ASSESSMENT OF LEVELS OF LEAD, CADMIUM, COPPER, IRON, AND ZINC IN SOIL, WATER AND PLANTS AROUND GOLD MINES IN ANKA LOCAL GOVERNMENT AREA, ZAMFARA STATE

BY

YAHAYA Z. YA'U
SPS/12/MCH/00023

A DISSERTATION SUBMITTED TO THE DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY, FACULTY OF SCIENCE, BAYERO UNIVERSITY, KANO IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE (M.Sc) IN ANALYTICAL CHEMISTRY

APRIL, 2016

DECLARATION

I hereby declare that this work is the product of my own research effort undertaken under the supervision of Prof. A. A. Audu and has not been presented and will not be presented elsewhere for the award of a degree or certificate. All sources have been duly acknowledged.

Sign__________________________ Date_____________________

Yahaya Zakari Ya'u
SPS/12/MCH/00023

CERTIFICATION

I certify that this research work was carried out by Yahaya Zakari Ya'u (SPS/12/MCH/00023) in the Department of Pure and Industrial Chemistry, Bayero University, Kano under my supervision.

Sign_________________________ Date____________________

Prof. A. A. Audu
Department of Pure and Industrial Chemistry,
Bayero University, Kano.

APPROVAL

This dissertation has been examined and approved for the award of degree of Master of Science (M.Sc) in Analytical Chemistry of Bayero University, Kano.

Dr. M. D Faruruwa

External Examiner **Date**

Prof. M. I Mohammed

Internal Examiner **Date**

Prof. A. A. Audu **Date**

(Supervisor)

Dr. Haruna Musa **Date**

(HOD/Chief Examiner)

Prof S. Y. Mudi **Date**

(SPS Representative)

DEDICATION

This dissertation is dedicated to my beloved parents Alh. Ya’u Mua’zu and Haj. Aishatu Abdullahi for the relentless parental and financial support given to me.

ACKNOWLEDGEMENT

With gratitude to Almighty Allah Who enabled me to carry out this research, my profound gratitude to my supervisor Prof. A. A. Audu, who spared his time to guide, direct, teach, encourage and effectively supervise the research work.

My sincere gratitude to all my lecturers in the Department of Pure and Industrial Chemistry, particularly the Head of Department, Dr. Haruna Musa, postgraduate coordinator Dr. Umar Sani and all the laboratory personnel whose effort made this research work a reality.

I am grateful to the support, encouragement and understanding, I enjoyed from all my course mates particularly Umar Abdullahi Shatima, Muhd Sani, Attahiru Muhammad, Jamilu Abdulrauf and others too numerous to mention.

I am also indebted to my elder brothers Mustapha and Sani, my sisters Faiza, Ummi, and Balkisu for the helping hand they render throughout this program.

Finally, I am grateful to my closest friends at home; EL-amin, Auwalu designor, Nass, Shuaib Sani, Yahaya Isya Gaya and Maryam Bapph Yaya for their advice encouragement and relentless prayers toward the success of this research work. Thank you so much.

TABLE OF CONTENTS

CHAPTERONE

CHAPTER TWO

CHAPTER THREE

CHAPTER FOUR

CHAPTER FIVE

LIST OF APPENDICES

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Mining and agriculture have continue to supply most of the basic raw materials used by modern civilization, however, the discovery of precious stones has make rural farmers to abandoned their farms and support their livelihoods by the exploitation of natural resources in their vicinity which often result in environmental degradation. This research was conducted to assess the levels of contamination caused by the mining activities in Anka local government area of Zamfara state by determining the levels of Zn, Pb, Fe, Cu and Cd in soil, grains and different water sources collected from four villages where the inhabitants are actively involved in gold mining and processing activities. The mean concentration of these heavy metals obtained after hot acid digestion were; copper (92.58 ±23.04 mg $kg-^1$ at the mining site, 65.07 ±15.00 at the farmlands, 65.65 ±19.21 mg $kg-^1$ at the residential areas). Lead was not detected in all the borehole water of the study area but was observed in some wells and all of the pond water samples with an average concentration of 0.07 ±0.01 mg/L for well water and 0.83 ±0.42 mg/L for pond water. Elevated lead concentration was however observed in all the soil samples with average concentration of 1956.75 ±537.41 mg $kg-^1$ at the mining sites, 617.60 ±358.34 at farmlands and 511.83 ±213.91 mg $kg-^1$ at residential area. These results are similar with values reported from other mining areas. The concentration of some of the metals analysed are quite above the maximum permissible limit set by WHO and NASREA and therefore such soil and water sources are considered contaminated by those heavy metals.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Mining

Mining is the extraction of valuable minerals and other materials from the ground; it may have been the second of humankind's earliest endeavors granted that agriculture was the first. The two industries ranked together as the primary or basic industries of early civilization, only little has changed in the importance of these industries since the beginning of civilization and they continue to supply all the basic raw materials used by modern civilization (Willard, 2005). However, unless adequate precautions are taken mining can be accompanied by serious negative impacts on the environment and human health (Bakau, 1993). Most people in rural areas in sub-saharan Africa are poverty stricken, they support their livelihoods by the exploitation of natural resources in their vicinity which often result in environmental degradation (Thomas *et al.,* 2003).

1.1.1 Artisinal Small Scale Mining

Broadly speaking, artisanal and small-scale mining (ASM) refers to informal mining activities carried out by individuals, groups, families or cooperatives using low technology or with minimal machinery. It is difficult to estimate the extent of ASM due to the lack of a common definition, its use of seasonal and occasional workers, and a lack of official statistics. In 1999 there were a reported 13 million people working directly in ASM, with the livelihoods of a further 80-100 million people affected indirectly. A more recent estimate notes that these numbers have likely risen in response to higher gold and commodity prices, and that there are now at least 25 million artisanal miners, with 150-170 million people indirectly reliant on ASM. In Africa, increased participation in ASM has been linked to; poverty, decline in the viability of agriculture, or as a way to supplement agricultural income.

Even though some people are encourage to enter this sector by the potential for high profits. Due to its broad perspective, ASM is often characterized by its key features which include:

a. Lack or much reduced degree of mechanization and great amount of physically demanding work.
b. Low level of occupational safety and health care which can be seen through lack of basic safety equipment, like helmet, safety boots, working gloves and dust mask, because its seen by the miners as something that does not contribute directly to their daily income and therefore has inferior priority.
c. Deficient qualification of the personnel on all levels of the operation.
d. Inefficiency in the exploitation and processing of the mineral production (low recovery of values).
e. Exploitation of marginal and/or very small deposits, which are not economically exploitable by mechanized mining.
f. Low level of productivity.
g. Low level of salaries and income.
h. Periodical operation by local peasants or according to the market price development.
i. Lack of social security.
j. Insufficient consideration of environmental issues.

From the economic point of view, ASM can contribute to development by providing employment, increasing local purchasing power, stimulating local economic growth and slowing urban migration. However, this sector also creates social, environmental and financial challenges that may undermine development such as environmental degradation, pollution of waterways through mercury use, dam construction, a build-up of silt, poor sanitation, and effluent dumped in rivers. Generally, Small-scale mining can be extremely environmentally damaging and often has serious health and safety consequences for workers and surrounding communities. This is usually due to poor practices in mining and processing of target minerals. Monitoring and enforcement of environmental regulations is hampered by informality, the remote location of mine operations, and lack of resources, as such, governments in many countries regard ASM as an illegal activity (Thomas *et al*., 2003). Anthropogenic heavy metal contamination is becoming widespread with ubiquitous nature of heavy metals in the environment. Anthropogenic sources of heavy metal pollution include but not limited to mining, iron smelting, fossil burning and municipal and industrial waste disposal (Abdu and Yusuf, 2013). During mining, a fine grind of the ore is often necessary to release metals and minerals, so the mining industry produces enormous quantities of fine rock particles, in sizes ranging from sand-sized down to as low as a few microns (USEPA, 1994). These fine-grained wastes are known as "tailings". By far, the larger proportion of ore mined in most industry sectors ultimately becomes tailings that must be disposed of. In the gold industry, only a few hundredths of an ounce of gold may be produced for every ton of dry tailings generated (USEPA, 1994). Tailings need to be properly managed because they constitute a major source of release of many trace elements into the environment (Antwi-Agyei *et al.,* 2009).

Ores and minerals are rich sources of heavy metals such as chromium, iron, lead, manganese, nickel and zinc (Sahu *et al*., 2004). During mining, the ores and minerals are explored thereby freeing these heavy metals. It is therefore known that, the soil, over a gold mining region is always polluted by heavy metals, which are released from gold mining activities. It’s also believed that the activity of Cyprus Mining Cooperation in Lefke was responsible for air, water and land pollution of the area (Stone, 2000). Potential environmental impacts of mining on the environment include poisonous air emission, fugitive dust blown to the surrounding area, non-reused overburdens, waste rocks, tailings, loss of plant population, reduction in localized groundwater recharge and loss of fish population from water pollution Rasheed and Amuda (2014). Because these metals are toxic to living organisms, there are several cases where pollutant's related ingestion of contaminated food has led to human death. Such researches on ecological risk assessment of heavy metals in the polluted soil had gotten more and more attention. It was found that the results of the ecological risk assessment can reveal the possibility for soil to be polluted, and even for the ecology to be harmed by concerned heavy metals (Yao-guo *et al.*, 2010).

1.2 Soil

Soil is a natural resource essential for the food production and global economy; it also plays many important roles in the environment. As being situated at the interface between the atmosphere and the lithosphere it acts as a filter and a buffer: it may weaken and degrade environmentally harmful compounds protecting the air quality. It also has an interface with hydrosphere and therefore it affects surface and groundwater quality. Furthermore, soil, as a part of biosphere, provides nutrient-bearing environment that sustains the growth of plant and animals. As a habitat and protecting media of flora and fauna it contributes to the maintaining of the global nutrient cycling as well as biomass production, whether by natural vegetation growing or plant cultivation. Beside these ecological functions, soil is ground to build and live on, raw material and reserve of cultural heritage (Monika and Marija, 2011). Because soil quality and its utilization are directly linked, each of above mentioned functions or use mode requires a certain soil quality level. Otherwise, any change of soil quality may affect its utilization potential, Harris *et al.* (1996) define the soil quality as a capacity of the certain soil volume in given conditions (land use, relief, and climate) to protect water and air quality, to sustain plant and animal growth, promoting thus the human health. A healthy soil is essential for human health because what is in the soil affects the health, safety and quality of the food that is derived from the soil (Uduma and Jimoh, 2014). Out of total degraded land on the global scale that are estimated to 1,965 mha, about 55% was water eroded, about 28% wind eroded, and about 12% is polluted by chemicals (Adriano *et al.*, 1995). From the standpoint of soil degradation, the presence of some trace elements in a toxic concentration may be due to both natural and anthropogenic factors. Therefore, it may become quite difficult to discriminate among the different causes. The parent material largely influences trace metals content in many soil types, with concentration sometimes exceeding the critical values (Palumbo *et al.*, 2000; Romić and Romić, 2003; Salonen and Korkka-Niemi, 2007). Some metals, such as Ni, Cr and Mn, are contained as trace elements in some rock types of volcanic and metamorphic origin (Alloway, 1995). During weathering processes the primary crystalline structures of some rock minerals are completely broken, relevant chemical elements may be thus either adsorbed in the topsoil or transported towards surface water or ground water targets (Huang and Hu, 2008). Soil buffer capacity may be defined as its ability to postpone the negative effects of more or less continuous input of toxic substances by inactivation of contaminants (Moolenar and Lexmond, 1999). This inactivation can generally be reached by effective binding of contaminant and soil particles, or by forming of insoluble complexes. When the contaminant input exceeds the level of so-called “critical content”, their buffer capacity is getting overcome as well and then the soil is characterized as polluted (De Haan, 1996). Generally, two main types of soil pollution may be distinguished: diffuse pollution or non-point source, and point source (O'Shea, 2002). The example of the non-point source is atmospheric deposition as a result of urban transport and construction activities, as well as mineral fertilizer application in agriculture. Diffuse sources of pollution are not easy to control, and the best methods for soil pollution control often depend on the legal regulations and management strategies. It becomes easier to control point sources of pollution, because it usually refers to the single source that is easy to identify (local pollution caused by chance, accidentally or undertaking prohibited activities like artisanal small scale mining) (Monika and Marija, 2011).

1.2.1 Soil pH

The soil reaction is the pre-eminent factor controlling the chemical behaviour of metal and many other important processes in the soil. The pH of a soil applies to the H^+ ion concentration in the solution present in soil pore which is in dynamic equilibrium with the predominantly negatively charged surfaces of the soil particles. Hydrogen ions are strongly attracted to the surface negative charges, and they have power to replace most other cat ions. Soil pH is affected by the changes in redox potential which occur in soils that become water logged periodically (Bache, 1979 and Wild, 1988). The significance of soil pH lies in its influence on availability of soil nutrient, solubility of toxic nutrient elements in the soil, physical breakdown of root cells, cation exchange capacity etc. Soil pH is therefore among the most informative measurement that can be made to determine soil characteristics (Dagari, 2012).

Soils have several mechanisms which serve to buffer pH to varying extents, including hydroxyl aluminum ions, CO_2, carbonate and cat ion exchange reactions, (Bache, 1979). However, even with the buffering mechanism, soil pH differs significantly due to localized variations within soil. Soil generally has pH value within the range 4 – 8.5 owing to buffering by Al at the lower end and $CaCO_3$ at the upper end range (Wild, 1988).

1.3 Plant

Virtually all human nutrition depends on plants, directly or indirectly. Some animals are mainly herbivores. Much of human nutrition depends on cereals, especially corn, wheat and rice or other staple crops such as potato, cassava, and legumes. Other plants that are eaten include fruits, vegetables, nuts, herbs, spices and edible flowers. Beverages from plants include coffee, tea, wine, beer and alcohol. Sugar is obtained mainly from sugar cane and sugar beet. Cooking oils are made from corn, soybean, canola, safflower, sunflower, olive and others. Food additives such as gum arabic, guar gum, locust bean gum, starch and pectin are all plant based. When grown on contaminated soil or irrigated with water contaminated by heavy metals, plants can accumulate these heavy metals and the accumulated heavy metals will then be transferred to the animal and eventually contaminating the food chain (Abdu and Yusuf 2013). Plants can also be used to remove, stabilize and detoxify organic and inorganic pollutants including heavy metals from air, soil and liquid through phytoremediation processes (Salt *et al.,* 1999). Another important role plants play in the environment is creating the oxygenated atmosphere of earth and removing carbon dioxide from the atmosphere, thereby initiating the process of controlling Earth's climate (Keddy, 2007).

1.4 Water

Water played a crucial part in the origin of life and it still has essential role in maintaining plant and animal life. The presence of water in the cells and body fluids such as blood accounts for approximately sixty percent of the body’s weight. Nearly all the processes essential for life depend on reactions that take place in aqueous solutions such as digestion of food in the stomach, or the transport of oxygen around the body (Philip, 1996).Water is vital both as a solvent in which many of the body’s solutes dissolve and as an essential part of many metabolic processes within the body. It is used to break bonds in order to generate smaller molecules like glucose, fatty acids and amino acids used as fuels for energy. Most living organisms can survive only for short periods without water, therefore it plays a key role in prevention of diseases, drinking eight glasses of water daily can decrease the risk of colon cancer by 45% and bladder cancer by 50% (Oparaocha *et al.,* 2010). Water is also used in many industrial processes and in machines such as the steam turbines and heat exchangers. Water in its natural environment is characterized by impurities. Being a universal solvent, water contains dissolved solids, gases and hosts a number of microorganisms. Only about 3% of water sources on earth, including both surface water (rivers, lakes, streams and reservoirs) and ground water are good in terms of quality or freshness (Oparaocha *et al*., 2010). Largest percentage of the water sources are polluted either naturally or by human activities. Pollution in the cities and other industrial establishments has profound influence on water resources and consequential effect on the health of the human residing in such areas. Several pollutants affect human and animal health. However, non-degradable pollutants like trace metals are often a greater concern to researchers more than other pollutants (Ganeshamurthy *et al*., 2008). Industrial revolution that occurred in 1800 increased the extent of water pollution by human activities, and the greatest offenders have been food processors, the pulp and paper industry, metal producers and chemical manufacturers (Awofolu, 2005). Surface water bodies like rivers, rivulets, streams and lakes are the first to receive trace metals generated in various industrial processes and waste producing sources. Drinking water bodies and other aquifers near agricultural land irrigated with polluted waters of rivers and stream become contaminated. However, lower concentration of heavy metals in ground water indicates that metals are accumulated mostly in the surface soil and only a small portion leaches into the ground water (Ganeshamurthy *et al*., 2008). According to the United Nations Human Development Report, the water and sanitation crisis claims more lives through disease than any war claims through weapons. Every year, approximately 1.4 million children die from unavailable, clean drinking water; and 3.6 million people die each year from water-related diseases. Of that large number, 84% are children and 98% of them are living in the developing world (Water Facts, 2010). Water therefore requires purification to make it portable. Trace metal pollution can be tackled by using primary and secondary treatment of waste water before disposal or discharge. In recent times, biological method has been used to solve problems of trace metals pollution as organisms and plants have the ability to absorb trace metals (Bioremediation) in exceptionally large proportions (Selvapathy and Sreedhar, 1991).

1.5 Heavy Metals

Out of the ninety elements found in the earth's crust, 53 of them are regarded as heavy metals as their densities are higher than 5 g/cm^3. From the geochemical point of view, trace metals are regarded as metals whose percentage in rock composition does not exceed 0.1%. Some of these elements are essential for normal growth and development of living organisms. From the physiological point of view some of them are called micronutrients or microelements. Some of these metals such as lead and cadmium have no beneficial properties, and are toxic even in small concentrations (Radojevic and Bashkin, 1999). The issue of toxicity is usually merely a matter of quantity, with the range varying for each element (Monika and Marija, 2011). The presence of these metals in excess of the concentrations quoted by World Health Organization (W.H.O) can cause various ailments (Allan *et al.*, 2000). For instance, nickel which is known to be essential for some microorganisms and animals but not to plants. It becomes toxic at higher concentration to even the microorganisms (Dara, 2006). Excessive intake of copper may cause hemolysis, hepatotoxic and nephrotoxic effects. Inhalation of air borne copper causes irritation of the respiratory tract and mental fume fever (ATSDR, 2002). Among the various inorganic pollutants, trace element are toxic, dangerous and harmful because of their carcinogenic nature (Indu *et al.*, 2010), non-biodegradable nature, long biological half-lives and their potential to accumulate in different body parts Rasheed and Amuda (2014). Man, animals and plants take up these metals from the environment and long term deposition leads to adverse reactions. Environmental impact of heavy metals such as cadmium, lead, mercury and arsenic as well as their health effects has been a source of major concern such as seen in the outbreak of itai-itai disease in Japan (Morikawh *et al.*, 1992) due to the consumption of rice containing high levels of cadmium and minamata disease in 1956 caused by the consumption of mercury contaminated fish (Akagi *et al.*, 1995).

1.5.1 Toxicity of Heavy Metals

High levels of trace elements may pose an important hazard to human health and the environment, not only because of their direct toxic effects on organisms but also due to their further potential for increasing exposure along the food chain through bioaccumulation (Lambers *et al.*, 1998). The ability of heavy metals to disrupt the function of essential biological molecule such as proteins, enzymes and deoxyribonucleic acids (DNA), is the cause of their toxicity while the displacement of certain essential metals by similar metals is another. For example, cadmium can substitute for zinc in certain proteins that require zinc in their structure to function. This alteration can lead to toxic consequences. In a similar way, lead can substitute for calcium in bone. Usually small doses in the micrograms range are taken up by those that are continually exposed to these metals, over a period of time; adverse toxic effects may occur as a result of long term low level exposures thus producing sings of toxicity on individual. (Ewers and Schlipkoter, 1991).

1.6 Zamfara State and the Lead Poisining

Zamfara State is located in northwestern Nigeria and has an estimated population of 3.6 million people, and approximately 20% are children < 5 years of age (UNEP, 2010). Although farming is the major livelihood in Zamfara State, gold ore processing increasingly constitutes an important income source in selected areas. From February–April 2010, Médecins Sans Frontières (MSF) and local public health officials reported the dead of over 40 children from the 200 children (with less than 5 years of age) that have suffered from convulsion among four villages of Zamfara State. The unprecedented level of morbidity and mortality raised suspicion about other incidental diseases such as malaria and bacterial infections; however, laboratory tests failed to demonstrate microorganisms in most patients, and the illnesses did not respond to anti-malarial and empiric antibiotics. During May 2010, the Nigerian Federal Ministry of Health assembled a multidisciplinary team consisting of representatives from the Nigerian Field Epidemiology and Laboratory Training Program (NFELTP), Zamfara State Ministry of Health, the center for disease control (CDC), and the World Health Organization (WHO) to join MSF in investigating the outbreak (CDC 2010).

Environmental causes were suspected because of a recent increase in gold ore–processing activities in the region. Diagnostic tests on eight symptomatic children revealed blood lead levels (BLLs) of 168–370 µg/dL, levels known to be fatal in children. During May–June 2010, the team surveyed the two most-affected villages and confirmed lead poisoning as the cause of the outbreak (CDC 2010; Dooyema *et al.,* 2012). Lead-rich gold ore was identified in both villages and gold ore–processing activities had begun during the previous 12 months inside a majority of family compounds. The soil-lead levels in 85% of family compounds exceeded the U.S. Environmental Protection Agency (EPA) soil-lead standard [400 parts per million (ppm)] for areas of bare soil where children play (U.S. EPA 2003). Factors associated with child mortality in the two surveyed villages were the child's age, maternal participation in ore processing, and environmental factors such as primary water source type and soil-lead level of the family compound (Dooyema *et al.,* 2012). The investigation concluded that 118 child fatalities were strongly associated with gold ore processing (Yi-Chun *et al.,*2012).

1.7 Principles of Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectrophotometer (AAS) is a widely employed technique for trace and ultra-trace elemental analysis of complex matrices by measuring the absorbed radiation by the chemical element of interest. In principle a solution (generally aqueous) containing the metallic element is aspirated in the form of an aerosol into a high temperature flame, the flame evaporates the solvent and decomposes the compound containing the element to create gaseous state atoms of the element. In this experiment an air-acetylene flame is used as the vaporization method, this technique is often called Flame Atomic Absorption Spectroscopy (FAAS). A beam of monochromatic light with a resonance wavelength is then passed through the flame while the atoms of the element in the flame absorb some of the light, the amount of light absorbed is directly dependent upon the concentration of the element in the solution being vaporized in the flame. The radiation source is a hollow cathode lamp which contains substantial proportions of the element to be analyzed. A beam of electromagnetic radiation characteristic of a particular element can be passed through the atomic vapor and monitored by a photomultiplier tube (PMT) detector. If the sample contains that particular element, its atoms will selectively absorb some of the electromagnetic radiation, thereby attenuating the beam and causing the detector signal to decrease. This absorbance is proportional to the concentration of that element in the vapor and hence in the original sample (Garcia *et al.,* 2008).

1.8 Aim of the Research

- The aim of this work is to determine the levels and seasonal variation of heavy metals (Zn, Pb, Fe, Cu and Cd), in grains, soil and water collected from four villages of Anka local government area and compare the result obtained with national (e.g. NASREA, DPR) and international (e.g. WHO) standard guide lines.

- To assess the extent of environmental pollution caused by the activities of artisan small scale gold miners by comparing results obtained with back ground concentration

1.9 Objectives of the Research

i. To analise the collected samples using atomic absorption spectroscopy (AAS)
ii. To compare the results obtained with background (control) concentration.
iii. To compare the result with national and international guide lines for their levels in water, grains and soil.

1.10 Scope of the Research

This research will involve the sampling of water, soil and grains of the areas around the identified gold mines in Bagega, Dareta, Abare and Duza of Anka local government area, one of the areas known to be affected by the famous lead poisoning crisis in Zamfara state of Nigeria, and the subsequent determination of some heavy metals using atomic absorption spectrometer.

