nishijo *et al.*, 1995). The International Agency for Research on cancer has classified cadmium as a human carcinogen (group 1), for prostrate and kidney cancer, on the basis of sufficient evidence in both humans and experimental animals (IARC, 1993).

2.2 Soil

Soil is a mixture of organic matter, gases, minerals, liquids and organisms that together support life. Earth's body of soil, called the pedosphere has four important functions as a medium for plant growth, as a means of water storage, supply and purification, as a modifier of Earth's atmosphere and as a habitat for organisms (McCarthy, 2006).

The mineral content of plants also depends on factors such as the natural content of trace elements in the environment, their level in mineral fertilizers and fertilizer doses. In the soil, a natural source of these metals is bedrock (Antisari *et al.,* 2015).

Heavy metals dynamics in the soil and their uptake by plants depend on soil properties, which play a key role in the bioavailability of these metals. The level of compounds accumulation in plants depends on, amongst others, soil type, PH, humidity, and micronutrients content, as well as on the time of crop harvesting (Yang-Ghang *et al.,* 2016).

To be available for uptake by plants, heavy metals must be present in the soil solution.

There is considerable evidence that the chemical specification of heavy metals in solution affects their availability and toxicity to plants (Parker *et al.,* 1995). For example, Cu^{2+} (Graham, 1981) and Cd^{2+} (Cabrera *et al.,* 1988) have shown a high level of correlation with the activity of free metals ions in soil solution rather than with total elements concentration in soils when plants uptake these metals. Soluble heavy metals concentrations in soils are likely to be influenced to some extent by the total concentrations of heavy metals present in soils. Thus in uncontaminated soils, heavy metals bioavailability is likely to be related to the nature of soil parent material and the degree of soil weathering (McLaren, 2003). In case of contaminated soils, solution heavy metals concentrations are likely to increase with total contaminant loading. Colloids in soil that are able to sorb heavy metals will therefore have a major influence in controlling heavy metals availability to plants.

Plants absorb heavy metals from soil the surface 25cm depth zone of soil is the most affected by such pollutants resulting from anthropogenic activities. Heavy metals accumulate in this soil layer due to the relatively high organic matter content.

This plant part of interest for direct transfer of metal pollutants to humans is the edible parts such as grains, vegetables, is readily taken up by plants and translocated to aerial plant parts where it accumulates (Satarug *et al.*, 2003)

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

The study area which is Azara town is situated at Nasarawa State. The state is within the Middle Benue Trough of Nigeria which lies between latitude 7o 45' and 9o 25'N of the equator and between longitude 7° and 9° 37' E of the Greenwich Meridian. Azara mining site is located in Awe Local Government Area of Nasarawa State. The geographical coordinates 8° 221 North, 9° 151

East and has an altitude of 181.5m above sea level (Obaje, *et. al.,* 2006)

3.2 Samples and Processing

Samples of the edible vegetables were randomly collected from main farmlands around the community. The samples were collected from these growing areas during the cultivation season.

A total of five samples of vegetables were collected (bitterleaf (*Vernonia amygdalina*), melon (*Cucumis reticulatus*), okro (*Abelmuschus esculentus*), Amaranthus (*Amaranthus dubius*), waterleaf (*Talinum fruticosum*). All samples were collected and stored in polythene bags according to their type and brought to the laboratory for preparation and treatment. For Copper, Cadmium, Lead and Zinc analyses, vegetables samples were washed with distilled water to eliminate particles. The leafy stalks were removed from all samples and these were and dried on a sheet of paper to eliminate excess moisture. After drying each, samples were weighed and oven dried at 60°C to a constant weight. Each oven dried sample was ground in a mortar until it could pass through a 60 mesh sieve. The samples were stored in clean, dry, high density polythene bottles with screw caps. Bottles were prewashed with nitric acid, rinsed with deionized water, dried and leached with 5% nitric acid to avoid metal contamination.

Samples were precisely weighed (2.0g each) and ground in a mortar followed by wet digestion with HNO_3:$HClO_4$ (2:1) in a conical flask for 2-3 hours on a sand bath (Radwan &Salama 2006). Some 10ml of Hcl was added, digested samples were filtered with 0.45µm pore size cellulose nitrate membrane filter paper (Millipore) and the volume was increased to 100ml with distilled water and bottles were store until atomic absorption spectrophotometer was ready to read samples.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Heavy Metals Concentration in Vegetables

Results

Table 1 showed the concentration of heavy metals in vegetables from random sites in Azara town with the WHO maximum permissible level in vegetables only Barite showed to be slightly high.

Table 2 showed the concentration of heavy metals in different soils collected at random in Azara town with the WHO maximum permissible level in soil only Barite showed to be slightly high.

