

Review on Measurement of Heavy Metals and their Health Implications using Atomic Absorption Spectroscopy Technique in Some Parts of Nigeria

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Abstract: *The Contamination caused by heavy metals in the environment has attracted global attention owing to its abundance, persistence and environmental toxicity. Both natural and anthropogenic activities are responsible for the abundant of heavy metals in the environment. However, anthropogenic activities can effortlessly generate heavy metals in sediment, soils, and water that pollute the human and aquatic environment. Heavy metals are toxic environmental substances which may accumulate in a food chain and pose threat to the health of humans. The present study reviewed the presence of heavy metals and their health implications in some part of the country. Heavy metal has been reported in different literature both local and international to have cause toxic effect on man and the environment. Common sources of heavy metals are from mining and industrial wastes, vehicle emissions, lead acid batteries, fertilizers, paints treated woods, aging water supply infrastructures and micro plastic floating in oceans. Some heavy metals such as Cd and Pb may be present in children's toys and high level that exceeds regulatory standards. Since, the diversity of environmental contaminants increased exponentially, with countless anthropogenic sources. Therefore, the diverse and emerging issues of food security and environmental quality have become a Nigerians concern, particularly their inextricable association with human health. Based on this reviewed work, it was observed a higher level of heavy metal concentrations in areas like Kano, adamawa, Niger Delta and those with low level include Ekiti & Kaduna state e.t.c.*

Keywords: Heavy metals, AAS, Contamination

1. Introduction

Heavy metals such as lead (Pb), cadmium (Cd), iron (Fe) and manganese (Mn) are always part of life due to nature and human activities. Metals generally are natural components of the Earth's crust and therefore are major constituents of soil. Every 10³ Kg of normal soil contains at least 200 g chromium, 80 g nickel, 16 g lead, 0.5 g mercury and 0.2 g cadmium theoretically. Therefore it may not be easy to assign a definite cause for an increase in metal content of a soil sample without recourse to the background level of the metal (Oti *et al*, 2012). Heavy metals are generally metallic compound with relatively high density and are toxic or poisonous at low concentration. This group of metals include Mercury (Hg), Cadmium (Cd), Arsenic (As), Chromium (Cr), Lead (Pb), Zinc (Zn), Copper (Cu), Iron (Fe) and Calcium (Ca). They are usually natural components of the earth. There are different sources of heavy metals which are pollutants to the environment and living organisms and their sources include chemicals and physical weathering of igneous and metamorphic rocks (Abdullahi, 2019). Also, other contributions include the decomposition of plant and animal detritus, precipitation of atmospheric depositions, airborne particles from volcanic activity, wind erosion, forest fire, plant exudates and oceanic spray. Heavy metal contamination of fruits and vegetables are common phenomenon and fruits and vegetables are important components of human diet. Fruits and vegetables are rich sources of vitamins, minerals, and fibers, and also have beneficial anti oxidative effects. Conversely, intake of heavy metal-contaminated fruits and

vegetables pose a serious risk to the human health. (Abdullahi, 2019). Contaminated food items by heavy metals are one of the most important aspects of food quality assurance. Moreover, rapid and unorganized urban and industrial developments have contributed to the elevated levels of heavy metals in the urban environment of developing countries such as Nigeria, Iran and Ind. Often times, emissions of heavy metals from industries and vehicles are deposited on the vegetable surfaces during their harvest, transport and marketing (Abdullahi, 2019). The high level of heavy metals concentration observed in vegetables from selected market in Anambra State, Nigeria. The prolonged consumption of unsafe concentrations of heavy metals through foodstuffs may lead to the chronic accumulation of heavy metals in the kidney and liver of humans causing disruption of numerous biochemical processes, leading to cardiovascular, nervous, kidney and bone diseases (Abdullahi, 2019).