1.11 Justification for the Research

It is on record that a lot of work has been done on different pollutants around artisanal gold mines located in various local governments of Zamfara state. Yi-Chun *et al*. (2010) conducted a Village-Level Investigation of Childhood Lead Poisoning Associated with Gold Ore Processing in three local government areas (Anka, Bukkuyum, and Maru.) of Zamfara state. While in 2011, Yusuf et al. also reported contamination of farmlands and various water sources with Pb in the villages of Abare beyond permissible limits. In 2013, during the period when contaminated soils were being excavated and replaced by clean soils, Abdu and Yusuf assess the level of lead (Pb) contamination in farmlands, crop plants and water sources and the health risk assessment based on life time exposure through ingestion and inhalation of lead contaminated soil and dust in Abare village of Zamfara State. Kabiru *et al*., (2013) conducted a research on the prevalence and determinants of childhood lead poisoning in Kawaye, a village located in Zamfara's Anka local government area (LGA). It is clear that since after the excavation of the contaminated soil and it is subsequent replacement by clean soils, no work has been done to access the levels of these contaminants in those areas hence the need to carry out this work.

CHAPTER TWO

2.0 LITRATURE REVIEW

Our green planet has been contaminated from day to day by different contaminants. One of the most serious contaminant groups is the heavy metals. The ecosystem has been contaminated by high concentration of heavy metals released into the biosphere by human activity. Industrial activities, energy production, construction, urban waste treatment, and vehicle exhaust are some of the sources causing large quantities of heavy metal contamination in atmosphere, water, and soil (Nyle and Ray 1999).

Mark *et al.,* (2014) conducted a research that assessed the levels of heavy metal contaminations of drinking water sources due to illegal gold mining activities in bagega, sunke and dareta villages of Zamfara state, Nigeria. The result of their work shows that the water in Bagega showed high concentration of Pb with a value of 15600 ppm much above the limit set by WHO (2008). The two remaining villages Sunke and Dareta had Pd concentration values of 549 and 445 ppm respectively far above the limit set by WHO (2008). Also, the work revealed high concentration of Fe and Zn, where the highest concentration of Zn was observed in Sunke village with a value of 2560 ppm twice more than the limit set by WHO (2008). They conclude that in terms of toxicological point of view, the concentrations of all the nine (9) heavy metals analyzed i.e Co, Cd, Zn, Cu, Ni, Pb, Mn, Fe, and Cr were above the limit set by Federal Environmental Protection Agency (FEPA) Nigeria 1998, and that of WHO in all the villages under investigation. They believed that the levels of these heavy metals pose a significant concern on the health of the local population. Abdu and Yusuf (2013) used atomic absorption spectrophotometer (AAS) to assess the level of lead (Pb) contamination in farmlands, crop plants and water sources and the health risk in one of the Pb-contaminated villages of Zamfara State. They found that the average concentrations of

Cd, Pb and Zn were 17.5, 1266 and 985 mg kg-^{1}, respectively, in soil, which were far beyond minimum threshold values worldwide (300 mgkg-1 for Cd in EU and UK, 150 mg kg-1 for Pb in USA and 70 mg kg-1 for Zn in Canada) (Abdu *et al*., 2011). They concluded that the high concentrations of Pb in both soil and plant and the estimated health risk may have posed a health hazard for the environment and the ecosystem as a whole, and that based on data description, the primary input of this heavy metal in the soil is the soil parent material. Both human and natural activities influenced concentrations of Pb in the plant material. Processing of contaminated gold ore in this village has been responsible for the severe Pb pollution. They also suggested that remediation studies are required to tackle Pb contamination in the farm lands.

Yusuf *et al.* (2011) also reported contamination of farmlands and various water sources with Pb beyond permissible limits in the affected villages of Zamfara state. They concluded that this Contamination could occur due to deposition of lead from dust and underground water movement even from landfills that are not well protected. Lar *et al.* (2013) conducted the assessment of lead, mercury and arsenic in soils of Anka area, Zamfara state Nigeria. The data from their work revealed that the soils in the study area are significantly contaminated, showing high level of toxic elements than normal distribution. The ranges of concentration are: Pb (6.91-4157ppm), As (7.43-173.2ppm) and Hg (2.15-12.92ppm). They therefore underscored the continued and urgent need of high-quality investigation of lead exposure in regions where health is poor and where no data currently exist.

Uduma and Jimoh (2014) carried out a research on the assessment of Pb enrichment and depletion in selected contaminated arable soils of Nigeria. In their work, lead (Pb) concentration was determined in the vicinity of mining and dumping sites which include the contaminated villages of Zamfara state. They found that the enrichment factors for the soil samples ranged over 7.7 – 36.9, (indicating significant to extremely high enrichment) and that there was no lead depletion in all soil samples assessed. They conclude that the locations of the studied areas in the anthropogenically affected zones are characterized by lead enrichment of all the tested soils, and in all cases well exceeding even 100% (EF > 2) against matrix and pointed that this poses serious debilitating effects on the agro – ecosystems, since lead has no known essential functions in plants metabolism.

Dahiru *et al.*, (2013) employed atomic absorption spectrometer in determining Cadmium, Copper, Lead and Zinc levels in sorghum and millet grown in the city of Kano and its environs. The result of their work shows generally that zinc accumulated more than any other metal in both tissues (leaves and grains) of the two crops, while the level of lead in the crops' grains was almost eight times lower than that of the leaf. The remaining three metals (Cadmium, Copper and Zinc) also showed lower levels in the grains compared to that of the leaf, but not as low as that of lead. Low uptake and low translocation of lead in shoot of the cereals was attributed to lack of specific carriers which in case of other metals may in significant way influence the percentage of the elements accumulation in their grains (Weber and Hrynczuk, 2000). They conclude that very little amount of the metals were trans located to the shoot, and the metals accumulation was more in the leaf than in the grain of the two cereals and that the cereals consumable parts of the crops grown on the studied soils are therefore safe for consumption.

Emmanuel *et al.* (2013) reported the comparative study of mineral elements distribution in sorghum and millet from minna and bida, north central Nigeria. They employed

Colorimetric, flame photometric, EDTA titrimetric and atomic absorption spectrophotometric methods for the determination of the mineral elements. The analysis showed that sorghum in Minna was high in copper while sorghum in Bida relatively contained same amount of calcium, phosphorus and phosphate. Millet in Minna contained high value of sodium, potassium, and magnesium while millet in Bida was high in zinc. The results also revealed that the level of potassium was higher followed by Mg, PO4, Na, Cu, Ca, P and Zn. The study revealed that the levels of mineral elements in the cereals were within permissible limits for daily consumption and compare favorably with those reported for similar food stuffs from other parts of the world.

Antwi-Agyei *et al.* (2009) reported the use of atomic absorption spectrometer in determining the concentration of; As, Cu, Pb and Zn in the soil of areas surrounding both active and decommissioned tailings dams of Obuasi gold mine in Ghana. They found that the average concentrations of As, Cu, Pb and Zn in soils around the active tailings dams were respectively 581±130, 39.64 ± 3.02, 24.22 ± 2.62 and 72.64 ± 8.01 mg/kg. Soils in the vicinity of the decommissioned tailings dam registered increased values - 1711 ± 172, 71.44 ± 5.27, 38.67 ± 3.59 and 168.1 ± 36.2 mg/kg for As, Cu, Pb and Zn respectively. They conclude that both types of the tailings dams impacted adjoining soils with greater concentrations of the trace elements when compared to undisturbed control soils.

Yao-guo *et al.* (2010) uses flame atomic absorption spectrophotometer to determine the concentrations of Hg, Cd, Pb, Cu, Cr, As and Zn in soil crop and residents' hair samples of Xiaoqinling gold mining region in China. The results were used to assess the potential ecological risks of those trace elements, which showed that, these metals in soil were ranked by severity of ecological risk as Hg＞Cd＞Pb＞Cu＞Cr＞As＞Zn. He therefore conclude that those heavy metals in the soil had a high potential ecological risk, and had been affecting the crops' growing and yield, and even the residents' health by building up along the food chain.

Ali *et al*., (2013) evaluated the concentration of heavy metals (Lead, Cadmium, and Hg) in drinking tap water of Ahvaz city of Iran by atomic absorption spectroscopic methods. In this work, the Concentrations of Pb and Cd were determined by electro thermal method, while that of Hg was determined using cold vapor technique. Result shows that concentrations of

Cd in drinking water (about 0.0012 mg/L) are below standard limits of World Health Organization (WHO), while that of Pb crossed WHO standard limits among all samples. Approximately 33% of samples show high concentration of Hg in comparisons to national standards of 0.006 mg/L. The study showed concentration of selected heavy metal (Pb and Hg) in drinking water of Ahvaz is higher than standards levels and therefore recommends further studies to determine the sources and cause of the pollution.

Mohammad *et al.* (2010) employed inductive coupled plasma-mass spectrophotometer (ICPMS) to determine the concentration of up to fifteen trace elements including lead in the regional ground water of western Uttar Pradesh, India. The study reveals that Fe, Mn, Sr, Cr, Al and Pb are generally present at a concentration above the World Health Organization (WHO) permissible limit in ground water of the area of investigation. It was also found that the increasing concentration of these elements in the ground water of the study area is mainly originating from industrial effluents of sugar mills, pulp and paper factories, cooperative distilleries and municipal waste water. It was therefore, concluded that, the effects of large scale industrialization in the study area and laxity in proper treatment of effluents before discharging these into the river system are now showing up in the form of deterioration of ground water quality.

Sezgin *et al.* (2013) employed Graphite Furnace Atomic Absorption Spectrometry (GFAAS) coupled with Ni matrix modifier (for Pb and Cd) and Pd-Mg mixture as matrix modifier (in the case of As) to determine the concentration of arsenic, lead and cadmium at trace levels in tap and bottled water samples consumed in the west part of Turkey. Detection limits for As, Cd, and Pb was found to be 2.0, 0.036 and 0.25 ng/mL, respectively. In all water samples, concentration of cadmium was found to be lower than detection limits. Lead concentration in the samples analyzed varied between N.D. (not detected) and 12.66±0.68 ng/mL. The highest concentration of arsenic was determined as 11.54 ± 2.79 ng/mL.

2.1 Lead (Pb)

Lead is a bluish gray or gray-white metal with a bright silvery luster. It is soft, malleable and a poor conductor of electricity, but is resistant to corrosion (ATSDR, 2007). Lead is the 82nd element on the periodic table, with four stable isotopes (i.e., 204, 206, 207, and 208) and a density of 11.34 g/cm^3 at 20°C. It exists in three oxidation states [Pb(0), Pb(II), and Pb(IV)] (ATSDR, 2007). Even at low levels, it has no biological or physiological essentiality as a nutrient (Abdu and Yusuf, 2013). It was used in pipes, drains, and soldering materials for many years. When ingested, the target organs are bones, brains, blood and soft tissues like liver and kidney (Phillip, 1996). Chronic exposure to Pb may result in birth defects, mental retardation, autism, psychosis, allergies, dyslexia, hyperactivity, weight loss, shaky hands, muscular weakness and paralysis. Lead has been upgraded to a probable human carcinogen based on sufficient evidence for carcinogenic effects in humans (Rousseau *et al.*, 2005).

2.1.2 Cadmium (Cd)

Cadmium is a metal (with atomic number, 48; relative atomic mass, 112.41) found in the earth’s crust, associated with zinc, lead, and copper ores. Cadmium is a soft, silver-white metal and released to soil, water, and air by non-ferrous metal mining and refining, manufacture and application of phosphate fertilizers, fossil fuel combustion, and waste incineration and disposal. Cadmium (as oxide, chloride, and sulfate) exists in air as particles or vapors (from high temperature processes) and transported long distances in the atmosphere, where it will be deposited (wet or dry) onto soils and water surfaces (ATSDR, 2012). The deposited cadmium and its compounds may travel through soil, and its mobility depends on several factors such as pH and amount of organic matter, which will vary depending on the local environment. Generally, cadmium binds strongly to organic matter where it will be immobile in soil, thus entering the food-chain through foliar absorption or root uptake. The rate of up take depends on a variety of factors including deposition rates, type of soil, humus content, and presence of other elements, such as zinc (UNEP, 2008). It has been noted that some heavy metals (for instance lead, cadmium, and mercury) have an estrogenic activity; that is as an endocrine disruptor (Erfurth *et. al.*, 2001).

While in water, cadmium exists as the hydrated ion or as ionic complexes with other inorganic or organic substances. Soluble forms migrate in water while insoluble forms are immobilized and deposited and absorbed to sediments (ATSDR, 2012). It is used in nickel–cadmium (Ni–Cd) batteries, pigments, coatings and plating, stabilizers for plastics, non-ferrous alloys, semiconductors and photovoltaic devices (USGS, 2008).

Low levels of cadmium have been measured in most foodstuffs such as leafy vegetables (e.g. lettuce, spinach), starchy roots (e.g. potatoes), cereals and grains, nuts and pulses (UNEP, 2008; EFSA, 2009). Exposure is primarily via ingestion of food and, to a lesser extent, via inhalation of ambient air, ingestion of drinking-water, contaminated soil or dust (CDC, 2005).

Cadmium (Cd) is among the major environmental concern to the agricultural system as its residence time in soil is over thousands years (ATSDR, 2005). Cadmium ranks seventh as toxic substances posing the most significant potential threat to human health and ranks third in the heavy metals subdivision behind lead and mercury (ATSDR, 2011). Cadmium is classified as a Group 1 IARC carcinogen and neurotoxin (Cao *et al.*, 2009; ATSDR, 2012).

2.1.3 Copper (Cu)

Copper is a microelement essential to all organisms and is an essential constituent of many enzymes of oxidation-reduction reaction (Raven and Johnson, 1986). Deficient or excessive supply of copper can cause significant modification of biochemical process in plants, leading to lower yields and quality of agricultural crops (Gauch, 1974). Copper is responsible for the oxidation and absorption of iron and vitamin c during digestion and act as a catalyst in the formation of hemoglobin (Comings, 1986), ingestion of its soluble salts gives rise to gastroenteritis. Exposure to copper fumes may occur in high concentration in metal refineries. This is clinically characterized by febrile reaction with sweating, headache and pains in the trunk and limbs (Gosselin *et la.*, 1984). High doses of copper can cause anemia, liver and kidney damage, stomach and intestinal irritation. When copper ends up in soil, it strongly attaches to organic matter and minerals. As a result copper does not travel very far after release and then enters ground water. A plant has limited chance of survival in soils with high level of copper (Comings, 1986).

2.1.4 Iron (Fe)

Iron is a metal in the first transition series. It is by mass the most common element on earth, forming much of earth outer and inner core. It is the fourth most common element on Earth crust. The presence of iron in rocky planets like earth is due to its abundant production as a result of fusion in high-mass stars. Iron exists in a wide range of oxidation states of +2 to +6, although +2 and +3 are the most common. Elemental iron occurs in meteoroids and other low oxygen environments, but is reactive to oxygen and water. Fresh iron surfaces appear lustrous silvery-gray, but oxide in normal air give hydrated iron oxides, commonly known as rust. Unlike many other metals which form passivating oxide layers, iron oxides occupy more volume than iron metal, and thus iron oxides flakes off and expose fresh surfaces for corrosion.

Pure iron is soft not obtainable by smelting but it is significantly hardened and strengthened by impurities such as carbon from the smelting process. A certain proportion of carbon (between 0.002% and 2.1%) produces steel, which may be up to 1000 times harder than pure iron. Crude iron metal is produced in blast furnaces, where ore is reduced by coke to pig iron, which has high carbon content. Further refinement with oxygen reduces the carbon content to the correct proportion to make steel. Steels and low carbon iron alloys along with metal are by far the most common metals in industrial use, due to their great range of desirable properties and the abundance of iron.

Iron plays an important role in biology, forming complexes with molecular oxygen in hemoglobin and myoglobin; these two compounds are common oxygen transport proteins in vertebrates. Iron is also the metals used at the active site of many important redox enzymes dealing with cellular respiration and oxidation and reduction in plants and animals (http:en.wikipedia.org/wiki/iron). Most tropical soils are rich in iron. It occurs mainly as pyrites or ferromagnetic minerals such as biotite, hornblende and limonite. Small amounts are present in soil solution. But concentration of ferrous ion (Fe^{2+}) may be high enough to reach toxic level (Moravic *et al.*, 1986).

2.1.5 Zinc (Zn)

Zinc is an essential element involved in metabolic functions. It is important for both man and plant healthy growth (Jeffrey, 1989). Exposure to zinc fume leads to nausea and constriction in the chest leading to coughing with labored breathing and severe headache. Inhalation causes muscular pains and vomiting (Fosmire, 1990). Zinc is rapidly absorbed from the gastro-intestinal tract and is stored in all tissues of the body especially the liver, kidney, muscles and pancreas. The male reproductive system is reported to accumulate large concentration of body zinc (Bremner, 1973). Karez *et al*, (1983) reported the variation in concentration of zinc in human teeth with sex and age of individuals and also the levels of zinc in selected algae species varied from 307±63.5 to 18.7±22ug depending on species and location and also analyzed the differences in the physiology and tolerance of several lichens species with respect to zinc. Results indicated that most species accumulate high amount of zinc. Zinc is an essential element in all organisms and plays some roles in the biosynthesis of enzymes, auxins and proteins (Bremner, 1973).

Zinc concentration in plants exceeding 250mg/Kg prevents normal growth and is an indication of environmental pollution (Mohammad, 2005). Zinc deficiency is common in alkaline and calcareous soils, where solubility is reduced and in acidic sandy soils where leaching occurs. Use of fertilizers, farmyard manures and the incorporation of organic residue are some of the ways of correcting zinc deficiency. Water soluble-zinc that is located in soils can contaminate ground water, it also interrupt activities of soil by negatively influencing the activity of microorganisms and earthworms. High level of zinc can cause damage to pancreas, and can also cause stomach cramps, skin irritation, vomiting and nausea (Mohammad, 2005).

CHAPTER THREE

3.0 Materials and Method

3.1 Study Area

The study area (fig. 3.1) is within the coordinates range between longitude 5°48E to 600°53E and latitude 11°58N to 12°15N, Anka local government of Zamfara state Nigeria.

3.2 Sampling Materials

The materials used for the soil sampling include the following tools; cutlass, metal hoe, ruler, polyethylene bags, plastic trowel and a GPS.

3.3 Sampling procedure

A total of two hundred and ten samples (consisting of soil, water and grain) were collected during the 2014 dry season (December) and the 2015 raining season (September to October) from different locations in the villages of Bagega, Dareta, Abare and Duza all in Anka Local Government area of Zamfara state. The Soil samples were collected at a depth of l0cm from the residential, farms and the mining sites of each of the village under study. A total of forty one soil samples were collected, each of which were separately stored in a polythene bag (Ayodele and Gaya, 1998). Thirty six water samples were taken from wells, ponds and boreholes encountered within and outside the villages. A total of twenty eight samples of the grains were obtained through random sampling, where seven (7) millet samples were collected from each of the four villages under study. A background soil sample was also collected at a distance of about two kilometers from the last house and/or ore processing areas around the village.

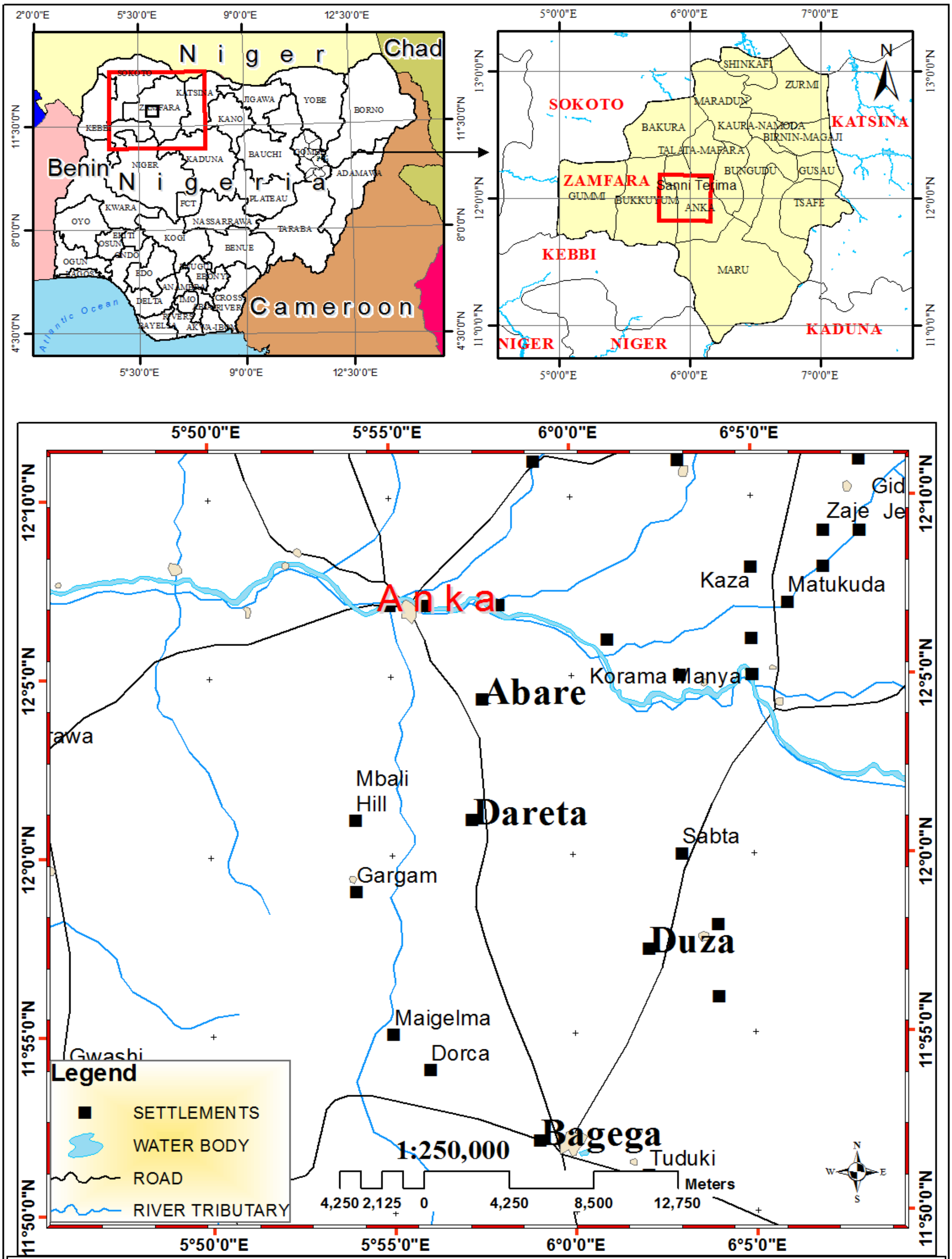


Fig. 3.1 Map of Anka Local Government Showing the Study Areas.

3.4 Sample Pre-Treatment

The soil samples were air dried, grounded and sieved using a 200mm mesh. The samples were then oven dried at 65°C, until a constant weight was obtained and were then kept for analysis. The water sample was preserved by the addition of three milliliters (3 mls) of concentrated nitric acid (HNO_3) at the point of collection. The grain samples were cleaned with deionized water and air – dried. The leaves and the grains of the dried plant were separated, ground and sieved through 0.5 mm mesh. The resulting powder was oven dried and kept for analysis (Dahiru, *et. al.,* 2013).

3.5 pH Measurement

pH measurement: To 10g of pre-treated soil in a $50cm^3$ beaker, $25cm^3$ of deionised water was added. The suspension was stirred several times for 30 minutes with a glass rod and then allowed to stand for 30 minutes for the suspended clay to settle. Electrodes were then inserted into the suspension to measure the pH and readings were recorded (Dagari, 2012). The procedure was repeated three more times.

3.6.0 Digestion of Samples

3.6.1 Digestion of Soil Samples

To 100 mg of the powdered soil sample in a 100 ml beaker, 2 mL of conc. HNO_3 + 6 mL conc. HCl was added and the beaker covered with watch glass. The solution was heated for 6 h on a sand-bath at a temperature of 250 ºC in a fume cupboard to dryness and then left to cool; 2 mL of HCl were added to re-dissolve the dry sample. 10 mL of distilled water was then added and heated for 5 min. The extract were cooled, the content filtered into 25ml volumetric flask and made to mark with distilled water (Lar *et. al.,* 2013).

