# EVALUATION OF HEAVY METALS IN WATER SAMPLES, IN AZARA COMMUNITY OF NASARAWA STATE

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NOVEMBER, 2019

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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

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# DECLARATION

I hereby declare that this project Title "Evaluation of Heavy Metals in Water Samples, in Azara Community" 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.

**SOLOMON ENJUGU JOSEPH**

# CERTIFICATION

This project "Evaluation of Heavy Metals in Water Samples, in Azara Community" meets the egulations governing the award of postgraduate diploma, of the school of Postgraduate studies, Nasarawa State University, Keffi, and is approved for its contribution to knowledge.

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# DEDICATION

The work is dedicated to God Almighty for His goodness and mercy upon my life and guiding me through the period of the research work.

# ACKNOWLEDGEMENT

First and foremost, praises and thanks to God, the Almighty, for His showers of blessings and who helped me throughout my research work (only because you made a way).

I would like to express my deep and sincere gratitude to Dr. Moses Zaruwa the pioneer of this studies, my research supervisors, Dr. Mike Enemali and Dr. Bawa Muhammed for giving me the opportunity to conduct this research and providing invaluable guidance throughout this research. Their dynamism, vision, sincerity and motivation have deeply inspired me. They taught me the methodology to carry out the research and to present the research works as clearly as possible. It was a great privilege and honor to work and study under their guidance.

Words can't express how grateful I am to my parents for their love, prayers, care and sacrifices for educating and preparing me for my future. I am very much thankful to my siblings and friends for their understanding, prayers and continuing support to complete this research work.

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# ABSTRACT

The study assessed levels of some heavy metals (Cd, Cr, Cu, Fe, Mg, Mn and Ca) in drinking water sources in Azara, community where mining activities is ongoing. Fourteen (14) water samples were collected from river, Stream, boreholes, hand dug wells, in the community. Heavy metals were analyzed using Atomic Absorption Spectrophotometry. The analyzed results were compared with the permissible limits as prescribed by the Federal Ministry of Environment of Nigeria. Results revealed that the levels of the heavy metals in all the samples analyzed are below the maximum limit. However, one sample obtained from the River was found to have 0.137mg/dl copper which is above the permissible limit (0.10 mg/dl).

# CHAPTER ONE

# INTRODUCTION

Heavy metals are defined as metallic elements that have a relatively high density compared to water (Bennett *et al.*, 2013). With the assumption that heaviness and toxicity are inter-related, heavy metals also include metalloids, such as arsenic, that are able to induce toxicity at low level of exposure. In recent years, there has been an increasing ecological and global public health concern associated with environmental contamination by these metals. Also, human exposure has risen dramatically as a result of an exponential increase of their use in several industrial, agricultural, domestic and technological application. Reported sources of heavy metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents, and atmospheric sources. Environmental pollution is very prominent in point source areas such as mining, foundries and smelters, and other metal-based industrial operations (He *et al.*, 2015).

Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water. Their multiple industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment; raising concerns over their potential effects on human health and the environment. Their toxicity depends on several factors including the dose, route of exposure, and chemical species, as well as the age, gender, genetics, and nutritional status of exposed individuals. Because of their high degree of toxicity, arsenic, cadmium, chromium, lead, and mercury rank among the priority metals that are of public health significance. These metallic elements are considered systemic toxicants that are known to induce multiple organ damage, even at lower levels of exposure. They are also classified as human carcinogens (known or probable) according to the U.S. Environmental Protection Agency, and the International Agency for Research on Cancer.

Although heavy metals are naturally occurring elements that are found throughout the earth's crust, most environmental contamination and human exposure result from anthropogenic activities such as mining and smelting operations, industrial production and use, and domestic and agricultural use of metals and metal-containing compounds (Jan *et al.*, 2009). Environmental contamination can also occur through metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of heavy metals, sediment re-suspension and metal evaporation from water resources to soil and ground water. Natural phenomena such as weathering and volcanic eruptions have also been reported to significantly contribute to heavy metal pollution. Industrial sources include metal processing in refineries, coal burning in power plants, petroleum combustion, nuclear power stations and high tension lines, plastics, textiles, microelectronics, wood preservation and paper processing plants (Nriagu, 1989).

It has been reported that metals such as cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se) and zinc (Zn) are essential nutrients that are required for various biochemical and physiological functions. Inadequate supply of these micro-nutrients results in a variety of deficiency diseases or syndromes. Heavy metals are also considered as trace elements because of their presence in trace concentrations (ppb range to less than 10ppm) in various environmental matrices. Their bioavailability is influenced by physical factors such as temperature, phase association, adsorption and sequestration. It is also affected by chemical factors that influence speciation at thermodynamic equilibrium, complexation kinetics, lipid solubility and octanol/water partition coefficients. Biological factors such as species characteristics, trophic interactions, and biochemical/physiological adaptation, also play an important role (Verkleji, 1993).

The essential heavy metals exert biochemical and physiological functions in plants and animals. They are important constituents of several key enzymes and play important roles in various oxidation-reduction reactions (WHO/FAO/IAEA, 1996). Copper for example serves as an essential co-factor for several oxidative stress-related enzymes including catalase, superoxide dismutase, peroxidase, cytochrome c oxidases, ferroxidases, monoamine oxidase, and dopamine β-monooxygenase. Hence, it is an essential nutrient that is incorporated into a number of metallo enzymes involved in hemoglobin formation, carbohydrate metabolism, catecholamine biosynthesis, and cross-linking of collagen, elastin, and hair keratin. The ability of copper to cycle between an oxidized state, Cu (II), and reduced state, Cu (I), is used by cuproenzymes involved in redox reactions. However, it is this property of copper that also makes it potentially toxic because the transitions between Cu(II) and Cu (I) can result in the generation of superoxide and hydroxyl radicals. Also, excessive exposure to copper has been linked to cellular damage leading to Wilson disease in humans (Agency for Toxic Substances and Disease Registry (ATSDR) 2002).

Similar to copper, several other essential elements are required for biologic functioning; however, an excess amount of such metals produces cellular and tissue damage leading to a variety of adverse effects and human diseases. For some including chromium and copper, there is a very narrow range of concentrations between beneficial and toxic effects. Other metals such as aluminium (Al), antinomy (Sb), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), cadmium (Cd), gallium (Ga), germanium (Ge), gold (Au), indium (In), lead (Pb), lithium (Li), mercury (Hg), nickel (Ni), platinum (Pt), silver (Ag), strontium (Sr), tellurium (Te), thallium (Tl), tin (Sn), titanium (Ti), vanadium (V) and uranium (U) have no established biological functions and are considered as non-essential metals (Chang *et al.,* 1996).

In biological systems, heavy metals have been reported to affect cellular organelles and components such as cell membrane, mitochondrial, lysosome, endoplasmic reticulum, nuclei, and some enzymes involved in metabolism, detoxification, and damage repair (Wang *et al.*, 2001). Metal ions have been found to interact with cell components such as DNA and nuclear proteins, causing DNA damage and conformational changes that may lead to cell cycle modulation, carcinogenesis or apoptosis. Several studies have demonstrated that reactive oxygen species (ROS) production and oxidative stress play a key role in the toxicity and carcinogenicity of metals such as arsenic, cadmium, chromium, lead, and mercury. Because of their high degree of toxicity, these five elements rank among the priority metals that are of great public health significance. They are all systemic toxicants that are known to induce multiple organ damage, even at lower levels of exposure. These metals are also classified as either "known" or "probable" human carcinogens based on epidemiological and experimental studies showing an association between exposure and cancer incidence in humans and animals based on documentations by United States Environmental Protection Agency (U.S. EPA), and the International Agency for Research on Cancer (IARC),

Heavy metal-induced toxicity and carcinogenicity involves many mechanistic aspects, some of which are not clearly elucidated or understood. However, each metal is known to have unique features and physic-chemical properties that confer to its specific toxicological mechanisms of action. Introduction should be short and concise. transfer most of the information in introduction to literature review.

### 1.1 Statement of Research Problem

Human activities have drastically changed the biochemical cycles and balance of some heavy metals. Between 1850 and 1990, production of copper, lead and zinc increased 10-fold (Nriagu 1995; CACAR 2003). The main anthropogenic sources of heavy metals are various industrial processes, mining, foundries, and smelters, combustion of fossil fuel and gasoline, and waste incinerators. The major heavy metals of concern to EMEP are Hg, Cd and Pb, because they are the most toxic and have known serious effects on e.g. human health. Environmental exposure to high concentrations of heavy metals has been linked with e.g. various cancers and kidney damage.

## 1.2 Research Question(s)

Ho. Are there significant variations in heavy metals concentrations in different water sample?

H1. Are there likely effects of mining activities on heavy metal concentrations in these different water samples?

## 1.3 Justification

Anthropological activities including mining have been commonly associated with heavy metals toxicity. A handful of heavy metals are of great health significance and the concentrations of these heavy metals in food and water must be within permissible standard limits. The concentrations of these heavy metals vary between geographical locations and other contributing factors.