Heavy metals contaminated food is estimated by one source to account for 30% of human cancers. Mining activities, atmospheric pollution such as (industrial emission, automobile exhaust, brick kiln emission, etc.), industrial wastes such as (wastewater discharges, solid waste dumping, and sludge disposal on the land), and agricultural practices (fertilizers and pesticides) are all possible sources of heavy metals contamination, possibly deposited heavy metals on the surface of market food crops that ensure heavy metals exposure via their consumption by human population. Furthermore, the aforementioned activities both anthropogenic and natural, accumulate heavy metals in the

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soil, water, food crops, and finally become a part of human bodies (Muhammad *et al.*, 2014). However, food consumption is considered as the key pathway to human exposure, contributing up to 90% as compared to other exposure pathways. Heavy metals (*viz.*, Cd, Pb, Cr, Ni, As, and Hg) are extremely toxic, owing to their persistent in nature. Long-term human exposure to these metals via the food chain may produce some adverse impacts (*e.g.*, heart, kidney, brain, and bone diseases). Additionally, heavy metals such as Cd and Pb may cause mutagenesis, and carcinogenesis. Lead is also responsible for elevated blood pressure and renal infection, improper hemoglobin synthesis, and damage to the reproductive system. Manganese may cause Parkinson's disease as result of iron oxide deposition. Zinc and Cu concentrations above recommended levels in food are suspected to cause toxicity in humans and animals (Muhammad *et al.*, 2014).

Atomic absorption spectroscopy can simply be defined as the absorption of light by activated atoms. Such absorption occurs on very narrow spectral lines, the so-called absorption or resonance lines, their theoretical spectral width being of the order of 0.001 Å. The lines are entirely characteristic and specific for each element and to date no two elements have been found to possess an identical resonance line. If monochromatic light of a specific wavelength is provided, it will be absorbed only by atoms of that element whose resonance line is identical with the wavelength of the light source and not by any others. A field of atoms is "opaque" for monochromatic light when resonance line and source wavelength match, but for other wavelengths it is translucent. The degree of opacity is proportional to the total number of absorbing atoms. It follows then that with a beam of specific monochromatic light the concentration of an element can be determined in a mixture of atomic species. Atomic absorption will take place only in a field of free, neutral, activated atoms. Atomic absorption cannot be brought about by ions, by atoms bound in compounds, or by a molecular gas. When metals are heated to their boiling point, they vaporize as free atoms, provided that interaction with other elements is prevented, and it is for this reason that atomic absorption spectroscopy in its present form has found its most extensive applications in the analysis of the metallic elements

2. Methodology

The samples collected such as environmental, geological and biological samples by different researchers in some part of this country were prepared according to the conditions required by the AAS technique. After preparation is done then the samples taken to the analysis, the atomic absorption spectrometer (AAS) was used for the analysis of these samples according to manufacture instruction. In order to determine the heavy metals the lamp was put into the turner and the operation condition such as wave length and slit width adjusted as required. The instrument was optimized for maximum sensitivity using the wavelength and lamp of alignment knob. The numbers and values of the

standards were fed into the system with the correct burner in place; air was turned on, followed by acetylene at the appropriate pressure. The flame was ignited and left for about some minutes. The absorbance of the blank was adjusted to zero after which the reading of the standard sample with concentration in mg/kg for each of the metal were taken. This was repeated for each parameter to be obtained in each of the given sample. The equipment was then put in the analytical mode and the individual sample was measured and recorded by aspirating each sample in the instrument. The concentration of the heavy metal in the samples was determined. The above is the simple principle of AAS as it applied to determine the heavy metal concentrations. The Principle and basic operation of AAS is presented below:

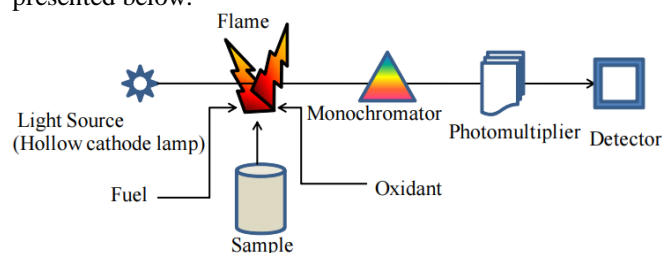


Figure 1: Schematic diagram showing the principle and working of atomic absorption spectroscopy (AAS) (Vijay *et al.*, 2017).