3.6.2 Digestion of Grain Samples

To one gram of the pretreated sample in a 50ml beaker, 10ml concentrated HNO_3 was added, the beaker was covered with a watch glass and heated on a sand bath for 45mins. After cooling, 5ml of 70 % $HClO_4$ was added and the mixture was further boiled until white fume is observed. After cooling 20ml distill water was added and heated until a clear solution was obtained. The mixture was cooled, filtered through filter paper and transferred quantitatively to a 50ml volumetric flask. It is then made to the mark with distilled water (Zeng 2004).

3.6.3 Digestion of Water Samples

1000cm^3 of the water sample was placed on a hot plate and evaporated to about 50 cm^3 in a 1000 cm^3 beaker. 20 cm^3 of 0.1M nitric acid (HNO_3) was added to the resultant water sample and heated at about 120c^0 until a clear solution was obtained. The sample was allowed to cool to 120c^0, filtered with filter paper, and transferred into a 100 cm^3 volumetric flask and made up to the mark with de ionized water. The resultant solution was then transferred to a cleaned 100 cm^3 plastic container and analyzed with atomic absorption spectroscopy (Fatima, 2015).

3.7.0 Preparation of Standards

In preparation of standards, chemicals of analytical grade purity and deionised water were used. All glassware and plastic containers were washed with detergents, rinsed with distilled water and then soaked in 10% HNO_3 for 24 hour. They were then washed with deionised water and dried in an oven at 80^{o}C for 24 hours (Dagari, 2012).

3.7.1 1000mg/dm^3 Iron solution

To an accurately weighed 7.003g of ammonium ferrous sulphate [$(NH_4)_2SO_4$ $FeSO_4$] in a 400cm^3 beaker, 10cm^3 of 10% nitric acid was added. The solution was transferred into a 1000cm^3 volumetric flask and made to mark with deionised water, 10cm^3 of 1000mg/dm^3

iron solution was pipetted into a 100cm^3 volumetric flask, diluted and made to mark with deionised water. Standards of 1.0, 2.0, 4.0 6.0, 8.0 and 10.0 mg/dm^3 were prepared by dilution to mark of 1.0, 2.0, 4.0 6.0, 8.0 and 10.0cm^3 of 100mg/dm^3 iron solution in 100cm^3 volumetric flasks respectively.

3.7.2 1000mg/dm^3 Copper solution

3.801g of copper (II) nitrate was dissolved in a 400cm^3 beaker containing 10cm^3 of 10% nitric acid. The solution was transferred into a 1000cm^3 volumetric flask and made to mark with deionised water.Standards working solution of 0.40, 1.00, 2.00, 4.00, 6.00 and 8.00 mg/dm^3 were prepared by dilution to mark of 0.40, 1.00, 2.00, 4.00, 6.00 and 8.00cm^3 of 100mg/dm^3 copper solution in 100cm^3 volumetric flasks respectively.

3.7.3 1000mg/dm^3 Zinc solution

4.551g of zinc (II) nitrate was dissolved in a 400cm^{3}beaker containing 10cm^3 of 10% nitric acid. The solution was transferred into a 1000cm^3 volumetric flask and made to mark with deionised water. Standards of 1.00, 2.00, 4.00, 6.00, 8.00 and 10.00 mg/dm^3 were prepared by dilution to mark of 0.40, 1.00, 2.00, 4.00, 6.00 and 8.00cm^3 of 100mg/dm^3 zinc solution in 100cm^3 volumetric flasks respectively.

3.7.4 1000mg/dm^3 lead solution

1.598g of lead (II) nitrate was dissolved in a 400cm^3 beaker containing 10cm^3 of 10% nitric acid. The solution was transferred into a 1000cm^3 volumetric flask and made to mark with deionised water. Standards working solution of 0.60, 1.00, 4.00, 6.00, 8.00 and 10.00 mg/dm^3 were prepared by dilution to mark of 0.60, 1.00, 4.00, 6.00, 8.00 and 10.00cm^3 of 100mg/dm^3 lead solution in 100cm^3 volumetric flasks respectively.

3.7.5 1000mg/dm^3 Cadmium solution

2.103g of cadmium (II) nitrate was dissolved in a 400cm^{3}beaker containing 10cm^3 of 10% nitric acid. The solution was transferred into a 1000cm^3 volumetric flask and made to mark with deionised water. Standards of 0.50, 1.00, 2.00, 3.00, and 4.00 mg/dm^3 were prepared by dilution to mark of 0.50, 1.00, 2.00, 3.00, and 4.00cm^3 of 100mg/dm^3 cadmium solution in 100cm^3 volumetric flasks respectively.

3.8 Statistical Treatment

All data presented are mean values of three replicate measurements. One way analysis of variance (ANOVA) in randomized complete block design was performed to check the variability of the results among the villages; this was accomplished using Statistical Package for Social Scientists (SPSS, version 17.0).

CHAPTER FOUR

4.0 Results and Discusion

4.1 pH

The pH of the soils samples analyzed is as shown in Table 4.1. The mean value of the soil pH was 6.95 ± 0.69 for dry season and 6.67 ± 0.74 for rainy season. Sample BSS1 shows the highest pH value of 8.02 while sample ASR2 recorded the lowest pH value of 5.85 in the dry season. The distribution of these values showed that the soil samples possessed higher pH values in dry season compared to the corresponding value in the rainy season. This may be due to rainfall, fertilizer application, plant root activity and weathering (Alloway, 1997). The results obtained compared well with those obtained from similar works like that of Tekwa *et al.* (2011) who reported a mean pH of 5.41 in the soil of Mubi area, North Eastern Nigeria. Also, a pH range of 5.60 to 5.82 were reported from the soil of Mambila plateau (Earnest, 2010). Edward *et al.* (2011) also reported a pH range of 5.6 to 8.3 in the Densu River Basin, Ghana.

The pH of the water samples was 7.24 ±0.72 for dry season and 7.22 ±0.63 for rainy season. Sample DPW 2 shows the highest pH of 7.98 while samples BGW 1 and ABW 3 recorded the lowest pH of 6.11. Five wells, two boreholes and one pond recorded pH range of 6.11– 6.4 which is above the 6.5– 9.2 range recommended by NASREA (Ezigbo, 2011), all other values fall within the recommended range (Mark *et al.*, 2014). The result however is in close agreement with Mark *et al.* (2014) who reported a pH range 6.6 – 7.7 of drinking water sources in Anka local government, Zamfara State – Nigeria. Hassan *et al.* (2011) also reported a pH range 5.8 – 7.5 of different water sources in Bukkuyum and Anka local government of Zamfara state. Akagha (2010) also reported a pH range of 4.5 to 6.74 of underground water and three satellite river stations in Owerri local government area of Imo state Nigeria

Table 4.1: The dry and rainy season pH of soil and water samples.

S/N	Sample code	pH of Water samples DRS	pH of Water samples RNS	Sample code	pH of Soil samples DRS	pH of Soil samples RNS
1	DWW1	7.03	7.54	ASS1	7.45	7.28
2	DBW1	6.41	7.30	DSS1	6.27	6.03
3	DBW2	7.25	7.67	BSS1	8.02	7.25
4	BGW1	6.11	6.83	ZSS1	6.96	5.47
5	DPW 1	6.41	7.49	BSF1	6.70	5.36
6	BPW2	6.54	6.23	DSF1	7.46	6.97
7	DPW2	7.98	8.32	ASF1	6.23	6.43
8	BGW2	8.04	7.34	ZSF1	7.19	7.32
9	BPW2	8.23	6.33	ASR1	6.68	5.21
10	BGB1	6.65	6.56	BSR1	6.77	6.23
11	BGW2	7.98	6.84	DSR1	8.01	7.43
12	DWW3	7.34	7.16	ZSR1	7.98	6.74
13	ABW3	6.11	8.51	ZSS 2	7.94	7.55
14	DWW2	7.93	7.64	ZSF 2	6.27	6.84
15	BGB2	8.07	7.89	ZSR 2	6.77	5.57
16	ZWW1	8.21	8.20	BSS 2	6.50	5.34
17	ZWW2	6.76	6.66	BSR 2	7.40	5.83
18	ZBW1	6.21	7.42	BSF 2	6.43	7.43
19	ZBW2	8.04	7.71	ASS 2	7.16	7.35

		pH of Water samples		Sample code	pH of Soil samples	
S/N	Sample code	DRS	RNS		DRS	RNS
20	ZPW1	6.87	6.38	ASF 2	6.56	6.34
21	ABW1	6.89	6.63	DSS 2	7.29	7.23
22	BWW3	7.51	7.25	DSR 2	6.11	7.06
23	APW1	6.02	6.89	DSF 2	7.14	5.98
24	AWW2	6.57	7.01	ASS 3	5.88	6.94
25	ABW2	8.17	7.69	BSS 3	7.95	6.32
26	APW2	6.95	6.31	DSS 3	8.00	7.55
27	AWW1	7.39	7.06	ZSS 3	7.11	7.54
28	AWW3	7.28	7.18	ASF 3	7.88	6.64
29	DWW3	6.84	6.25	BSF 3	6.29	7.53
30	ZBW3	8.14	8.11	ZSF 3	5.89	5.88
31	Z6W3	8.13	7.95	DSF 3	7.16	6.01
32	ZBW3	6.54	6.42	ASR 3	6.33	7.34
33	APW3	7.23	7.99	BSR 3	6.93	6.38
34	DPW3	6.75	7.54	DSR 3	7.56	7.43
35	ZPW3	7.38	6.74	ZSR 3	5.90	7.55
36	ZPW2	7.76	7.11	ASF 4	7.36	6.39
37	MEAN	7.24	7.22	BCTR	6.96	6.23
38	STD	0.72	0.63	ACTR	0.69	6.29
				MEAN	6.95	6.66
				STD	0.69	0.74

Key

DSF	Dareta farms soil	BSF	Bagega farms soil
DSR	Dareta residential soil	BSR	Bagega residentin soil
DSS	Dareta mining site soil	BSR	Bagega mining site soil
DBW	Dareta borehole water	BBW	Bagega borehole water
DWW	Dareta well water	BWW	Bagega well water
DPW	Dareta pound water	BPW	Bagega pound water

ASF	Abare farm soil	ZSF	Duza farms soil
ASR	Abare residential soil	ZSR	Duza residential soil
ASS	Abare mining site soil	ZSS	Duza minig site soil
ABW	Abare borehole water	ZBW	Duza borehole water
AWW	Abare well water	ZWW	Duza well water
APW	Abare pound water	ZPW	Dauza pound water
DRS	Dry Season	CTR	Control (back ground sample)
RNS	Rainy Season		

4.2.0 Metals in the soil

The dry and the corresponding rainy season concentration of the heavy metals in all the samples analyzed are shown in appendix 1.

Figure 4.1 to 4.5 showed the mean concentration of zinc, copper, iron, lead, and cadmium in soil, water and millet from Dareta village. The mean concentration of metals in the soil during dry season was; 94.23 ± 24.37, 67.32 ± 47.06, 746.21 ± 227.87, 720.09 ± 521.87 and 6.25 ± 4.67 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd respectively, while 76.15 ± 9.37, 61.87 ± 13.38, 619.45 ± 94.31, 464.66 ± 344.57 and 5.86 ± 2.32 mg kg-^{1} was recorded for rainy season samples.

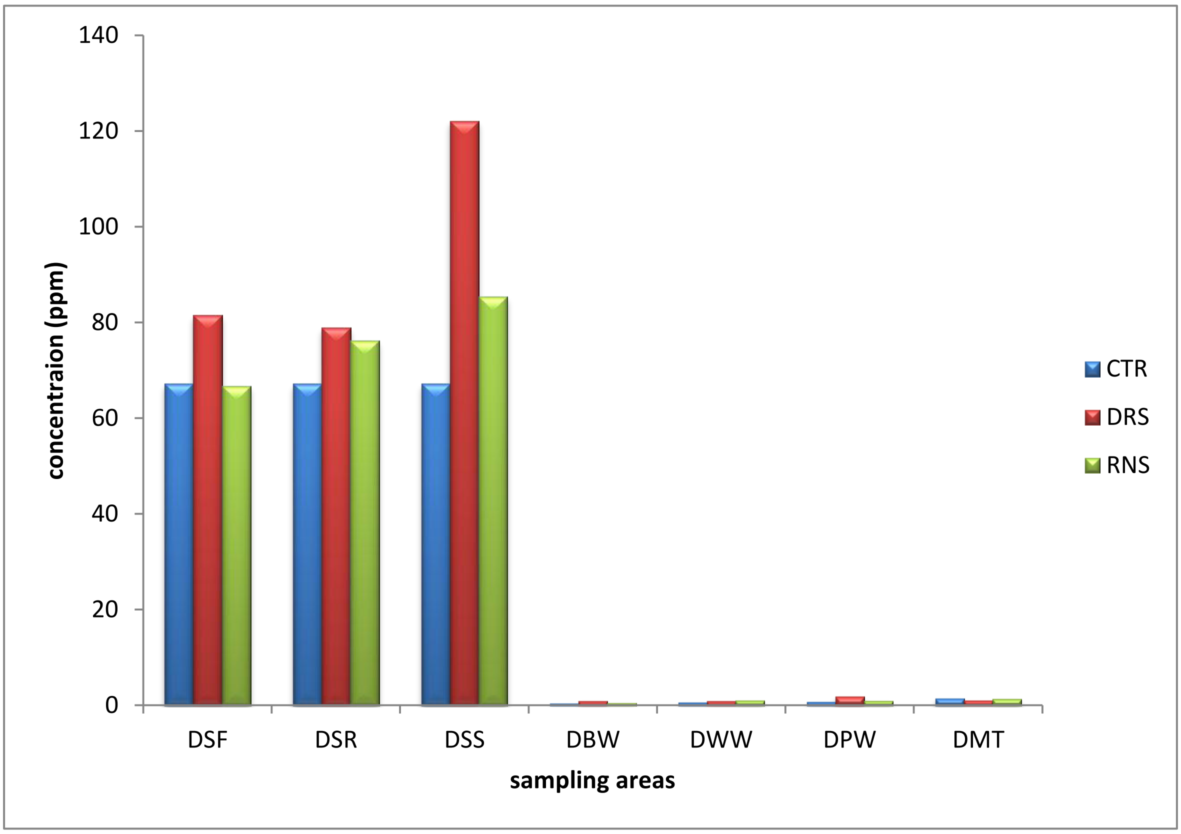


Fig. 4.1: Mean concentration of zinc in soil, water and millet samples analysed from Dareta village.

Key

CTR: Control (Background)	DRS: Dry season concentration
RNS: Rainy season concentration	DSF: Dareta Farm soil
DSR: Dareta Residential soil	DSS: Dareta Mining site
DBW: Dareta Borehole Water	DWW: Dareta Well Water
DPW: Dareta Pond Water	DMT: Dareta Millet

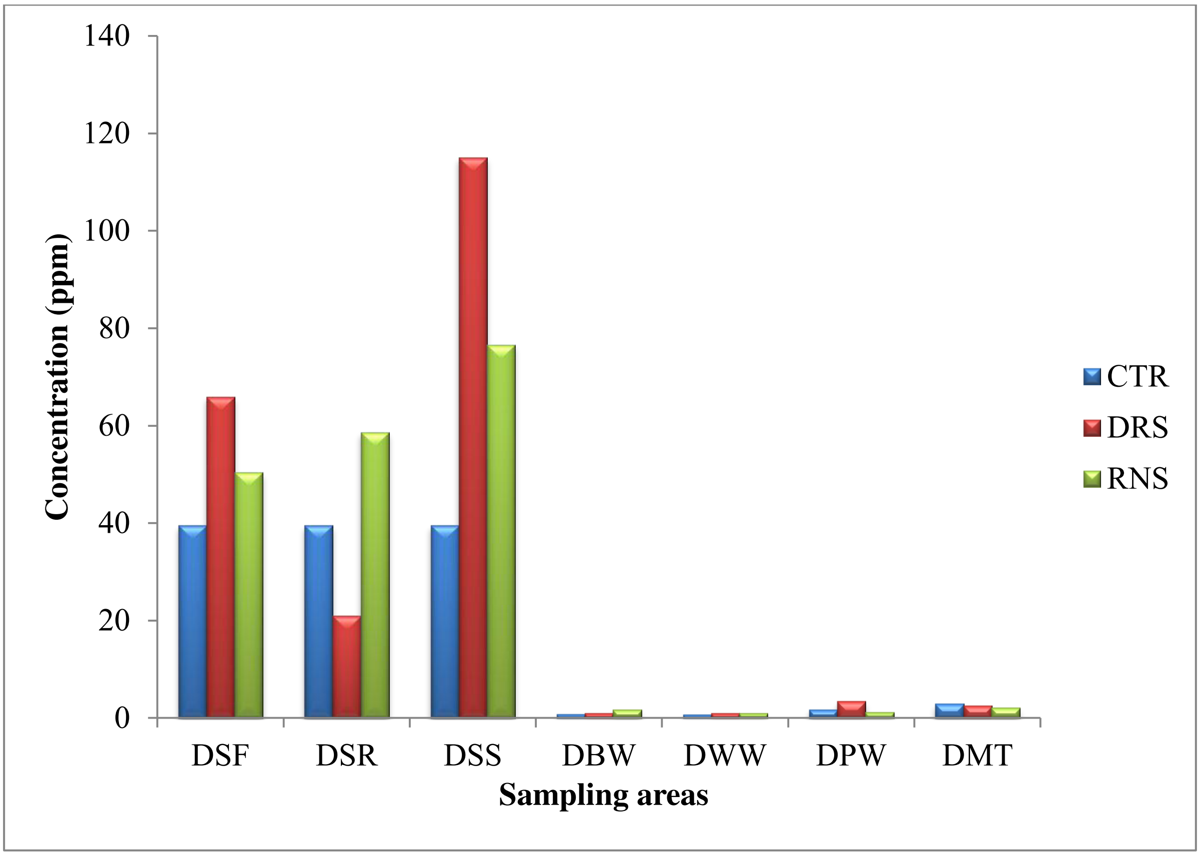
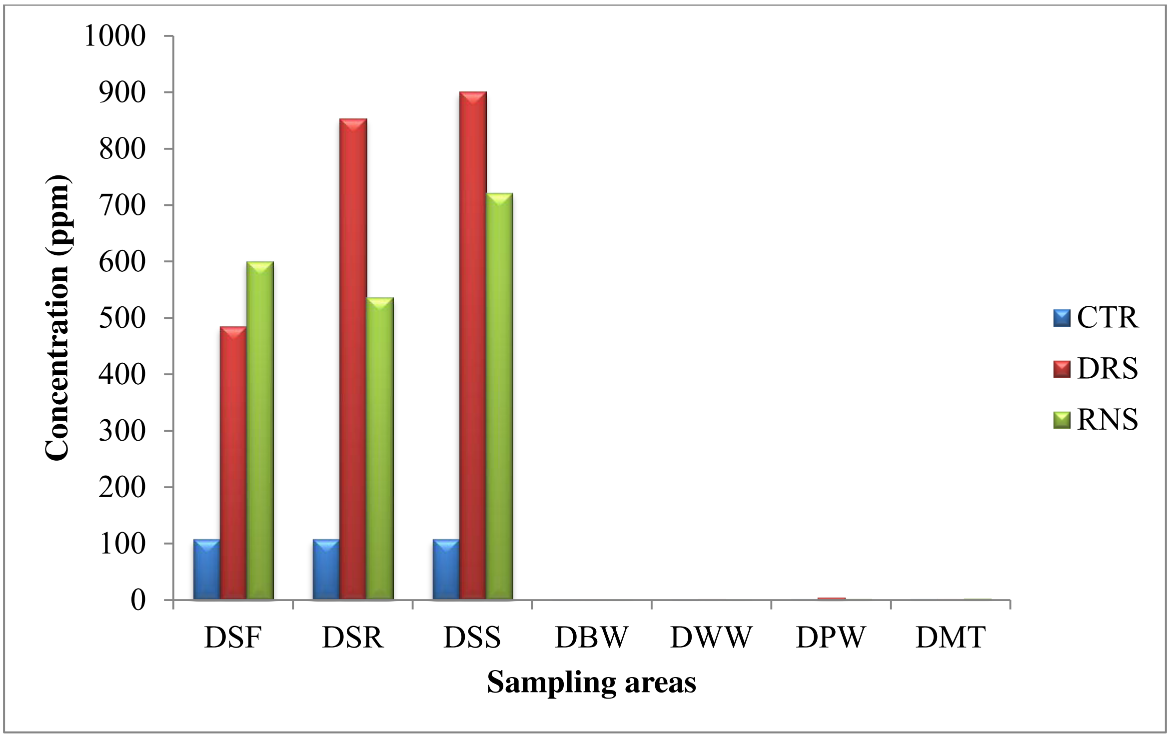


Fig. 4.2: Mean concentration of copper in soil, water and millet samples analysed from Dareta village.



Figu. 4.3: Mean concentration of iron in soil, water and millet samples analysed from Dareta village.

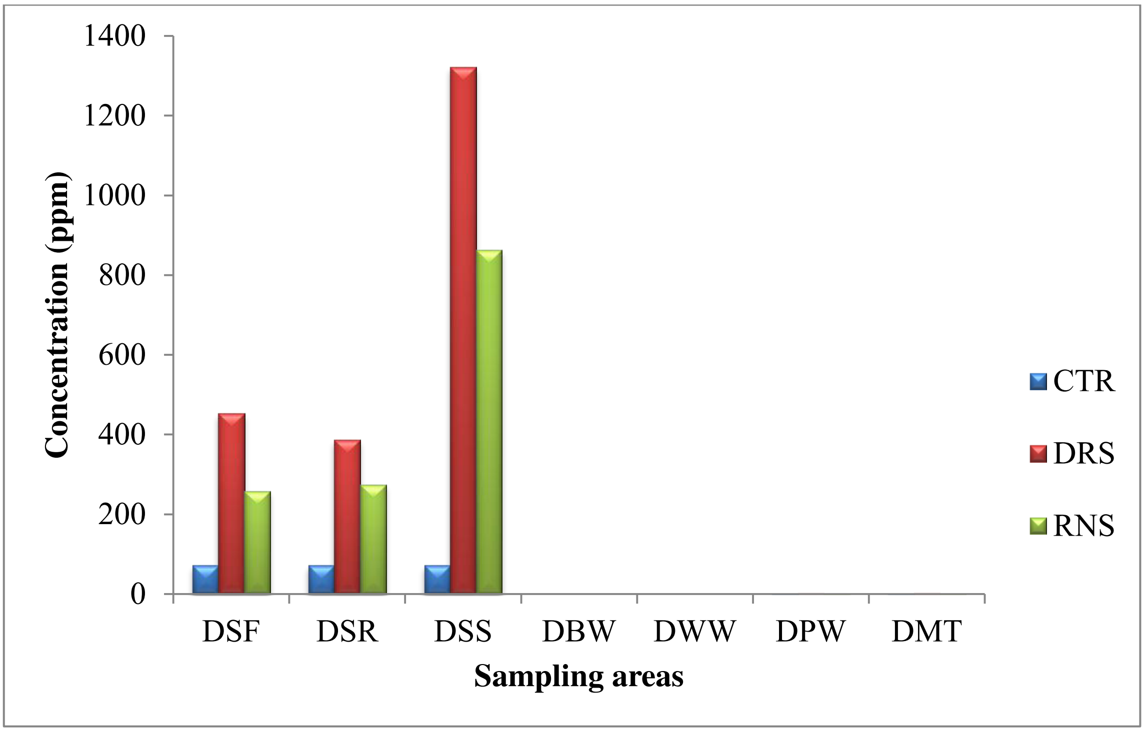


Fig.4.4: Mean concentration of lead in soil, water and millet samples analysed from Dareta village.