## 1.5 Aims and Objectives

The aim of this study is to determine the concentration of some heavy metals in different water sources in Azara community

In other to achieve this aim, the research is design to evaluate the concentration of Cr,Cd,Fe,Cu, Mg, Ca and Mn in the following water sources from Azara community.

(i) River

(ii) Stream

(iii) Borehole

(iv)Well

# CHAPTER TWO

# LITERATURE REVIEW

Technological advancements that led to improved life standards, has raised new challenges with respect to environmental safety, as unrestrained industrialization and urbanization without proper emission controls and pollution abatement have put human lives at risk (Bennett *et al.*, 2013). In developing countries, a need for economic growth that generally relies on agricultural and industrial development has bypassed environmental protection guidelines to a greater extent (Ikhuoria, and Okieimen, 2014). Heavy metals including metalloids, such as arsenic, are widely utilized to sustain the living standards of the modern world. In addition to natural sources, the amount of metals entering the environment through anthropogenic activities ranging from coal driven power plants to waste incinerators has increased tremendously. Owing to their prevalence, risk of human exposure to such metals continues to increase. In the past, inadequate regulation of recycling programs has led to accidental exposure. For example, the Itai-Itai and Minimiata disasters threatened public health and raised concerns regarding their safety in the environment. Because water and soil pollution represent the most important problems being faced by both developed and developing countries, metals in the environment are now wide spread environmental contaminants that pose a continuous threat to mankind. Overall, metal toxicity arising from different sources is a problem of increasing significance from an ecological, evolutionary, nutritional, and environmental perspective (Nagajyoti *et al.*, 2010). Heavy metal contamination is increasingly being recognized as dramatic in large parts of the developing world (Cheng, 2003). Contamination of dietary substances by chemicals and non-essential elements such as heavy metals is known to have a series of adverse effects on the body of humans and animals (D'Souza, and Peretiatko, 2012). Because they are ubiquitous and recalcitrant, their entry into the body poses a potential health risk to human populations. Metals can escape control mechanisms such as homeostasis, transport, compartmentalization, and binding to specified cell constituents, thus they can have toxic and even lethal effects. Heavy metals can cause malfunctioning of the cellular processes via displacement of essential metals from their respective sites. Oxidative deterioration of biological macromolecules has been found to be primarily due to binding of metals to DNA and nuclear proteins. Symptoms are often the first indicators of contamination, and as such help to identify the contaminant. Symptoms that arise as a result of metal poisoning include intellectual disability in children, dementia in adults, central nervous system disorders, kidney diseases, liver diseases, insomnia, emotional instability, depression and vision disturbances [9,10]. In short, toxicity associated with exposure to metals if unrecognized or inappropriately treated represents a clinically significant medical problem, having greater impact on increasing the morbidity and mortality rate. Having broader applicability in domestic, industrial, and agricultural purposes, their widespread distribution in the environment raises serious concerns over their potential health effects on humans. Although toxicity that arises from sudden exposure to substantial quantities of metals (such as from occupational exposure) typically affects multiple organ systems, severity of the health outcomes of toxic metals depends on the type and form of the element, route and duration of the exposure, and, to a greater extent, on a person's individual susceptibility (Jan *et al.*, 2011).

### 2.1 Heavy Metals

Heavy metals are naturally occurring elements, and are present in varying concentrations in all ecosystems. There is a huge number of heavy metals. They are found in elemental form and in a variety of other chemical compounds. Those that are volatile and those that become attached to fine particles can be widely transported on very large scales. Each form or compound has different properties which also affect what happens to it in food web, and how toxic it is. Human activities have drastically changed the biochemical cycles and balance of some heavy metals. Between 1850 and 1990, production of copper, lead and zinc increased 10-fold (Nriagu and Pacyna, 1998; CACAR 2003). The main anthropogenic sources of heavy metals are various industrial processes, mining, foundries, smelters, combustion of fossil fuel and gasoline, and waste incinerators. The major heavy metals of concern are Hg, Cd and Pb, because they are the most toxic and have known serious effects on e.g. human health. Environmental exposure to high concentrations of heavy metals has been linked with e.g. various cancers and kidney damage. There are considerably more measurements data on Hg, Cd and Pb in Europe than for other metals.

Table 2.1 Classification of elements according to toxicity and availability (Wood, 1974).

| Non-critical Accessible | Toxic but rare | Very toxic |
|---|---|---|
| Al | Ba | Ag |
| Br | Cs | As |
| C | Ga | Au |
| Ca | Hf | Be |
| Cl | Ir | Bi |
| F | La | Cd |
| Fe | Nb | Co |
| H | Re | Cu |
| K | Rh | Hg |
| Li | Ru | Ni |
| Mg | Ta | Pb |
| Na | Ti | Pd |
| O | | |
| P | | |
| Rb | | |
| S | | |
| Sr | | |

Table 2.2: Maximum permissible concentration of various metals in natural water for the protection of human health (EPA, 1987).

| | Maximum permissible level | |
|---|---|---|
| Metals | $mg/m^3$ | $\mu mol/m^3$ |
| Mercury | 0.144 | 1.72 |
| Lead | 5 | 24 |
| Cadmium | 10 | 89 |
| Selenium | 10 | 127 |
| Thallium | 13 | 64 |
| Nickel | 13.4 | 228 |
| Silver | 50 | 464 |
| Manganese | 50 | 910 |
| Chromium | 50 | 962 |
| Iron | 300 | 5372 |
| Barium | 1000 | 7281 |

As a fact, metals are elements and they have been an intrinsic component of the environment to which human and animals are adapted. Therefore, a "natural" exposure to all metals may thus be harmless to a human being. Many "trace metals" are even fundamental for growth and metabolism at low concentrations as they serve a biological function. Heavy metals only exert their harmful effect when exposure is excessive. The United States Environment Protection Agency (EPA, 1987) has recommended the maximum permissible concentrations of some toxic metals for the protection of human health as given in (Table 2.2). Lead is primarily of interest because of its toxic effect and it therefore may cause either acute or sub-acute health effects in a human population.

These metallic elements (mercury, arsenic, and lead) that are able to induce toxicity even at lower levels of exposure are considered systemic toxicants. Occupying the top position on the list of

hazardous substances, the following sections provide insight into the mechanisms through which these metals exert their toxicity within the body of living organisms

### 2.1.1 Cadmium:

Humans are exposed to cadmium by inhalation and ingestion although the main health impacts recorded in the literature are through dietary exposure (kidney and bone damage) and inhalation from smoking tobacco and occupational exposure (lung damage). Dietary intake accounts for 90% of all exposure in non-smokers. Cadmium in the environment is toxic to plants and animals and many micro-organisms (Gulson *et al.*, 2003). Cadmium does not degrade in the environment to less toxic products which contributes to its bioaccumulation in the kidneys and liver of vertebrates and invertebrates. Cadmium enters the environment from a variety of anthropogenic sources (Skoczynska, 2008). Wastewater is key source of environmental cadmium contamination and diffuse pollution occurs through industrial air emissions and widespread use of fertilizers on agricultural soils. Plants (including rice and tobacco) that are grown in contaminated soils take up cadmium and lead to human dietary (and inhalation) exposures (Karrari *et al.*, 2012). However, human exposure also occurs when cadmium contaminated soils are disturbed and the dust is inhaled. Diets high in meat (especially liver and kidneys) or products from marine mammals may result in a particularly high intake of cadmium. Cadmium is not considered essential for biological function in humans. The main human organ impacted by cadmium exposure is the kidney in both the general population and the occupationally exposed. Tobacco smokers are considered to be at particular risk as are people with low iron levels. A secondary critical effect is skeletal damage as a secondary response to kidney damage or direct action on the bone cells by the cadmium (Gulson *et al.*, 2003).

### 2.1.2 Copper:

Copper is a naturally-occurring metallic element that occurs in soil at an average concentration of about 50 parts per million (ppm). It is present in all animals and plants and is an essential nutrient for humans and animals in small amounts. The major sources of environmental copper releases include the mining, smelting and refining of copper, industries producing products from copper such as wire, pipes and sheet metal, and fossil fuel combustion (Skoczynska, 2008). Water pipes are often made of copper and bath fixtures may be made from brass and bronze alloys that contain copper. The principal source of copper in drinking water results from the leaching of copper from pipes and bath fixtures due to acidic water. Blue-green stains left in bath fixtures are a sign of the presence of copper in water (Gulson *et al.*, 2003). Other releases of copper to the environment include agricultural use against plant diseases and treatments applied to water bodies to eliminate algae. Health Effects Absorption/Metabolism Studies investigating oral absorption of copper have found the percentage absorbed ranging from 24-60 percent. Factors affecting the amount absorbed include the amount of copper in the diet and competition with other metals found in food such as iron and zinc. There are no studies examining inhalation exposure to copper. The amount of dermal absorption is also not known, but a few studies indicate that it is very low. Beneficial Effects Copper is a component of several enzymes necessary for normal metabolic functions in humans. The Recommended Daily Allowance (RDA) of copper for adults is 0.9 milligrams (mg). The median intake of copper from the typical U.S. diet ranges from 1 to 1.6 mg/day (Ahamed and Siddiqui, 2012).