The condition for the AAS analysis is given in the table 1 below:

Table 1: Showing the flame type, Temperature and Suitable elements for AAS analysis

Flame type	Approximate Temp. (°C)	Element suitable for analysis
Air-coal gas	1800 °C	Cu, Zn, Pb, Cd, alkali metals
Air-propane	1900 °C	Same as above and volatile elements, noble metals
Air-acetylene (lean)	2300 °C	Alkaline earth metal
Air-acetylene (rich)	2300 °C	Sn, Ba, Cr etc.
N ₂ O/acetylene	2955 °C	Al, V, Ti, Ta, Be, Se etc.

3. Overview Summary of the Results and Discussion

The table 2 below is safe recommended values of heavy metals according to the Food and Agriculture Organization and World Health Organization.

Table 2: Safe permissible limit for heavy metals according to the Food and Agriculture Organization/World Health Organization (FAO/WHO 2001 to 2007)

Heavy metals	Safe permissible limits [mg/kg]
Mn	500
Ni	66.9
Cd	0.2
Pb	0.3
Cr	2.3
Fe	425
Cu	40
Zn	60

The table 3 below is the summary of the results obtained from the articles and papers reviewed together with the

locations, samples analyzed, and the references. This table gives a quick overview of some articles reviewed in work.

Table 3: Summary of the results analyzed by AAS

Sample	Location	Findings	References
Irish potatoes and Soils	Dahwol-vwana, Jos-south L.G.A, Plateau state	Pb, Cd and Zn	Sanda, 2015
wheat, millet, millet pap, maize, maize pap, groundnut, kuli-kuli and ose-oji	Port Harcourt	Zn, Fe, Cu, Pb & Cd	Felagha & Ogbolosingha, 2018
grey waste water, soil and vegetables	Shinko and Fagge area of Yola an Kano	Fe, Zn, Mn & Cu	Chiroma <i>et al</i> (2014)
rice, maize, millet, guinea corn and wheat	Kaduna	Cu, Zn & Fe	Sulyman <i>et al</i> (2015)
pork muscles (free ranger pigs & confined pigs)	Nsukka Central Market	Zn, Fe, Cu,Cr, Ni, Pb & Cd	Chisom, (2009)
Water	Sharada, Bompai and Dambatta (Kano).	Zn, Pb, Cr, Cu, Ni, Co, Ag, Fe & Mn	Bala <i>et al</i> , (2008)
fruit spices(Black pepper, Ginger, Garden sage, Thyme, Nutmeg)	local markets in Nigeria	Pb,Cd, Co & Se	OBIAGELI, (2015)
Soils	Geriyo, Adamawa	Fe, Zn, Mn, Cu, Cd, Cr & Pb	Haliru <i>et al</i> , (2014)
Soils and Water	Ikogosi Warm Spring, Ondo State	Cu, Cd, Zn, As, Cr & Ar	Adegoke <i>et al</i> ,(2009)
Industrial Discharges	Lagos	Pd ,Cu,Cd, Mn & Fe	Kolawole & Abinbola, (2011)
Soil	Niger Delta	Cd, Mn, Ni, Pb & Zn	ATUMAH, (2017)

The heavy metals concentrations of agricultural soils taken from the depth of 0-30 cm from two different control sites of sewage irrigation area geriyo, adamawa state was determined using atomic absorption spectrophotometer standard method. The trace and heavy metals identified at site I&II include: Fe, Zn, Mn, Cu, Cd, Cr and Pb and their respective concentrations are presented in the table 4 below.