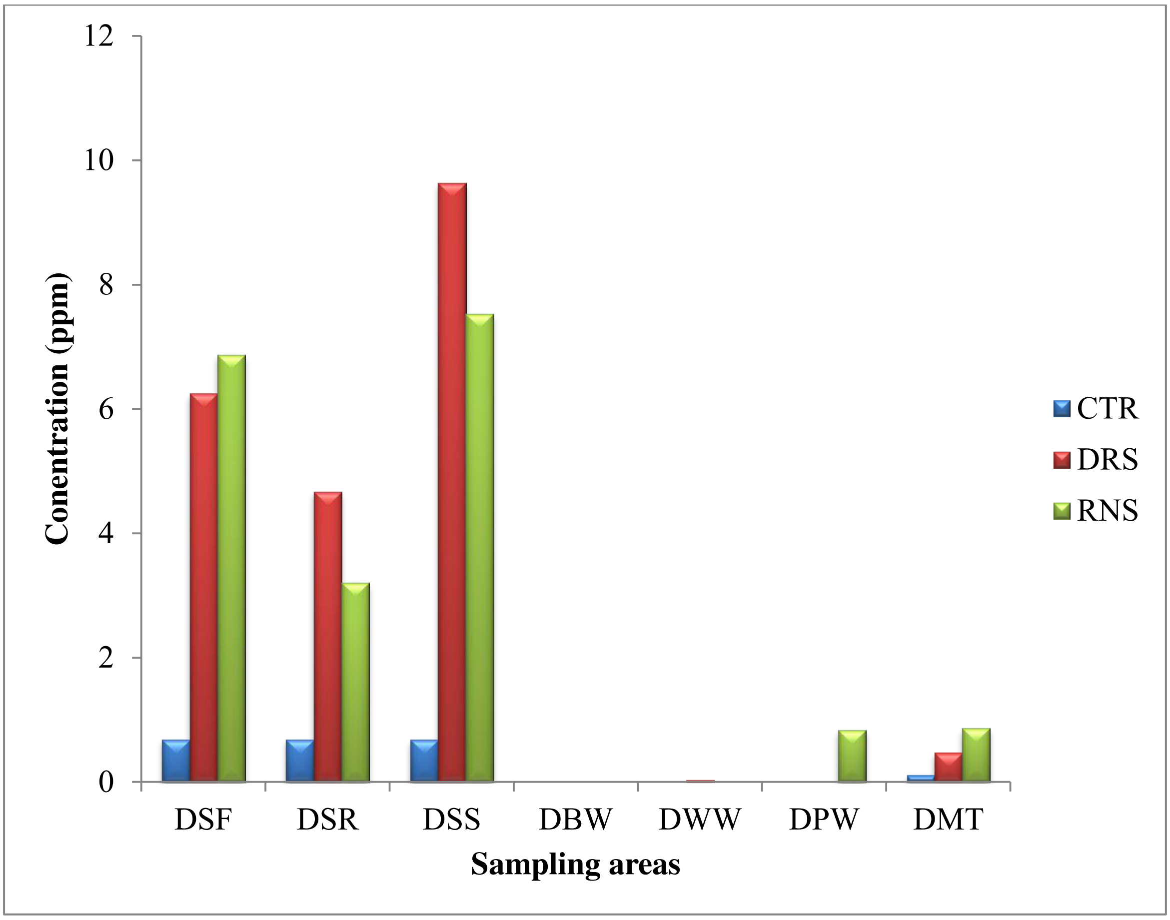


Fig. 4.5: Mean concentration of cadmium in soil, water and millet samples analysed from Dareta village.

The combined mean concentration of all sampling points from the villages under study showed generally that samples collected from the mining and crushing sites of the village exhibit elevated mean concentration recording a highest value of 1321.51 ± 137.04 mg kg-^{1} for lead (Fig. 4.4), while the lowest concentration was 3.20 ± 0.61 mg kg-^{1} of cadmium (Fig. 4.5) recorded by samples collected from farm lands of the villages under study. Most of the results obtained in dry season exhibit elevated concentration than the corresponding rainy season results, this may be due to the fact that these heavy metals might have dissolve and disperse into surrounding streams as a result of rainwater runoff and percolation through contaminated soil (Mark *et al*., 2014) and the seasonal nature of the mining processes in most of the villages due to the engagement of the local miners in to farming during rainy season (Thomas *et al.,* 2003), which in turn can reduce the amount of the contaminants released to the environment. Generally there was an increase in the levels of zinc at all sampling points around the mining communities compared to the levels obtained from the background soil, this indicate that the activities of the local miners contributes to the increase in the levels of heavy metals at and around the mining areas. Similar values were reported by Antwi-Agyei *et al.,* (2009) who reported the mean concentration of; 168.1 ± 108.7, 71.44 ± 15.8, 38.67 ± 10.76 mg kg-^{1} for Zn, Cu, and Pb around goldmine tailings dams at Obuasi, Ghana. Yao-guo *et al.,* (2010) also reported 118.6 ± 85.26, 54.13 ± 71.18, 216.93 ± 487.83 and 0.55 ± 3.91 mg kg-^{1} as the mean concentration of Zn, Cu, Pb and Cd of polluted soil over Xiaoqinling gold mining region, Shaanxi, China. Tobias *et al.,* (2013) also reported a mean concentration of 10.92 ± 8.77, 39.0 ± 28.43, 784.09 ± 45.74, 71.00 ± 64.89 and 5.21 ± 1.47 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd in soil of Aba city, Nigeria. Higher average values of 985, 1266 and 17.5 mg kg-^{1} for Zn, Pb and Cd from contaminated farmlands of Abare village, Zamfara State, Nigeria was reported by Abdu and Yusuf (2013) but the higher values may be as the result of the contaminated dust arising from an excavation processes that was going on at the time of their sampling. The values obtained in this research does not exceeds the maximum allowable values of 300 – 600 mg kg-^{1} (NASREA), 200 mg kg-^{1} WHO permissible concentration (Ezigbo, 2011) for zinc, 100 mg kg-^{1} for Cu (Kabata-Pendias, 2011 and Chiroma *et al.,* 2014), 5000 mg kg-^{1} for Fe (Chiroma *et al*., 2014). The mining site and the farm lands of Dareta (Fig. 4.5) showed concentration higher than the 3 – 6 mg kg-^{1} cadmium in soil set by NASREA but below 10 mg kg-^{1} set by WHO (Ezigbo, 2011), while Pb concentration at the mining site of Dareta village (fig. 4.4) was above the 500 mg kg-^{1} permissible limit set by NASREA (Ezigbo, 2011).

The combine mean concentration of metals in all water sources during dry season was; 1.18 ± 0.55, 3.41 ± 0.61, 1.70 ± 2.14, 1.31 ± 0.22 and 0.21 ± 0.03 mg/L for Zn, Cu, Fe, Pb and Cd respectively, while 0.79 ± 0.29, 2.17 ± 0.42, 0.89 ± 0.62, 0.83 ± 0.26 and 0.01 ± 0.01 mg/L was recorded for rainy season samples. The trend showed that samples collected from ponds exhibit elevated concentration while the lowest values were mostly from borehole water. Pb (Fig. 4.4), Cd (Fig. 4.5) and Cu (Fig. 4.2) were not detected in borehole water of Dareta, Fe (Fig. 4.3) shows the highest concentration of 4.14 ± 1.58 mg/L obtained in pond water, while Cd showed the lowest concentration of 0.006 mg kg-^{1} from well water sample. This may be as a result of extra natural filtration procedure that the underground water sources (the wells and boreholes) might have undergoes which the surface water (pounds) lacks. The elevated concentration of zinc in the pond water may be due to indiscriminate washing of the crushed rocks by the local miners around most of the pounds available and the dust fallout on the open ponds from the air carrying dust generated during the crushing procedure (Antwi-Agyei *et al.*, 2009). Heavy metals associated with gold mining waste might have also dissolve and disperse into surrounding streams as a result of rainwater percolation through the waste or dispersed as particles through erosion processes (Mark *et al*., 2014). The results obtained compared to those obtained by Rasheed and Amuda (2014) who reported a mean concentration of 3.18 ± 2.305, 1.02 ± 0.89 and 0.014 ± 0.004 mg/L for Zn, Cu and Pb in Surface Water of Kutcheri, Zamfara State, Nigeria. Cobbina *et al*. (2013) also reported 0.15 ± 0.026, 6.65 ± 7.841 and 0.005 ± 0 mg/L for Zn, Fe and Cd mg/L in drinking water sources in the Talensi-Nabdam district, Tongo. Much higher values of 29, 23, 314, 165 and 15 mg/L for Zn, Cu, Fe, Pb and Cd were however reported in drinking water contaminated due to illegal gold mining activities in Dareta, Sunke and Bagega of Zamfara State, Nigeria (Mark *et al.*, 2014) large difference observed may be due to the fact that it's extremely difficult for different individuals to name and sample the same location and therefore showed the non-uniform deposition of these metals by human activities and not the natural distribution. Most of the borehole water and few well water conformed with the maximum permissible limit of 1.5, 0.5, 0.3, 0.01 and 0.01 mg/L for Zn, Cu, Fe, Pb and Cd set by NASREA/WHO (Tobias *et al.,* 2013). While all ponds and a few well water samples showed concentration above the maximum permissible limits.

The mean concentration of metals in grain samples during dry season was; 1.61 ± 0.43, 2.49 ± 0.83, 2.51 ± 1.64, 2.42 ± 0.80 and 0.39 ± 0.12 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd respectively, while 1.74 ± 0.67, 2.06 ± 0.46, 2.49 ± 0.70, 1.94 ± 1.0 and 0.33 ± 0.31 mg kg-^{1} was recorded for rainy season samples. Cd (Fig. 4.5) recorded the lowest mean concentration of 0.39 ± 0.12 mg kg-^{1} while Cu (Fig. 4.2) had the highest concentration of 1.61 ± 0.43 mg kg-^{1}. The values observed did not followed a particular pattern, however this may be due to different factors such as soil pH, soil organic matter, levels of the bio-available fraction of the heavy metals, fertilizer application, the ability of the crop plants to absorb heavy metals etc, which can all affect the levels of heavy metals in the grains (Zhuang *et al.,* 2009 and Kabata-Pendias, 2011). The results obtained from this study is consistent with mean concentration of

0.71, 0.18, 0.15 and 0.16 mg kg-^{1} for Zn, Cu, Pb and Cd in millet samples grown in the city of Kano and its environs (Dahiru *et al*., 2013). 1.97, 3.65, 0.582 and 3.26 mg kg-^{1} for Zn, Cu, Fe and Pb in millet reported by Tudunwada *et al.* (2007) when they used tannery sludge as soil amendment for cereals on small-holder farms in Kano, Nigeria. Emmanuel *et al*. (2013) also reported 0.29 ± 0.16 and 0.59 ± 0.35 mg kg-^{1} for Zn and Cu in Millet from Minna and Bida.

Figure 4.6 to 4.10 showed the mean concentration of zinc, copper, iron, lead, and cadmium in soil, water and millet from Bagega village. The mean concentration of metals in the soil during dry season was; 84.42 ± 11.61, 43.74 ± 16.60, 438.39 ± 362.88, 1293.30 ± 976.15 and 2.00 ± 1.15 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd respectively, while 75.67 ± 9.49, 59.03 ± 13.72, 287.34 ± 246.96, 1022.65 ± 868.93 and 1.40 ± 0.57 mg kg-^{1} was recorded for rainy season samples. The combined mean concentration of all sampling points from the villages under study showed generally that samples collected from the mining and crushing sites of the village exhibit elevated mean concentration recording a highest value of 2399.12 ± 568.59 mg kg-^{1} for lead (Fig. 4.9), while the lowest concentration was 1.04 ± 0.43 mg kg-^{1} of cadmium (Fig. 4.10) recorded by samples collected from farm lands of Bagega village. Most of the results obtained in dry season exhibit elevated concentration than the corresponding rainy season results, this may be due to the fact that these heavy metals might have dissolve and disperse into surrounding streams as a result of rainwater runoff and percolation through contaminated soil (Mark *et al*., 2014) and the seasonal nature of the mining processes in most of the villages due to the engagement of the local miners in to farming during rainy season (Thomas *et al.*, 2003), which in turn can reduce the amount of the contaminants released to the environment.

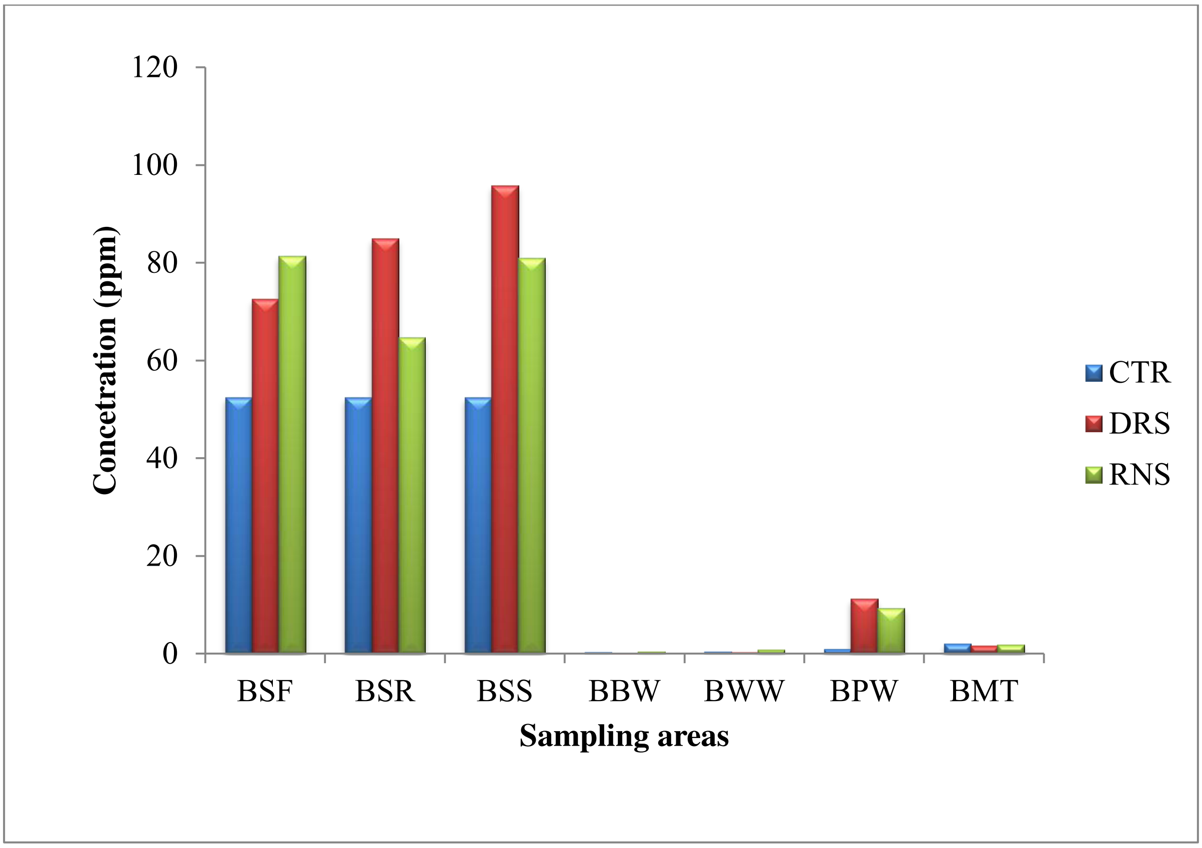


Fig. 4.6: Mean concentration of zinc in soil, water and millet samples analysed from Bagega village.

Key

CTR: Control (Background),	DRS: Dry season concentration
RNS: Rainy season concentration,	BSF: Bagega Farm soil
BSR: Bagega Residential soil,	BSS: Bagega Mining site
BBW: Bagega Borehole Water,	BWW: Bagega Well Water
BPW: Bagega Pond Water,	BMT: Bagega Millet

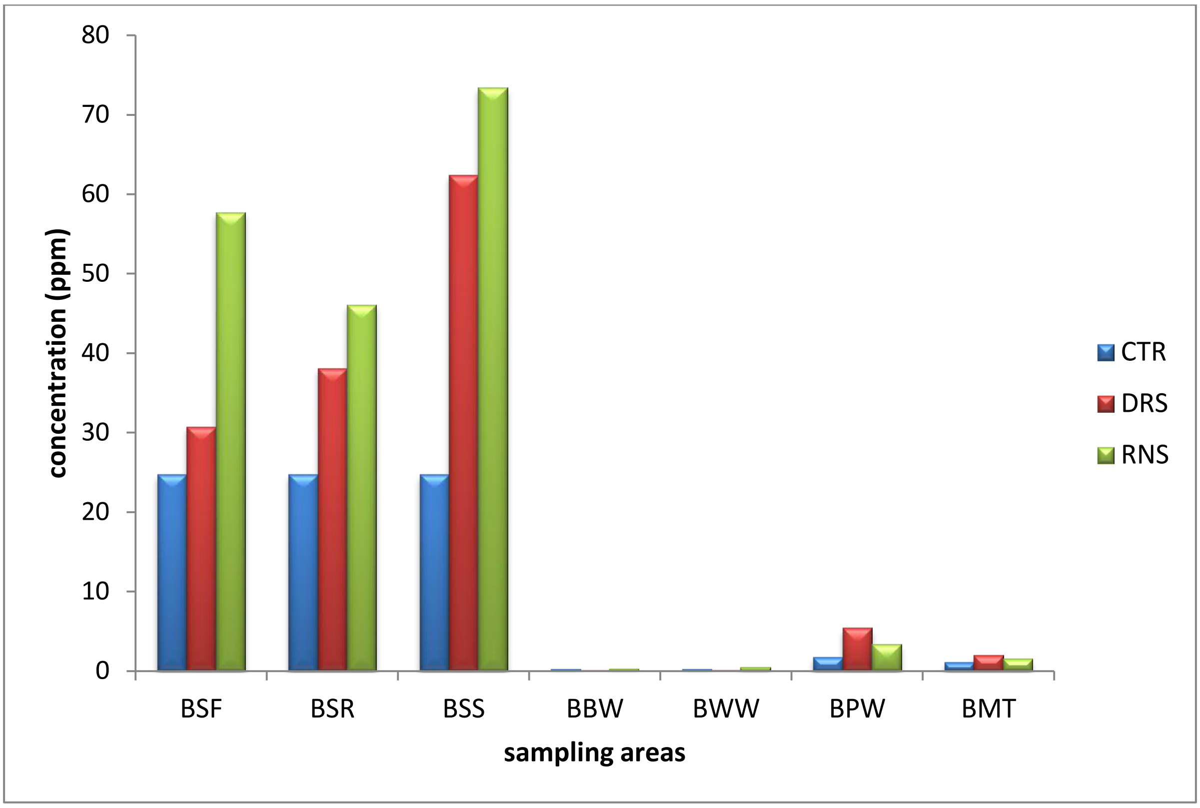


Fig. 4.7: Mean concentration of copper in soil, water and millet samples analysed from Bagega village.

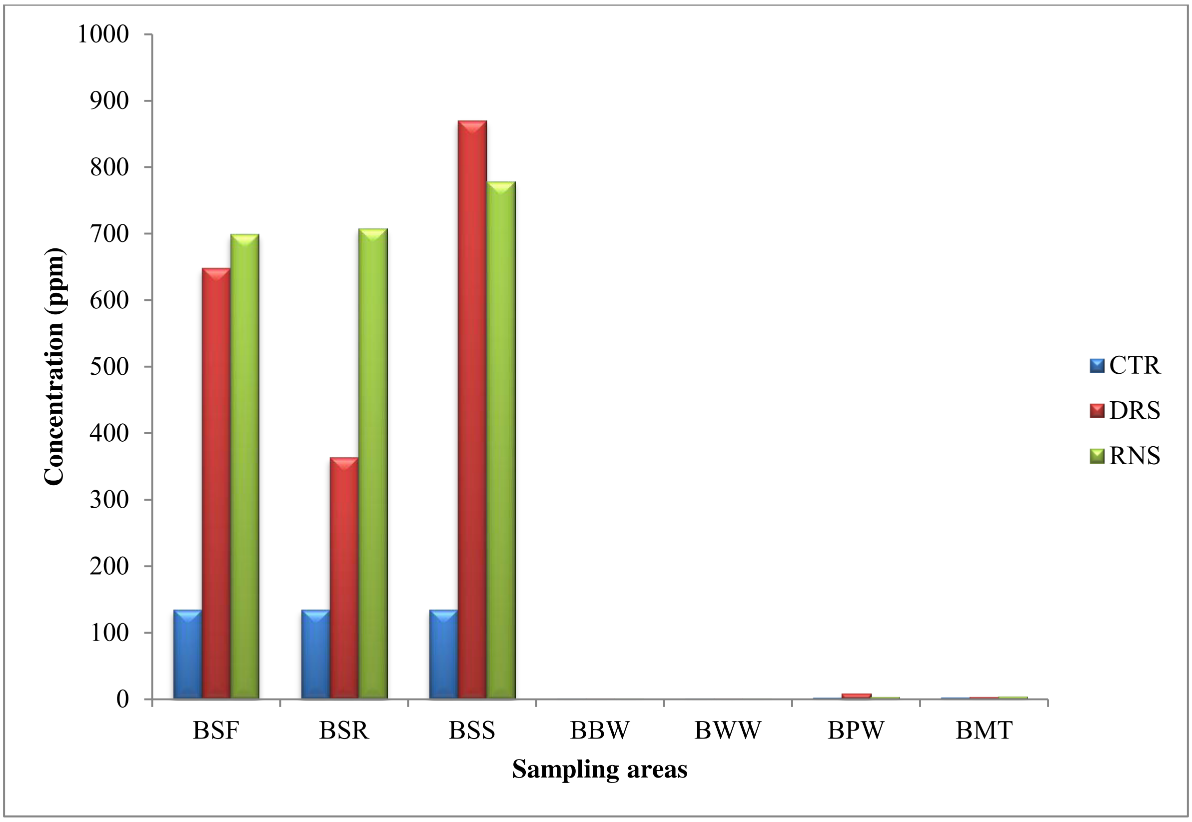


Fig. 4.8: Mean concentration of iron in soil, water and millet samples analysed from Bagega village.

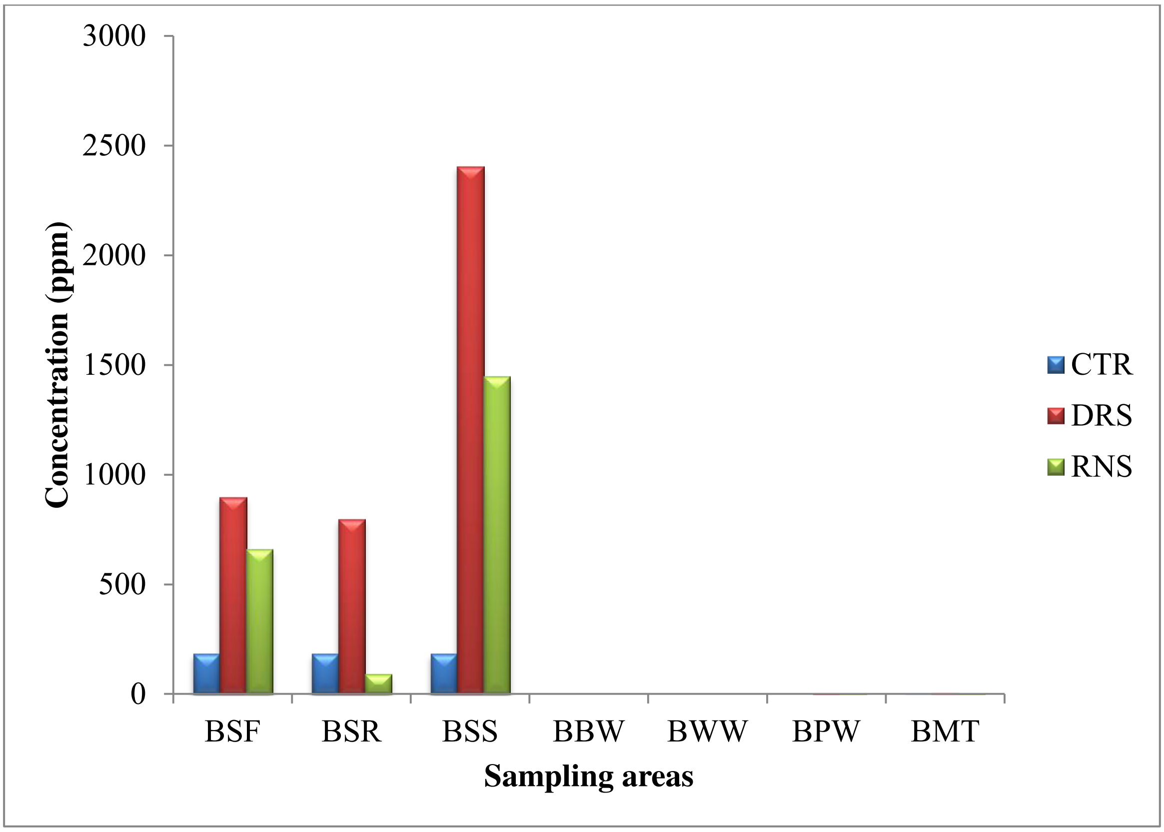


Fig. 4.9: Mean concentration of lead in soil, water and millet samples analysed from Bagega village.