The safe highest level of intake for an extended period of time (chronic exposure) is 10 mg/day. Food sources rich in copper include shellfish, organ meats, nuts, beans and cocoa. Effects of copper deficiency can include anemia, low numbers of white blood cells, osteoporosis in infants and children, and defects in connective tissue leading to skeletal problems. Short-Term (Acute) Effects Acute poisoning from ingestion of excessive copper can cause temporary gastrointestinal distress with symptoms such as nausea, vomiting, and abdominal pain. Liver toxicity was seen in doses high enough that resulted in death. 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 (Ahamed and Siddiqui, 2012). However, at high enough levels, chronic overexposure to copper can damage the liver and kidneys. Wilson's disease is an inherited (genetic) disorder in which copper builds up in the liver. Symptoms of liver toxicity (jaundice, swelling, pain) usually do not appear until adolescence. Carcinogenicity (ability to cause cancer) although some studies of workers exposed to copper have shown increased cancer risks, they were also exposed in the workplace to other chemicals with carcinogenic potential. Increased cancer risk has not been found in animal studies (Gulson *et al.*, 2003). Copper is currently categorized by the EPA as a Group D carcinogen (inadequate evidence to classify) and has not yet been reviewed for placement into one of the new cancer classification categories. Reproductive/Developmental Effects There are no reports of developmental effects occurring in humans exposed to elevated levels of copper. 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 (Ahamed and Siddiqui, 2012).

### 2.1.3 Magnesium (Mg)

Magnesium is an active component of several enzyme systems in which thymine pyrophosphate is a cofactor. Oxidative phosphorylation is greatly reduced in the absence of magnesium. Mg is also an essential activator for the phosphate-transferring enzymes myokinase, diphophopyridinenucleotide kinase, and creatine kinase. It also activates pyruvic acid carboxylase, pyruvic acid oxidase, and the condensing enzyme for the reactions in the citric acid cycle. It is also a constituent of bones, teeth, enzyme cofactor, (kinases, etc) (Murray *et al.*, (2000). The health status of the digestive system and the kidneys significantly influence magnesium status. Magnesium is absorbed in the intestines and then transported through the blood to cells and tissues. Approximately one-third to one-half of dietary magnesium is absorbed into the body. Gastrointestinal disorders that impair absorption such as Crohn's disease can limit the body's ability to absorb magnesium. These disorders can deplete the body's stores of magnesium and in extreme cases may result in magnesium deficiency. When a magnesium-deficient diet is fed to young chicks, it leads to poor growth and feathering, decreased muscle tone, ataxia, progressive incoordination and convulsions followed by death (Merck, 1986). Chronic or excessive vomiting and diarrhea may also result in magnesium depletion. Deficiency diseases or symptoms is secondary to malabsorption or diarrhoea, alcoholism. Acute magnesium deficiency results in vasodilation, with erythemia and hyperaemia appearing a few days on the deficient diet. Neuromuscular hyperirritability increases with the continuation of the deficiency, and may be followed eventually by cardiac arrhythmia and generalized tremours. A common form of magenesium-deficiency tetany in ruminants is called grass tetany or wheat wheat-pasture poisoning. This condition occurs in ruminants grazing on rapidly growing young grasses or cereal crops and develops very quickly. Toxicity disease or symptoms of magnesium deficiency in humans include depressed deep tendon reflexes and respiration (Murray *et al.*, 2000). Sources include leafy green vegetables (containing chlorophyll).

### 2.1.4 Calcium (Ca)

Calcium functions as a constituent of bones and teeth, regulation of nerve and muscle function. In blood coagulation, calcium activates the conversion of prothrombin to thrombin and also takes part in milk clotting. It plays a vital role in enzyme activation. Calcium activates large number of enzymes such as adenosine triphosphatase (ATPase), succinic dehydrogenase, lipase etc. It is also required for membrane permeability, involved in muscle contraction, normal transmission of nerve impulses and in neuromuscular excitability. A reduced extracellular blood calcium increases the irritability of nerve tissue, and very low levels may cause spontaneous discharges of nerve impulses leading to tetany and convulsions (Murray *et al.*, 2000). Calcium absorption requires calcium-binding proteins and is regulated by vitamin D, sunlight, parathyroid hormone and thyrocalcitonin. Thyrocalcitonin decreases plasma calcium and phosphate levels whereas parathyroid hormone increases them. Dietary calcium and phosphorus are absorbed mainly in the upper small intestine, particularly the duodenum and the amount absorbed is dependent on source, calcium-phosphorus ratio, intestinal pH, lactose intake and dietary levels of calcium, phosphorus, vitamin D, iron, aluminium, manganese and fat. The greater the need, the more efficient the absorption. Absorption of calcium and phosphorus is facilitated by a low intestinal pH which is necessary for their solubility and thus normal gastric secretion of hydrochloric acid or $H^+$ is necessary for efficient absorption. Achlorhydria decreases absorption of these minerals. The low pH of the duodenum accounts for the greater absorption in that area. Lactose also enhances the aborption of calcium (Horsfall *et al.*, 2014).

In children, calcium deficiency causes rickets due to insufficient calcification by calcium phosphate of the bones in growing children. The bones therefore remain soft and deformed by the body weight. In adults, it causes osteomalacia, a generalized demineralization of bones. It may also contribute to osteoporosis, a metabolic disorder resulting in decalcification of bone with a high incidence of fracture, that is, a condition where calcium is withdrawn from the bones and the bones become weak and porous and then breaks (Horsfall *et al.*, 2014; Murray *et al.*, 2000). Calcium deficiency also affects the dentition of both children and adult. Toxicity symptoms occur with excess absorption due to hypervitaminosis D or hypercalcaemia due to hyperparathyroidism, or idiopathic hypercalcaemia. Excess calcium depresses cardiac activity and leads to respiratory and cardiac failure; it may cause the heart to stop in systole, although, normally, calcium ions increase the strength and duration of cardiac muscle contraction. Excess calcium and phosphorus are excreted by the kidney. Ca and P excreted in faeces are largely the Lee, and Aronoff 2003). Growing, pregnant and especially lactating humans and animals require liberal amounts of calcium and phosphorus. Parturient paresis, or milk fever, in cows is associated with calcium metabolism.

### 2.1.5 Chromium (Cr)

Chromium is an essential element for animals and humans (Frieden, 2012). It has been found in nucleoproteins isolated from beef liver and also in RNA preparations (Uppala *et al.*, 2005). It could play a role in maintaining the configuration of the RNA molecule, because Cr has been shown to be particularly effective as a cross-linking agent for collagen. Cr has also been identified as the active ingredient of the glucose tolerant factor (Brown, 2003), a dietary factor required to maintain normal glucose tolerance in the rat. Trivalent chromium is a constituent of ''glucose tolerance factor'' (GTF), which binds to and activates/potentiates insulin action (Murray *et al.*, 2000). Chromium compounds have a wide variety of industrial uses, including production of stainless steel and other alloys, high-melting refractory materials, pigments and mordants for paints and dyes, tanned leather goods and chrome plating (Frieden, 2012). Cr affects the action of insulin in protein metabolism, as indicated by rats fed chromium-deficient diets repleted by chromium (Roginski and Mertz, 2008). Insulin-mediated amino acid transport into tissues was enhanced and incorporation of labelled glycine, serine and methionine into heart protein was greater in chromium-supplemented animals.

### 2.1.6 Iron (Fe)

Iron functions as haemoglobin in the transport of oxygen. Fe is an important constituent of succinate dehydrogenase as well as a part of the haeme of haemoglobin (Hb), myoglobin and the cytochromes (Chandra, 2000). Iron is required for proper myelination of spinal cord and white matter of cerebellar folds in brain and is a cofactor for a number of enzymes involved in neurotransmitter synthesis (Larkin and Rao, 1990). Iron is involved in synthesis and packaging of neurotransmitters, their uptake and degradation into other iron-containing proteins which may directly or indirectly alter brain function (Beard, 2001).

Iron exists in the blood mainly as haemoglobin in the erythrocytes and as transferrin in the plasma. It is transported as transferrin; stored as ferritin or haemosiderin and it is lost in sloughed cells and by bleeding (Murray *et al.*, 2000). Fe is required for making Hb and it is a prooxidant which is also needed by microorganisms for proliferation (Beard, 2001). Biologically important compounds of iron are haemoglobin, myoglobin, cytochromes, catalases and peroxidase (Malhotra, 1998). Factors effecting the absorption of iron are: low phosphate diet which increases iron absorption, whereas high phosphate diet decreases iron absorption by forming insoluble iron phosphates. Adrenocortical hormones (glucocorticoids) play a role in regulating the level of plasma iron. During stress, when the hypothalamus, adenohypophysis, and adrenal cortex are activated, regardless of the source, the plasma iron decreases (Horsfall *et al.*, 2003). Iron in ferrous form is more soluble and is readily absorbed than the ferric form. Phytic acid and oxalic acid decreases iron absorption by forming iron phytate and iron oxalate. The absorption of iron is inhibited by profuse diarrhoea, malabsorption syndrome, achlorohydria, dissertion of small intestine and partial or total gastrectomy (Malhotra, 1998).