Table 3 showed the WHO standard of maximum permissible level insoil and vegetables.

Heavy metals concentration in vegetables

Metals (g)	Melon	Okro	Amaranths
Copper	0.9006	0.6599	0.4639
Lead	0.6308	1.0903	1.1038
Cadmium	0.0121	0.0263	0.0159
Zinc	0.2285	1.0260	1.0260
Barite	1.0568	0.0215	0.5612

4.2 Heavy Metals in Soil

Metals (g)	Red soil	Brown soil	Clay soil
Copper	0.6311	0.5033	9.2045
Lead	0.6277	1.8625	2.5106
Cadmium	0.0206	0.0185	0.0144
Barite	0.1382	0.5670	0.7650
Zinc	0.2290	0.1220	0.0150

The maximum allowable limits of heavy metals in soils and vegetables have been established by standard regulatory bodies such as World Health Organization (WHO), Food and Agricultural Organization (FAO).

Chemical element	Maximum permissible level in soil (μg/g)	Maximum permissible level in vegetables (μg/g)
As	20	-
Cd	3	0.10
Co	50	50.00
Cr	100	-
Cu	100	73.00
Fe	50000	425.00
Mn	2000	500.00
Ni	50	67.00
Pb	100	0.30
Se	10	-
Zn	300	100
$BaSO_4$	0.10	0.10

WHO, 1995

Heavy metal poisoning symptoms actually varies and might include vomiting, pain in stomach, sweating, diarrhoea, nausea and bad metallic taste in mouth depending on the natures well as quantity of heavy metals that enters the body. If unrecognized or inappropriately treated, heavy metals toxicity can result in significant illness and reduced quality of life (Ferner, 2001)

Plants have the ability to accumulate heavy metals from various sources including irrigation, soil erosion, and runoff, air depositions of dust and aerosol, and discharges of wastewater (Labonne *et al.,* 2001; Goodwin *et al.,* 2003). However, very low levels of pollution may have no apparent impact on the vegetable itself, which would show no obvious signs of illness but may decrease the sufficient of good vegetables.

4.3 Toxicity of Lead to Life

Lead is a protoplasmic poison with affinity for the matter of our brains. It invades neurons, damages a cell, nerve synapse and dendrites, and reduces the number of oxygen carrying red blood cells. It combines with phosphorus and enters the blood stream where it moves to the spleen, liver, and kidneys. After it has done its damage to the spleen, liver, and kidneys, it then goes to the bones, which become its permanent storage site. If the phosphorus intake is inadequate, the body will liberate lead from the bones and put it back into the blood stream so that it can do another round of damage to liver, spleen, kidneys and brains. Therefore the poor and malnourished are at particular risk when it comes to lead poisoning.

Lead is known to cause both immediate and long term health problems, especially with children. It is toxic when swallowed, eaten or inhaled. Children are at the highest risk for lead poisoning, simply because their bodies absorb over 50% of all they come in contact with, as compared to an adult who only absorb 10%. Children under the age of seven (7) are the most vulnerable as their nervous systems are undeveloped and easily damaged (Landrigan *et al.*, 2002). Also, lead tastes sweet and so small children who have access to lead paint chips enjoy its taste and are eager to chew down. Over a long period of time these children offer suffer from brain damage. They lose the ability to carry out normal metal functions. Eventually in later life lead poisoning reduces intelligence, causes memory loss, promotes peripheral neuropathy and deteriorates thinking. It can also cause bone pain, gout, high blood pressure, iron deficiency, anaemia, headaches, muscle tremor, hallucinations, and numbness and tingling in the extremities (Hazard Substances Data Bank (HSDB), 2009).

Other forms of lead poisoning can occur. For example people who work in factories where lead is used can inhale lead fumes. The amount of fumes inhaled at any one time maybe small but over months and years, the lead in person's body can build up. This kind of lead poisoning can lead to nerve damage and problems with the gastrointestinal system (stomach and intestines) which ca be seen as nausea, vomiting, extreme tiredness, high blood pressure, and convulsions (spasm) (Sanders *et al.,* 2009).

The symptoms initially present as fatigue, irritability, abdominal pain, constipation, and lack of appetite. Children frequently become hyperactive and aggressive, with a shortened attention span, sensor motor deficits, and disordered behaviour, which are the same symptoms as emotional trauma (HSDB, 2009).

4.4 Toxicity of Copper to Life

Copper is an essential micronutrients for both plants and animals. A healthy human has no more than about 2milligrams of copper for every kilogram of body weight (Gscheidner & Eyring, 1991).

Some people are born without the ability to eliminate copper from their bodies and as such the amount of copper they retain increases, the copper level can become so high it begins to affect the brain, liver or kidneys resulting in mental illness and death. Fortunately this problem can be treated. The person can be given a chemical that combines with the copper and the damaging effects on the body are reduced or eliminated (HSDB, 2009).