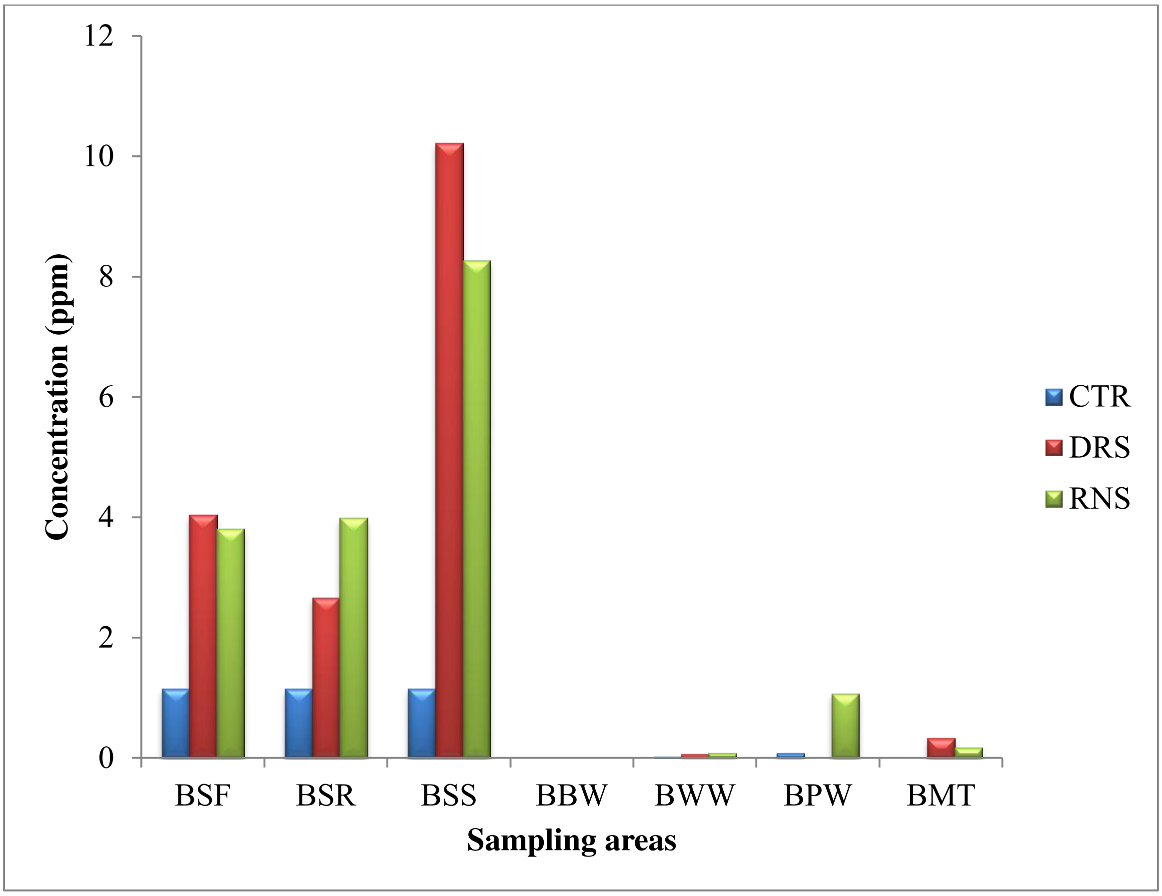


Fig. 4.10: Mean concentration of cadmium in soil, water and millet samples analysed from Bagega village.

Generally there was an increase in the levels of zinc at all sampling points around the mining communities compared to the levels obtained from the background soil, this indicate that the activities of the local miners contributes to the increase in the levels of heavy metals at and around the mining areas. Similar values were reported by Antwi-Agyei *et al.,* (2009) who reported the mean concentration of; 168.1 ± 108.7, 71.44 ± 15.8, 38.67 ± 10.76 mg kg^{-1} for Zn, Cu, and Pb around goldmine tailings dams at Obuasi, Ghana. Yao-guo *et al.,* (2010) also reported 118.6 ± 85.26, 54.13 ± 71.18, 216.93 ± 487.83 and 0.55 ± 3.91 mg kg^{-1} as the mean concentration of Zn, Cu, Pb and Cd of polluted soil over Xiaoqinling gold mining region, Shaanxi, China. Tobias *et al.,* (2013) also reported a mean concentration of 10.92 ± 8.77, 39.0 ± 28.43, 784.09 ± 45.74, 71.00 ± 64.89 and 5.21 ± 1.47 mg kg^{-1} for Zn, Cu, Fe, Pb and Cd in soil of Aba city, Nigeria. Higher average values of 985, 1266 and 17.5 mg kg^{-1} for Zn, Pb and Cd from contaminated farmlands of Abare village, Zamfara State, Nigeria was reported by Abdu and Yusuf (2013) but the higher values may be as the result of the contaminated dust arising from an excavation processes that was going on at the time of their sampling. The values obtained in this research does not exceeds the maximum allowable values of 300 – 600 mg kg^{-1} (NASREA), 200 mg kg^{-1} WHO permissible concentration (Ezigbo, 2011) for zinc, 100 mg kg^{-1} for Cu (Kabata-Pendias, 2011 and Chiroma *et al.,* 2014), 5000 mg kg^{-1} for Fe (Chiroma *et al*., 2014). The mining site and the farm lands of Dareta (Fig. 4.5) showed concentration higher than the 3 – 6 mg kg^{-1} cadmium in soil set by NASREA but below 10 mg kg^{-1} set by WHO (Ezigbo, 2011), while Pb concentration of the mining site (Fig. 4.4) was above the 500 mg kg^{-1} permissible limit set by NASREA (Ezibbo, 2011).

The combine mean concentration of metals in all water sources for dry season was; 3.85 ± 6.37, 5.40 ± 0.00, 0.80 ± 1.11, 0.18 ± 0.14 and 0.38 ± 0.45 mg kg^{-1} for Zn, Cu, Fe, Pb and Cd respectively, while 3.52 ± 0.05, 3.36 ± 0.00, 0.36 ± 0.38, 0.17 ± 0.12 and 0.16 ± 0.12 mg kg-^{1} was recorded for rainy season samples. The trend showed that samples collected from ponds exhibit elevated concentration while the lowest values were mostly from borehole water. Pb (Fig 4.4), Cd (Fig. 4.5) and Cu (Fig. 4.2) were not detected in borehole water of Bagega, Fe (Fig. 4.3) shows the highest concentration of 4.14 ± 1.58 mg kg-^{1} obtained in pond water, while Cd showed the lowest concentration of 0.006 mg kg-^{1} from well water sample. This may be as a result of extra natural filtration procedure that the underground water sources (the wells and boreholes) might have undergoes which the surface water (ponds) lacks. The elevated concentration of zinc in the pond water may be due to indiscriminate washing of the crushed rocks by the local miners around most of the pounds available and the dust fallout on the open ponds from the air carrying dust generated during the crushing procedure (Antwi-Agyei *et al.*, 2009). Heavy metals associated with Gold mining waste might have also dissolve and disperse into surrounding streams as a result of rainwater percolation through the waste or dispersed as particles through erosion processes (Mark *et al.*, 2014). The results obtained compared to those obtained by Rasheed and Amuda (2014) who reported a mean concentration of 3.18 ± 2.305, 1.02 ± 0.89 and 0.014 ± 0.004 mg/L for Zn, Cu and Pb in Surface Water of Kutcheri, Zamfara State, Nigeria. Cobbina *et al.* (2013) also reported 0.15 ± 0.026, 6.65 ± 7.841 and 0.005 ± 0 mg/L for Zn, Fe and Cd mg/L in drinking water sources in the Talensi-Nabdam district, Tongo. Much higher values of 29, 23, 314, 165 and 15 mg/L for Zn, Cu, Fe, Pb and Cd were however reported in drinking water contaminated due to illegal gold mining activities in Dareta, Sunke and Bagega of Zamfara State, Nigeria (Mark *et al.*, 2014) large difference observed may be due to the fact that it's extremely difficult for different individuals to name and sample the same location and therefore showed the non-uniform deposition of these metals by human activities and not the natural distribution. Most of the borehole water and a few well water conformed with the maximum permissible limit of 1.5, 0.5, 0.3, 0.01 and 0.01 mg/L for Zn, Cu, Fe, Pb and Cd set by NASREA/WHO (Tobias *et. al.*, 2013). While all ponds and a few well water samples showed concentration above the maximum permissible limits.

The mean concentration of metals in grain samples during dry season was; 1.61 ± 0.43, 2.49 ± 0.83, 2.51 ± 1.64, 2.42 ± 0.80 and 0.39 ± 0.12 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd respectively, while 1.74 ± 0.67, 2.06 ± 0.46, 2.49 ± 0.70, 1.94 ± 1.0 and 0.33 ± 0.31 mg kg-^{1} was recorded for rainy season samples. Cd (Fig. 4.5) recorded the lowest mean concentration of 0.39 ± 0.12 mg kg-^{1} while Cu (Fig. 4.2) had the highest concentration of 1.61 ± 0.43 mg kg-^{1}. The values observed did not followed a particular pattern, however this may be due to different factors such as soil pH, soil organic matter, levels of the bio-available fraction of the heavy metals, fertilizer application, the ability of the crop plants to absorb heavy metals etc, which can all affect the levels of heavy metals in the grains (Zhuang *et al.,* 2009 and Kabata-Pendias, 2011). The results obtained from this study is consistent with mean concentration of 0.71, 0.18, 0.15 and 0.16 mg kg-^{1} for Zn, Cu, Pb and Cd in millet samples grown in the city of Kano and its environs (Dahiru *et al*., 2013). 1.97, 3.65, 0.582 and 3.26 mg kg-^{1} for Zn, Cu, Fe and Pb in millet reported by Tudunwada *et al.,* (2007) when they used tannery sludge as soil amendment for cereals on small-holder farms in Kano, Nigeria. Emmanuel *et al*., (2013) also reported 0.29 ± 0.16 and 0.59 ± 0.35 mg kg-^{1} for Zn and Cu in Millet from Minna and Bida.

Figure 4.11 to 4.15 showed the mean concentration of zinc, copper, iron, lead, and cadmium in soil, water and millet from Abare village. The mean concentration of metals in the soil during dry season was; 61.96 ± 20.12, 37.15 ± 4.99, 627.16 ± 254.02, 1366.51 ± 901.46 and 5.64 ± 4.02 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd respectively, while 56.02 ± 30.58, 24.69 ± 4.01, 728.63 ± 43.67, 731.87 ± 681.69 and 5.35 ± 2.52 mg kg-^{1} was recorded for rainy season samples. The combined mean concentration of all sampling points from the villages under study showed generally that samples collected from the mining and crushing sites of the village exhibit elevated mean concentration recording a highest value of 2405.77 ± 748.16 mg kg-^{1} for lead (Fig. 4.14), while the lowest concentration was 2.55 ± 0.86 mg kg-^{1} of cadmium (Fig. 4.15) recorded by samples collected from farm lands of Abare village. Most of the results obtained in dry season exhibit elevated concentration than the corresponding rainy season results, this may be due to the fact that these heavy metals might have dissolve and disperse into surrounding streams as a result of rainwater runoff and percolation through contaminated soil (Mark *et al*., 2014) and the seasonal nature of the mining processes in most of the villages due to the engagement of the local miners in to farming during rainy season (Thomas, 2003), which in turn can reduce the amount of the contaminants released to the environment. Generally there was an increase in the levels of zinc at all sampling points around the mining communities compared to the levels (52.49, 24.73, 118.14, 102.47 and 1.31 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd) obtained from the background soil, this indicate that the activities of the local miners contributes to the increase in the levels of heavy metals at and around the mining areas. Similar values were reported by Antwi-Agyei *et al.,* (2009) who reported the mean concentration of; 168.1 ± 108.7, 71.44 ± 15.8, 38.67 ± 10.76 mg kg-^{1} for Zn, Cu, and Pb around goldmine tailings dams at Obuasi, Ghana.

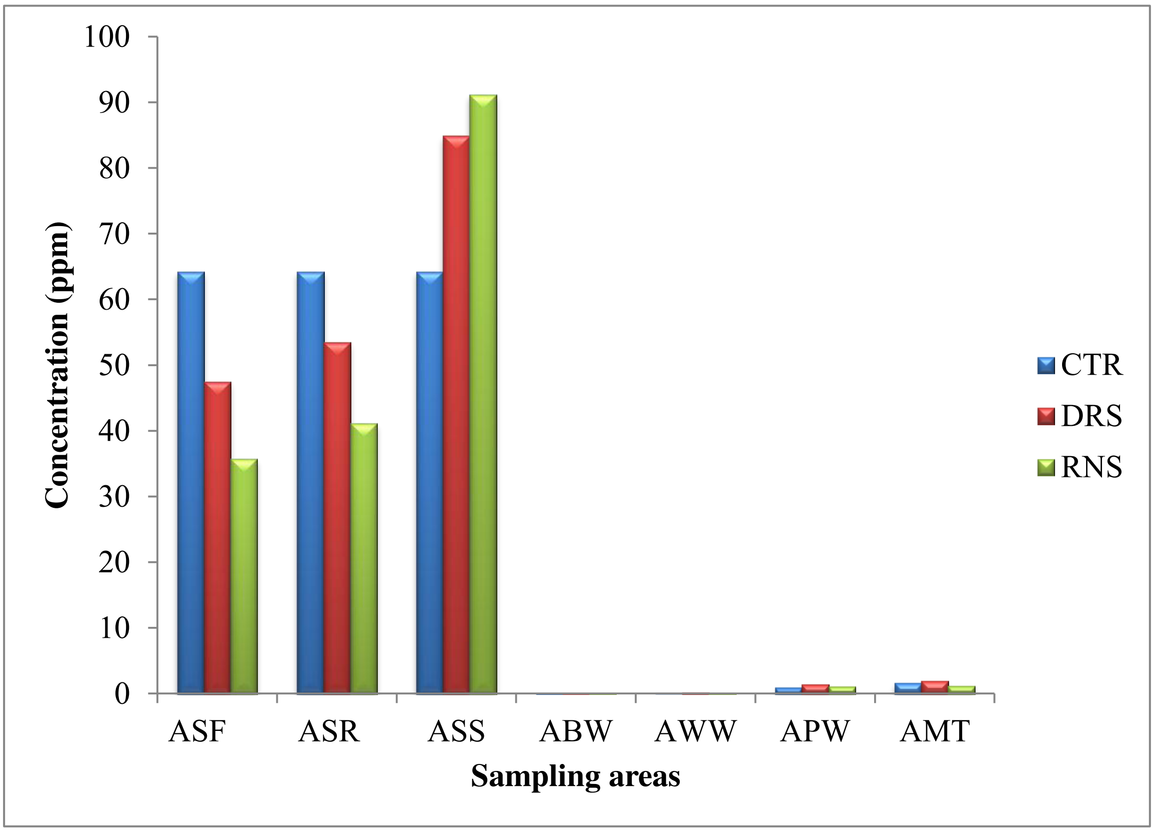


Fig. 4.11: Mean concentration of zinc in soil, water and millet samples analysed from Abare village.

Key

CTR: Control (Background)

DRS: Dry season concentration

RNS: Rainy season concentration

ASF: Abare Farm soil

ASR: Abare Residential soil

ASS: Abare Mining site

ABW: Abare Borehole Water

AWW: Abare Well Water

APW: Abare Pond Water

AMT: Abare Millet

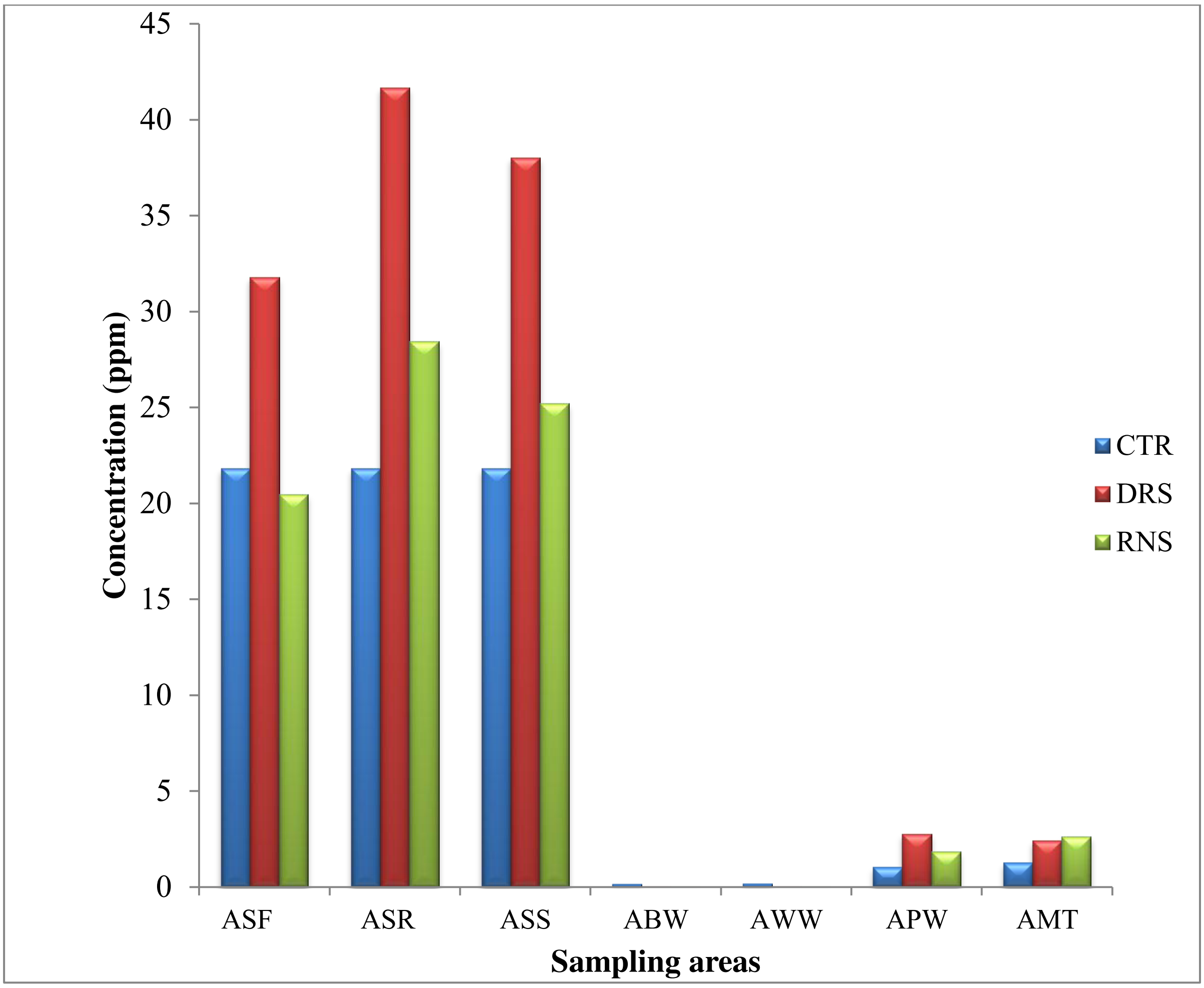


Fig. 4.12: Mean concentration of copper in soil, water and millet samples analysed from Abare village.

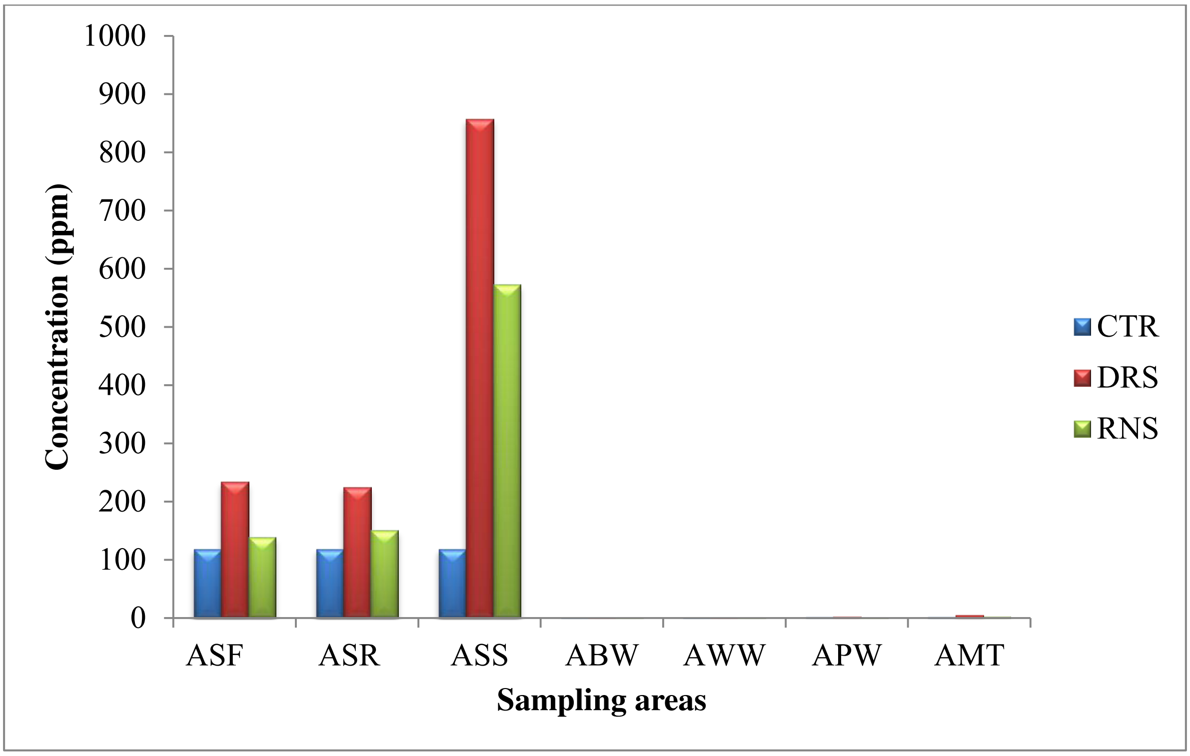


Fig. 4.13: Mean concentration of iron in soil, water and millet samples analysed from Abare village.

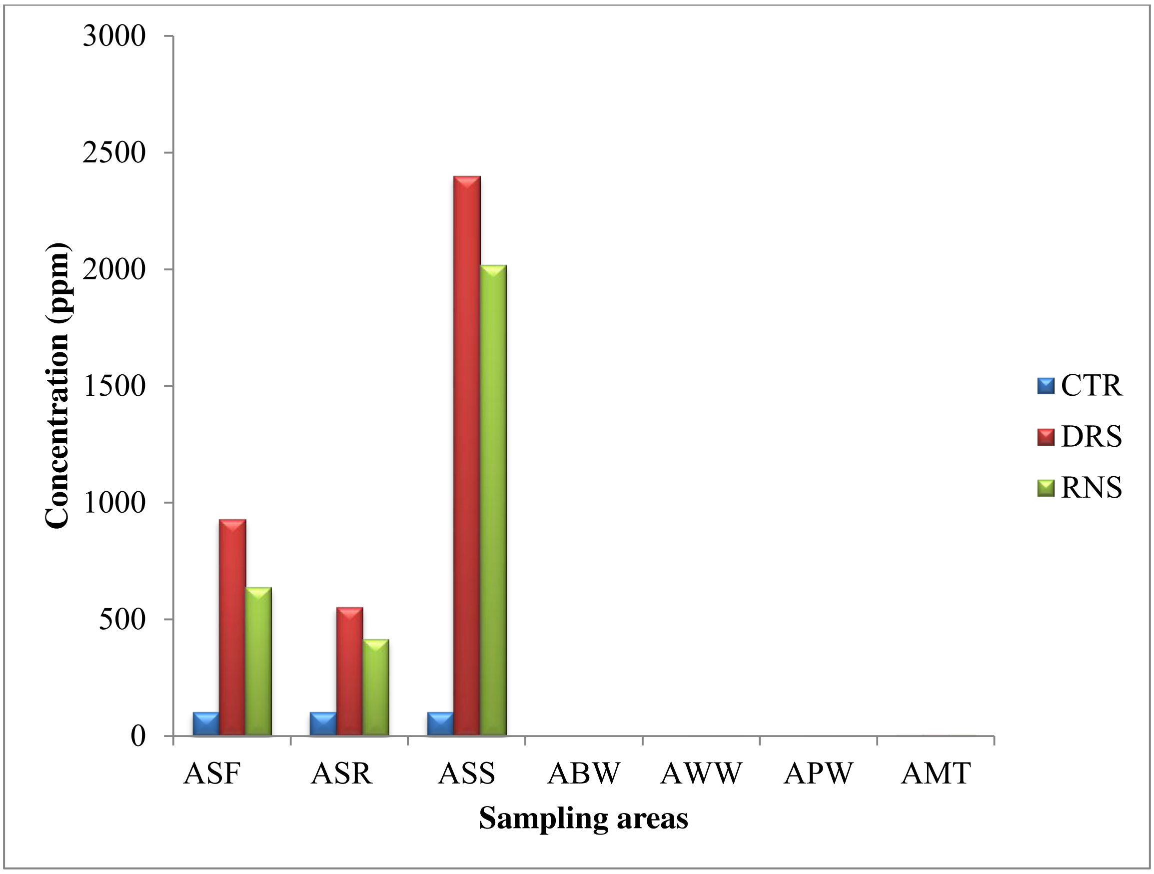


Fig. 4.14: Mean concentration of lead in soil, water and millet samples analysed from Abare village.