Fe deficiency is associated with alterations in many metabolic processes that may impact brain functioning, among whom are neurotransmitter metabolism, protein synthesis, organogenesis etc (Beard, 2001). Early iron deficiency has also been reported to affect GABA metabolism in adult rats (Frieden, 2012). Fe accumulation has been related to some neurologic disorders such as Alzheimer disease, Parkinson disease, type-1 neuro-degeneration with brain iron accumulation and other disorders (Horsfall *et al.*, 2003). Brain is quite sensitive to dietary iron depletion and uses a host of mechanisms to regulate iron flux homostatically (Brown, 2003).

The pig is born with low iron stores and develops an iron deficiency anaemia if not provided with supplementary iron. The factors causing the onset of anaemia in piglets are its relatively low iron stores at birth, its high growth rate early in life, and the low level of iron in sow milk. If the pig is given iron supplements at birth, the total red cell mass or volume per unit of body weight increases from birth to three weeks of age (Frieden, 2012). Iron deficiency anaemia also occurs at birth in other animals like dogs, cats, cattle, etc. but it is more pronounced in pigs. Excessive accumulation of iron in the liver, pancreas, heart, lungs and other tissues cause haemosiderosis and when this is accompanied by bronze pigmentation of the skin, the condition is called haemochromatosis (Malhotra, 1998; Murray *et al.*, 2000). Sources include red meat, spleen, heart, liver, kidney, fish, egg yolk, nuts, legumes, molasses, iron cooking ware, dark green leafy vegetables.

### 2.1.7 Manganese (Mn)

Manganese is a cofactor of hydrolase, decarboxylase, and transferase enzymes (Murray *et al.*, 2000). It is involved in glycoprotein and proteoglycan synthesis and is a component of mitochondrial superoxide dismutase. Manganese is a co-factor in phosphohydrolases and phosphotransferases involved in the synthesis of proteoglycans in cartilage. Mn is a part of enzymes involved in urea formation, pyruvate metabolism and the galactotransferase of connective tissue biosynthesis (Chandra, 1990). Mn activates several important enzyme systems and in this capacity it is required for the synthesis of acid mucopolysaccharides, such as chondroitin sulphate, to form the matrices of bones and egg shells. Consequently, skeletal deformities and defects in shell quality occur when the manganese intake is inadequate.

Increased absorption of manganese has been reported during pregnancy in sows (Merck, 2006) and with coccidiosis infection in chickens (Uppala *et al.*, 2005). Mn deficiency has been demonstrated in several animal species including laboratory animals, pigs, poultry, and possibly in cattle. Its severity depends greatly on the degree and duration of the deficiency and on the maturity of the animal (Horsfall *et al.*, 2003). Manganese deficiency presents with the following signs; in pigs, lameness, enlarged hock joints, and shortened legs, in cattle, leg deformities with overknuckling, in chicks, poults and ducklings, perosis or slipped tendon; and in chick embryos, nutritional chondrodystrophy.

## 2.2 Cytotoxic Mechanisms of Heavy Metals

Heavy metal induced toxicity has been studied extensively and reported by various workers. Having the potential to produce highly reactive chemical entities such as free radicals, heavy metals are known to cause oxidation of sulfhydryl groups of proteins, depletion of protein, DNA damage, lipid peroxidation, and several other effects. The underlying factors making the greatest contribution to toxicity for different metals involves generation of reactive oxygen (ROS) and nitrogen (RNS)species that disturb cell redox systems. ROS that are distinguished by their high chemical reactivity, include free radicals such as superoxide (O2,´), hydroxyl (OH,), peroxyl (RO2,) and alkoxyl (RO,), as well as certain non-radicals such as peroxynitrite (ONOO´) and H2O2, which are either oxidizing agents or get easily converted to radicals.

## 2.3 Azara and Mining

The magnitude and significance of impact on environment due to mining varies from mineral to mineral and also on the potential of the surrounding environment to absorb the negative effects of mining, geographical disposition of mineral deposits and size and method of mining A major environmental problem relating to mining in many parts of the developing world is uncontrolled discharge of contaminated water (or decant) from abandoned mines operations (Ranjna *et al.,* 2013).

Baryte is the chief constituent of lithopone paint and it is also extensively used as an inert volume and weight filler in drilling mud, rubber, glass, paper and highly used in several chemical industries. Veins of barites up to 1.8m wide and more than a kilometer 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 barites have been proved more recently in the Azara area by the Nigerian Mining Corporation in this area, and 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).

Baryte was first detected in Azara in the early 1960s (Courtesy of Geological Survey of Nigeria, 1965). The Nigeria Baryte Mining and Processing Company (NBMPC) Ltd., incorporated in 1988 was charged with the exploration and exploitation of baryte in Azara and any part of Nigeria where baryte was found.

Contaminants and toxic compounds from mining activities jeopardizes quality of surface and underground water by making it unsafe for drinking and industrial usage, disturbing the hydrology of the area (Roy *et. al*., 2003). In Africa (Nigeria inclusive), poverty coupled with poor policy frameworks to address mining activities and the mining industry is a major threat to environmental sustainability (Oelofse, and Turton, 2008). With the increasing number of artisan's miners in Africa, water quality has been polluted due to contamination (Oelofse and Turton, 2008). The release to the environment of mining waste can result in profound irreversible destruction of ecosystem. In many cases the polluted sites may never be fully restored, for pollution is so persistent that there is no available remedy (EEB, 2000).

Due to improper planning and negligence on mining regulations, an appreciable amount of environmental degradation and ecological damage to water occurs in almost every mining site in Nigeria. The key questions are whether surface and groundwater supplies will remain fit for human consumption, and whether the quality of water in mining sites will remain adequate to support human and wildlife (Anirudha, 2005). Baryte can dissolve in water and, when dissolved, can cause an environmental and health hazard (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 as component. In most developing countries like Nigeria, underground and river water has remained a major source of water to the teaming population of the people in the rural areas. Baryte mining affects quality of water resources, both surface and groundwater, at various stages of the life cycle of the mine and even after its closure of the mine (Younger *et. al.*, 2002; Ishaya, 2008). Estimation of the quality of water is extremely important for proper assessment of the associated hazards. These issues must be addressed within the context of the environmental requirements in place in the jurisdiction within which the mining occurs (Oden, 2012).

# CHAPTER THREE

# MATERIALS AND METHODS

## 3.1 Study Area

The study area Azara is located in Awe Local Government area of Nasarawa state between latitude of 8.32° N to 8.53° N and longitude 8.18° E and 8.30° E within the Middle Benue Trough of Nigeria. The state has an area of 27,117 km$^2$ and awe LGA population of 112,574 at the 2006 census. The activities predominant in the place are mining. Mining processes are in thousands of tons. Azara mining site is located in Awe Local Government Area of Nasarawa State and has an altitude of 181.5m Above Sea Level (Obaje, 2006).