Table 4: The trace and heavy metals identified at site I&II agricultural soils in geriyo adamawa by Haliru *et al* (2014)

Analyte	Concentrations at Site I [mg/kg]	Concentrations at Site II [mg/kg]
Fe	89.90	294.7
Zn	74.39	310.2
Mn	12.79	131.9
Cu	15.09	254.8
Cd	9.89	240.2
Cr	11.2	199.6
Pb	7.18	159.2

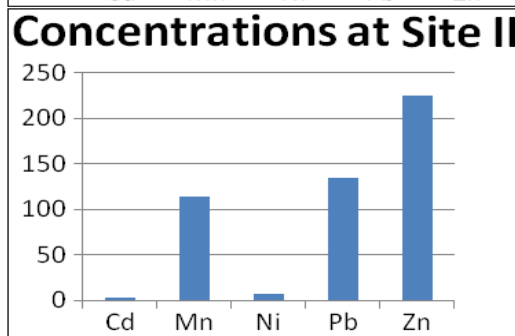
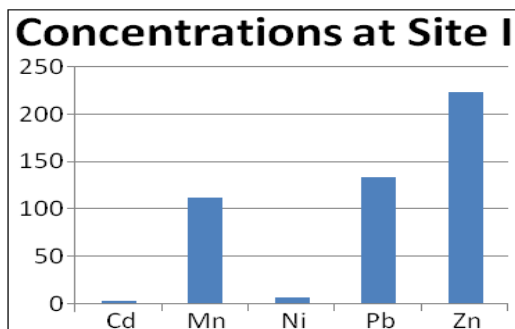


Figure 2&3 Bar chart showing concentrations at site I&II

The levels of trace and heavy metals of site II agricultural soil is much higher than site I and the control site with the concentration levels of Cu, Cd, Cr and Pb are levels in soil set out by EU, UK and US. It was revealed that there are negative effects of these concentrations on plant and ground water (Haliru *et al*, 2014). In the figure above Zn and Pb have the highest concentrations. In the monitoring the concentrations of Cd, Mn, Ni, Pb and Zn, soil samples were collected from Egbaoma marginal oil field OML 38 in onshore Niger Delta. Atomic Absorption Spectrometer (AAS) was applied to determine the above heavy metals concentrations (Atumah,2017). The concentrations of the above heavy metals are presented in the table 5 below:

Table 5: heavy metals concentrations obtained from Egbaoma marginal oil field OML 38 in onshore Niger Delta by Atumah (2017)

Analytes	Concentrations in [mg/kg]
Cd	3.32
Mn	112.75
Ni	7.05
Pb	134
Zn	223.38

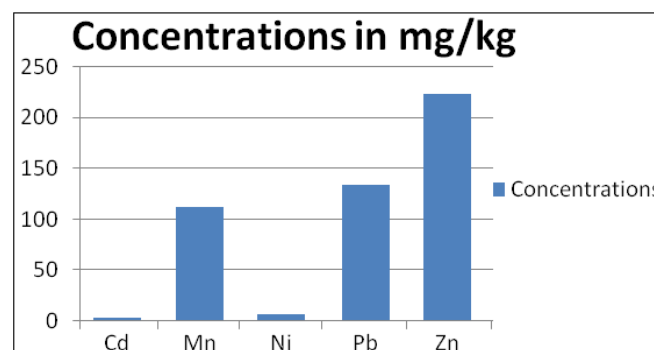


Figure 4: Bar chart showing the concentrations of heavy metals in mg/kg

The obtained results above show that Zinc having the greatest concentration value follow by the Lead. The greater level of Zinc, Lead, Manganese and Nickel is associated with the petroleum spillage from the wells because the crude oil of Nigeria is rich in such elements. For this reason regular environmental monitoring is recommended in that area in order to protect the environment from pollution hazard and human health implications (Atumah, 2017). Sulyman *et al*, (2015) have investigated the presence of heavy metals in rice, maize, millet, guinea corn and wheat using AAS technique. The results obtained are given in the table 6:

Table 6 show the presence of heavy metals in rice, maize, millet, guinea corn investigated by Sulyman *et al* (2015) using AAS.