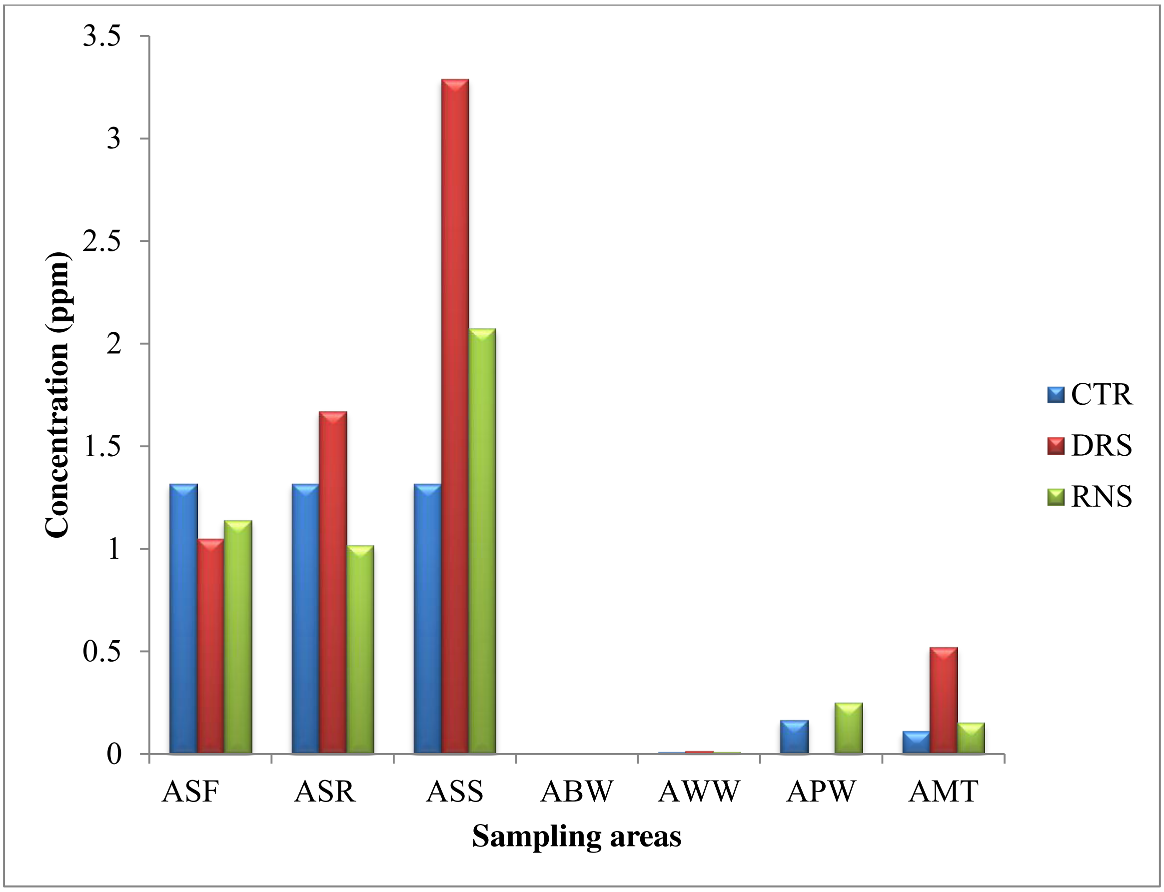


Fig. 4.15: Mean concentration of cadmium in soil, water and millet samples analysed from Abare village.

Yao-guo *et al.,* (2010) also reported 118.6 ± 85.26, 54.13 ± 71.18, 216.93 ± 487.83 and 0.55 ± 3.91 mg kg-^{1} as the mean concentration of Zn, Cu, Pb and Cd of polluted soil over Xiaoqinling gold mining region, Shaanxi, China. Tobias (2013) also reported a mean concentration of 10.92 ± 8.77, 39.0 ± 28.43, 784.09 ± 45.74, 71.00 ± 64.89 and 5.21 ± 1.47 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd in soil of Aba city, Nigeria. Higher average values of 985, 1266 and 17.5 mg kg-^{1} for Zn, Pb and Cd from contaminated farmlands of Abare village, Zamfara State, Nigeria was reported by Abdu and Yusuf (2013) but the higher values may be as the result of the contaminated dust arising from an excavation processes that was going on at the time of their sampling. The values obtained in this research does not exceeds the maximum allowable values of 300 – 600 mg kg-^{1} (NASREA), 200 mg kg-^{1} WHO permissible concentration (Ezigbo, 2011) for zinc, 100 mg kg-^{1} for Cu (Kabata-Pendias, 2011 and Chiroma *et al.,* 2014), 5000 mg kg-^{1} for Fe (Chiroma *et al.*, 2014). The mining site and the farm lands of Dareta (Fig. 4.5) showed concentration higher than the 3 – 6 mg kg-^{1} cadmium in soil set by NASREA but below 10 mg kg-^{1} set by WHO (Ezigbo, 2011), while Pb concentration of the mining site (Fig. 4.4) was above the 500 mg kg-^{1} permissible limit set by NASREA (Ezigbo, 2011).

The combine mean concentration of metals in all water sources during dry season was; 0.54 ± 0.75, 2.76 ± 0.00, 3.01 ± 3.01, 0.83 ± 0.00 and 0.93 ± 1.30 mg/L for Zn, Cu, Fe, Pb and Cd respectively, while 0.37 ± 0.59, 1.83 ± 0.00, 1.25 ± 1.82, 0.73 ± 0.00 and 0.54 ± 0.75 mg/L was recorded for rainy season samples, all against a background concentration of 0.34 ± 0.49, ND, 0.74 ± 0.94, ND and 0.008 ± 0.00 mg/L for Zn, Cu, Fe, Pb and Cd. The trend showed that samples collected from ponds exhibit elevated concentration while the lowest values were mostly from borehole water. Cu (Fig. 4.12) and Pb were not detected in both boreholes and wells water of Abare village while Cd was not detected in borehole water only.

Fe (Fig 4.13) shows the highest concentration of 8.49 ± 2.57 mg/L obtained in pond water, while Zn (Fig. 4.11) showed the lowest concentration of 0.05 ± 0.01 mg/L in borehole water sample. This may be as a result of extra natural filtration procedure that the underground water sources (the wells and boreholes) might have undergoes which the surface water (pounds) lacks. The elevated concentration of zinc in the pond water may be due to indiscriminate washing of the crushed rocks by the local miners around most of the pounds available and the dust fallout on the open ponds from the air carrying dust generated during the crushing procedure (Antwi-Agyei *et al.*, 2009). Heavy metals associated with Gold mining waste might have also dissolve and disperse into surrounding streams as a result of rainwater percolation through the waste or dispersed as particles through erosion processes (Mark *et al*., 2014). The results obtained compared to those obtained by Rasheed and Amuda (2014) who reported a mean concentration of 3.18 ± 2.305, 1.02 ± 0.89 and 0.014 ± 0.004 mg/L for Zn, Cu and Pb in Surface Water of Kutcheri, Zamfara State, Nigeria. Cobbina *et al.* (2013) also reported 0.15 ± 0.026, 6.65 ± 7.841 and 0.005 ± 0 mg/L for Zn, Fe and Cd mg/L in drinking water sources in the Talensi-Nabdam district, Tongo. Much higher values of 29, 23, 314, 165 and 15 mg/L for Zn, Cu, Fe, Pb and Cd were however reported in drinking water contaminated due to illegal gold mining activities in Dareta, Sunke and Bagega of Zamfara State, Nigeria (Mark *et al.*, 2014) large difference observed may be due to the fact that it's extremely difficult for different individuals to name and sample the same location and therefore showed the non-uniform deposition of these metals by human activities and not the natural distribution. Most of the borehole water and a few well water conformed with the maximum permissible limit of 1.5, 0.5, 0.3, 0.01 and 0.01 mg/L for Zn, Cu, Fe, Pb and Cd set by NASREA/WHO (Tobias *et. al.*, 2013). While all ponds and a few well water samples showed concentration above the maximum permissible limits.

The mean concentration of metals in grain samples obtained from Abare during dry season was; 1.58 ± 0.38, 1.98 ± 0.09, 4.56 ± 0.79, 3.00 ± 0.68 and 0.52 ± 0.11 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd respectively, while 1.81 ± 0.74, 1.49 ± 0.079, 2.35 ± 0.84, 3.51 ± 0.97 and 0.15 ± 0.47 mg kg-^{1} was recorded for rainy season samples. Cd recorded the lowest mean concentration of 0.25 ± 0.05 mg kg-^{1} while Fe had the highest concentration of 4.56 ± 0.43 mg kg-^{1}. The values observed did not followed a particular pattern, however this may be due to different factors such as soil pH, soil organic matter, levels of the bio-available fraction of the heavy metals, fertilizer application, the ability of the crop plants to absorb heavy metals etc, which can all affect the levels of heavy metals in the grains (Zhuang *et al.,* 2009 and Kabata-Pendias, 2011). The result obtained from this study is consistent with mean concentration of 0.71, 0.18, 0.15 and 0.16 mg kg-^{1} for Zn, Cu, Pb and Cd in millet samples grown in the city of Kano and its environs (Dahiru *et al*., 2013). 1.97, 3.65, 0.582 and 3.26 mg kg-^{1} for Zn, Cu, Fe and Pb in millet reported by Tudunwada *et al.,* (2007) when they used tannery sludge as soil amendment for cereals on small-holder farms in Kano, Nigeria. Emmanuel *et al*., (2013) also reported 0.29 ± 0.16 and 0.59 ± 0.35 mg kg-^{1} for Zn and Cu in Millet from Minna and Bida.

Figure 4.16 to 4.20 showed the mean concentration of zinc, copper, iron, lead, and cadmium in soil, water and millet from Duza village. The mean concentration of metals in the soil during dry season was; 57.12 ± 11.06, 33.34 ± 10.11, 411.72 ± 438.38, 734.99 ± 838.48 and 2.48 ± 1.43 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd respectively, while 57.22 ± 14.80, 29.75 ± 10.72, 372.97 ± 393.34, 731.29 ± 894.74 and 1.74 ± 1.76 mg kg-^{1} was recorded for rainy season samples. The results of all sampling points in Duza villages showed generally that samples collected from the mining and crushing sites of the village exhibit elevated mean concentration recording a highest value of 1700.59 ± 437.15 mg kg-^{1} for lead (Fig. 4.19), while the lowest concentration was 1.16 ± 0.56 mg kg-^{1} of cadmium (Fig. 4.20) recorded by samples collected from residential areas of Duza village. Most of the results obtained in dry season exhibit elevated concentration than the corresponding rainy season results, this may be due to the fact that these heavy metals might have dissolve and disperse into surrounding streams as a result of rainwater runoff and percolation through contaminated soil (Mark *et al.*, 2014) and the seasonal nature of the mining processes in most of the villages due to the engagement of the local miners in to farming during rainy season (Thomas *et. al.*, 2003), which in turn can reduce the amount of the contaminants released to the environment. Generally there was an increase in the levels of zinc at all sampling points around the mining communities compared to the levels (52.49, 24.73, 118.14, 102.47 and 1.31 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd) obtained from the background soil, this indicate that the activities of the local miners contributes to the increase in the levels of heavy metals at and around the mining areas. Similar values were reported by Antwi-Agyei *et al.,* (2009) who reported the mean concentration of; 168.1 ± 108.7, 71.44 ± 15.8, 38.67 ± 10.76 mg kg-^{1} for Zn, Cu, and Pb around goldmine tailings dams at Obuasi, Ghana. Yao-guo *et al.,* (2010) also reported 118.6 ± 85.26, 54.13 ± 71.18, 216.93 ± 487.83 and 0.55 ± 3.91 mg kg-^{1} as the mean concentration of Zn, Cu, Pb and Cd of polluted soil over Xiaoqinling gold mining region, Shaanxi, China.

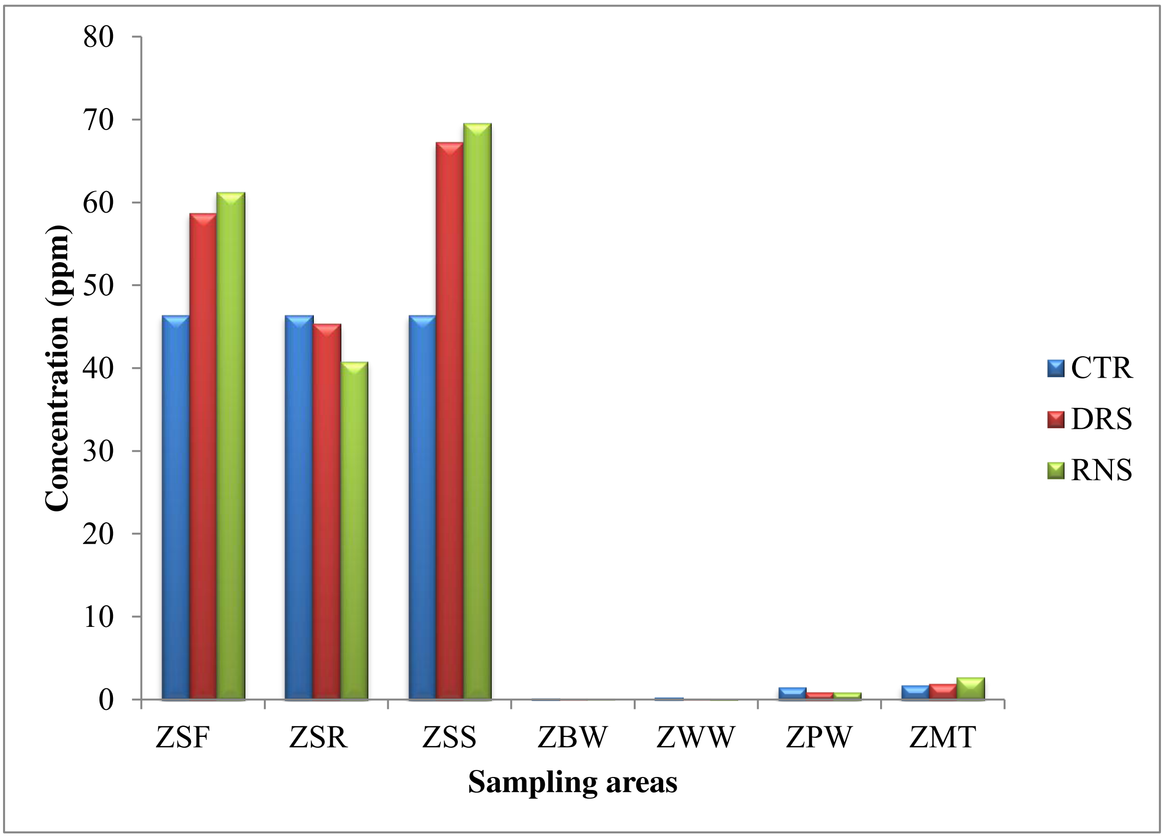


Fig. 4.16: Mean concentration of zinc in soil, water and millet samples analysed from Duza village.

Key

CTR: Control (Background)

DRS: Dry season concentration

RNS: Rainy season concentration

DSF: Duza Farm soil

DSR: Duza Residential soil

DSS: Duza Mining site

DBW: Duza Borehole Water

DWW: Duza Well Water

DPW: Duza Pond Water

DMT: Duza Millet

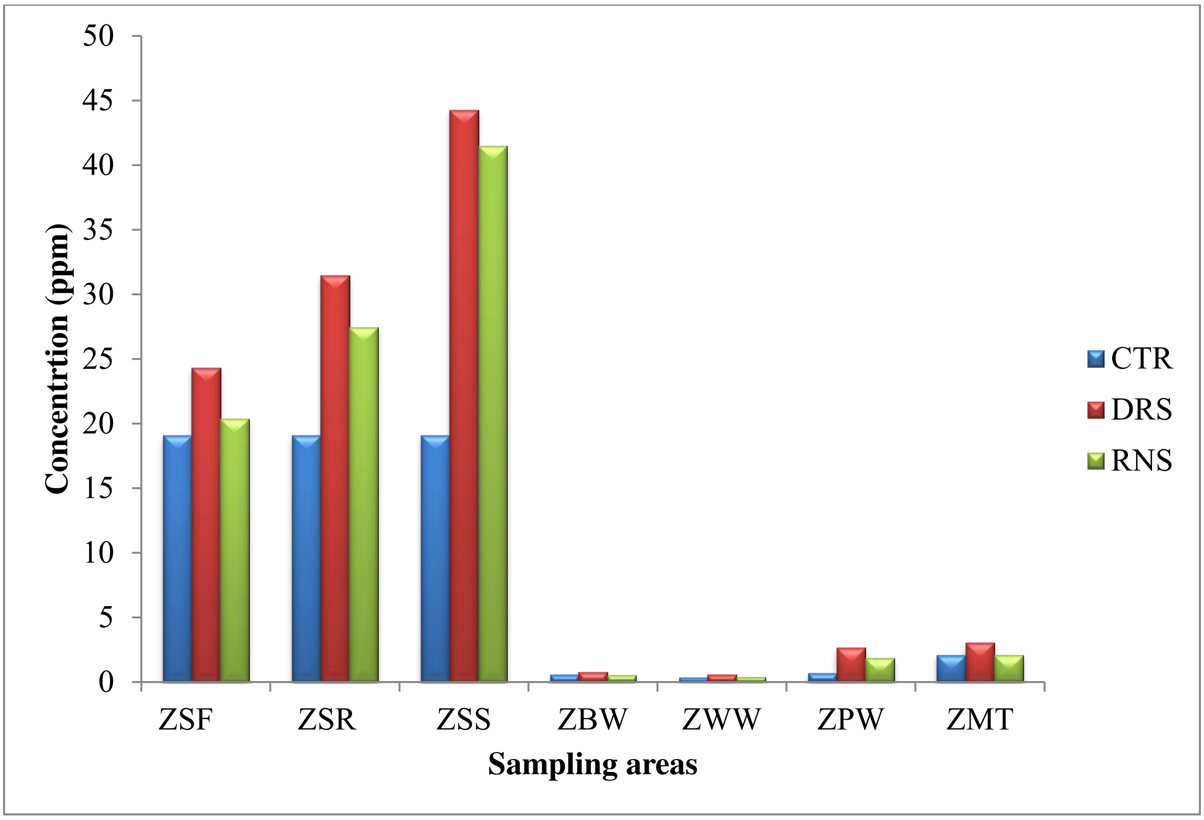


Fig. 4.17: Mean concentration of copper in soil, water and millet samples analysed from Duza village.

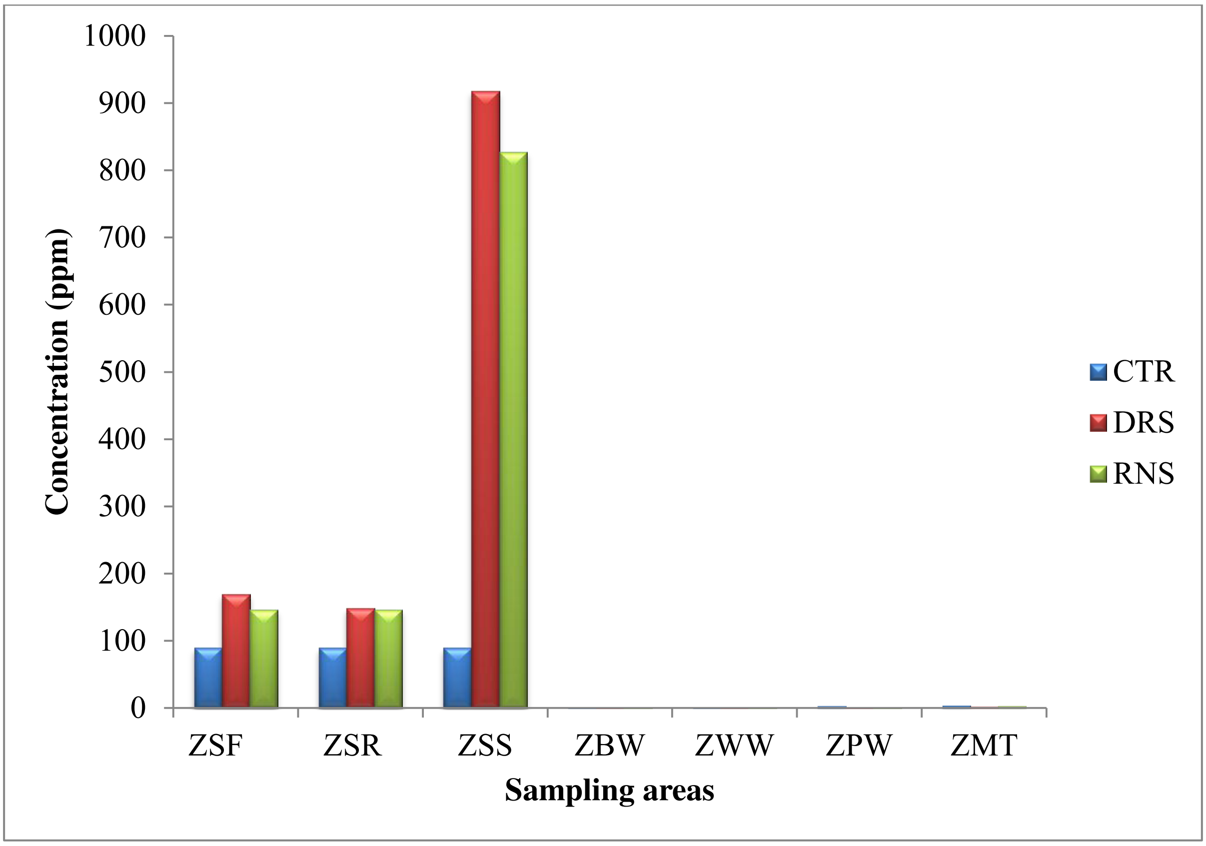


Fig.: 4.18: Mean concentration of iron in soil, water and millet samples analysed from Duza village.

