ASSESSMENT OF POLLUTION STATUS IN ASHA AND SABOEREGI MINING AREAS OF NIGER STATE, NIGERIA

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Declaration

I declare that the work in this Thesis entitled "ASSESSMENT OF POLLUTION STATUS IN ASHA AND SABOEREGI MINING AREAS OF NIGER STATE, NIGERIA" has been carried out by me in the Department of Chemistry. The information derived from literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other Institution.

_____ _____

Peter Jibrin GANA Date

Certification

This Thesis entitled "ASSESSMENT OF POLLUTION STATUS IN ASHA AND SABOEREGI MINING AREAS OF NIGER STATE, NIGERIA" by Peter Jibrin GANA meets the regulations governing the award of the Ph.D Analytical Chemistry of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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Dedication

This research work is dedicated to my beloved wife Leah and our children, Blessing (Yaya), Paul (Ebenezer) and Comfort (Kaka Yebo) for all their love, support and sacrifice.

Acknowledgement

I give special thanks to the Most High God, the Giver and the Sustainer of my life for allowing me to see the completion of this work. All glory, honour and adoration be unto Him now and forever. Amen.

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Table of Contents

Chapter Six

List of Figures

List of Tables

List of Appendices

List of Abbreviations

AAS	–	Atomic Absorption Spectrophotometer
AMD	_	Acid Mine Drainage
ANOVA	–	Analysis of Variance
AOAC	–	Association of Analytical Chemists
APHA	–	American Public Health Association
AR	–	Analytical Reagent
ATSDR	–	Agency for Toxic Substances and Disease Registry
BDL	–	Bellow Detection Limit
BOD	–	Biochemical Oxygen Demand
CEC	–	Cation Exchange Capacity
Cmol	–	Centimole
CNS	–	Central Nervous System
COD	–	Chemical Oxygen Demand
COND	–	Conductivity
DO	–	Dissolved Oxygen
DTPA	–	Diethylenetriamine Pentaacetate
EC	–	Electrical Conductivity
EDTA	–	Ethylene Diaminetetra Acetic Acid
FAO	–	Food and Agricultural Organization
FEPA	–	Federal Environmental Protection Agency
IARC	–	International Agency for Research on Cancer
LGA	–	Local Government Area
MESS	–	Multi-Element Standard Solution
nm	–	Nanometer
NTU	–	Nephelometric Turbidity Units
OM	–	Organic Matter
SON	–	Standard Organization of Nigeria
SpGr	–	Specific Gravity
TDS	–	Total Dissolved Solid
TS	–	Total Solid
TSS	–	Total Suspended Solids
UNDP	–	United Nations Development Program
USEPA	–	United State Environmental Protection Agency
USPH	–	United State Public Health
WHO	–	World Health Organization

Abstract

This research work investigated the water and soil pollution status of Asha and Saboeregi mining areas of Niger State using standard analytical methods. The physico-chemical parameters of water (pH, turbidity, total dissolved solids, electrical conductivity, dis-solved oxygen, chloride, alkalinity, sulphide, colour, suspended solid, total solid, bio-chemical oxygen demand, chemical oxygen demand, nitrate and phosphate) as well as soil (pH, organic carbon, organic matter, available phosphorus, cation exchange capacity, sand, silt and clay) were determined. The water, soils and *Sorghum bicolor* grains were analysed using atomic absorption spectrophotometer to determine the concentrations of Au, Cd, Cu, Fe, Mn, Pb and Zn. Statistical analysis on the results were carried out using One –way analysis of variance (ANOVA). The results indicated that of the fifteen physical and chemical properties of waters from Rivers Gbako and Tangale studied, seven of the properties (turbidity, alkalinity, sulphide,, colour, suspended solid, nitrate and phosphate) exceeded the acceptable World Health Organisation (WHO) standard limits for surface waters while four of these properties (total dissolved solid, electrical conductivity, chloride and biochemical oxygen demand) were found to be below the acceptable WHO standard limits for surface waters and the remaining three properties (pH, dissolved oxygen and chemical oxygen demand) were within the acceptable WHO standard limits for surface waters during the period of study. The distribution of heavy metals in surface water of Rivers Gbako and Tangale indicates that anthropogenic activity was an important factor contributing to increased metals (Au, Cd, Cu, Fe, Mn, Pb and Zn) concentration in the water. The metal concentrations were higher than the values obtained for control sites except for Cd and Pb. The metal concentrations were also higher than the recommended limits given by Joint Food Organization and World Health Organization (FAO/WHO). The soils at Asha mining site were sandy loam while those of Saboeregi were sandy clay loam in texture and showed Saboeregi soils had better structural stability, water holding capacity and high nutrient. The concentrations of the metals (Au, Cd, Cu, Fe, Mn, Pb and Zn) in the soils from the mining sites were higher than the corresponding values from the control sites, and also higher than the recommended limits given by Joint FoodOrganization and World Health Organization (FAO/WHO). The index of geo-accumulation (Igeo) showed that soils at the two study sites (Asha and Saboeregi) were extremely polluted with Fe with Igeo value of 7.43. Heavily to extremely polluted with Mn with Igeo value of 4.41 and heavily polluted with Zn with Igeo value of 3.66. The concentrations of the metals (Au, Cd, Cu, Fe, Mn, Pb and Zn) in the *Sorghum* grains harvested from the mining sites were higher than the corresponding values from the control site with the exception of Cd and Pb, and also higher than the recommended limits given by Joint Food Organization and World Health Organization (FAO/WHO) with the exception of Cu and Mn.

CHAPTER ONE

1.0 INTRODUCTION

Pollution may be defined as the contamination of earth's environment with materials that interfere with human health, quality of life or natural functioning of ecosystem. Such contaminants may be gases causing air pollution, solids/liquids causing water, food and land pollution or sound causing sound pollution. Most of these pollutions except few (such as volcanic eruptions) are caused by human activities. Pollution has been aggravated by marked increase in global population, poverty, increased industrialisation, and urbanisation in developed countries since the beginning of the 20th century.Thus environmental pollution is largely associated with the past and present industrial activities which immensely contributed to the release of significant level of metals to the environment (Dolam *et al*., 2006).

The use of metals in human history has yielded great benefits as well as unexpected harmful consequences. Metals as a group share some common properties. However, while sharing common properties, metals exhibit wide ranges with respect to one another, in both chemical behaviour and measured values of those common properties. Historically, it has been the exploitation of these properties of metals and the dependence of the modern technological development that led to the increasing demand for these metals. It is their chemical and radioactive behaviour in biological systems (toxicity, mutagenicity, and carcinogenicity), realized within the past century, which pose the most serious risks. The elements of greatest concern include Pb, Cd and Hg, and As. Other different types of metals, like Be, Sr, and Ba (alkaline earth metals), and U and Th (rare earth metals) also pose problems (Lake *et al*., 1984; Pickering, 1986).

1.1 The Research Problem

The Mining operations take a heavy toll on the environment and its associated biota through the removal of vegetation, topsoil and the displacement of fauna.The release of heavy metals from the mining waste is particularly problematic as they do not chemically break down in the environment. They settle or persist in streams or land for long period of time, providing a long-term source of pollution to the surrounding inhabitant's especially human health. In most cases the extent of this threat is not known as the heavy metal level is sometimes not established. Frequent exposure to mine waste may lead to chronic or acute disease.

Other environmental problems in mining include the release of metallic smoke and dust into the atmosphere, dumping of waste rock, tailings or slag, and the discharge of mine pit water or waste water.

1.2 Justification of the Study

Mining of mineral resources has assumed prime importance globally, contributing immensely to the national wealth with associated socio-economic benefits.World Health Organization (WHO , 2011) estimates that about a quarter of the diseases facing mankind today occur due to prolonged exposure to environmental pollution (Prüss-Üstün and Corvalán, 2006; Kimani, 2007).

With rapid increase in mining process of extracting metals and minerals from the earth, the effects on the environment (if protective measures are not taken) can be unnaturally high in concentrations of some chemicals, such as arsenic, sulphuric acid, and mercury (Nordstrom *et al.*, 2000). Runoff of soil or rock debris -although non-toxic- also devastates the surrounding vegetation. There is an additional potential for massive contamination of the area surrounding mines due to the metals removed from the ground with the ore. Large amount of water produced from mine drainage, mine

cooling, aqueous extraction and other mining processes increases the potential of these chemicals to contaminate ground and surface water (Adler *et al*., 2007).

It is therefore of utmost importance to monitor the mining environment constantly, to prevent disasters arising from the introduction of heavy metals into the soil, water and plants. Monitoring the levels of heavy metals in the soil will also provide an indication to policy-makers of the pressing need to enforce compliance by various companies and industries.

1.3 Aim and Objectives

The aim of this study is to determine the level of pollution caused by mining activities on soil, water and plants in Asha and Saboeregi areas of Niger State. This aim will be achieved through the following objectives:

i. Determination of physico-chemical properties and the concentration of heavy metals (Au, Cd, Cu, Fe, Mn, Pb, and Zn) in soil and
ii. Determination of physico-chemical properties and the concentration of heavy metals (Au, Cd, Cu, Fe, Mn, Pb, and Zn) in water within the study area
iii. Determination of these metals in the *Sorghum bicolor* grains cultivated within the area
iv. Establishment of relationship between soil properties and the heavy metals in the soils, water and grains.
v. Determination of pollution index in order to ascertain the pollution status of the soil at the mining sites.
vi. Speciation of Au, Cd, Cu, Fe, Mn, Pb, and Zn metals in the soil using sequential extraction procedure in order to establish the bioavailability of the metals.

CHAPTER TWO

2.0 LITERATURE REVIEW

Mining is the extraction of valuable mineral deposits or other geological materials from the earth (Nwajiuba, 2000). Natural resources (metallic, non-metallic minerals and fossil fuels) are important in the development of any country. The general importance of the mining sector in Nigeria has been documented to include foreign exchange, employment and economic development. Mining and its waste leads to several geo-environmental disasters on land, water and plants. It has huge socio-economic effects on the population residing in the impacted area especially in terms of livelihood and health. Once this happens, it becomes a news item and comes into focus for geoenvironmental evaluation (Obaje *et al.*, 2005).

Mining and processing of heavy metals led to environmental degradation. The magnitude and intensity depend on the type of chemicals and processes used, the efforts taken in the management of waste as well as on environmental fragility of the location. It also involves extreme disturbance to local residents by increased diseases, water pollution and destruction of farmland thereby violating the rights of local communities (Tekedil and Srivastav, 2015). Some of the contaminants are even classified as human carcinogens by International and Federal Health Agencies (EPA, 2012).