Copper deficiency or excess can be a problem. Deficiency causes anaemia, connective tissue, nerve and nervous system abnormalities. Although because of copper pipes, and the fact that many copper rich foods are somewhat additives, deficiency is seldom a problem. The exception would be in the case of Menke's disease, which is rare genetic disease that causes copper mal-absorption in infants males. Wilson's disease on the other hand, is a genetic disease that causes copper overload. Excess copper in the human system is generally caused by copper pipes, especially in newer houses or houses that have brass faucets, which have copper in them. Hot water leaches more copper from the pipes than cold water, so it is always important to use cold water of the day run through the pipes for a minute or two before using it, as excess copper accumulates in water that's stored in the pipes overnight (ATSDR,1989). Inhaling copper dust and fumes can affect the respiratory tract and cause nausea and diarrhoea. It will also decrease the body's haemoglobin and erythrocytes count, it can affect the liver and endocrine system, in addiction it can cause eye irritation, headaches and muscles aches (HSDB, 2009).

4.5 Toxicity of Cadmium to Life

Cadmium is toxic to every body system and should never be mined in the first place. Almost all of the cadmium we are exposed to gets absorbed. Cadmium like all heavy metals accumulates over a life time. It is stored in fat, which keeps it from circulating in the blood.

Cadmium is first transported to the liver through the blood. There it is bond to proteins to form complexes that are transported to the kidneys where it accumulates and damages the liver, causing anaemia. Cadmium accumulates in kidneys, where it damages filtering mechanisms. This causes the excretion of essential proteins and sugars from the body and further kidney damage. It also impairs calcium metabolism and contributes to osteoporosis and ostoe-malacia. It takes a very long time before cadmium that has accumulated in kidney is excreted from human body. Other health effects that can be caused by cadmium are:

i. Diarrhoea, stomach pains and severe vomiting
ii. Bone fracture
iii. Reproductive failure and possibly even infertility
iv. Damage to the central nervous system
v. Damage to the immune system
vi. Psychological disorder
vii. Possibly DNA damage or cancer development (HSDB, 2009)

4.6 Toxicity of Barium to Life

Barium is a very abundant, naturally occurring metal and is used for a variety of industrial purposes.

Large amounts of barium intake can cause, high blood pressure, changes in heart rhythm or paralysis and possibly death.

4.7 Toxicity of Zinc to Life

Zinc, a ubiquitous trace element essential as a catalytic, structural and regulatory ion, is indispensable for growth and development of microorganisms, plants, and animals (Mocchengiani *et al.*, 2000)

Mass poisoning has been reported following the drinking of acidic beverages kept in galvanized containers; fever, nausea, vomiting, stomach cramps, and diarrhoea occurred 3–12 hours after ingestion. Food poisoning attributable to the use of galvanized zinc containers in food preparation has also been reported; symptoms occurred within 24 hours and included nausea, vomiting, and diarrhoea, sometimes accompanied by bleeding and abdominal cramps (Elinder *et al.*, 1986) Manifest copper deficiency, which is the major consequence of the chronic ingestion of zinc (Cousins *et al.*,1990), has been caused by zinc therapy (150–405 mg/day) for coeliac disease, sickle cell anaemia, and acrodermatitis enteropathica (Porter *et al.*,1977, Prasad *et al.*, 1987).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The aim of this study is to evaluate the presence of heavy metals in soil and different vegetables in Azara town in Nasarawa state. This study shows the values of bioaccumulation levels which differs depending on heavy metals. The variation in the accumulation levels of the different metals and in different vegetables maybe due to the mining activities, runoff of the fertilizer and pesticide residue use for agricultural purposes are also discharged.

The value bio-accumulation for the selected metals was found to be lower than the WHO permissible standard both in soil and vegetables except for Barite which was slightly higher.

All the elements selected for this study are important elements that are needed in the body, but it is unfortunate that bio-accumulation leads to toxicity both in humans and animals; this shows that in a long run, most inhabitants in the study area might be affected negatively. However the soil in Azara town can be prevented by the application of phytoremediation. Phytoremediation is a bioremediation process that uses various types of plants to remove, transfer, stabilize and destroy contaminants in the soil

5.2 Recommendations

There is a need for a continuous monitoring of contamination level of heavy metals especially Barite, Lead, and Cadmium since they can accumulate to toxic levels and also because the habitants depend on these lands for farming. Further research should be carried out and the frequency of the sampling should take into consideration the types of heavy metals, seasonal flows of crop cultivation to show which season heavy metals accumulates the more and other factors which may change during and after data might have been collected.

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