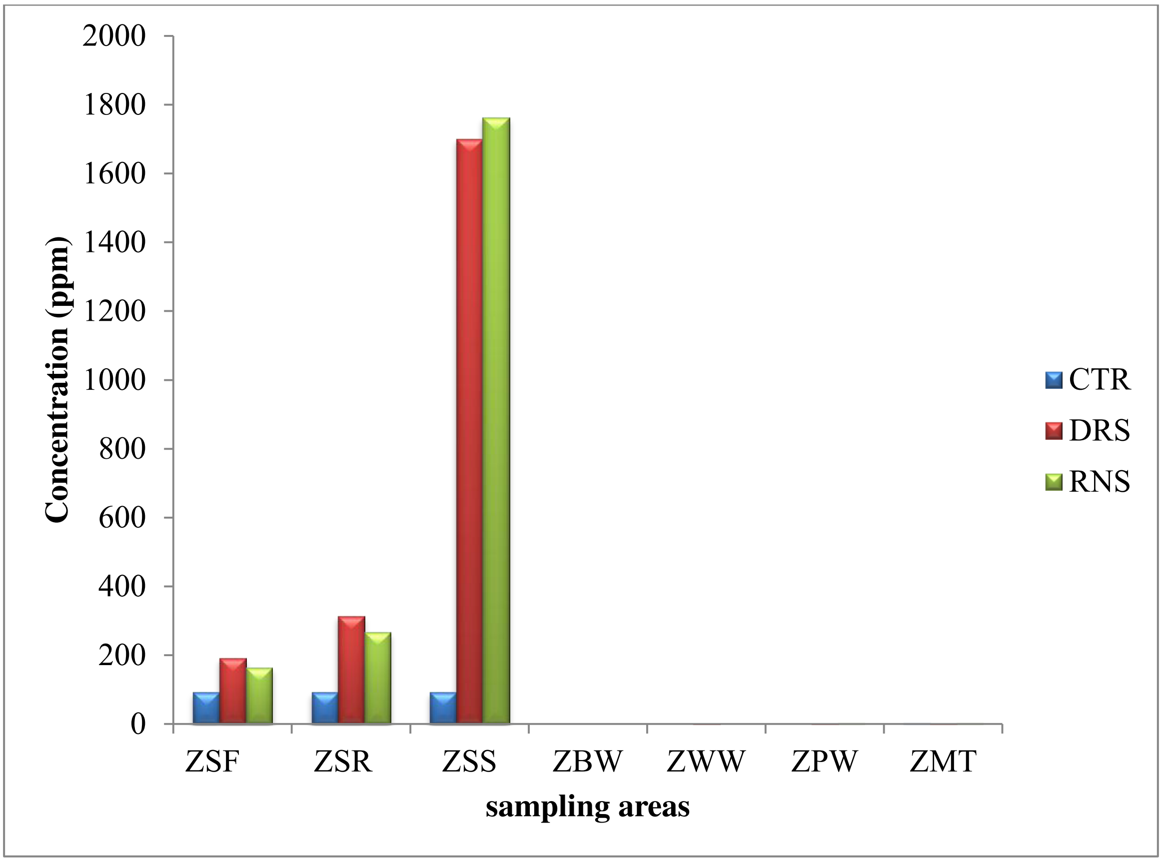


Fig. 4.19: Mean concentration of lead in soil, water and millet samples analysed from Duza village.

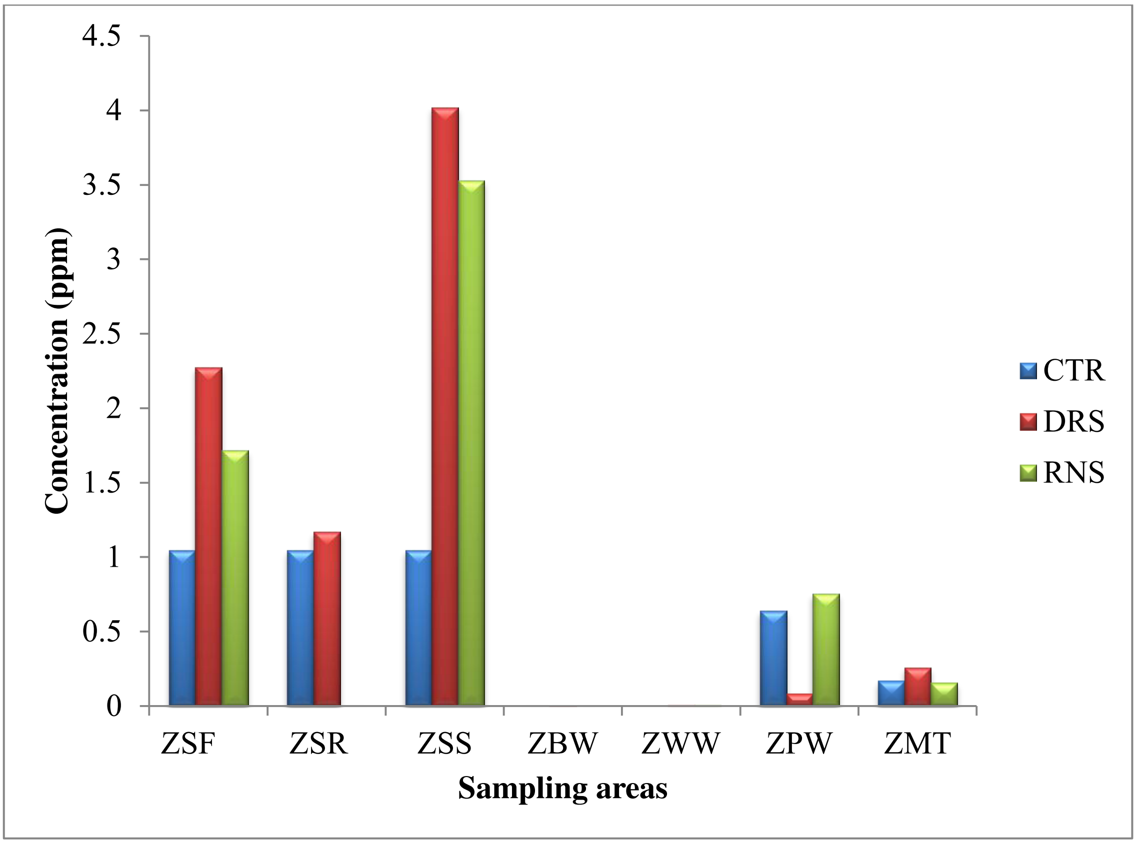


Fig. 4.20: Mean concentration of cadmium in soil, water and millet samples analysed from Duza village.

Tobias *et. al.*, (2013) also reported a mean concentration of 10.92 ± 8.77, 39.0 ± 28.43, 784.09 ± 45.74, 71.00 ± 64.89 and 5.21 ± 1.47 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd in soil of Aba city, Nigeria. Higher average values of 985, 1266 and 17.5 mg kg-^{1} for Zn, Pb and Cd from contaminated farmlands of Abare village, Zamfara State, Nigeria was reported by Abdu and Yusuf (2013) but the higher values may be as the result of the contaminated dust arising from an excavation processes that was going on at the time of their sampling. The values obtained in this research does not exceeds the maximum allowable values of 300 – 600 mg kg-^{1} (NASREA), 200 mg kg-^{1} WHO permissible concentration (Ezigbo, 2011) for zinc, 100 mg kg-^{1} for Cu (Kabata-Pendias, 2011 and Chiroma *et al.,* 2014), 5000 mg kg-^{1} for Fe (Chiroma *et al*., 2014). The mining site and the farm lands of Dareta (Fig. 4.5) showed concentration higher than the 3 – 6 mg kg-^{1} cadmium in soil set by NASREA but below 10 mg kg-^{1} set by WHO (Ezigbo, 2011), while Pb concentration of the mining site (Fig. 4.4) was above the 500 mg kg-^{1} permissible limit set by NASREA (Ezigbo, 2011).

The combine mean concentration of metals in all water sources of Duza village during dry season was; 0.33 ± 0.46, 2.65 ± 0.00, 0.37 ± 0.11, 0.48 ± 0.59 and 0.05 ± 0.03 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd respectively, while 0.32 ± 0.45, 1.84 ± 0.00, 0.30 ± 0.12, 1.74 ± 0.00 and 0.75 ± 0.00 mg kg-^{1} was recorded for rainy season samples, all against a background concentration of 0.64 ± 0.75, 0.69 ± 0.00, 0.90 ± 1.36, ND and 0.63 ± 0.00 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd. The trend showed that samples collected from ponds exhibit elevated concentration while the lowest values were mostly from borehole water. Cu (Fig. 4.17), Pb (Fig 4.19) and Cd (Fig. 4.20) were not detected in most of the boreholes and wells water of Duza village but ponds water had the highest concentration of Cu with a mean value of 2.65 ± 0.21 mg kg-^{1}, while Zn (Fig. 4.16) showed the lowest concentration of 0.07 ± 0.02 mg kg-^{1} in both wells and boreholes water samples. This may be as a result of extra natural filtration procedure that the underground water sources (the wells and boreholes) might have undergoes which the surface water (pounds) lacks. The elevated concentration of zinc in the pond water may be due to indiscriminate washing of the crushed rocks by the local miners around most of the pounds available and the dust fallout on the open ponds from the air carrying dust generated during the crushing procedure (Antwi-Agyei *et al.*, 2009). Heavy metals associated with Gold mining waste might have also dissolve and disperse into surrounding streams as a result of rainwater percolation through the waste or dispersed as particles through erosion processes (Mark *et al.*, 2014). The results obtained compared to those obtained by Rasheed and Amuda (2014) who reported a mean concentration of 3.18 ± 2.305, 1.02 ± 0.89 and 0.014 ± 0.004 mg/L for Zn, Cu and Pb in Surface Water of Kutcheri, Zamfara State, Nigeria. Cobbina *et al.* (2013) also reported 0.15 ± 0.026, 6.65 ± 7.841 and 0.005 ± 0 mg/L for Zn, Fe and Cd mg/L in drinking water sources in the Talensi-Nabdam district, Tongo. Much higher values of 29, 23, 314, 165 and 15 mg/L for Zn, Cu, Fe, Pb and Cd were however reported in drinking water contaminated due to illegal gold mining activities in Dareta, Sunke and Bagega of Zamfara State, Nigeria (Mark *et al.*, 2014) large difference observed may be due to difference of sampling point which therefore shows non-uniform deposition of these metals by human activities and not the natural distribution. Most of the borehole water and a few well water conformed with the maximum permissible limit of 1.5, 0.5, 0.3, 0.01 and 0.01 mg/L for Zn, Cu, Fe, Pb and Cd set by NASREA/WHO (Tobias, 2013). While all ponds and a few well water samples showed concentration above the maximum permissible limits.

The mean concentration of metals in grain samples obtained from Duza during dry season was; 1.01 ± 0.28, 2.54 ± 0.46, 1.42 ± 0.41, 1.56 ± 0.21 and 0.25 ± 0.05 mg kg-^{1} for Zn, Cu, Fe, Pb and Cd respectively, while 1.30 ± 0.61, 2.06 ± 0.68, 2.27 ± 0.58, 1.84 ± 0.09 and 0.15

± 0.01 mg kg-^{1} was recorded for rainy season samples. Cd recorded the lowest mean concentration of 0.52 ± 0.07 mg kg-^{1} while Fe had the highest concentration of 2.27 ± 0.61 mg kg-^{1}. The values observed did not followed a particular pattern, however this may be due to different factors such as soil pH, soil organic matter, levels of the bio-available fraction of the heavy metals, fertilizer application, the ability of the crop plants to absorb heavy metals etc, which can all affect the levels of heavy metals in the grains (Zhuang *et al.,* 2009 and Kabata-Pendias, 2011). The results obtained from this study is consistent with mean concentration of 0.71, 0.18, 0.15 and 0.16 mg kg-^{1} for Zn, Cu, Pb and Cd in millet samples grown in the city of Kano and its environs (Dahiru *et al*., 2013). 1.97, 3.65, 0.582 and 3.26 mg kg-^{1} for Zn, Cu, Fe and Pb in millet reported by Tudunwada *et al.,* (2007) when they used tannery sludge as soil amendment for cereals on small-holder farms in Kano, Nigeria. Emmanuel *et al*., (2013) also reported 0.29 ± 0.16 and 0.59 ± 0.35 mg kg-^{1} for Zn and Cu in Millet from Minna and Bida.

CHAPTER FIVE

5.0 Summary, Conclusion and Recommendations

5.1 Summary

The pH and the heavy metals concentration of the soil, water and grains samples were analysed. The pH of the soil samples ranged from slightly acidic to slightly basic, while the heavy metals concentration of water and soil of the sampled villages showed elevated concentration in and around areas where ore processing activities are carried out compared to those areas that are not exposed to the mining activities, while the concentration of the heavy metals in the grain samples did not follow a particular pattern. The heavy metals concentration in the soil samples was found to be in this order Cd < Cu < Zn < Fe < Pb while it follows this order Pb < Cu < Cd < Fe < Zn in the water samples.

5.2 Conclusion

Soil samples collected from the four villages in Anka local government of Zamfara state were found to have an elevated concentration of heavy metals compared to the background concentration obtained in samples collected at a distance of about two kilometers from the last residential and ore processing areas. The concentrations of heavy metals in soil varied significantly within villages, suggesting human factor in the dispersion of these heavy metals as suggested by UNEP (2010). Water in ponds was often highly contaminated. However, no boreholes were found to have been contaminated, indicating that heavy metals contamination most likely has not spread throughout the groundwater aquifer. The heavy metals found in wells and ponds was likely to have come from external sources (processing) rather than naturally occurring (UNEP, 2010). The grain samples showed heavy metals levels similar to those reported in the literature, though the concentration did not follow a particular pattern as so many factors can affect the levels of heavy metals in the grains samples such as pH, dissolved organic matter, and the ability of the crop plant to absorbed heavy metals (Kabata-Pendias, 2011). Most of the rainy season results are comparatively lower than the corresponding dry season concentration.

5.3 Recommendation

- Efforts should be made by concern authorities to ensure that mining and processing activities are restricted to specific areas that are far from either farms or residential areas.
- Efforts should also be made for the provision of proffer ways of handling and disposal of waste generated during the mining processes and also to avoid dumping same in water ways.
- The local authorities should be empowered to imposed this recommendation.
- Further study should be made to evaluate the ecological risk associated with levels of these heavy metals in soil, plants and all consumable goods of the affected area.

REFERENCES

Abdu N, Abdulkadir A, Agbenin J. O, and Buerkert A (2011). Vertical distr-ibution of heavy metals in waste water irrigated-vegetable garden soils of three West African cities. *Nutr. Cycl. Agroecosyst*. 89:387-397.

Abdu, N. and Yusuf, A.A (2013). Human Health Risk Characterization of Lead Pollution in Contaminated Farmlands of Abare Village, Zamfara State, Nigeria. *African journal of Environmental Science and Technology*. Vol.7(9), pp. 911-916.

Adriano, D.C., Chlopecka, A., Kaplan, D.I., Clijsters, H., and Vangronsveld, J. (1995). Soil Contamination and Remediation: Philosophy, Science and Technology. Third International Conference on the Biogeochemistry of Trace Elements, Paris, 15-19 May, 1995. (INRA editions, Paris, France), pp 317-322

Ajigo, I.O., K.D. Tsuwang, and U.A. Lar. (2014). Assessment of Lead, Mercury and Arsenic in Soils of Anka Area, North western Nigeria. *International Journal of Science, Environment and Technology,* Vol. 3, No 1, 2014, 187 – 197

Akagha, I. C., (2010). Analyses of Some Selected Heavy Metals And Contaminants in Underground Water And Three Satellite River Stations in Owerri Local Government Area of Imo State. A thesis submitted to the department of pure and industrial chemistry, faculty of natural sciences Nnamdi Azikiwe University Awka, pp 49-50

Akagi, H., Malm, O. and Kinjo, Y. (1995). Methyl mercury Pollution in Amazon Brazil. *Science Total Environ* 175: 85-95.

Ali, A., Parisa, Z. and Roohollah, S. (2013).*Mercury and Lead Contamination Study of Drinking Water in Ahvaz,Iran*. International Journal of Farming and Allied Sciences Available online at www.ijfas.com. Retrieved on 17 Dec. 2015.

Allan, H. S., Elena, O. L. and Mahfuzar, R. (2000). *Contamination of Drinking Water by Arsenic in Bangladesh*, Bulletin of World Health Organization, 2000, 78(9). pp 3.

Alloway, B. J. (1997). Chemical Principal of Environmental Pollution, 2nd edn, Blackie Academic and Professional, Chapman Hall, London 190-216.

Alloway, B.J. (1995). *The Mobilisation of Trace Elements in Soils, in: Prost R., ed. Contaminated Soils*: Third International Conference on the Biogeochemistry of Trace Elements, Paris, 15 -19 May 1995. (INRA editions, Paris, France). 283-384.

Antwi-Agyei, P., Hogarh J. N. and Foli G. (2009). Trace Elements Contamination Of Soils Around Gold Mine Tailings Dams At Obuasi, Ghana. *African Journal of Environmental Science and Technology* Vol. 3(11), pp. 353-359

ATSDR, (2002). Toxicological Profile for copper (Draft for public comment Atlanta, GA, U.S. Department of Health and Human Service, Agency for Toxic Substance and Human Services, Public Health Service, Agency for Toxic Substance and Disease Registry (subcontract No. ATSDR-2051999-00024), (accessed 18.11.13.).

ATSDR, (2005). *Toxicological Profile for Arsenic*. U.S. Agency for Toxic Substances and Diseases Registry http://www.atsdr.cdc.gov/toxprofiles/tp2.pdf. (accessed 18.11.13.).

ATSDR, (2011).*The Priority List of Hazardous Substances, 2011*. Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Public Health Services, Atlanta, GA (accessed 18.11.13.).

ATSDR, (2012).*ToxicologicalProfile for Cadmium*.Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Public Health Services, Atlanta, GA. (accessed 18.11.13.).

ATSDR.(2007).*Toxicological profile for lead*. Agency for Toxic Substances and Disease Registry, Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. Accessed at: http://www.atsdr.cdc.gov/toxprofiles/tp13.html. (accessed 18.11.13.).

Awofolu, O. R. (2005). A Survey of Trace Metals in Vegetation, Soil and Lower Animals Along Some Selected Major Roads, Metropolitan city of Lagos, *Environmental Monitoring Assessment*. 105: 441.

Ayodele, J.T and Gaya U.M. (1998). Chromium, Manganese and Zinc in Kano Municipality street Dust, Nigeria *J. Chem.Soc* (23):24-34.

Bache, B.W. (1979). *The Encyclopaedia of Science*3rd Edition, Fairbridge, R.W and Finkl, C.W. Dowden, Hutchinson and Ross, Stroudsburg.pp 487 – 490.

Bakau F. (1993). Pollution Prevention and Abatement Guideline for the Mining Industry Jointly Sponsored by World Bank.UNIDO and UNEP.

Bremner. J. N. (1973). Inorganic Forms of Nitrogen, Method of Soil analysis. 3rd edn, Am. Soc. Inc. Madison Wisconsin. USA. 126-130.

Cao,Y.,Chen,A.,Radcliffe,J.,Dietrich,K.N.,Jones,R.L.,Caldwell,K., and Rogan,W.J., (2009). Postnatal Cadmium Exposure, Neuro-Development, And Blood Pressure In Children At 2, 5, And 7 Years Of Age. *Environmental Health Perspective*.117,1580–1586.

CDC (2005). Third National Report on Human Exposure to Environmental Chemicals, U.S Department of Healthand Human Services, Public Health Services.Center for Disease Control and Prevention (CDC). Availableat: http://www.cdc.gov/exposurereport/ (Asseced on 13.09.2014).

CDC (2010). Outbreak of acute lead poisoning among children aged < 5 years - Zamfara, Nigeria.Available:http://www.cdc.gov/mmwr/preview/mmwrhtml/mm5927a3.htm?s_cid=mm5927a3_w [accessed 22 August 2012].

Chiroma T. M , Ebewele R. And Hymore F.K (*2014*).*Comparative Assessement of Heavy Metal Levels in Soil, Vegetables and Urban Grey Waste Water Used for Irrigation in Yola and Kano* International Refereed Journal of Engineering and Science (IRJES) *Volume 3, Issue 2, PP.01-09*

Cobbina, S. J., Myilla, M, and Michael, K. (2013). Small Scale Gold Mining and Heavy Metal Pollution: Assessment of Drinking Water Sources in Datuku in The Talensi Nabdam District. *International journal of scientific & technology research* volume 2, issue 1

Comings, J. N. (1986)."The Science of Medicine" Annual Review, 23 (45):54.

Dagari, M. S., (2012): Effects of Organic Amendments on Lead Uptake by Cowpea. An unpublished Phd. Thesis submitted to the department of Pure and Industrial Chemistry Bayero University Kano. 60-73

Dahiru M. F., U. A. Birnin Yauri, and Sani M. D., (2013). Cadmium, Copper, Lead and Zinc levels in sorghum and millet grown in the city of Kano and its environs. *Global Advanced Research Journal of Environmental Science and Toxicology*, Vol. 2(3) pp. 082-085.

Dara, S. S. (2006). Environmental Chemistry and Control. S. Chand Publisher and Company Ltd. Ram Nagar, New Delhi pp. 177-216.

De Haan, F.A.M. (1996). Soil Quality Evaluation. In: Soil pollution and soil protection. Ed. F.A.M. de Haan, M.I. Visser-Reyneveld. Wageningen Agricultural University and International Training Centre (PHLO). Wageningen. pp. 1 -17.

Dooyema C.A., Neri A,, Lo Y.C., Durant J, Dargan P.I., and Swarthout T. (2012). Outbreak Of Fatal Childhood Lead Poisoning Related To Artisanal Gold Mining In Northwestern Nigeria. *Environmental Health Perspective* 120: 601–607.

Earnest, W.I, (2010). Analytical Study of soil in Mambila plateau An MSc dissertation. Department of Chemistry, Federal university of Technology, Yola.Pp 26-31.

EC, (2007). Mercury, Lead, Cadmium, Tin and Arsenic in Food: European Commission Factsheet on Food Contaminants (2007):

Edward K.P.B., Thomas T.A, Shiloh D. O., Samuel Y. G., and AbassG. (2011). *Multivariate cluster analysis of some major and trace elements distribution in an unsaturated zone profile, Densu river basin, Ghana*". African Journal of Environmental Science and Technology Vol. 5(3), pp. 155-167.

EFSA. (2009). Cadmium in Food. Scientific Opinion of the Panel on Contaminants in the Food Chain. TheEFSA Journal, 980: 1–139.

Elele and Adamu S., (2014). Heavy Metal Contaminations of Drinking Water Sources due toIllegal Gold Mining Activities in Zamfara State – Nigeria", *Journal of Chemistry and Biochemistry,* Vol. 2, No. 1, pp. 31-44

Emmanuel M., Adegboyega O., and Bankole M. T. (2013). Comparative Study of Mineral Elements Distribution in Sorghum and Millet from Minna and Bida, North Central Nigeria. *International Journal of Food Nutrition and Safety.*

Erfurth, E. M., Gerhardsson, L., Nilsson, A., Rylander, L., Schutz, A., Skerfving, S.and Borjesson, J. (2001). *Arch. Environ. Health,* 56, 449.

Ewers, U. and Schlipkoter, H. W. (1991).*Chronic Toxicity Of Metal Compounds*: Merian, E (ed). Metals and their compounds in the environment VCH. Verlag Segsellschaft Mbh, Weinhein New York: 591-603.

Ezigbo V.O., (2011). *Determination of the Trace Metal Concentration in the Soil of Nnewi North Local Government Area*. Journal of vasic physical research:vol 2,no. 1 pp.82-85

Fatima, B. S. (2015): Physicochemical Analysis of Water and Sediment from Some Dams in Katsina State. An unpublished Phd. Thesis submitted to the department of Pure and Industrial Chemistry Bayero University Kano.

Fosmire, G. J. (1990). Zinc Toxicity. *American Journal of Clinical Nutrition.*

Gadde, R .R., Laitinen H.A. (1974). Studies of .Heavy Metals adsorption by Hydrousion and Manganese oxide. Analytical Chem. 46: 2022-2026.

Ganeshamurthy, A. N., Varalakshmi, L. R. and Sumangala, H. P. (2008). Environmental Risks Associated with Heavy Metals Contamination in Soil, Water and Plants in Urban and Periurban Agriculture, *Journal of Horticultural Science.* Vol. 3(1) 1-29.

Garcia, R., Torres, M.C., and Baez, A. (2008). Determination of trace elements in total suspended particles at the south west of Mexico City from 2003-2004 Rev. *Chemistry and Ecology,* 24(2): 157-167

Gauch, G.H. (1974). Inorganic Plant Nutrtion. 4th edn. Dawden Huchiason and Sons. Inc. Strousboug, France, 15-18.