Small-Scale Mining is a means of livelihood adopted primarily in rural areas (Veiga, 2003). This is sometimes called informal sector, which is outside the legal and regulatory framework (Azubike, 2011). When not formalized, organized, planned and controlled, Artisanal and Small-Scale Mining can be viewed negatively by governments and environmentalists, because of its potential for environmental degradation (Oramal *et al.*, 2015). Some of these menaces are depletion of the environment such as land degradation, devegetation, lost of aquatic animals, pollution of water and air. Most

artisanal miners work in difficult and often very hazardous conditions in the absence of the required safe mining regulations to safeguard their operations (Veiga, 2003). Apart from environmental problems, health issues are not left out in gold mining operations. The use of gravity concentration methods such as panning and sluicing during processing is a potential health risk. Toxic materials are released into the environment, posing large health risk to the miners, their families and surrounding communities (Azubike, 2011). Thus, gold mining operations are particularly hazardous, because of the nature of chemicals (such as mercury amalgam and cyanide) used for its extraction (CDC, 2010).

Despite serious dangers encountered in this activity, artisanal gold mining operations continue to spread due to rise in the demand for gold and unattractive nature of other means of livelihoods such as farming in the rural areas where the mineral is substantially available. In March 2010, Médecins Sans Frontières (MSF) discovered an epidemic of lead poisoning in Zamfara state in North–Western Nigeria particularly in Anka and Bukkuyum Local Government Areas of the state (MSF, 2010).Subsequent investigations by the Centers for Disease Control and Prevention (CDC 2010), the World Health Organization (WHO) and the Zamfara State Ministry of Health (ZMoH) confirmed that hundreds of children under age of five were at risk of death or serious acute and chronic health issues due to extremely high levels of lead and mercury (WHO, 2011). At least 10,000 people were estimated to be affected overall (MSF, 2010). The source of the outbreak was associated with artisanal gold ore processing that occurs in the villages (Azubike, 2011) and the medium through which the people were affected include drinking water, food, inhalation of contaminated dust, oral ingestion of particles especially by children and through breast feeding. Mining of gold has been left in the hands of artisanal miners who do not have enough resources, adequate equipment

and technology required for the mining activities. Niger State in North Central, Nigeria is a major gold field (Ako *et al*., 2014), but does not get the required attention from Government. Most of themining activities are left in the hands of the unskilled miners.

2.1 Effect of Mining on Aquatic Life

Water pollution around the mining and smelting areas has been clearly demonstrated by high concentrations of heavy metals in water, sediments, and aquatic organisms (Nirmal *et al*., 2011). Contamination of water bodies occur in a number of ways simply classified as geochemical processes and human activities (Galadima *et al*., 2010). Besides the contamination from the weathering and leaching processes of mine tailings, untreated mine drainage also contributes large amount of heavy metals to nearby streams and rivers (Nirmal *et al*., 2011).

Several studies have reported the dangers mining activities pose to both aquatic and terrestrial life as indicated by Mkpuma *et al*., (2015). For instance, it was reported that in 1995 more than four billion litres of wastewater that contained cyanide, slipped into a tributary of the Essequiboin Guyana and the tailings dam, which was filled with cyanide waste and collapsed. All the fish in the river died, plant and animal life were completely destroyed, and floodplain soils were heavily poisoned, making the land unsuitable for agricultural activities (Eisler and Wiemeyer, 2004). The main source of drinking water for the local people was also polluted. A similar incident happened at the Kahuzi-Biega National Park, Congo, in 1980 where a large number of animals were killed within a period of 15-20 years as a result of extraction of tantalum and cassiterite at the park (Mkpuma *et al*., 2015).In Indonesia a case ofpoisonous wastes (arsenic and mercury) dumped by a gold mining company occurred which had serious impact on the environment. Fishes were killed and people in the surrounding area suffered from

various illnesses like persistent headache, skin rashes, tumours and difficulty in breathing (Gray and Page, 2008).

Mine drainage is another component of mining processes that interact with other chemicals to cause a variety of effects on aquatic life that are difficult to separate into individual components. Toxicity is dependent on discharge volume, pH, total acidity, and concentration of dissolved metals. pH is the most critical component, since the lower the pH, the more severe the potential effects of mine drainage on aquatic life; most organisms have a well-defined range of pH tolerance. If the pH falls below the tolerance range, death will occur due to respiratory or osmoregulatory failure (Kimmel, 1983). Low pH causes a disturbance of the balance of sodium and chloride ions in the blood of aquatic animals. At low pH, hydrogen ions may be taken into cells and sodium ions expelled (Morris *et al*., 1989). Mayflies and stoneflies that normally live in neutral water experience a greater loss of sodium in their haemolymph when exposed to low pH than do acid-tolerant species of stoneflies, such as *Leuctra* and *Amphinenntra*, whose sodium uptake is only slightly reduced by low pH (Sutcliffe and Hildrew, 1989).

Acid waters typically have fewer species, lower in abundance and biomass of macro-invertebrates than near-neutral pH waters (Potts and McWilliams, 1989). Attempts have been made to specifically identify limiting factors affecting aquatic lives. Two factors investigated were interruption of the food chain and direct effects of low pH levels on aquatic life. Macro invertebrates are often grouped by their feeding habits, and assemblages of invertebrates in acidified waters appear to be related to food availability. The fauna of low pH streams is usually composed of shredders (organisms that eat leaves that fall into the stream), collectors (organisms that filter or gather particles of organic matter from the water), and predators. Low pH tends to eliminate species that feed on algae (scrapers or grazers) and may inhibit growth of bacteria which

help break down leaves to make them more easily digestible and also serve as a food source. These observations led early investigators to theorize that low pH levels reduced the food sources for invertebrates, thereby indirectly reducing their numbers. This is partially true however; other studies showed that direct effects of low pH on aquatic life are more critical than their food sources (NRC, 1992; Rosemond *et al*., 1992).

2.2 The Effect of Mining Processes on the Ecosystem

According to Weed and Rutschky (1971), the entire ecosystems are affected by the physical perturbations of mining operations, as well as the chemical alterations in soil and water. Mining activities can result to soil compaction and conversely, removal of the topsoil. These alterations disrupt nutrient dynamics by minimizing the availability of nitrogen and phosphorus, lower the pH through the acidification of the soil and can introduce toxic metals and acids. Depending on the scale and nature of the mining operation, these effects can be localized to the mining site or can extend to nearby aquatic systems (Weed and Rutschky, 1971).

Other effects of mining processes on the ecosystem are releases of gases that may be harmful to downwind residents and to nearby wildlife, airborne contaminants that can affect farms and ranches and enter the food supply chain. The ultimate effect of coal mining is denser pollution and destruction of ozone when the fuel is burned (Mielke *et al*., 2003).Studies indicated that the chemicals may accumulate in fruits, leaves, crops and soils around mining sites. These may cause severe contamination of water sources(Bartrem *et al*., 2014; Oramah *et al*., 2015).

2.3 Effect of Mining Proceses on Physicochemical Parameters

2.3.1 pH

This is a measure of acidity and alkalinity of a solution or water. It is used to express the intensity of acidic or alkalinity of a water sample, which actually indicates the concentration of hydrogen ions present (Mason, 1993). The acid mine drainage, discharge of effluents, acidic precipitation, runoff, microbial activities and decay process change the pH of water. Acid mine drainage affects pH resulting in reduced acid neutralizing capacity and lowers pH. Low pH increases the solubility processes of heavy metal compounds, which increase contamination in the environment. Anderson *et al*. (2000) found that the degree of solubility determines the toxicity of the heavy metals and that they are more toxic at low pH of less than 4.5 because they are more mobile.

The significance of pH includes changes that occurs when wastewater is discharged into the environment. At pH values between 6.7 and 8.6 for instance, aquatic environments are well balanced (WHO, 1998; RMPC, 2006). However, at pH less than 5 or more than 9, most aquatic species are affected. The pH varies with the amount of dissolved materials in the water.

Studies in Norway and Sweden indicated extinction of fish populations often resulted from chronic reproductive failure because of acidification induced effects on sensitive developmental stages (Brungs *et al*., 1998). Acid stress (pH 4.0 -5.0) also has caused fish mortality by interfering with the physiological mechanisms regulating active ion exchange across gill membranes (Brungs *et al*., 1998).

2.3.2 Turbidity

This is the measure of the relative cloudiness of water. Turbidity is caused by suspended solid matter scattering light as it passes through water. Water turbidity arises from suspended inorganic substances, dispersed organic substances, micro-organisms amongst others. Turbidity is important because it affects both the acceptability of water to consumers, and the selection and efficiency of treatment processes, particularly the

efficiency of disinfection with chlorine since it exerts a chlorine demand and protects microorganisms and may also stimulate the growth of bacteria (RMPC, 2006). Highly turbid water full of suspended material has many effects on the surface water. If water surface of a river is excessively turbid over long periods its health and productivity can be greatly diminished. Highly turbid water can influence the amount of dissolved oxygen in three ways. First turbid waters interfere with light penetration in the water, thereby reducing the amount of light reaching the bottom, making it less suitable for plant growth. Fewer aquatic plants will be the result and therefore less photosynthesis and less dissolved oxygen. Dissolved oxygen concentrations are also influced by high turbidity and its relationship to water temperature. Suspended particles absorbed heat, which causes water temperature to increase, thereby resulting in less oxygen because warm water holds less oxygen than cold water. High turbidity may also be caused by high levels of dead organic matter called detritus. Detritus can include leaves, twigs and other plant and animal wastes which lead to depletion of oxygen as they are decomposed by bacterial (EPA,2012,).