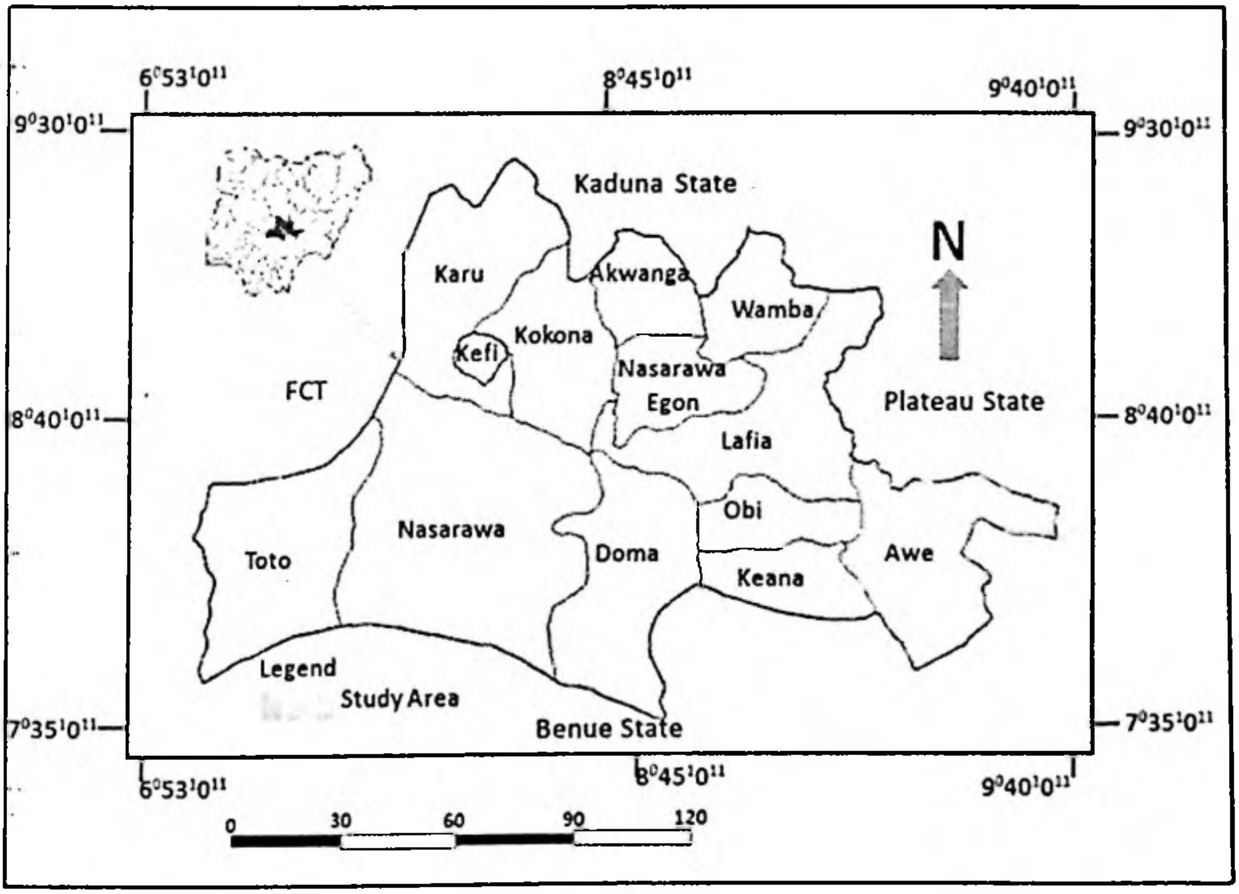

Figure 3.1: Map of study area.

## 3.2 Sample Collection and Preparation

A total of fourteen water samples were collected in nitric acid washed plastic bottles. Four samples from Azara Stream (Kogi Wusse), and Surface running water, three samples from Boreholes, Hand dug well respectively. All the sampling bottles were washed with sample water to reduce contamination. The water samples were collected in a clean polyethylene bottles, because glass bottles absorb metals and therefore will cause inaccuracy in analysis. The water was filtered through a 0.45 micro meter membrane filter as soon as possible after collection. For the digestion, 1 L of each sample was measured into a clean digestion flask. 9 ml of concentrated HNO3 and 3 ml of concentrated HCl was added into the sample in the digestion flask (USEPA, 1986; Bader, 2011). The whole samples was heated in a hot plate until all the brownish fumes was expelled out (Nitrogenous Compound) which confirm that the sample is digested and the samples was allowed to cool at room temperature. A few millilitres of distilled water was added and the mixture was filtered into 25 ml standard flask and it was transferred into plastic reagent bottle for Atomic Absorption Spectrometry (AAS).

The Atomic Absorption Spectrometry is a spectroanalytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state. The technique measures the concentrations of elements in digested samples down to parts per million (ppm) in a sample.

### 3.2.1 Digestion of Water Sample

The EPA vigorous digestion method described by Gregg (1989) was adopted. 100ml of each of the representative water samples were transferred into Pyrex beakers containing 10ml of concentrated HNO3. The samples were boiled slowly and then evaporated on a hot plate to the lowest possible volume (about 20ml). The beakers were allowed to cool and another 5ml of Conc. HNO3 was added. Heating was continued with the addition of Conc. HNO3 as necessary until digestion was complete. The samples were evaporated again to dryness (but not baked) and the beakers were cooled, followed by the addition of 5ml of HCl solution (1:1 v/v). The solutions were then warmed and 5ml of 5M NaOH was added, then filtered. The filtrates were transferred to 100ml volumetric flasks and diluted to the mark with distilled water. These solutions were then used for the elemental analysis.

### 3.2.2 Metal Analysis

A total of nine metallic elements were determined in the pre – treated samples of water using Atomic Absorption Spectrophotometry as described by Gregg (1989). These include Al, Cr, Mn, Fe, Cu, Ca, Mg, and Cd.

# CHAPTER FOUR

# RESULTS AND DISCUSSION

## 4.1 Results

### 4.1.1 Concentration of heavy metals in different water samples.

## 4.2 Discussion

Findings from the fourteen underground water samples collected in this study area depicts that the concentration of iron, Copper, manganese, chromium and cadmium are all within the permissible limit as prescribe by the Federal Ministry of Water Resources. The copper content of all the water samples except sample one fell within the permissible limit. The permissible limit as prescribe by FME as 0.1mg/l while the result of sample one is 0.137mg/l. Copper is an essential element for living organisms, including humans, and-in small amounts-necessary in our diet to ensure good health. However, too much copper as observed in sample one can cause adverse health effects such as vomiting, diarrhea, stomach cramps, and nausea. It has also been associated with liver damage and kidney disease. Though, the human body has a natural mechanism for maintaining the proper level of copper in it. However, children under one-year old that have not yet developed this mechanism, as a result, are more vulnerable to the toxic effects of copper. People with Wilson's disease also have a problem with maintaining the proper balance of copper and should also exercise particular care in limiting exposure to copper. Childhood Cirrhosis associated with excessive copper concentrations (Nirmal *et. al.,* 2011; Ishaya *et. al.,* 2016). The copper content of most of the underground water does not exceed prescribe limits, although concentrations can be higher in well water and in hard water where mining activities takes place.

TABLE 4.1: CONCENTRATIONS OF HEAVY METALS IN WATER SAMPLES PRESENTED AS MEAN ± STANDARD ERROR OF MEAN (SEM) IN mg/dl

| HEAVY METAL (Mg/kg) | STANDARD | RIVER | STREAM | BOREHOL | WELL |
|---|---|---|---|---|---|
| Fe | 1.50 | 0.11 ± 0.02 | 0.11 ± 0.00 | 0.11 ± 0.01 | 0.11 ± 0.00 |
| Cu | 0.10 | 0.05 ± 0.03 | 0.21 ± 0.00 | 0.21 ± 0.00 | 0.02 ± 0.00 |
| Mn | 0.20 | 0.23 ± 0.00 | 0.21 ± 0.00 | 0.02 ± 0.00 | 0.02 ± 0.00 |
| Cr | 1.00 | 0.23 ± 0.01 | 0.21 ± 0.00 | 0.02 ± 0.01 | 0.02 ± 0.00 |
| Cd | 1.00 | 0.03 ± 0.01 | 0.03 ± 0.00 | 0.03 ± 0.00 | 0.02 ± 0.01 |
| Ca | 150 | 175.47 ± 8.19 | 184.02 ± 4.27 | 166.97 ± 12.87 | 164.02 ± 4.27 |
| Mg | 50.0 | 34.24 ± 7.00 | 30.05 ± 4.28 | 30.00 ± 4.30 | 38.57 ± 4.27 |

The comparison of mean concentration of these metals with the standard for fresh water in river, stream, borehole, and well indicates the mean concentrations of Fe, Cu, Mn, Mg, Cr, Cd, Ca, were lower than the standards for fresh water except Mg and Ca which were higher.

Table 4.1 shows all results of heavy metals in River, Stream, Borehole and Well water samples. All the heavy metals were below the maximum permissible limits as prescribed by Federal Ministry of Environment, except Calcium and Magnesium (Fig 4.2) which shows a concentration of 150mg/kg and 50mg/kg respectively. The total heavy metal content of the fourteen water samples showed that thirteen samples fell within the permissible limit of the Federal Ministry of Environment. However, sample one from the stream contains a greater concentration of copper. Contrary to the findings of this study, water supplies from groundwater around solid minerals mining often encounter significant levels of contamination (Langan, 2009).

The Calcium content of all the fourteen water samples were above the permissible (150mg/l) limit of the Federal Ministry of Environments shown in Fig 4.2, 4.4, 4.6 and 4.8. Calcium homeostasis is tightly regulated by 1, 25 dihydroxyvitamin D, which controls the absorption and elimination of calcium in the intestinal lumen. When calcium is absorbed in excess of need, the excess is excreted by the kidney in healthy people without renal impairment. However, in people with milk alkali syndrome, excess calcium precipitates hypercalcemia, metabolic alkalosis and renal insufficiency. Milk-alkali syndrome is characterized by high blood calcium and metabolic alkalosis caused by taking in too much calcium and absorbable alkali; common sources of calcium and alkali are dietary supplements taken to prevent osteoporosis and antacids. If untreated, milk-alkali syndrome may lead to kidney failure or death. Although calcium can interact with iron, zinc, magnesium and phosphorus within the intestine, thereby reducing the absorption of these minerals, available data do not suggest that these minerals are depleted when humans consume diets containing calcium above the recommended levels (Langan, 2009; Ishaya *et. al.,* 2014).

Magnesium content of two underground water samples (samples 4 and 12) are above the permissible limit of 50 mg/l with result of 51.4 mg/l while sample 51.4mg/l respectively(Appendix). Excess magnesium causes hyper magnesaemia associated with a significantly decreased ability to excrete magnesium. Increased intake of magnesium in water may cause a temporal adaptable change in bowel habits (diarrhoea), but seldom causes hypermagnesaemia in persons with normal kidney function. Drinking water with high magnesium can have a laxative effect, although research suggests that consumers adapt to these levels as exposures continue. Laxative effects have also been associated with excess intake of magnesium in water (Langan, 2009, Ishaya and Abaje, 2009).