Samples	Cu	Zn	Fe
Rice	1.58mg/kg	0.70mg/kg	8.24mg/kg
Maize	0.98mg/kg	2.01mg/kg	5.99mg/kg
Millet	5.23mg/kg	4.51mg/kg	10.54mg/kg
Guinea	0.90mg/kg	2.04mg/kg	18.97mg/kg
Wheat	2.41mg/kg	11.32mg/kg	13.61mg/kg
permissible limit	40	60	425

The levels of heavy metals determined in the analyzed cereal samples were found to be below the permissible limit set by FAO/WHO; hence, the concentration of these heavy metals in the selected cereals analyzed, may not pose a health hazard in the population and can as well serve as good and dependable sources of essential trace metals to the human population (Sulyman *et al*, 2015). From the results above it shows that Cu has the highest concentration in millet and least in Guinea corn, while Zn have the highest concentration in millet and least in rice, while Fe has the highest concentration in Guinea corn and least in maize. OBIAGELI, (2015) have applied AAS in the determination of heavy metals concentrations such as lead (Pb), Cadmium (Cd), Cobalt (Co) and Selenium (Se) in common fruit spices collected from local markets in Nigeria. The research showed differences in metal concentrations according to the locations. In all locations of this research, the obtained results are tabulated as follows:

Table 7: Results obtained in common fruit spices collected from local markets in Nigeria

Heavy metals	Range of Concentrations [mg/kg]
Pb	12 to 30
Cd	1.20 to 3.00
Co	0 to 0.60
Se	0 to 12.05

Some of these concentrations are above the standard limit approved by WHO and FAO. No risk from daily intake of the most of fruit spices under study for hazardous Pb, Cd, Co and Se if the human take about 20g of spices per day. But there are dangerous from thyme and ginger for lead.

Adegoke *et al*, (2009) conducted a research on heavy metals such as Cu, Cd, Zn, As and Cr in the soil ($\mu\text{g/g}$) and water (ppm) samples collected at Ikogosi Warm Spring, Ekiti

State using AAS. The results obtained showed that the average concentrations ($\mu\text{g/g}$) of the heavy metals in the soil are 5.29 $\mu\text{g/g}$ for Cu, 1.50 $\mu\text{g/g}$ for Cd, 46.72 $\mu\text{g/g}$ for Zn, 10.50 $\mu\text{g/g}$ for As and 339.78 $\mu\text{g/g}$ for Cr. The average concentrations (ppm) of the heavy metals in the water are 4.8 $\mu\text{g/g}$ for Cu, 0.15 $\mu\text{g/g}$ for Cd, 4.17 $\mu\text{g/g}$ for Zn, 0.57 $\mu\text{g/g}$ for Ar and 1.46 $\mu\text{g/g}$ for Cr. In the overall, the average concentration of chromium is the highest in the soil with concentration of 339.78 $\mu\text{g/g}$ with cadmium having the lowest value of 1.50 $\mu\text{g/g}$ while in water sample copper had the highest level with concentration of 4.80ppm and cadmium had the lowest concentration with value of 0.15ppm. All these concentrations are within the standard levels.

Bala *et al*, (2008) detected some heavy metals such as Zn, Pb, Cr, Cu, Ni, Co, Ag, Fe and Mn in water collected from two areas (polluted and controlled site) of Kano state, Using AAS method. The results obtained show that the mean values of all heavy metals (with the exception of Zn) in water samples from the polluted areas studied were significantly higher than in the control site. These mean values have also exceeded the acceptable limits. So these Industrial effluents discharged into the environment pose a serious threat to our agricultural products and health.