2.3.3 Total dissolved solids

This is a measure of the combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro-granular (colloidal sol) suspended form. Elevated levels of (TDS) have been suggested as stressors to aquatic life in Central Appalachian streams influenced by coal mining (Bodkin *et al.*, 2007; Pond *et al*., 2008). In coalfield streams, TDS is most often dominated by the dissolved ions SO_4^{2-} and HCO_3^- , with elevated concentrations (relative to reference) of Ca^{2+}, Mg^{2+}, Na^+ , K^+ , and Cl^- (Mount *et al*., 1997; Pond *et al*., 2008). In mine-influenced streams of the Central Appalachians, in-stream TDS concentration can exceed 2,000 mg/dm^3 (Pond *et al*., 2008). Aquatic bioassays have exposed organisms to a wide range

of TDS concentrations. The organisms used in such toxicity testing include common indicator species, such as the cladocerans,*Ceriodaphnia dubia* and *Daphnia magna*, the amphipod,*Hyalella azteca*, and the midge,*Chironomus tentans*, as well as indigenous species such as the mayfly *Isonychia* sp. Kennedy *et al*., (2003) exposed *C. dubia* to sulfate-dominated mine effluent and observed significant effects on survival and reproduction at specific conductivities of approximately 6,000 and 3,700 μS/cm (approx. 4,200 & 2,590 mg/dm^3 TDS), respectively. Soucek and Kennedy (2005) observed lethal effects of sulfate to *H. azteca* (512 mg/dm^3), *C. dubia* (2,050 mg/dm^3), and *C. tentans* (14,134 mg/ dm^3). Chapman *et al*., (2000) also found reductions in survival and growth of *C. tentans* from simulated mine effluent of approximately 2,000 mg/ dm^3 TDS.

To investigate the effects of TDS on a species representative of populations observed to be impacted at field sites, Kennedy *et al*., (2004) collected mayflies of the genus *Isonychia* from an unpolluted stream. They then exposed the mayflies to simulated mine effluent for seven days and observed a significant effect on survival at a conductivity of ~1,500 μS/cm (~1,050 mg/ dm^3 TDS). These laboratory experiments illustrate a clear biological response to elevated TDS, though the results differ among studies, suggesting that TDS tolerance varies widely among different test organisms. Additional research has shown that TDS toxicity is dependent upon the type and combination of ions in solution. Acute toxicity tests conducted by Mount *et al*., (1997) exposed *C. dubia* and *D. magna* to 2,453 different solutions of various ion combinations. They found the relative toxicity of individual ions to be: $K^+ > HCO^{3-} \approx Mg^{2+} > Cl^- > SO_4^{2-}$. They also found that toxicity of K^+, Cl^- , and SO_4^{2-} was reduced in solutions with more than one cation present. Soucek and Kennedy (2005) also found that sulphate toxicity was reduced for *C. dubia* and *H. azteca* when water hardness

(Ca^{2+} and Mg^{2+}) was increased. Increased chloride concentration also reduced sulfate toxicity to *H. azteca*.

These studies suggest that the biological response to in-stream mineral solutions depends on TDS composition and ion interactions, as well as overall ionic strength or TDS concentration. Field data have shown that the biotic response to elevated TDS also occurs outside the laboratory with indigenous species. Many recent studies of eastern coal mining-influenced streams have found that benthic macroinvertebrate community structure is altered in mining influenced streams relative to community structure in streams uninfluenced by mining (Green *et al*., 2000; Pond *et al*., 2008). In those studies, most mining-influenced streams were observed to be elevated in conductivity/TDS and in all cases, one of those water changes.

2.3.4 Electrical conductivity

The conductivity of water is said to depend on the quantity of dissolved salts present and for dilute solutions it is approximately proportional to the total dissolved solid (TDS) content. The presence of dissolved salts in water increases its electrical conductivity, which varies according to the temperature. Drinking water has a conductivity ranging between 50 and 500 μS/cm. Domestic water has conductivities above 1000 μS/cm (Nkuli, 2008).

The recommended limit of conductivity for water required for direct abstraction to supply is 400 μS/cm (RMPC, 2006). Conductivity depends upon the number of ions or charged particles dissolved in water and their mobility. Water conductivity increases with increasing mobility of ions in water (Nkuli, 2008).

Conductivity and TDS are used to measure the water quality very high values of dissolved ionic matter are good indicator of possible water pollution sites. Industrial

discharges, mine waste, sewage and agricultural run-off for instance can raise conductivity of surface and groundwater (WHO, 1998).

2.3.5 Dissolved oxygen

There are two main sources of dissolved oxygen in stream water: the atmosphere and photosynthesis. Waves and tumbling water mix air into the water where oxygen readily dissolves until saturation occurs. Oxygen is also introduced by aquatic plants and algae as a byproduct of photosynthesis. The amount of oxygen that dissolves is limited by physical condition, such as water temperature and atmospheric pressure. Assuming a constant atmospheric pressure, low water temperatures produce a higher potential dissolved oxygen level than do high water temperatures. Fish growth and activity usually require 5-6 mg/dm^3 of dissolved oxygen. Low dissolved oxygen levels indicate an excessive demand on the oxygen of the system. The build up of organic material from human activities is one source of oxygen depletion.

Micro-organisms in the stream consume oxygen as they decompose sewage, urban and agricultural runoff, and discharge from food-processing plants, meat-packaging plants, and dairies. Natural organic materials, such as leaves, accumulate in the stream and create an oxygen demand as they decompose. Some pollutants, such as acid mine drainage, produce direct chemical demands on oxygen in the water. Dissolved oxygen is consumed in the oxidation-reduction reactions of introduced chemical compounds, such as nitrate (NO_3^-) and ammonia (NH_3), sulphate (SO_4^{2-}) and sulphite (SO_3^{2-}), and ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions (Exploring the Environment, 2004).

2.3.6 Chloride

Chloride is one of the most important parameter in assessing the quality of water.Chloride contents indicate domestic as well as industrial pollution and in addition

higher concentrations of chlorides indicate higher degree of pollution (Chatterjee and Raziuddin, 2002). Chloride levels above 140 mg/dm^3 are considered to be toxic for plants (Flood, 1996).

2.3.7 Total alkalinity

Alkalinity of the water source is more significant than its pH because it takes into account the principal constituents that influence the water's ability to regulate the pH of the medium. Alkalinity increases as the amount of dissolved carbonates and bicarbonates increase (Radha *et al*., 2007).

2.3.8 Sulphide

The mining sector uses large quanties of water, though some mines do reuse much of their water intake. Mining activities and other geochemical processes throws sulphide-containing minerals into the air, where they oxidise and react with water to form sulphuric acid (equations 2.1-2.3). This together with various trace elements impacts water both from the surface and underground mines (Duruibe*et al*., 2007).

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad 2.1$$

$$2FeSO_4 + 2H_2SO_4 \rightarrow Fe_2(SO_4)_3 + SO_2 + 2H_2O \quad 2.2$$

$$Fe_2(SO_4)_3 + 2FeAsS + 9/2O_2 + 3H_2O \rightarrow 2H_3AsO_4 + 4FeSO_4 + S \quad 2.3$$

2.3.9 Colour

Colour changes typical of creeks affected by AMD start as orange, red, or yellow-brown as the ferrous iron solution is diluted. The pH rises as the AMD mixes with the receiving stream, causing the ferrous iron to precipitate out as ferric iron. Farther downstream, the stream is white as aluminum oxide deposits along rocks and the streambed. The iron and aluminum deposits tend to form a sludge-like material, which inhibits algae, insect, and fish growth, and damages their habitat. Benthic

(bottom-dwelling) organisms are particularly sensitive to this type of pollution. Following the orange iron and white aluminum deposits, the streams can then take on turquoise-blue or green colors as copper and other metals begin to precipitate from solution (Brodie, 1990).

2.3.10 Suspended solid

Suspended solids include clay, silt, plankton, industrial waste, and sewage. Soil erosion introduces soil and mineral particles to surface water. Stream bed sediments can be stirred up by organisms feeding off the bottom. Particles remain suspended by water currents for some time. Urban runoff introduces a wide variety of particles to stream water. Algal growth from added nutrients and sunlight can also increase turbidity.

As the amount of suspended solids increases, photosynthesis decreases, fish gills become clogged, and eggs are smothered. Material settling into spaces between rocks makes these microhabitats unsuitable for the macroinvertebrates living there. Surface water temperature also rises as suspended particles near the surface absorb heat from the sunlight, which in turn affects dissolved oxygen levels (Otilia *et al*., 2006).

2.3.11 Total solids

This is the sum of dissolved and suspended solids. The quantity of dissolved material is mainly determined by the solubility of rocks and soils that the water contacts. Water that flows through limestone and gypsum dissolves calcium, carbonates, and sulfates, resulting in high total dissolved solid levels. The amount of material dissolved in a water sample affects its ability to conduct electricity. Total dissolved solids can be estimated by measuring conductivity, because as total solids increase, conductivity also increases.

Run-off from urban areas can carry salt from streets, fertilizers from lawns, along with other types of materials to contribute dissolved solids. Wastewater treatment plants can add phosphorus, nitrogen, and organic matter. Leaves and other plant materials dumped into streams are another source of dissolved solids. Soil particles are introduced by soil erosion and runoff. Decayed plant and animal matter is naturally converted to particulate matter within the water.

High concentrations of total solids can lower water quality and cause water balance problems for individual organisms. Low concentrations may limit the growth of different aquatic life. High concentrations of dissolved solids can lead to laxative effects and unpleasant mineral taste in drinking water (Antwi-Agyei *et al*., 2009).

2.3.12 Biological oxygen demand

BOD is a measure of the quantity of oxygen used by micro-organisms (e.g. aerobic bacteria) in the oxidation of organic matter. Critical study of BOD gives an idea of the oxidizable matter actually present in a waste sample and allows pollution load evaluation to be established (Yisa, 2004).

The organic matter available for decomposition has both natural and human origins. Nutrients are the main culprit for high BOD in river water. Calm stretches of water ways also collect organic wastes that settle out from upstream. Swamps, bogs, and vegetation along the water provide organic matter for decomposition.

Human activities can result in point source and nonpoint source contribution. Discharge from wastewater treatment plants, pulp and paper mills, meat-packing plants, and food-processing plants are examples of point sources of organic matter. Urban runoff is a nonpoint source provider. Rain and melting snow carry sewage from improper sewer connections into storm drains. Nutrients from lawn fertilizers, leaves, grass clippings, and paper from residential areas also find their way to the water.

Nitrates, phosphates, and other nutrients are carried from fields by agricultural runoff. Chemical oxidation of sulfides, ferrous ions, and ammonia also consume oxygen in water (Clair *et al*., 2003).

2.3.13 Chemical oxygen demand

This is an indicative of the measure of the amount of oxygen that can be consumed by reactions in a measured solution. It can be used to quantify the amount of oxidizable pollutants found in the surface water (e.g lakes and rivers) or wastewater. It is useful in terms of water quality by providing a metric to determine the effect an effluent will have on the receiving body much like BOD (Clair *et al*.,2003).