There were significant similarities between total hardness and calcium glaringly exceeded the permissible limits as prescribe by FME. The source of the calcium and total hardness are undoubtedly the baryte mining within the drainage basin. The high amount of calcium in the form of carbonate usually results to the hardness of the water from the mining ponds. Temporally the hardness of the water is removed by boiling the water. This will impact economically on the users of the underground water for laundry purposes, as much money will be spent on soap and boiling to soften the water (Ndinwa and Ohwona, 2014).

# CHAPTER FIVE

## CONCLUSION AND RECOMMENDATION

### 5.1 CONCLUSION

The study reveals that all water samples analyzed contain heavy metals within permissible limits of the Federal Ministry of Environment and Water Resources of Nigeria (2019) except one sample from the river which contains copper above the permissible limits. The study therefore concludes that most of the water from different sources in Azara community are safe and fit for human consumption.

### 5.2 RECOMMENDATIONS

We recommend further research should be carried out at the agricultural site close to the minning area on the level of heavy metals plants absorbed in that environment.

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# APPENDIX

Heavy metal concentration of Water samples and Permissible limits (FME). 1-4, River, 5-8 Stream, 9-11 Borehole, 12-14, Well

| **S/N** | **(units in mg/dl)** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** | **13** | **14** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Iron | 0.109 | 0.111 | 0.108 | 0.107 | 0.110 | 0.109 | 0.110 | 0.109 | 0.108 | 0.112 | 0.111 | 0.101 | 0.113 | 0.111 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | Copper | 0.0137 | 0.0221 | 0.0221 | 0.0221 | 0.0219 | 0.0221 | 0.0221 | 0.0222 | 0.0221 | 0.0221 | 0.0221 | 0.0221 | 0.0221 | 0.022 |
| 3 | Manganese | 0.0026 | 0.0222 | 0.0222 | 0.0221 | 0.0223 | 0.0221 | 0.002 | 0.0222 | 0.0221 | 0.0220 | 0.0221 | 0.0221 | 0.0019 | 0.002 |
| 4 | Chro | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.002 | 0.00 | 0.00 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | m | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 1 | | 1 | 1 |
| | iu | 2 | 4 | 5 | 1 | 1 | 1 | 2 | 1 | 1 | 0 | 8 | | 9 | 9 |
| | m | | | | | | | | | | | | | | |
| 5 | C | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. | 0. |
| | a | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | d | 2 | 2 | 2 | 3 | 2 | 2 | 3 | 3 | 3 | 2 | 2 | 2 | 2 | 2 |
| | m | 9 | 8 | 7 | 2 | 5 | 9 | 1 | 1 | | 9 | 9 | 4 | 9 | 8 |
| | iu | | | | | | | | | | | | | | |
| | m | | | | | | | | | | | | | | |

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | C | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 1 |
|  | al | 7 | 8 | 5 | 8 | 8 | 7 | 8 | 8 | 0 | 5 | 5 | 8 | 8 | 7 | 5 |
|  | ci | 1. | 8. | 4. | 8. | 8. | 1. | 8. | 8. | 5. | 4. | 4. | 8. | 8. | 1. | 0. |
|  | u | 2 | 3 | 1 | 3 | 3 | 2 | 3 | 3 | 6 | 1 | 1 | 3 | 3 | 2 |  |
|  | m |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 7 | M | 3 | 3 | 1 | 5 | 3 | 3 | 3 | 1 | 3 | 3 | 1 | 5 | 3 | 3 | 5 |
|  | a | 4. | 4. | 7. | 1. | 4. | 4. | 4. | 7. | 4. | 4. | 7. | 1. | 4. | 4. | 0 |
|  | g | 2 | 2 | 1 | 4 | 3 | 3 | 4 | 2 | 3 | 3 | 1 | 4 | 3 | 3 |  |
|  | n | 4 | 4 |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | es |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | iu |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | m |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |

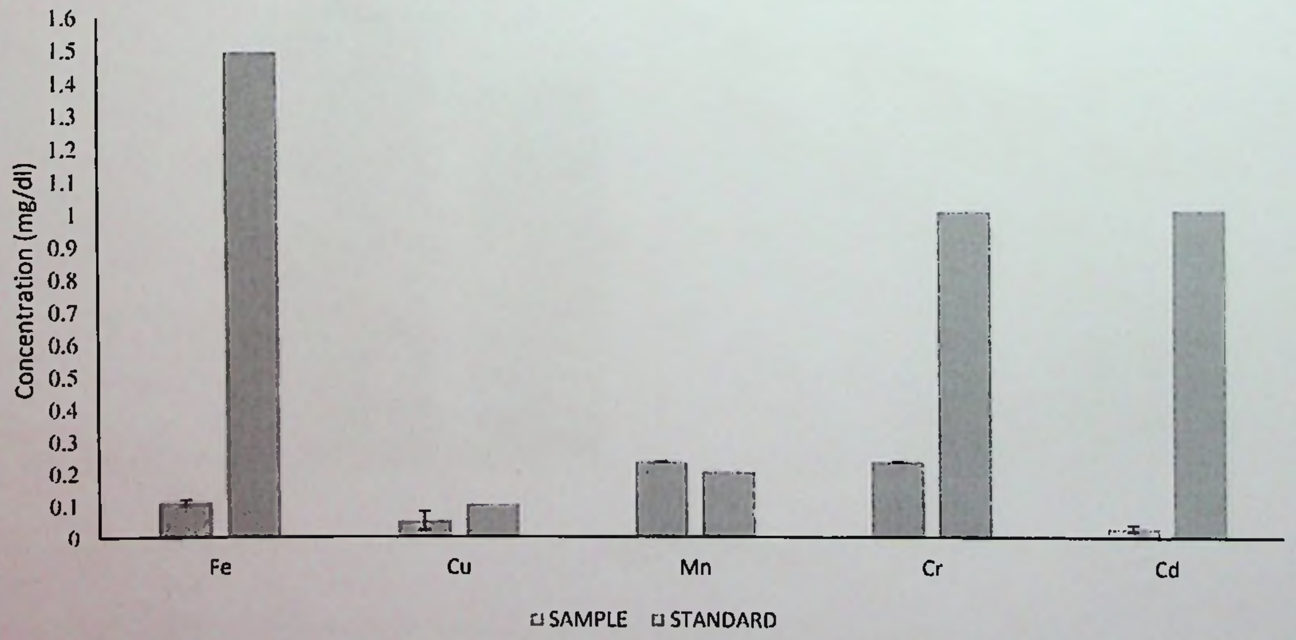

FIG 4.1: Concentrations of Heavy metals in River water sample

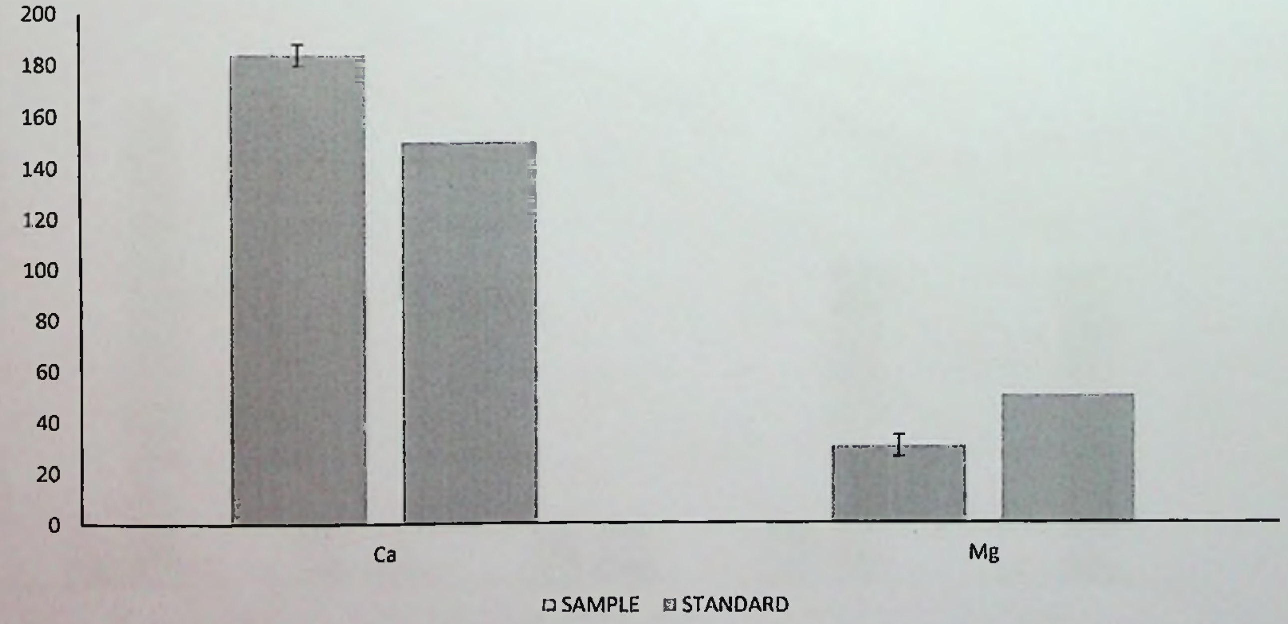

Fig 4.2 Concentrations of Calcium and Magnesium in River water sample

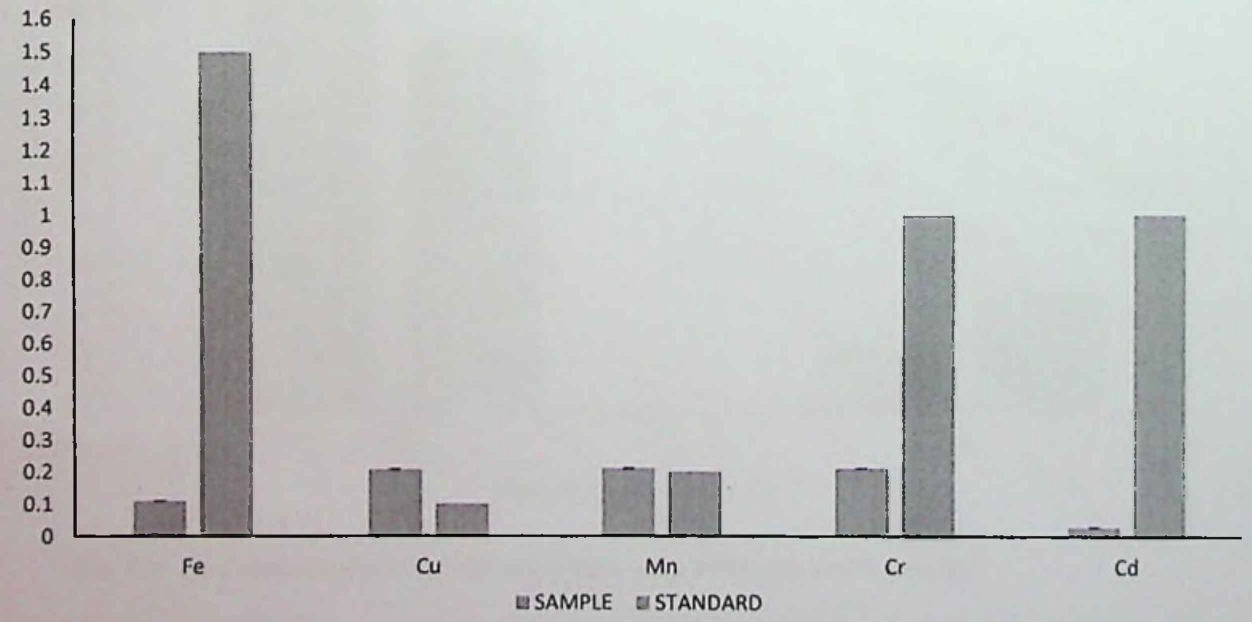

Fig 4.3 Concentrations of Heavy metals in Stream water sample

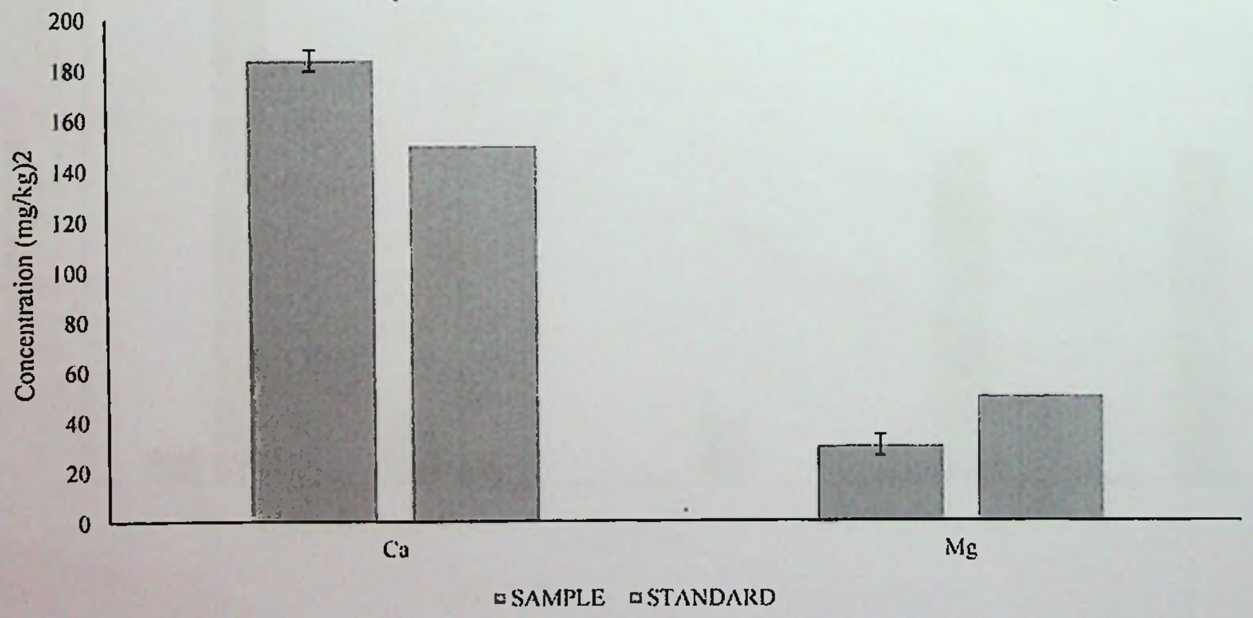

Fig 4.4 Concentrations of Calcium and Magnesium in Stream water sample