Gosselin, R. E., R.P Smith., H. C. (1984). Clinical Toxicology of Commercial Products 5th edn, Baltimore Williams and Wikins, Washington D.C. 289.

Harris, R.F.D., Karlen, D.L. and Mulla, D.J. (1996). *A Conceptual Framework For Assessment And Management Of Soil Quality And Health, Methods For Assessing Soil Quality*. Ed. Doran J.W., A.J. Jones, Soil Science Society of America, Special Publication, 49: 61-82.

Hassan S. A., Dogara B. and Cordelia N. O. (2011). Impacts Of Local Gold Mining On Drinking Water Quality In Zamfara State, Nigeria, Paper presented at the 2nd

National Water and Sanitation Conference held at the Conference Centre, National Water Resources Institute, Kaduna, Nigeria on 23 - 25 March, 2011.

Huang, C. and Hu, B., (2008). Silica-coated magnetic nanoparticles modified with c-mercapto propyl trimethoxy silane for fast and selective solid phase extraction of trace amounts of Cd, Cu, Hg, and Pb in environmental and biological samples prior to their determination by inductively coupled plasma mass spectrometry Spectrochim. Acta Part B 63, 437–444.

IARC. (1993). Beryllium, cadmium, mercury, and exposures in the glass manufacturing industry. Working Group views and expert opinions, Lyon, 9–16 February 1993.IARC MonogrEvalCarcinog Risks Hum, 58: 1–415. PMID:8022054.

Indu, V. N.; Kailash, S.; Arumugam, M.; Gangadhar, K.; and Clarson, D. (2010). Trace Metal Quality of Meenachil River at Kottayam Kerela (India) by Principal Component Analysis, World Applied Sciences Journal 9(10): 1100-1107.

Irén L. (2004), Sorghum and Millets, in Cultivated Plants, Primarily as Food Sources, [Ed. György Füleky], in Encyclopedia of Life Support Systems (EOLSS), Developed under the Auspices of the UNESCO, Eolss Publishers, Oxford ,UK, [http://www.eolss.net] accessed on 20.12.2015

Jeffrey, G. H. (1989). Vogel's Textbook of Quantitative Chemical Analysis, 5th edn, London, UK 477-48.

Kabata-Pendias A., (2011) Trace Elementsin Soil and Plants, fourth ed. CRC Press, Taylor and Francis Group, LLC pp.24

Kabiru I.G, Idris S.H, Kabir S, Patrick M.N, Gabriele P, Hafiz M.A, Habib Y, Nasir S and Akin O. (2013). Prevalence and Determinants of Childhood Lead Poisoning in Zamfara State, Nigeria. *Journal of Health and Pollution* 2-8.

Karez, R. S., Engelbert and U. Sommer. (1983). Effects of epiphytic load on optical properties and photosynthetic potential of the sea grasses- Thalasia Testudinum Marina, Eondon 48(l):85-93.

Keddy, P. A. (2007) Plants and Vegetation. Cambridge: Cambridge University Press. ISBN 978-0-521-86480-0.

Lambers, H., Chapin, F.S., Pons, T.L., (1998); Plant Physiological Ecology. Springer-Verlag, Med 1994;14:423-444.

Lar U., Tsuwang K., Gusikit R. and Mangs A. (2013) Lead and Mercury Contamination Associated with Artisanal Gold Mining in Anka, Zamfara State, North Western Nigeria: The Continued Unabated Zamfara Lead Poisoning *Journal of Earth Science and Engineering* 3 (2013) 764-775.

Majid S. Ghaderian , Ali A. Ghotbi R. (2012): Accumulation of copper and other heavy metals by plants growing on Sarcheshmeh copper mining area, Iran. *Journal of Geochemical research.* pp 2-6

Mark O A O, Raymond L N, Ugoeze U E & Adamu S. (2014): Heavy Metal Contaminations of Drinking Water Sources due to Illegal Gold Mining Activities in Zamfara State Nigeria. *Journal of Chemistry and Biochemistry*

Mohammad M.A.K, Rashid U and Habibah L. (2010). Study of Trace Element in Ground Water of Western Uttar Pradesh, India. *Scientific research and essays* vol. 5(20): 3175-3182.

Mohammad, I. M. (2005).Chemical Analysis for Assessing Potential Productivity of Soils from five Irrigation Areas of Kano State. An unpublished Ph.D. thesis submitted to the Department of Chemistry B.U.K 32-34,47-50.

Monika Z. and Marija R. (2011). Soil Contamination by Trace Metals: Geochemical Behaviour as anElement of Risk Assessment, Earth and Environmental Sciences, Dr. Imran Ahmad Dar (Ed.), ISBN: 978-953-307-468-9, Available from: http://www.intechopen.com/books/earth-and-environmental-sciences/soilcontamination-by-trace-metals-geochemical-behaviour-as-an-element-of-risk-assessment. Accessed on 25.06.2015

Moolenaar, S.W., Lexmond, T.M. (1999). General aspects of Cadmium, Copper, Zinc, and lead balance of agro-ecosystems, Journal of Industrial Ecology, 2 (4): 45-60.

Moravic J.E; Malik, U; Marihlad, K and Papayara, A. (1986). Effects of Fumes from Welding Industry. *Journal of Env. Pollution*. 27:77-83.

Morikawh, Y.; Nakaqama, H.; Tabata, M.; Senma, M.; Kitaqawa, Y.; Kawano, S.; Teranishi, H and Kido, T (1992): Study of an outbreak of itai-itai disease. Department of Public Health, Kanazawa Medical University, Ishikava Nihon EiseqakuZasshi 46(6) 1057-62.

Moruffdeen A.A., and Michael A.O. (2014): Geoenvironmental Assessment of Abandoned Mines and Quarries in South-western Nigeria. *Journal of Geochemical Exploration* 145 (2014) 148–168.

Naeem, K.; Yawar, W.; Akhter, P.; and Rehana, K. (2012). Atomic absorption spectrometric determination of cadmium and lead in soil after total digestion," Asia-Pacifc *Journal of Chemical Engineering,* vol. 7, pp. 295–301,

Nyle, C.B and Ray, R.W (1999): The Nature and Properties of Soil. Prentice Hall, Inc. USA pp 4-70.

Oparaocha, E. T.; Iroegbu, O. C.;and Obi, R. K. (2010): Assessment Of The Quality Of Drinking Water Sources, *Journal of Applied Biosciences* 32: 1964-1976.

O'Shea, L. (2002). An Economic Approach To Reducing Water Pollution: Point And Diffuse Sources, *Science of the Total Environment*, 282:49-63.

Palumbo, B., Angelone, M. and Bellanca, A. (2000). *Influence of inheritance and pedogenesis on heavy metal distribution in soils of Sicily, Italy*, Geoderma, 95 (3–4), 247–266.

Philip M. (1996); *Advanced Chemistry*, Low Price Edition, Cambridge University Press, Cambridge, United Kingdom. P. 558.

Polissar L. (1990). Pathways Of Human Exposure To Arsenic In A Community Surrounding A Copper Smelter.*Environmental. Res*. 53(1):29-47.

Radojevic M. and Bashkin V. N. (1999): Practical Environmental Analysis. The Royal Society of Chemistry, Cambridge United Kindom: 365-366.

Rasheed A. I. and Amuda A. K., (2014). Impacts of Artisanal Mining on Some Heavy Metals Concentration in Surface Water inKutcheri, Zamfara State North-Western Nigeria *Academic Journal of Interdisciplinary Studies*. Vol 3, no. 7p74

Raven, P.H and Johson G.B. (1986). Biology of Times, 4then. Mirrow College Publishing.St. Louis Toronto. *Santa Clara* 156-157."

Robinson R.A., and Stokes, R.H (1968). Electrolytic solutions, the measurement and interpretation of conductance, chemical potential and diffusion in solutions of simple electrolyte" 2nd rev. Ed, London

Romić. M and Romić D. (2003). Heavy Metals Distribution In Agricultural Top Soils In Urban Area. *Environmental Geology*, 43(7), 795-805.

Rousseau MC, Straif K, Siemiatycki J. (2005). IARC carcinogen update. *Environ Health Perspective*. p 4

Sahu S.K. Pradan K.C and Sarangi (2004). Soil pollution in Orissa.Pp 13-15. Department of Soil Science and Agriculture, Bhubaneswar India.

Salonen, V. and Korkka-Niemi, K. (2007); Influence of parent sediments on the concentration of heavy metals in urban and suburban soils in Turku, Finland, Applied Geochemistry, 22, 906–918.

Salt, D, Prince, R, Baker, A, Raskin, I, & Pickering, I. (1999). Zinc ligands in the metal

Selvapathy, P. and Sreedhar P. (1991): Heavy Metal Removal by Water Hyacinth. *Journal 0f Industrial Public Health* Engg., 3, 11-17.

Sezgin, B.; Tolga, Y.; Nihan, T.; Mehmet, D.; Kemal F. A.; Onur, M. and Abdullah, K., (2013). Determination of As, Cd, and Pb in Tap Water and Bottled Water Samples by Using Optimized GFAAS System with Pd-Mg and Ni as Matrix Modifiers.Journal of Spectroscopy. pp 2-3

Steven G. *(2008):* Suggested Practices to Reduce Zinc Concentrations in Industrial Stormwater Discharges. Washington State Department of Ecology, Environmental Assessment Program for Water Quality Program. pp 4-7

Stone L. (2000). The social Effects of Mining and the C.M.C. Mine Problem. pp 212.

Tekwa, I., Shehu, H., and Maunde, S., (2011). Soil nutrient status and productivity potentials of lithosols in Mubi Area, North Eastern Nigeria, *Agriculture and Biology journal of North America*. 24: 211-119.

Thomas H., Felix H., and Michael P. (2003). Artisanal & Small-Scale Mining, Challenges and Opportunities. Mining Miner\als and Sustainable Development Projekt-Consult GmbH January 2003. No. 70 available at;*http://pubs.iied.org/pdfs/9268IIED.pdf*

Tobias I., Ndubuisi E., EzejioforA. N., Udebuani1A. C., E. U. Ezeji1, E. A. Ayalogbu1, C. O. Azuwuike, L. A. Adjero, C. E. Ihejirika, C. O. Ujowundu, L. A. Nwaogu and K. O. Ngwogu. (2013). *Environmental Metals Pollutants Load of a Densely Populated and Heavily Industrialized Commercial City ofAba, Nigeria* Journal of Toxicology and Environmental Health Sciences Vol. 5(1) pp. 1-11.

Tsuwang K.D., Ajigo I.O. and Lar U.A. (2014). Assessment of Lead, Mercury and Arsenic in Soils of Anka area, north western Nigeria *International Journal of Science, Environment and Technology*, Vol. 3, No 1, 2014, 187 – 197

Tudunwada I. Y.1, E. U. Essiet, and S. G. Mohammed. (2007). *Effects of Tannery Sludge on Heavy Metals Concentration in Cereals on Small-holder Farms in Kano, Nigeria* Volume 35, Issue 2.

U.S. EPA, (2000)."*Arsenic Occurrence in Public Drinking Water Supplies.*" U.S. Environmental Protection Agency. http://www.epa.gov/OGWDW/arsenic/pdfs/occurrence.pdf EPA-815-R-00-023.

U.S. EPA.(2003). Superfund Lead-Contaminated Residential Sites Handbook. Available: http://www.epa.gov/superfund/lead/products/handbook.pdf [accessed 26 June 2012].

Uduma A. U., and Jimoh W. L. O. (2014). Assessment of Pb Enrichment and Depletion in Selected Contaminated Arable Soils of Nigeria Using Calcium as a Reference Element,

UNEP (2008).Interim Review of Scientific Information on Cadmium. Geneva: United Nations Environment Program.

UNEP, (2010).Lead Pollution and Poisoning Crisis Environmental Emergency Response Mission Zamfara State, Nigeria.September/October 2010.*Published in Switzerland, by the Joint UNEP/OCHA Environment Unit*

United Nations Economic and Social Council.Developments in Small-Scale Mining. Report of theSecretary General. April 1st, 1996. Available atwww.un.org/documents/ecosoc/c7/1996/ec71996-9.htm International Institute for Environment and Development (IIED).

USEPA (1994).*Design And Evaluation Of Tailings Dams*.Technical Report – EPA530-R-94-038. USEPA, Office of Solid Waste, Special Waste Branch, Washington, DC.

USGS, (2008).Mineral Commodity Summaries, Cadmium.pp.42−43.

Water facts, (2010). Retrieved from http//water.org/learn-about-the-water-crisis/facts/

Weber R, Hrynczuk B (2000). Effect of leaf and soil contaminations of heavy metals content in spring wheat crops. Nukleonika, 2, 137 –140.

WHO (2008).Guidelines for drinking water quality. World Health Organization, Geneva.

Wild, A. (1988), "*Russell's Soil Conditions and Plant Growth*" 11thedition, Longman London.pp212.

Willard L. (2005).An Introduction To Geology And Hard Rock Mining Rocky Mountain Mineral Law Foundation. Science and Technology Series.

World Journal of Agricultural Research. (2014). Vol. 2, No. 1, 5-11 Available online at http://pubs.sciepub.com/wjar/2/1/2.

Yao-guo, W., You-ning, X., Zhang, J., HU. S. (2010). Evaluation of ecological risk and primary empirical research on heavy metals in polluted soil over Xiaoqinling gold mining region, Shaanxi, China. Trans. Nonferrous Met. Soc. China 20. 688−694.

Yi-Chun, L.; Carrie, A. D.; Antonio, N.; James D.; Taran J.; Andrew M.; Lori de, R.; Douglas, T.; Lora, D.; Raymond, S. D.; Matthias, Y. S.; Luka, M. I.; Ossai, O.; Nasir, T. U.; Alhassan, H. D. and Mary, J. B. (2012). Childhood Lead Poisoning Associated with Gold Ore Processing: a Village-Level Investigation—Zamfara State, Nigeria. Environmental Health Perspectives, volume 120 | number 10

Yusuf, A.A., Abdu N, Tanimu B (2011). *Assessment Of Lead Contamination Of Farmlands In Abare Village*, Zamfara State. In: Hassan WA et al. (Eds). Mobilizing Agricultural Research Towards Attaining Food Security and Industrial Growth in Nigeria. Proceedings of the 45th Annual Conference of the Agricultural Society of Nigeria. pp. 487-491.

Zeng-Yei, H. (2004). Evaluating heavy metal contents in nine composts using four digestion methods. Journal of Bioresource Technology 95. 53–59

Zhuang, P., Shu W. , Li Z., Liao B., Li J. and Shao J. (2009).*Removal of Metals by Sorghum Plants from Contaminated Land. Journal of Environmental Sciences* 21. 1432–1437

APPENDICES

Appendix I: Mean heavy metals concentration (mg kg^{-1}) in grain samples analysed

S/TYP	CTR	DRS	RNS
DMT	1.738	1.894	2.664
BMT	1.638	1.971	1.180
AMT	2.014	1.587	1.810
ZMT	1.451	1.014	1.307
MEAN	1.710	1.616	1.740
STD	**0.234**	**0.434**	**0.673**

S/TYP			
DMT	0.240	1.915	1.042
BMT	2.012	3.212	1.36
AMT	2.428	3.003	3.516
ZMT	1.910	1.563	1.843
MEAN	1.647	2.423	1.940
STD	**0.964**	**0.807**	**1.100**

S/TYP			
DMT	0.11	0.473	0.86
BMT	ND	0.331	0.174
AMT	0.11	0.52	0.153
ZMT	0.17	0.258	0.156
MEAN	0.097	0.395	0.335
STD	**0.070**	**0.121**	**0.349**

S/TYP			
DMT	2.075	3.034	2.064
BMT	1.264	2.41	2.637
AMT	1.057	1.98	1.498
ZMT	2.892	2.543	2.06
MEAN	1.822	2.491	2.064
STD	**0.837**	**0.434**	**0.465**

S/TYP	CTR	DRS	RNS
DMT	1.01	0.978	1.856
BMT	2.478	3.087	3.512
AMT	1.837	4.562	2.357
ZMT	3.451	1.421	2.271
MEAN	2.194	2.512	2.499
STD	**1.031**	**1.640**	**0.709**

Appendix II: Mean heavy metals concentration (mg kg^{-1}) in soil samples analysed

Cu	CTR	DRS	RNS		CTR	DRS	RNS		CTR	DRS	RNS
ZSS	19.074	44.260	41.451	ZFS	19.074	24.300	20.374	ZRS	19.074	31.460	27.426
ASS	21.816	38.017	25.197	AFS	21.816	31.786	20.463	ARS	21.816	41.667	28.437
BSS	24.731	62.436	73.392	BFS	24.731	30.709	57.666	BRS	24.731	38.075	46.049
DSS	39.482	115.071	76.563	DFS	39.482	65.923	50.367	DRS	39.482	20.973	58.685
MEAN	26.275	64.946	54.151	MEAN	26.275	38.179	37.217	MEAN	26.275	33.043	40.149
STD	**9.102**	**34.985**	**24.981**	STD	**9.102**	**18.788**	**19.625**	STD	**9.102**	**9.090**	**15.027**

Fe	CTR	DRS	RNS		CTR	DRS	RNS		CTR	DRS	RNS
DSS	107.426	900.565	721.859	DFS	107.426	484.490	600.333	DRS	107.426	853.600	536.167
ASS	134.750	870.097	778.801	AFS	134.750	648.067	699.047	ARS	134.750	363.330	708.053
BSS	118.145	857.382	572.439	BFS	118.145	233.550	139.145	BRS	118.145	224.250	150.462
ZSS	89.376	917.790	827.164	ZFS	89.376	169.270	145.813	ZRS	89.376	148.129	145.941
MEAN	112.424	886.458	725.065	MEAN	112.424	383.844	396.084	MEAN	112.424	397.327	385.155
STD	**19.038**	**27.651**	**110.478**	STD	**19.038**	**222.541**	**295.611**	STD	**19.038**	**316.963**	**282.472**

Pb	CTR	DRS	RNS		CTR	DRS	RNS		CTR	DRS	RNS
DSS	71.439	1321.517	862.431	DFS	71.439	452.142	257.667	DRS	71.439	386.638	273.889
ASS	183.157	2405.770	1447.154	AFS	183.157	897.873	658.808	ARS	183.157	795.900	89.655
BSS	102.473	2399.125	2017.731	BFS	102.473	929.460	636.491	BRS	102.473	551.334	413.736
ZSS	92.719	1700.597	1762.719	ZFS	92.719	190.935	163.726	ZRS	92.719	313.460	267.436
MEAN	112.447	1956.752	1522.508	MEAN	112.447	617.602	429.173	MEAN	112.447	511.833	261.179
STD	**48.888**	**537.416**	**498.105**	STD	**48.888**	**358.342**	**255.336**	STD	**48.888**	**213.915**	**132.783**

Pb	CTR	DRS	RNS
DSS	0.680	9.633	7.522
ASS	1.152	10.218	8.270
BSS	1.316	3.290	2.073
ZSS	1.046	4.019	3.527
MEAN	1.048	6.790	5.348
STD	**0.269**	**3.640**	**3.017**

	CTR	DRS	RNS
DFS	0.680	6.250	6.867
AFS	1.152	4.035	3.810
BFS	1.316	1.047	1.140
ZFS	1.046	2.273	1.716
MEAN	1.048	3.401	3.383
STD	**0.269**	**2.260**	**2.590**

	CTR	DRS	RNS
DRS	0.680	4.670	3.204
ARS	1.152	2.667	3.990
BRS	1.316	1.670	1.016
ZRS	1.046	1.168	ND
MEAN	1.048	2.543	2.052
STD	**0.269**	**1.548**	**1.858**

Zn	CTR	DRS	RNS
ZSS	46.381	67.288	69.591
ASS	64.264	84.940	91.197
BSS	52.492	95.780	80.917
DSS	67.187	122.333	85.489
MEAN	57.581	92.585	81.798
STD	**9.802**	**23.047**	**9.160**

	CTR	DRS	RNS
ZFS	46.381	58.75	61.261
AFS	64.264	47.481	35.731
BFS	52.492	72.570	81.383
DFS	67.187	81.490	66.748
MEAN	57.581	65.072	61.280
STD	**9.802**	**15.002**	**19.033**

	CTR	DRS	RNS
ZRS	46.381	45.332	40.820
ARS	64.264	53.476	41.146
BRS	52.492	84.930	64.716
DRS	67.187	78.876	76.222
MEAN	57.581	65.653	55.726
STD	**9.802**	**19.215**	**17.660**

Appendix III: Mean heavy metals concentration (mg kg^{-1}) in Water samples analysed

	CTR	DRS	RNS
ZBW	0.162	0.074	0.070
ABW	0.042	0.056	0.044
BBW	0.321	0.049	0.414
DBW	0.400	0.880	0.461
MEAN	0.231	0.264	0.247
STD	**0.160**	**0.410**	**0.220**

	CTR	DRS	RNS
ZWW	0.249	0.070	0.05
AWW	0.085	0.170	0.013
BWW	0.346	0.296	0.798
DWW	0.561	0.850	1.004
MEAN	0.310	0.346	0.466
STD	**0.198**	**0.348**	**0.509**

	CTR	DRS	RNS
ZPW	1.510	0.873	0.846
APW	0.916	1.420	1.060
BPW	0.924	11.210	9.353
DPW	0.740	1.830	0.930
MEAN	1.022	3.833	3.047
STD	**0.335**	**4.933**	**4.204**

S/TYP	CTR	DRS	RNS
ZBW	ND	ND	ND
ABW	ND	ND	ND
BBW	ND	ND	ND
DBW	ND	ND	ND
MEAN			
STD			

S/TYP	CTR	DRS	RNS
ZWW	ND	ND	ND
AWW	ND	ND	ND
BWW	ND	ND	ND
DWW	ND	ND	ND
MEAN			
STD			

S/TYP	CTR	DRS	RNS
ZPW	0.692	2.656	1.840
APW	1.040	2.760	1.839
BPW	1.751	5.404	3.367
DPW	1.738	3.419	2.170
MEAN	1.305	3.559	2.304
STD	**0.526**	**1.275**	**0.725**

S/TYP	CTR	DRS	RNS
ZBW	0.085	0.341	0.285
ABW	0.301	0.273	0.279
BBW	0.210	0.067	0.070
DBW	0.143	0.110	0.093
MEAN	0.184	0.197	0.181
STD	**0.092**	**0.130**	**0.116**

S/TYP	CTR	DRS	RNS
DWW	0.260	0.862	0.114
AWW	0.101	0.264	0.125
BWW	0.263	0.251	0.220
ZWW	0.137	0.280	0.194
MEAN	0.190	0.414	0.163
STD	**0.083**	**0.298**	**0.051**

S/TYP	CTR	DRS	RNS
DPW	0.780	4.140	1.660
APW	1.834	8.497	3.367
BPW	1.692	2.090	0.796
ZPW	2.480	0.494	0.450
MEAN	1.696	3.805	1.568
STD	**0.700**	**3.465**	**1.302**

S/TYP	CTR	DRS	RNS
ZBW	ND	ND	ND
ABW	ND	ND	ND
BBW	ND	ND	ND
DBW	ND	ND	ND
MEAN			
STD			

S/TYP	CTR	DRS	RNS
DWW	ND	ND	ND
AWW	ND	ND	ND
BWW	ND	0.08	0.08
ZWW	ND	0.06	
MEAN		0.07	0.08
STD		**0.014**	

S/TYP	CTR	DRS	RNS
DPW	0.927	1.310	0.830
APW	ND	0.837	0.733
BPW	ND	0.280	0.260
ZPW	ND	0.904	1.745
MEAN	0.927	0.832	0.892
STD		**0.423**	**0.620**

	CTR	DRS	RNS
ZBW	ND	ND	ND
ABW	ND	ND	ND
BBW	ND	ND	ND
DBW	ND	ND	ND
MEAN			
STD			

DWW		0.006	0.007
AWW	0.008	0.013	0.010
BWW	0.019	0.067	0.079
ZWW	ND	0.030	ND
MEAN	0.013	0.029	0.032
STD	**0.007**	**0.027**	**0.040**

		`	`
DPW	0	0.433	0.030
APW	ND	1.852	1.071
BPW	0.164	0.710	0.249
ZPW	0.638	0.084	0.755
MEAN	0.267	0.769	0.526
STD	**0.331**	**0.765**	**0.473**