2.3.14 Nitrate

Nitrate is essential to crops but harmful to humans and animals if taken in high doses (Wetlands, 1999). Nitrates are naturally occurring substances that are vital for plant growth. Nitrates are component of animal manures and artificial fertilizers. They are highly soluble and easily washed away from fields which often contains large amounts of nitrate nitrogen (NO_3^-) to rivers, where eutrophication may result (Hoko, 2007). It may also percolate through the soil to ground sources of water supplies where they cause contamination to dangerous levels. Nitrate is of low toxicity and once absorbed into the blood stream, is rapidly excreted in urine or faeces and recycled in the saliva (Wetlands, 1999).

Blasting processesin the gold mines, use explosives that normally contain nitrogen compounds. Common examples of such agents are ammonium nitrate and fuel oil (ANFO), water gels and explosives. During blasting these gaseous compounds from the explosives are released to the mine wastes and the surrounding environment(Hoko, 2007).

2.3.15 Phosphate

Phosphate is a natural mineral found in the rock deposits the world over. For example in Florida most of the deposits are found in “Bone valley’’ in the heart of the Central Florida (Kent *et al.,* 2013). It is present in natural waters and usually found in the form of phosphates (PO_4^{-3}). Its ions are bonded to soil particles and in laundry detergents also end up in streams. Other sources of phosphorus include sewage, animal waste, soil erosion, fertilizers, and drained swamps and marshlands. By boosting nutrients in soil phosphate helps to promote rapid plant growth.

It acts as a "growth-limiting" factor of aquatic plants and algae. Excess phosphate creates blooms of extensive algal growth.One of the most visible consequences of phosphate in the mines is that of radioactive materials such as uranium/radium/radon is often coupled with phosphate and mining process tend to leave a higher concentration of these radioactive materials at mined lands. A study reported by Kent *et al.,* (2013) in Florida Institute of Phosphate Research indicated that foods grown on these lands did not pose a risk to human health.

Phosphorus (P) is an essential element classified as a macronutrient because of the relatively large amounts of phosphorus required by plants. Phosphorus is one of the three nutrients generally added to soils in fertilizers. It has been found by several scientists that the main role of phosphorus in soils is the transfer of energy. A sufficient number of phosphorus availability for plants stimulates early plant growth and hastens maturity. So, Phosphorus is essential for plant growth in coal mining area and mismanagement of soil phosphorus can pose a threat to water quality and soil quality directly or indirectly (Eva *et al*., 2017).

2.4 Effect of Heavy Metals from Acid Mine Drainage

Heavy metals increase the toxicity of mine drainage and also act as metabolic poisons. Iron, lead, and manganese are the most common heavy metals which can

compound the adverse effects of mine drainage. Heavy metals are generally less toxic at neutral pH. Trace metals such as, cadmium and mercury, which may also be present in mine drainage, are toxic at extremely low concentrations and may act synergistically to suppress algal growth and affect fish and benthos (Hoehn and Sizemore, 1977). Some fishes, such as brook trout, are tolerant of low pH, but addition of metals decreases that tolerance. In addition to dissolved metals, precipitated iron or aluminium hydroxide may form in streams receiving mine discharges with elevated metals concentrations. Ferric and aluminium hydroxides decrease oxygen availability as they form; the precipitate may coat gills and body surfaces, smother eggs, and cover the stream bottom, filling in crevices in rocks, and making the substrate unstable and unfit for habitation by benthic organisms (Hoehn and Sizemore, 1977). Scouring of iron flocculants increases turbidity and suspended solids and may inhibit fish feeding.

Iron precipitates at a pH greater than 3.5 and does not re-enter solution at higher pH. Precipitation of ferric hydroxide may result in a complete blanketing of the stream bottom, adversely affecting both macro invertebrates and fish (Hoehn and Sizemore, 1977). The severity is dependent on stream pH and the thickness of the precipitate. Generally, the effect of precipitated iron is less severe in alkaline conditions. Many fishes and macro invertebrates are tolerant of iron precipitate in alkaline water; however, total numbers and diversity are usually lower than in unaffected streams. Koryak *et al*., (1972) found that ferric hydroxide greatly diminished total biomass of benthic organisms and limited fish populations in streams with tolerable pH levels.

Manganese is another metal that is widely distributed in mine drainage. Manganese can be present in a variety of forms (complexes) with organic compounds. Manganese is difficult to remove from discharges because the pH must be raised to above 10.0 before manganese will precipitate. Manganese, therefore, is persistent and

can be carried for long distances downstream of a source of mine drainage. Less information is available on the effects of elevated manganese concentrations on aquatic life than the effects of iron and aluminium. Perhaps this is because manganese in mine drainage is usually associated with other metals which may have a more deleterious effect or mask the effect of the manganese. Manganese discharge limits have traditionally been based on the objectionable discoloration effects of manganese at concentrations as low as 0.2 mg/dm^3 in water supplies rather than effects on aquatic life (Adler and Rascher, 2007).

2.5 Fate of Heavy Metal in Soils

The extent to which natural background levels are exceeded (that is total metal content), and the ease of mobilization as well as bio-availability determine the impact of metal contamination in soils (Chlopecka *et al*., 1996). However, since heavy metals are not biodegradable, though may be bio-transformed, their persistence in soils seems to be virtually permanent.The half-lives of heavy metals also indicate that complete removal of metallic contaminant from soils is nearly impossible. For example, half-lives of Cd, Cu and Pb range between 15–1100 years, 310–1500 years and 740–5900 years respectively, depending on the soil type and their physicochemical properties (Alloway and Ayres, 1997). However, the accumulated heavy metals in soils are depleted slowly by leaching (into the ground and surface water), plant uptake deflation or erosion (Shiva *et al*., 2016).

2.6 Mobility of Heavy Metals in Soils

There is a close link between environmental hazards caused by heavy metals and their movement in soils. Heavy metals are only sparingly soluble in soils, and often occur predominantly in adsorbed state or as insoluble compounds, except for very acidic soils where acidification can increase the rates of their mobilization (Sherene, 2010). Li

and Shuman (1996) and Anitha (2011) also reported that sandy soils subjected to heavy rainfall or irrigation permit easy mobility of heavy metals.

Furthermore, leaching of heavy metals also depends on the magnitude and duration of their inputs into soils as well as on the soil binding capacity which is determined by the organic matter content. Low organic matter enhance the mobility of heavy metals in soils by either resulting in soil erosion or by leading to reduced cation exchange capacity which gives rise to inability of soil's capacity to adsorb heavy metal (Stigliani *et al*., 1991) .Thus the capacity of soils to adsorb and immobilize heavy metals is strongly determined by organic matter content, soil pH, redox potential, and salinity.

2.7 Plant Uptake of Heavy Metals in Soil

The uptake of heavy metals via plant roots is generally the most important pathway of absorption. The extent of heavy metal absorption by plant depends upon the ionic potential of the metal concerned (Foy, 1978). The ionic potential of a metal is defined as the ratio of its charge and ionic radius at a given state in the soil. Be^{2+} with an intermediate ionic potential of 5.9 (that is $2/0.34A^{o}$), has a tendency to get precipitated, while Cd^{2+}, with a lower ionic potential of 2.0 ($2/0.97A^{o}$), has a greater tendency to migrate (Salt and Kramer, 2000).

Miller and Mcfee (1983) reported that, the top soil provides more effective retention ability for metallic pollutants than the lower depth.This may likely be due to the presence of organic matter in the top soil. Therefore, the build-up of toxic metals in the most biologically active part of the soil, make the metals readily accessible to some plants.

The fate and transport of a heavy metal in soil depends significantly on the chemical form and speciation of the metal. Once in the soil, heavy metals are adsorbed by initial fast reactions (minutes, hours), followed by slow adsorption reactions (days, years) and are, therefore, redistributed into different chemical forms with varying bioavailability, mobility, and toxicity. This distribution is believed to be controlled by reactions of heavy metals in soils such as (i) mineral precipitation and dissolution, (ii) ion exchange, adsorption, and desorption, (iii) aqueous complexation, (iv)biological immobilization and mobilization, and (v) plant uptake (Raymond and Felix, 2011).

Kalaivanan and Ganeshamurthy (2015) reported that Plants growing in metal-contaminated sites exhibit altered metabolism, growth reduction, lower biomass production, and metal accumulation. Various physiological and biochemical processes in plants are affected by metal toxicities. The principal effect of plant elemental contamination is on the dietary and health requirements of animals and humans through the food chain.

2.8 Sources of Contamination and Distribution of some Heavy Metals

2.8.1 Gold

Gold mining is a global industry undertaken for its economic benefits of wealthy creation and employment. According to Dock (2005), mining is one of mankind's oldest industries. In African commercial scale mining provides important benefits in terms of exports/foreign exchange earnings and tax receipt to nineteen African countries (Hayumbu, and Mulenga, 2004). The African continent contains about 30% of the world's mineral resources, and possesses the largest known reserves of strategically important minerals, including gold (Edwards *et al.*, 2014).

Beside the socio-economic benefits of the mining industry in the developing countries such as Nigeria, the industry may be faced with three potential negative effects. The first one is the socio-economic dislocation all ill-prepared mining communities go through at mine closure, which arise from exploitation of a non-regenerative resources (Hayumbu and Mulenga, 2004). The second and third undesirable aspects arise when non-optimal management of mining operations results in environmental degradation and /or negative health impacts on miners and mining communities. Principal health problems among miners and mining communities from various countries that have been cited by the literature include respiratory disease, neoplasm/cancer, chronic hypertension, mental health and genetic impact (WHO, 1999) The major cause of these disease can be attributed to the heavy metal contamination and naturally occurring radioactive materials (ICRP, 1994).

Mining and industrial processing are among the main sources of heavy metal contamination in the environment. Mining activities, through milling operations coupled with grinding, concentrating ores and disposal of tailings, along with mill wastewater provide obvious sources of heavy metal contamination of the environment. It is, therefore, not surprising that the degree and extent of heavy metal pollution as a result of human activities has been one of the main topics studied in environmental geochemistry. Heavy metals can cause health problems at higher exposures and destroy aquatic organism when leached into water bodies. Metal contamination in aquatic environment has received huge concern due to their toxicity, abundance and persistence in the environmental and subsequent accumulation in the aquatic habitats. (Boamponsem *et al.,* 2010).

Gold Deposits in Nigeria

Gold in Nigeria is found in alluvial and eluvia placers and primary veins from several parts of super crustal (schist) belts in the northwest and southwest of Nigeria. The most important occurrences are found in Zamfara, Kaduna, Niger, Kebbi, Kogi and Osun states, all associated with the schist belts of northwest and southwest Nigeria. There are also a number of smaller occurrences beyond these major states (Baba *et al.*, 2011).