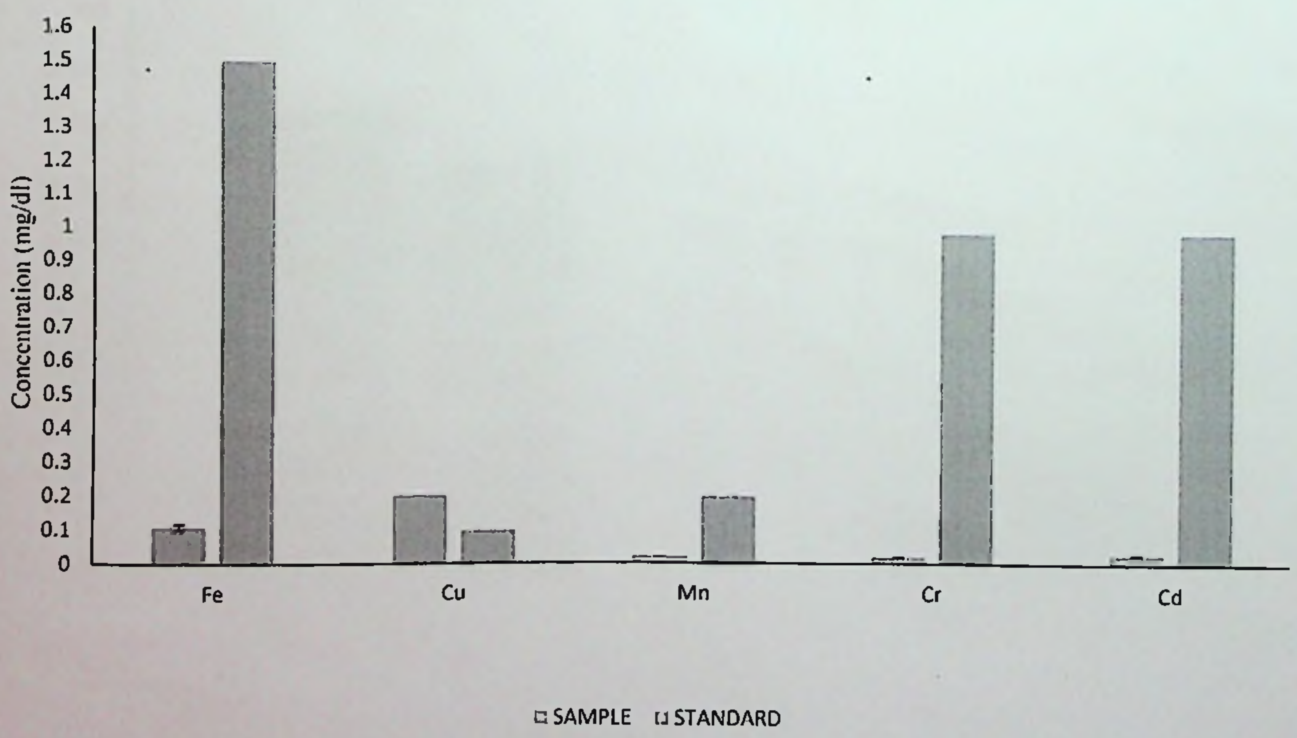

Fig 4.5 Concentrations of Heavy metals in Borehole water sample

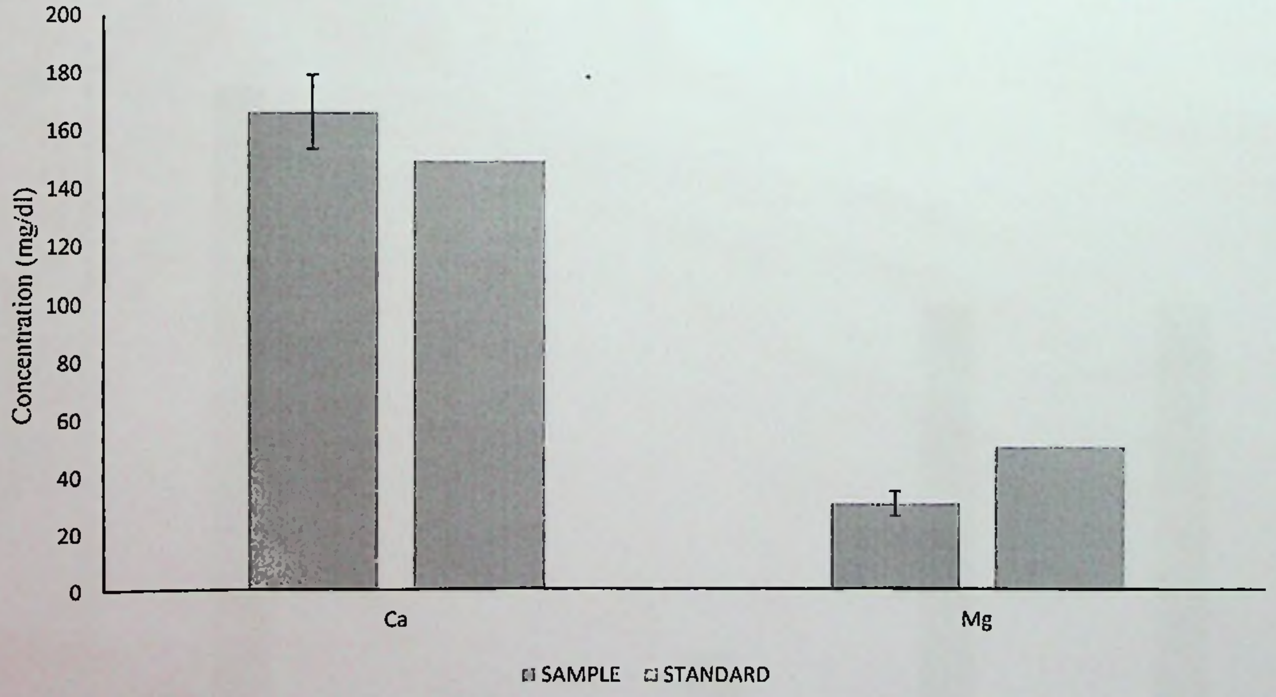

Fig 4.6 Concentrations of Calcium and Magnesium in Borehole water sample

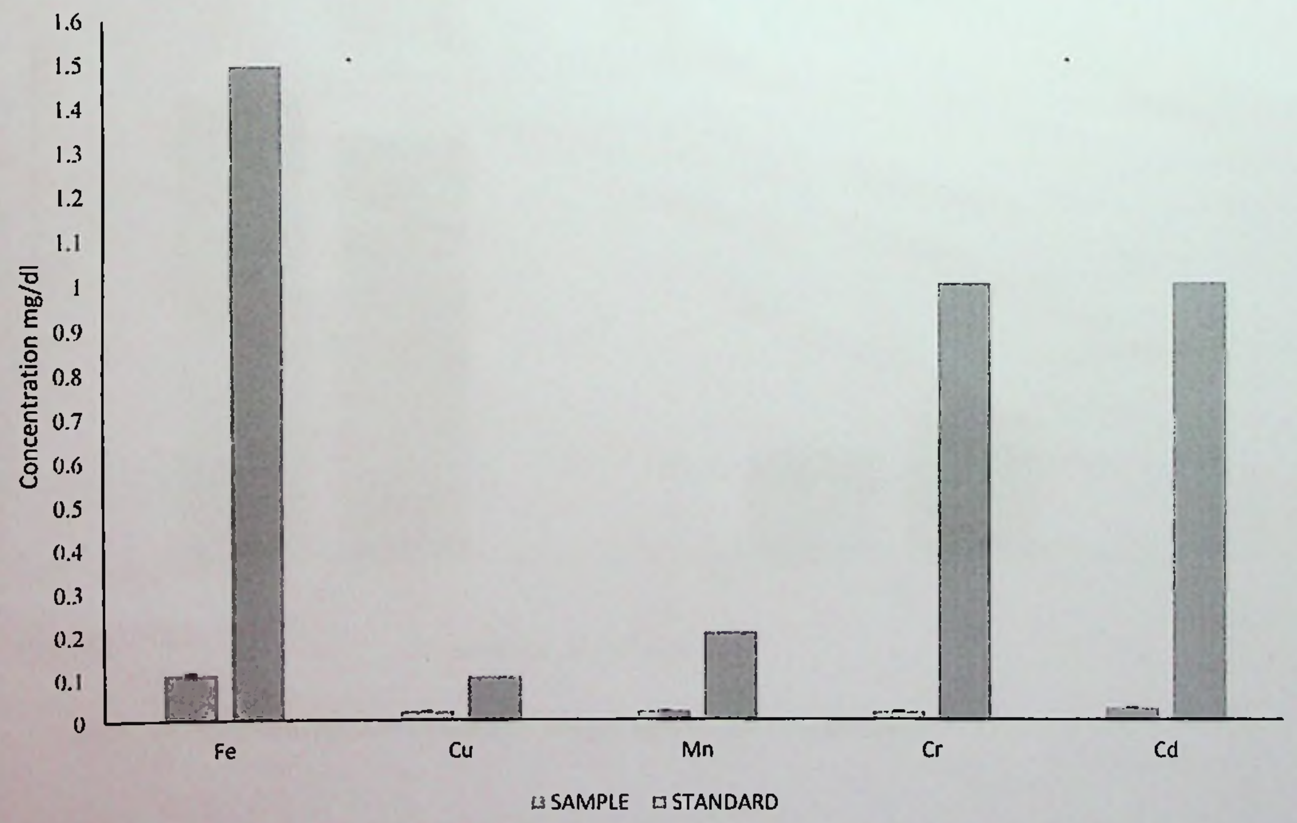

Fig 4.7 Concentrations of Heavy metal in Well water sample

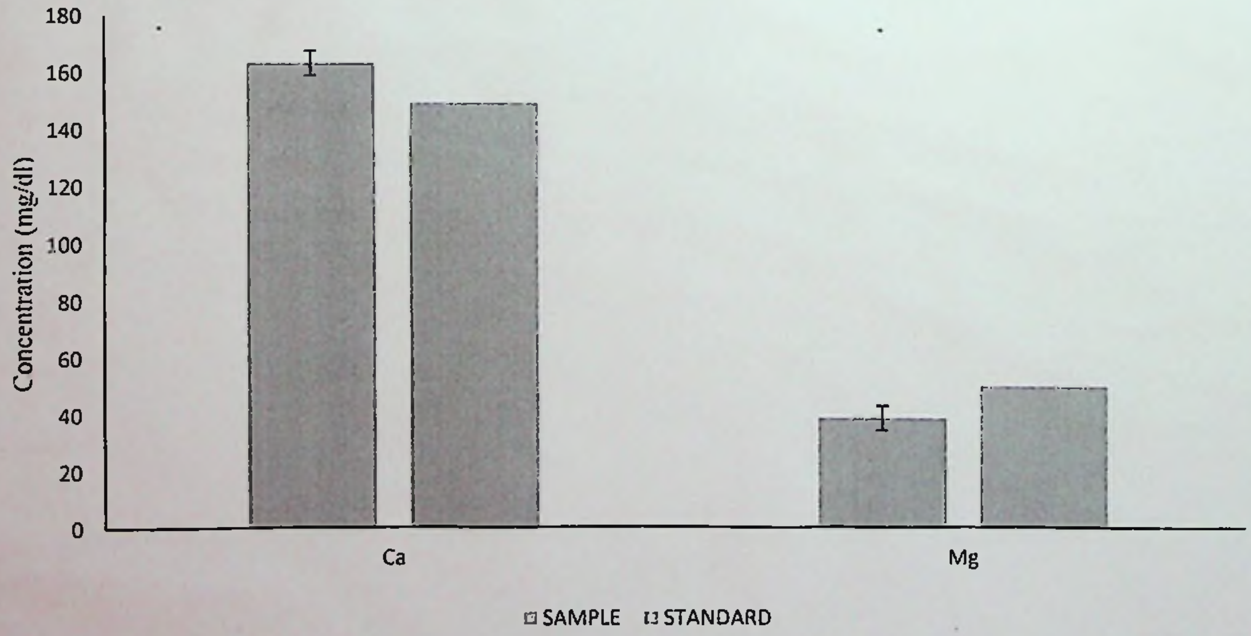

Fig 4.8 Concentrations of Calcium and Magnesium in Well water sample