Chiroma *et al* (2014) investigated the level of heavy metals present in the samples collected from urban irrigation sites of Yola and Kano. The samples collected include: grey waste water, soil and vegetables. The amount of heavy metals in the irrigation waters is beyond the maximum permissible levels of 0.5 $\mu\text{g/ml}$, 0.2 $\mu\text{g/ml}$, 0.2 $\mu\text{g/ml}$ and 0.017 $\mu\text{g/ml}$ for Fe, Zn, Mn and Cu respectively for irrigation waters used on all types of soils. The amount of Cu in all the farm soils is beyond the maximum permissible level in soils. The Kano farmland soils indicate higher levels of heavy metal soil contamination compared to Yola farmland soils. The level of metal in irrigation waters and farmland soils from the study areas ranged from very severe pollution to excessive pollution and slight contamination to severe pollutions respectively. The heavy metals also showed similar distribution pattern in parts of the same species of vegetables from both sites. Hence higher concentrations were observed in vegetable parts from the Kano sites compared to those from Yola sites.

4. Health Implications of some heavy metals above safe permissible limit

Skin exposure of the general public to chromium can occur from contact with products containing chromium. E.g preserved wood or chromium containing soil. Airborne chromium may contribute significantly to occupational exposure. High level exposed of chromium or its compounds, primarily by inhalation, may lead to irritating respiratory effects, possible circulatory effects, effects on stomach and blood, liver and kidney effects, can lead to dermal ulcers, effects on the renal, hematological and cardiovascular system and increased risk of death from lung cancer (Daniel *et al*, 2016). Long term exposure to the

elevated levels of cadmium in the environment has apparently increased the accumulation of cadmium in certain body organs (notably the kidney and liver). The transfer of cadmium into human foods is through air, water and soil. Of all the toxic metals released in large quantities to the environment, cadmium is generally regarded as the most likely to accumulate in human food chain (Chisom, 2009). Cadmium is extremely poisonous and toxic to humans. When inhaled it causes acute bronchitis, pneumonitis and inflammation in the liver. Cadmium toxicity causes a disease known as itai-itai (ouch ouch) resulting in death and physical deformities that sometimes extend to children born by affected mothers. This occurred in Japan, to people who ingested cadmium from eating rice grown in paddy fields flooded by water from a contaminated river (Chisom, 2009). Lead (Pb) is present in food, water, air, soil, paint, and other materials with which the general population comes in contact. Each are potential pathways for human Pb exposure via inhalation or ingestion. Exposure to lead mainly occurs through inhalation and ingestion. Essentially, 75% of airborne lead particles are less than 0.7 μ m in diameter. Because of this small size, a large fraction of inhaled lead may be deposited in the lungs. Worldwide, more than 80% of the daily intake of lead, in older children and adults, is derived from the ingestion of food, dirt and dust. Excessive exposure to lead may cause anemia, kidney disease, reproductive disorder, and neurological impairments such as seizures, mental retardation, and/or behavioral disorders. High blood lead levels in children may cause permanent deficiencies in growth and intelligence. In adults, high blood-lead concentrations may cause kidney disorders, infertility, and cancer. Extremely high concentrations (greater than 100 μ g/dl) usually result in death (Samaila, 2019). Exposure to low lead levels can cause system disorders, hyperactivity, hypertension, behavioural changes and learning difficulties in children. Some have gone as far as to blame antisocial behavior and criminality on sub-clinical Pb poisoning, although the evidence is tenuous (Chisom, 2009)