Elements Associated with Gold

Gold occurs in arsenian pyrite and is commonly associated with other elements such as Cu, Sb, Ni, Se, Hg, Tl, Ti, Zn, Ag, Co, Pb, and W (Olivo *et al.*, 2009). In the cyanidation method of gold processing, pure gold dissolves slowly in cyanide solution than gold containing small quantities of other metals (Jeffrey and Ritchie, 2001).Trace amount of lead, mercury thallium or bismuth reduce the passivation effect on gold surfaces thereby accelerating gold leaching rate (Marsden and House, 2006).

These metals can also have a detrimental effect on the adsorption of gold on to activated carbon and its subsequent elution by competing for adsorption sites and by consuming elution reagents.

The long history of gold mining at Obuasi, Ghana, has generated huge environmental legacy issues in the area. The most significant of the environmental challenges is that of the trace elements contamination. Other studies have made various findings regarding presence of trace elements in soils water sources and foodstuffs linked to the considerable level of naturally occurring arsenic bearing gold ores during gold extraction (Ahmad and Carboo, 2000; Kumi-Boateng, 2007).

Regarding the divalent metals (Zn, Cu and Pb), it was presumed that their relative abundance in the soils with respect to contamination in gold mining areas,

might be partly dependent on potential intrusions of the elements in to soil and their rate of mobility in the soil. Generally the selectivity of clay minerals and hydrous oxide absorbent surfaces in soil and sediments for divalent metals follow the order Pb>Cu>Zn. In this respect the rate of mobility of these three metals in such soils would increase in the reverse order (Zn > Cu > Pb) which is consistent with the findings in the study area.

Overall, the decreasing trend of element concentration in the Obuasi gold mining soil i.e. As > Zn > Cu > Pb is contrary to observations by Antwi-Agyei *et al.,* (2005) in which among other metals As Zn, Cu, and Pb were reported to decrease in soils around a gold base metal deposit in Ukraine in the order Pb > Zn > As > Cu at a distance of 400 – 700 m from the dump. This disagreement with the study at Obuasi might be attributed to differences in soil properties considering the two different locations involved.

In a related studies at eastern Mongolian, Altay, Aichler *et al.*,(2008) indicated new occurrences and indices of Au, Ag, Cu, Zn, Pb and (Ba) – As – Sb – Hg Mineralization were discovered in some of the prospective gold mine areas. Low gold contents accompany, also the As-Sb-Hg-(Ba) vain disseminated mineralization confined to acid volcanic rocks of the Permian Khar Argalantyn Fm. The Ag-rich base metal quartz veins in silicified marbles of the NeoProterozoic – Palaeozoic Maykhan Tsakhir Fm. In the Gobi Altay terrain, the occurrences and showing of slightly auriferous base metal (C, As, Zn, Pb, Ag) veins were ascertained in siliceous chlorite-sericite schist with layers of queenschists and quartzite's of the Carbon Tugrug Fm.

Similarly, according to Adetoyinbo *et al.,* (2011) the concentration of major element in the soil samples collected from five locations in the mining areas of Itagunmodi Osun state Nigeria and three locations outside the mining areas shows that the concentrations of the elements is higher within the mining site than outside mining

site. The concentration of heavy metals and other elements in antisanal Gold mining soils from Zamfara and Kebbi State were determined using XRF Technique by Girigisu *et al.*, (2012). Four out of the ten elements (Pb. Si, Rb and Fe) showed relatively high concentration.

The effect of gold mine activities on surface water quality (rivers) have been investigated by a number of researchers in many parts of the world; they generally acknowledge water quality deterioration due to the discharge of partially or untreated mine effluents, and/or accidental discharges, which can change the chemistry of water (McKinnon, 2002 ; Kaye, 2005).

The Central Rand goldfield of the Witwatersrand Basin, South Africa has been one of the most important gold mining areas in the world. It is, however, replete with gold mine tailings which have contributed significantly to water pollution as a result of acid mine drainage. Water quality is affected mainly by mine tailings and spillages, especially from active slimes dams, reprocessed tailings, as well as from footprints left behind after reprocessing. Water pollution studies undertaken over the past decade have established good baseline data on the state of the water environment of the Central Rand. Water quality information from the Rand Water Board, Water Research Commission and Crown Gold Recovery shows that the drainage systems on the East and Central Rand have been affected by AMD and have high salt loads (Mphephu, 2004).

Gold inspite of its ornamental value have been reported to have some health risk associated with gold miners. Gold miners were the first recorded victims of dengue fever in 1885 in tropical north-eastern Queensland. Other diseases such as silicosis (massive fibrosis of the lungs marked by shortness of breath and caused by inhalation of silica dusts, usually SiO_2) and phthisis (a historical term used to describe a wasting

condition, possibly pulmonary tuberculosis (PTB) have also been reported (Russell *et al*., 1996).

2.8.2 Cadmium

Cadmium is released into the environment through natural activities such as volcanic eruptions, weathering, river transport and some human activities such as mining, smelting, tobacco smoking, incineration of municipal waste, and manufacture of fertilizers (Chakraborty *et al.*, 2013).

Cadmium distributed in the environment will remain in soils and sediments for several decades. Plants gradually take up these metals which get accumulated in them and concentrate along the food chain, ultimately reaching the human body. In the US, more than 500,000 workers get exposed to toxic cadmium each year (Mutlu *et al.*, 2012). Researches have shown that in China the total area polluted by cadmium is more than 11,000 hectares and its annual amount of industrial waste of cadmium discharged into the environment is assessed to be more than 680 tons. In Japan and China, environmental cadmium exposure is comparatively higher than in any other country (Han *et al.*, 2009).

This metal was first used in World War I as a substitute for tin and in paint industries as a pigment. It is also being used in rechargeable batteries and about three-fourths of cadmium is used in alkaline batteries as an electrode component and the remaining part is used in coatings. It is used for special alloys production and also present in tobacco smoke, pigments and plating and as a plastic stabilizer (Martin and Griswold, 2009).

Humans may get exposed to this metal primarily by inhalation and ingestion and can suffer from acute and chronic intoxications. Once this metal gets absorbed by

humans, it will accumulate inside the body throughout life (Bernard, 2008). Cadmium is the seventh most toxic heavy metal as per Agency for Toxic Substances and Disease Registry (ATSDR, 2000) ranking. It is highly toxic to the kidney and it accumulates in the proximal tubular cells in higher concentrations. Cadmium concentration increases 3,000 fold when it binds to cystein-rich protein such as metallothionein. In the liver, the cystein-metallothionein complex causes hepatotoxicity and then it circulates to the kidney and gets accumulated in the renal tissue causing nephrotoxicity (ATSDR, 2000).

Cadmium has the capability to bind with cystein, glutamate, histidine and aspartate ligands and can lead to the deficiency of iron Cadmium can cause bone mineralization either through bone damage or by renal dysfunction. Studies on humans and animals have revealed that osteoporosis (skeletal damage) is a critical effect of cadmium exposure along with disturbances in cadmium metabolism, formation of renal stones and hypercalciuria. Inhaling higher levels of cadmium can cause severe damage to the lungs. If cadmium is ingested in higher amounts, it can lead to stomach irritation and result in vomiting and diarrhea. On very long exposure time at lower concentrations, it can become deposited in the kidney and finally lead to kidney disease, fragile bones and lung damage (Chakraborty *et al.*, 2013). Cadmium and zinc have the same oxidation states and hence cadmium can replace zinc present in metallothionein, thereby inhibiting it from acting as a free radical scavenger within the cell (Castagnetto *et al.*, 2002).

Cadmium interacts with essential nutrients through which it causes its toxic effects. Experimental analysis in animals has shown that 50% of cadmium gets absorbed in the lungs and less in the gastrointestinal tract. Premature birth and reduced birth weights are the issues that arise if cadmium exposure is high during human pregnancy (Henson and Chedrese, 2004).

Cadmium is predominantly found in fruits and vegetables due to its high rate of soil-to plant transfer. It is a highly toxic nonessential heavy metal that is well recognized for its adverse effect on the enzymatic systems of cells oxidative stress and for inducing nutritional deficiency in plants (Irfan *et al.*, 2013).

Cadmium is a toxic metal and hence utmost care must be taken to avoid its exposure to man and his environment because of its attendant health implications. Once accumulated in the kidney, high blood pressure, and kidney disease may occurred which may be difficult to remove by excretion. Cadmium directly damages nerve cells and also inhibits the release of acetylcholine and activates cholinesterase enzyme, resulting in a tendency for hyperactivity of the nervous system (Alloway, 1990).

2.8.3 Copper

Copper is reddish, with a bright metallic lustre in its metal state and is associated with soil silicate clays and soil organic matter. Copper in the soil can be categorised in terms of six pools: Cu adsorbed by hydrous oxides of Mn, Fe and Al; soluble ions; inorganic and organic complexes in soil solution; exchangeable Cu; stable organic complexes in humus and Cu adsorbed on the clay humus — colloidal complex (Adediran and Kramer,1987; Anderson, 1997).

Copper is used to produce wire and brass alloys and it is said to be the third most used metal in the world (VCI, 2011). It is an essential micronutrient required in the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. In plants, copper is especially important in seed production, disease resistance, and regulation of water. Copper is indeed essential, but in high doses it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth. While copper's interaction with the environment is complex,

research shows that most copper introduced into the environment becomes stable and results in a form which does not pose a risk to the environment. In fact, unlike some man-made materials, copper is not magnified in the body or bioaccumulated in the food chain. In soil, copper forms organic complexes implying that only a small fraction of copper will be found in solution as ionic copper, Cu(II) (Martínez and Motto, 2000).

A deficiency of copper, on the other hand, inhibits growth in mammals resulting in cardiovascular lesions and myelination of the spinal cord, and defects in pigmentation, bone and connective tissue formation, and reproduction (Bradl, 2004).

In general the toxic forms of copper are free ions and some inorganic complexes, whereas the organic and sorbed complex forms are harmless. Different factors decrease the toxicity of this heavy metal. For example, complexation and humic acid can improve the availability of Cu (II) to plants and other microorganisms and at the same time reduce the toxic effects of free Cu (II) (Stevenson and Chen, 1991; Bjuhr, 2007).

Copper is a trace element essential for healthy functioning of soil biological systems. However at elevated concentrations copper can be a potential toxicant. Consequently, an understanding of copper availability and toxicity to soil biota is essential for effective ecological assessment of metal impacts in soil. High levels of copper may cause metal fumes fever with flue like symptoms, hair and skin discoloration, dermatitis, irritation of the upper respiratory tract, metallic taste in the mouth and nausea (Manderova *et al.,* 2011; Lenntech, 2016). Copper accumulates in liver and brain copper toxicity is fundamental cause of Wilson's disease (Gebrekidan and Samuel, 2011). WHO has recommended the lower limit of acceptable range of oral intake of copper as 20 µg /kg body weight day^{-1}.

2.8.4 Iron

Iron is the most abundant transition metal in the earth's crust and occupies the 26th elemental position in the periodic table (USEPA, 1993). The source of iron in surface water is anthropogenic and is related to mining activities. The concentration of dissolved iron in the deep ocean is normally 0.6 nM or 33.5 × 10–9 mg/dm^3. In freshwater the concentration is very low with a detection level of 5 mg/dm^3 – ICP, whereas in groundwater the concentration of dissolved iron is very high with 20 mg/dm^3 (USEPA, 1993). In countries like Lithuania, many people have been exposed to elevated levels of iron through drinking water, as the collected groundwater exceeded the permissible limit set by the European Union Directive 98/83/EC on the quality of drinking water (Grazuleviciene *et al*., 2009). Iron is a most crucial element for growth and survival of almost all living organisms (Valko *et al*., 2005). It is one of the vital components of organisms like algae and of enzymes such as cytochromes and catalase, as well as of oxygen transporting proteins, such as hemoglobin and myoglobin (Vuori, 1995). Iron is an attractive transition metal for various biological redox processes due to its inter-conversion between ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions (Phippen *et al*., 2008).

Biologically it is the most important nutrient for most living creatures as it is the cofactor for many vital proteins and enzymes. Iron mediated reactions support most of the aerobic organisms in their respiration process. If it is not shielded properly, it can catalyze the reactions involving the formation of radicals which can damage biomolecules, cells, tissues and the whole organism (Albretsen, 2006). Iron poisoning has always been a topic of interest mainly to pediatricians. Children are highly susceptible to iron toxicity as they are exposed to a maximum of iron containing products (Albretsen, 2006). Iron toxicosis occurs in four stages. The first stage which occurs after 6 hrs of iron overdose is marked by gastrointestinal effects such as gastro

intestinal bleeding, vomiting and diarrhea (Osweiler *et al*., 1985). The second stage progresses within 6 to 24 hrs of overdose and it is considered as the latent period, a period of apparent medical recovery.

The third stage occurs between 12 to 96 hrs after the onset of certain clinical symptoms. This stage is characterized by shocks, hypotension, lethargy, tachycardia, hepatic necrosis, metabolic acidosis and sometimes death (Hillman, 2001). The fourth stage occurs within 2–6 weeks of iron overdose. This stage is marked by the formation of gastrointestinal ulcerations and development of strictures. Excess iron uptake is a serious problem in developed and meat eating countries and it increases the risk of cancer. Workers who are highly exposed to asbestos that contains almost 30% of iron are at high risk of asbestosis, which is the second most important cause for lung cancer (Nelson, 1992). It is said that asbestos associated cancer is linked to free radicals. Loose intracellular iron can also promote DNA damage. Iron can initiate cancer mainly by the process of oxidation of DNA molecules (Bhasin *et al*., 2002). Iron salts such as iron sulfate, iron sulfate monohydrate and iron sulfate heptahydrate are of low acute toxicity when exposure is through oral, dermal and inhalation routes and hence they have been placed in toxicity category 3.

Furthermore, iron salts are considered to be safe by the Food and Drug Administration and their toxic effects are very much negligible. Formation of free radicals is the outcome of iron toxicity (Ryan and Aust, 1992). During normal and pathological cell processing, byproducts such as superoxide and hydrogen peroxide are formed, which are considered to be free radicals (Fine, 2000). These free radicals are actually neutralized by enzymes such as superoxide dismutase, catalase and glutathione peroxidase but the superoxide molecule has the ability to release iron from ferritin and that free iron reacts with more and more of superoxide and hydrogen peroxide forming

highly toxic free radicals such as hydroxyl radical (McCord, 1998). Hydroxyl radicals are dangerous as they can inactivate certain enzymes, initiate lipid peroxidation, depolymerize polysaccharides and can cause DNA strand breaks. This can sometimes result in cell death (Hershko *et al.,* 1998).

Iron is not of toxicological significant. Evidence shows that in addition to its importance as an essential nutrient necessary for oxygen metabolism and mitochondrial function, iron exhibits a functional maturation of the skin. If the level of iron becomes toxic it can lead to multisystem organ failure, coma, convulsions and even death (Manoguerra *et al.,* 2005; Chang and Rangan, 2011).

2.8.5 Manganese

Manganese is a pinkish-grey, chemically active element. It is a hard metal and is very brittle.It is hard to melt, but easily oxidized. Manganese is reactive when pure, and as a powder it will burn in oxygen, it reacts with water (it rusts like iron) and dissolves in dilute acids (Ndinannyi, 2013).

Manganese is essential to iron and steel production. Manganese dioxide is also used as a catalyst. Manganese is used to decolorize glass and make violet coloured glass. Potassium permanganate is a potent oxidizer and used as a disinfectant. Other compounds that find applications are manganese oxide (MnO) and manganese carbonate ($MnCO_3$), the first goes into fertilizers and ceramics while the second is the starting material for making other manganese compounds (Birge *et al.,* 1977).

The major sources of man-made environmental Mn pollution arise from mining operations (Kharytonov *et al.,* 2003) and the manufacture of steel (Karnaukh and Lugovskoy, 2008; Zberovsky and Sobko, 2008). According to World Health Organization data, the daily intake of airborne Mn by the general population in areas

without Mn-emitting industries is lower than 2 µg/day. In areas with major foundry facilities, intake may rise to 4–6 µg/day, and in areas associated with ferro- or silico-manganese industries, it may be as high as 10 µg/day, with peak values exceeding 200 µg/day (IPCS, 1981).

Chronic Mn poisoning is a recognized health hazard associated with the mining and processing of Mn ores (Chashchin *et al*., 2009;Fang *et al*., 2009). Although the largest source of human exposure to Mn is via water and food, additional exposure may occur through air polluted with Mn emissions (IPCS, 1981). Mn poisoning has been linked to impaired motor skills, cognitive disorders, and metabolic processes (Solís-Vivanco et al., 2009).

Manganese is one of the most abundant metals in soils, where it occurs as oxides and hydroxides, and it cycles through its various oxidation states. Manganese occurs principally as pyrolusite (MnO_2), and to a lesser extent as rhodochrosite ($MnCO_3$). The main mining areas for manganese ores are South Africa, Russia, Ukraine, Georgia, Gabon and Australia (Briggs and Ficke, 1978).

This heavy metal is frequently associated with iron deposit and is known to block calcium channels and with chronic intoxication result in central nervous system (CNS) dopamine depletion. This latter condition duplicates almost all the symptomology of Parkinson's disease (Ndinannyi, 2013).

2.8.6 Lead

Human activities such as mining, manufacturing and fossil fuel burning has resulted in the accumulation of lead and its compounds in the environment. Lead is used for the production of batteries, cosmetics, metal products such as ammunitions, solder and lead based paints, gasoline, toys, lead bullets, plumbing pipes, pewter pitchers and

faucets. Its wide spread use has caused extensive environmental contamination and health problems in many parts of the world (Martin and Griswold, 2009).

In the US, more than 100 to 200,000 tons of lead per year is being released from vehicle exhausts. Some is taken up by plants, fixation to soil and flow into water bodies, hence human exposure of lead in the general population is either due to food or drinking water (Goyer, 1990).

Lead poisoning was considered to be a classic disease and the signs that were seen in children and adults were mainly pertaining to the central nervous system and the gastrointestinal tract (Markowitz, 2000). Lead poisoning can also occur from drinking water. The pipes that carry the water may be made of lead and its compounds which can contaminate the water (Brochin *et al.*, 2008). According to the Environmental Protection Agency (EPA, 2012), lead is considered a carcinogen. Lead has major effects on different parts of the body. Lead distribution in the body initially depends on the blood flow into various tissues and almost 95% of lead is deposited in the form of insoluble phosphate in skeletal bones (Papanikolaou *et al*., 2005).

Toxicity of lead can be either acute or chronic. Acute exposure can cause loss of appetite, headache, hypertension, abdominal pain, renal dysfunction, fatigue, sleeplessness, arthritis, hallucinations and vertigo. Acute exposure mainly occurs in the place of work and in some manufacturing industries which make use of lead. Chronic exposure of lead can result in mental retardation, birth defects, psychosis, autism, allergies, dyslexia, weight loss, hyperactivity, paralysis, muscular weakness,brain damage, kidney damage and may even cause death (Martin and Griswold, 2009). The increase in blood lead concentration can affect a person's IQ (Taylor *et al.*, 2012). Although lead poisoning is preventable yet it still remains a dangerous cause of diseases which can affect most of the organs. The plasma membrane moves into the interstitial

spaces of the brain when the blood brain barrier is exposed to elevated levels of lead concentration, resulting in a condition called edema (Teo *et al.,* 1997). It disrupts the intracellular second messenger systems and alters the functioning of the central nervous system, whose protection is highly important. Environmental and domestic sources of lead ions are the main cause of the disease but with proper precautionary measures it is possible to reduce the risk associated with lead toxicity (Brochin *et al.,* 2008).

Similarly Lead toxicity also disturbs various plant physiological processes and unlike other metals, such as zinc, copper and manganese, it does not have any biological function. A plant with high lead concentration fastens the production of reactive oxygen species (ROS), causing damage to lipid membrane that ultimately leads to damage of chlorophyll and photosynthetic processes and suppresses the overall growth of the plant (Najeeb *et al.,* 2014). Some research revealed that lead is capable of inhibiting the growth of tea plant by reducing biomass and debases the tea quality by changing the quality of its components. Even at low concentrations, lead treatment was found to cause huge instability in ion uptake by plants, which in turn leads to significant metabolic changes in photosynthetic capacity and ultimately in a strong inhibition of plant growth (Yongsheng *et al.,* 2011).