Copper (Cu) is a naturally-occurring metallic element that occurs in soil at an average concentration of about 50 parts per million (ppm). High levels of exposure to copper can cause destruction of red blood cells, possibly resulting in anemia. Long Term (Chronic) Effects Mammals have efficient mechanisms to regulate copper stores in the body such that they are generally protected from excess dietary copper levels. However, at high enough levels, chronic overexposure to copper can damage the liver and kidneys. Copper is currently categorized by the EPA as a Group D carcinogen. Developmental effects have been observed in a few studies of animals given high doses of copper, including delayed growth and development, delayed bone formation, and decreased litter size and body weights (Mahurpawar, 2015). Humans may be exposed to nickel by breathing air, drinking water, eating food or smoking cigarettes. Skin contact with nickel-contaminated soil or water may also result in nickel exposure. In small quantities nickel is essential, but when the uptake is too high it can be a danger to human health. An uptake of too large quantities

of nickel has the following consequences: Higher chances of development of lung cancer, nose cancer, larynx cancer and prostate cancer Sickness and dizziness after exposure to nickel gas Respiratory failure, Lung embolism, Birth defects, Asthma and chronic bronchitis, Allergic reactions such as skin rashes, mainly from jewelry, Heart disorders. Nickel fumes are respiratory irritants and may cause pneumonitis. Exposure to nickel and its compounds may result in the development of a dermatitis known as "nickel itch" in sensitized individuals. The first symptom is usually itching, which occurs up to 7 days before skin eruption occurs. The primary skin eruption is erythematous, or follicular, which may be followed by skin ulceration. Nickel sensitivity, once acquired, appears to persist indefinitely (Mahurpawar, 2015).

Arsenic is odorless and tasteless. Arsenic is a known carcinogen and can cause cancer of the skin, lungs, liver and bladder. Lower level exposure can cause nausea and vomiting, decreased production of red and white blood cells, abnormal heart rhythm, damage to blood vessels, and a sensation of "pins and needles" in hands and feet. Ingestion of very high levels can possibly result in death. Long-term low level exposure can cause a darkening of the skin and the appearance of small "corns" or "warts" on the palms, soles, and torso. Regulatory limits: Environmental Protection Agency (EPA) - 0.01 parts per million (ppm) in drinking water. Occupational Safety and Health Administration (OSHA) - 10 micrograms per cubic meter of workplace air (10 μ g/ m³) for 8 hour shifts and 40 hour work week (Martin & Griswold, 2009). Barium is not known to cause cancer. Short term exposure can cause vomiting, abdominal cramps, diarrhea, difficulties in breathing, increased or decreased blood pressure, numbness around the face, and muscle weakness. Large amounts of barium intake can cause, high blood pressure, changes in heart rhythm or paralysis and possibly death (Martin & Griswold, 2009). Regulatory limits: EPA - 2.0 parts per million (ppm) in drinking water (Martin & Griswold, 2009). Iron constitutes 5% of the earth's crust. It is generally abundant in most food stuffs, of plant as well as animal origin. The high exposure to Iron or excess iron intake may lead to cirrhosis of liver and haemochromatosis. The recommended daily dietary allowance for iron is 18mg for adults and 10 – 15mg for children (Chisom, 2009).

5. Conclusion

From the foregoing of this work observed a higher level of heavy metal concentrations in areas like Kano, Adamawa, Niger Delta and those with low level include Ekiti & Kaduna state e.t.c. Soil is a great reservoir for heavy metals contaminant as well as water, vegetables, cereal crops and biological sample such as pork meat. The contamination of these samples poses serious danger to the overall quality of human life. The most adverse effect of heavy metals is that they can be introduced into the soil through anthropogenic activities and into the crops and vegetables through the soils and finally into the food chain and threaten human health. Agricultural products growing on soils with high metal

concentrations are source of metal accumulations at levels harmful to human and animal health as well as to the bio-environment; these metals may have been mixed with groundwater by leaching which is great danger to aquatic and human lives. AAS is therefore an important technique for soil, plant, water, fertilizers analysis and other areas including medical, feed stock, environment, pollution, industrial effluents metallurgy, oil industry and general inorganic analysis.

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