The report of research studies of lead concentrations in samples from Nangodi in Ghana ranged from 0.005 to 0.791 mg/dm^3 with a mean of 0.250 ± 0.008 mg/dm^3, however, samples from Tinga in the same country recorded lead concentrations ranging from 0.001 to 0.227 mg/dm^3 with a mean of 0.031 ± 0.001 mg/dm^3. Samples from Nangodi that recorded the lowest lead concentration were HDWA and DB whilst the highest concentration was recorded from sample DA. Asamoah-Boateng (2009) reported lead concentrations that ranged from 0 to 2.710 mg/dm^{3}from surface waters samples in Newmont Ghana gold mining concession areas. Earlier study in Tinga

reported Pb concentrations that ranged from below detection limits to 0.188 mg/dm^3. Almost all samples from Nangodi exceeded the WHO stipulated limit of 0.010 mg/dm^{3}for drinking water.

However, Tinga samples recorded high values above the WHO permissible limit at various sampling points in the stream. The maximum concentration of Pb in Tinga was recorded in the stream where the processing of the mined minerals was done (GWP: gold washing pool in the stream, and AGWP: after gold washing pool in the stream) and the minimum was recorded in the second borehole (BHT2).

This suggests that runoff from domestic, industrial (such as improper disposal of acid lead batteries and wind-blown dust), and agricultural waste might be the main source of Pb pollution in the Tinga community. The high content of Pb in the stream could be due to weathering and leaching of lead from waste rocks dumps. Lead is one of the most significant toxicants of the heavy metals and the inorganic forms are absorbed through ingestion by food and water, and inhalation (Rajikovic, et al., 2008).

Lead is one of the most significant toxicants of the heavy metals and the inorganic forms are absorbed through ingestion by food and water, and inhalation (Rajikovic, et al., 2008). Lead is a possible human carcinogen and it is also a cumulative poison so that any increase in the lead burden should be avoided. A provisional tolerable daily intake is set as 3.5 μg of lead per kg of body weight for infants. Human health concerns associated with lead intoxication in children include brain damage, behavioral problems, anaemia, liver and kidney damage and hearing loss (Gohar and Mohammadi, 2010; Rajaganapathy *et al*., 2011) whereas in adults poor muscle coordination, nerve damage to the sense organs, increased blood pressure, hearing and vision impairment, reproductive problems and retarded fetal development ((Monisha *et al*., 2014).

2.8.7 Zinc

Zinc occurs naturally in soil (about 70 mg kg^{-1} in crustal rocks) (Davies and Jones, 1988) but zinc concentrations are rising unnaturally, due to anthropogenic additions. Most zinc is added during industrial activities, such as mining, coal, waste combustion and steel processing. Many foodstuffs contain certain concentrations of zinc. Drinking water also contains certain amounts of zinc, which may be higher when it is stored in metal tanks. Industrial sources or toxic waste sites may cause the concentrations of zinc in drinking water to reach levels that can cause health problems. Zinc is the third most used non-ferrous metal after aluminium and copper about 50% of production is used for galvanising steel to protect it from rust. Zinc compounds and dusts are used in cosmetics, plastics, rubber, ointments, sun screen creams, soaps, paints, ink, fertilisers and batteries. Around 30% of zinc used in the western world comes from recycling (Davies and Jones, 1988).

The world's zinc production is still on the rise which means that more zinc ends up in the environment. Water is polluted with zinc, due to the presence of large quantities present in the wastewater of industrial plants. A consequence is that zinc - polluted sludge is continually being deposited by rivers on their banks. Zinc may also increase the acidity of waters. Some fishes can accumulate zinc in their bodies, when they live in zinc -contaminated waterways. When zinc enters the bodies of these fishes, it is able to biomagnify up the food chain (Greany, 2005). Water-soluble zinc that is located in soils can contaminate groundwater. Plants often have a zinc uptake that their systems cannot handle, due to the accumulation of zinc in soils. Finally, zinc can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter (Greany, 2005).

Zn is an essential nutrient needed by the body for growth, development of bones, metabolism and wound-healing (Horn and Morris, 1990). Deficiency of zinc in the diet may lead to adverse health effects such as loss of appetite, decreased sense of taste and smell, lower ability to fight off infections, slow growth , delay in healing of wounds and skin sores. Whereas a short-term illness called metal fume fever can result when high levels of zinc dust or fumes are taken through breathing (Fairweather – Tait, 1988; Jeffery, 1992; Olorundare *et al*., 2011).

2.9 Chemical Speciation

The term 'speciation' in analytical chemistry refers to the separation and quantification of the different oxidation states or chemical forms of particular elements.

Thus, speciation (in Chemistry) of an individual element refers to its occurrence of or distribution among different species of various forms within the soil matrix (Masa *et al.*, 2013). Speciation analytics is the analytical activity of identifying and quantifying one or more chemical species of an element present in a sample. Species (in chemistry) denotes an element in a specific and unique molecular, electronic, or nuclear structure i.e. chemical species. Chemical extraction is employed to assess operationally defined metal fractions, which can be related to chemical species, as well as potentially mobile, bioavailable, or toxic phases of a sample. The mobile fraction is defined as the sum of the amount dissolved in the liquid phase and an amount which can be transferred into the liquid phase.

Speciation allows the determination of the availability and mobility or bioavailability of heavy metals in order to understand their chemical behaviour and fate: therefore useful environmental guideline for potential toxic hazard can be developed (Petit and Rucando, 1999; Jimoh, 2012).

2.9.1 The importance of chemical speciation

The chemical behaviours of any element in the environment depend on the nature of its components. Previously, the determination of total element concentration was considered to be sufficient for clinical and environmental considerations. Although the total concentrations of an elements is still difficult to know, and sometimes essential, the determination of species is necessary to fully understand the biogeochemical and toxicological behaviours of metals. Moroever it has been generally accepted that the ecological effects of metals (e.g. their bioavailability. and ecotoxicology) are related to such mobile fractions rather than the total concentration (Masa *et al.*, 2013).

In order to assess the reactivity of the species or binding form of heavy metals in solids materials various extraction media, electrolytes ($CaCl_2$ or $MgCl_2$), pH buffers of weak acids (ethanoic acid), chelating agents (EDTA or DTPA): reducing agents (NH_2OH), strong acids (HCl, HNO_3, HF) or basic reagents (NaOH and Na_2CO_3) have been widely used (Lund. 1990).

The understanding of the chemical nature of metal compounds in the atmosphere is important for three reasons. First, the toxicity of a metal is dependent upon the chemical forms. Second, environmental pathways in the global-cycles depend on the chemical forms of the respective metal, and third, trace metal compounds have an impact on the atmospheric chemistry which is related to catalytically active species (Masa *et al.*, 2013).

2.9.2 Tessier's sequential extraction scheme

One of the best - known sequential extraction schemes is that of modified Tessier's (Masa *et al.,* 2013). In this scheme heavy metals are distributed into six operationally defined fractions

Water soluble fraction (F1): This fraction contains water soluble metals which are the most mobile of all the heavy metals. They are also the most readily available for plant uptake; water soluble metals are usually extracted by distilled water (Ogunfowokan *et al*., 2013)

Exchangeable fraction (F2): This fraction involves weakly adsorbed metals retained on the solid surface by relatively weak electrostatic interaction. Remobilisation of metals can occur in this fraction due to adsorption desorption reactions and lowering of pH (Ahnstrom and Parker 1999; Narwal *et al.,* 1999). This fraction generally accounted for less than 2% of the total metals present in soils, the exceptions to this microelement, K, Ca, and Mn (Emmerson *et al.,* 2000). Exchangeable fraction is also known as an adsorbed fraction, it can be released by the action of cations such as K, Ca, Mg or (NH_4) displacing metals weakly bond to electrostatistically organic or inorganic sites (Beckett, 1989).

The common reagents used for the extraction of metals in this fraction are $MgCl_2$, sodium acetate (pH 5.4) and acetic acid (Tessier *et al*., 1979). Reagents used for this purpose are electrolytes in aqueous solution, such as salts of strong acids and bases or salts of weak acids and bases at pH 7. Other reagents showing similar properties have seldom been used, such as nitrate salts (to avoid complexation that is too strong or calcium salts (Ca^{2+} being more effective than Mg^{2+} or NH_4^+ in removing exchangeable ions). Results obtained with these reagents give good correlation with plant uptake (Gleyzes *et al*., 2002).

Carbonate bound fraction (F3): This fraction tends to be a major adsorbent for many metals. The most popular reagent use for the extraction of trace metals from carbonates phases in soils and sediments is 1M sodium acetate adjusted to pH 5.0 with acetic acid (Tessier *et al*., 1979).

Carbonate fraction is a loosely bound phase and bound to changes with environmental factors such as pH. The time lag for the complete solubilisation of carbonates depends on some factors such as the type and amount of the carbonate in the sample, particle size of the solid. Extraction of metals from carbonates phases enhances the leaching of metals specifically sorbed to organic and inorganic substrates (Tessier *et al*., 1979).

In general, this fraction is sensitive to pH changes, and metal release is achieved through dissolution of a fraction of the solid material at pH close to 5.0 (Gleyzes *et al*., 2002).

Iron and Manganese oxides fraction (F4): This fraction is referred to as the sink for heavy metals. Different reagents have been used for metal extraction in Fe-Mn oxide phases amongst are sodium dithionate in combination with sodium citrate and sodium bicarbonate in a varying concentration range (Beckett, 1989). Extraction with ascorbic acid / ammonium oxalate reagent offers great merits over others because high purity degree is achieved and does not attack silicates.

However, the most successful reagents for evaluating the total amount of metal ion associated with these minerals contain both a reducing reagent and a liable ligand able to retain released ions in a soluble form, the efficiency of the reagent being determined by its reduction potential and its ability to attack the different crystalline

forms of Fe and Mn oxyhydroxides. Hydroxylamine, oxalic acid and dithionite are the most commonly used reagents (Gleyzes *et al*., 2002**)**.

Organic matter bound fraction (F5): In this fraction metallic pollutant bound to this phase are assumed to stay in the soil for longer periods but may be immobilized by decomposition process (Kennedy *et al*., 1997). Under oxidizing conditions, degradation of organic matter can lead to a release of soluble trace metals bound to this component. The extracts obtained during this step are metals bound to sulphides (Marin *et al.,* 1997).

This organic fraction released in the oxidisable step is considered not to be bioavailable due to the fact that it is thought to be associated with stable high molecular weight humic substances that release small amount of metals in a slow manner (Filgueiras *et al*., 2002). The most commonly used reagents for the extraction of metals in organic phases is hydrogen peroxide with ammonium acetate re-adsorption or precipitation of released metals (Ure *et al.,* 1995). Other reagents such as H_2O_2 / ascorbic acid or HNO_3 + HCl have been used which can dissolve sulphides with enhanced selectivity, but on the other hand, silicates are attacked to some extent (Klock *et al.,* 1986). Oxidation with sodium hypochlorite has also been recommended (Shuman, 1983) but fraction of organically bond metals released showed considerable variability in different soil horizons (Papp *et al*., 1991).

Residual fraction (F6): Residual phase serve as a useful tool in the assessment of the long-term potential risk of heavy metal or toxic metals entering the biosphere. Digestion in strong acid such as nitric acid, hydrochloric acid or mixture such as aqua regia that do not dissolve the silicate matrix have been commonly used to leach out the recalcitrant metals that are bound to the sediment in the residual phase.

Residual phase give an estimate of the maximum amount of elements that are potentially mobilisable with changes in environmental conditions. Primary and secondary minerals containing metals in the crystalline lattice constitute the bulk of this fraction. Its destruction is achieved by digestion with strong acids, such as HF, $HClO_4$, HCl and HNO_3. This amount of associated metals is also associated by some authors as the difference between the total concentration and the sum of the fractions of the metals extracted during the previous steps (Gleyzes *et al.*, 2002). Separation from liquid from solid after each extraction was achieved by centrifugation.

2.10 Types of Mining Techniques

Mining techniques can be divided into two common excavation types:

(i) Surface mining

This type of mining produces about 85% of minerals and 98% of metallic ores. Usually divided into two categories of materials:

a. placer deposits, consisting of valuable minerals contained within river gravels, beach sands, and other unconsolidated materials;
b. Lode deposits, where valuable minerals are found in veins, in layers, or in mineral grains generally distributed throughout a mass of actual rock. This technique involves digging tunnels or shafts into the earth to reach buried ore deposits. Ore, for processing, and waste rock, for disposal, are brought to the surface through the tunnels and shafts.

(ii) Sub-surface mining

This technique is classified by the type of access shafts used, the extraction method or the technique used to reach the mineral deposit. Drift mining utilizes horizontal access tunnels, slope mining uses diagonally sloping access shafts and shaft

mining consists of vertical access shafts. Mining in hard and soft rock formations require different techniques (Bonnie, 2008).

The type of technique that is employed by the miners in the study areas is that of open earth surface mining .This is done by removing (stripping) surface vegetation, dirt and layers of bedrock in order to reach buried ore deposits (Cohen, 2000).

2.11 Soil Type in Niger State

Three major soil types can be found in the State. These include the ferruginous tropical soils, hydromorphic soils and ferrosols. The predominant soil type is the ferruginous tropical soils which are basically derived from the Basement Complex rocks, as well as from old sedimentary rocks. Hydromorphic or waterlogged soils are largely found in the extensive flood plain of the Niger River. The soils are poorly drained and are generally greyish or sometimes whitish in colour due to the high content of silt. Ferosols which developed on sandstone formations can be found within the Niger trough ((UNDP, 2004).

2.12 Mineral Resources in Niger State

The geological location of Niger State endows it with abundant mineral resources. Rich commercial deposits of various types of industrial minerals of high quality are available in the State which can be used for domestic and export purposes ((UNDP, 2004).

A number of minerals are being mined in the state from the following locations as indicated below:-

i. Gold in Chanchaga, Borgu, Katcha and Shiroro local government areas
ii. Manganese and Talc in Rafi local government area
iii. Tantalite in Magama local government area and

iv. Wiformite (Diorite) in Shiroro local government area.

v. Copper, Iron, Felspar & Lead Spread all over the State

vi. Cassertrite, Tantalite and Columbite in Borgu local government area

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 The Areas of Study

The study area is located in Niger State, Nigeria (Fig. 3.1), its landscape consists mostly of wooded savannah and includes the flood plains of the Kaduna River. The State has an area of 29,484 square miles (76,363 square km) and a population of 2,775,526 (UNDP, 2004).

3.2 Sampling Site

Two mining areas (Figures 3.1, 3.2 and 3.3) in Niger State, Nigeria (Asha on 09^0 56’ 29’’N; 06^0 47’ 05’’ E and Saboeregi on $09^0$24’ 08’’ N; $06^0$20’ 13’’E) were selected for the research work because of the on going mining activities.

Asha and Saboeregi mining areas which are in Shiroro and Katcha local Government Areas of Niger state, each has an estimated area of 1071 m x 97 m (0.980 Hectares) and 502 m x 298 m (1.5 Hectares) respectively. Soil control samples were obtained at a distance of 5km away from mining site from lands where mining activities were not going on.

3.2.1 Sample collection and treatment

Each mining site was divided into four (quadrants).The soil sampling spots in each quadrant were cleared of debris before sample collection. At each quadrant five samples were randomly collected to give a total of twenty (with spacing of 6 m apart) from 0-15cm depth of top soil with scooping stainless auger. The soil samples were collected in the months of September 2013 for the rainy season and February 2014 for the dry season.The soil samples were mixed together per quadrant and analyzed as compositesamples.

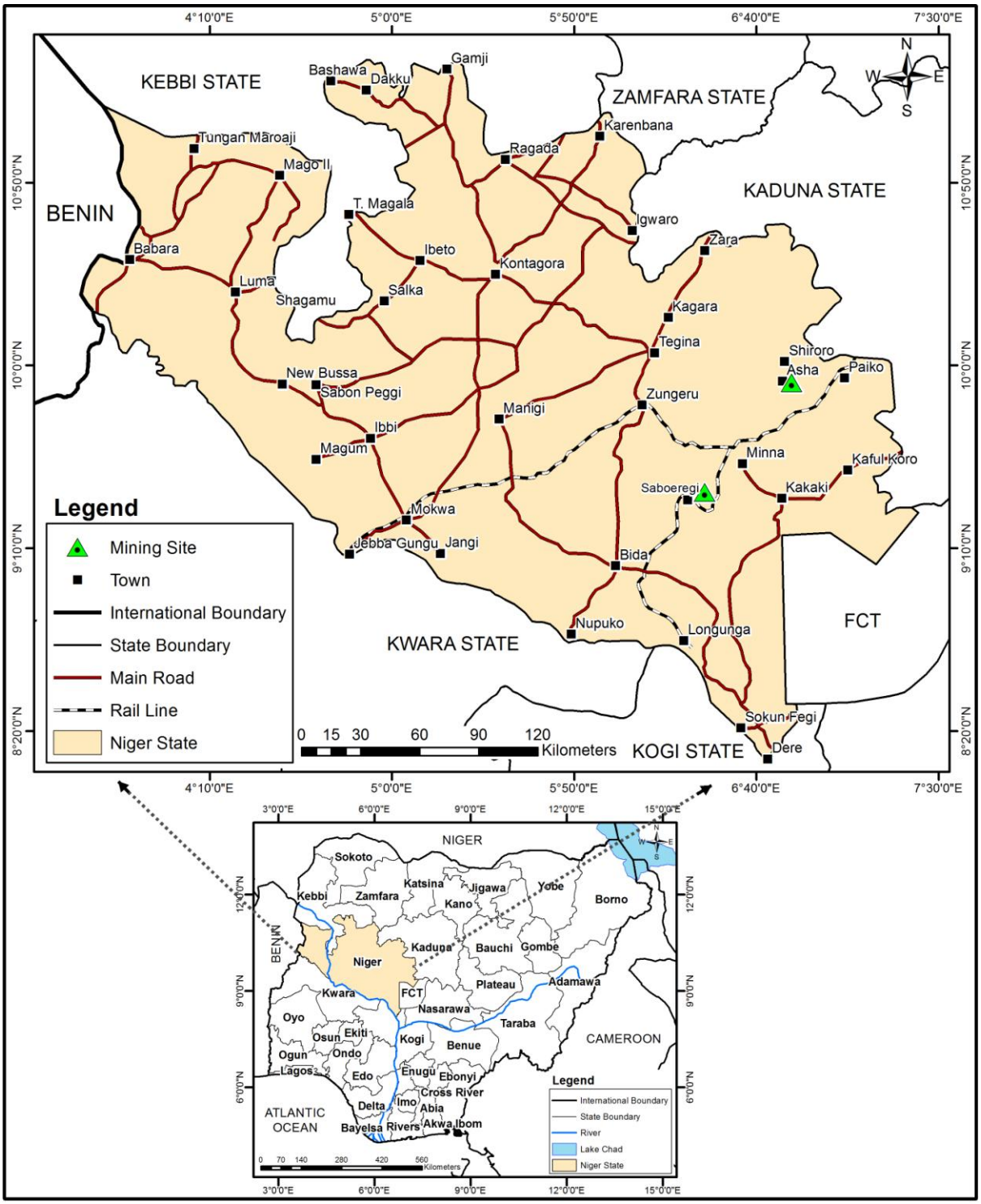


Figure3.1: MapofNigerStateshowingAshaandSaboeregimininingsites

Source: Adapted and modified from the administrative map of Niger State, 2016.

The *Sorghumbicolor* grain sampleswere collected from each quadrant, using a clean stainless steel pair of scissor and placed in polythene bags (Okonkwo and Marbe, 2004), in the month of December 2013 during the harvest period from the cultivated farm lands where soil samples were previously collected. The choice of *Sorghumbicolor*grains was based on its widespread availability throughout the study area.

Soil and *Sorghumbicolor* grains samples were also collected at a distance of 5 km away from the mining sites to serve as control. Soil and the *Sorghumbicolor* grains samples were placed in polythene bags and taken to the laboratory.

Soil and the *Sorghumbicolor* grains samples were air dried for 14 days, pulverized in a mortar, and sieved through 2 mm stainless steel sieves to obtain powdered samples which were stored in polythene bags ready for acid digestion and analysis (Bamgbose *et al*., 2000).

Water samples were obtained from two rivers Tangale (Fig. 3.2) and Gbako (Fig. 3.3) located within the two study mining areas. River Tangale is a tributary of River Kaduna. On the other hand River Gbako took its source from River Chanchaga and drained into River Niger.The water samples were collected between 9 am and 12.00 noon using plastic containers (2 dm^3) from each sampling points in the months of September 2013 for the rainy season and February 2014 for the dry season. The water samples were collected from seven points at a distance of 100 m from one point to another along each river. Also water samples were collected 1km upstream before the point of the mining operations to serve as control. Each water sample was divided into two; one portion was acidified with 2 cm^3 concentrated nitric acid to preserve it for metal analysis while the other portion was used for physicochemical analysis.

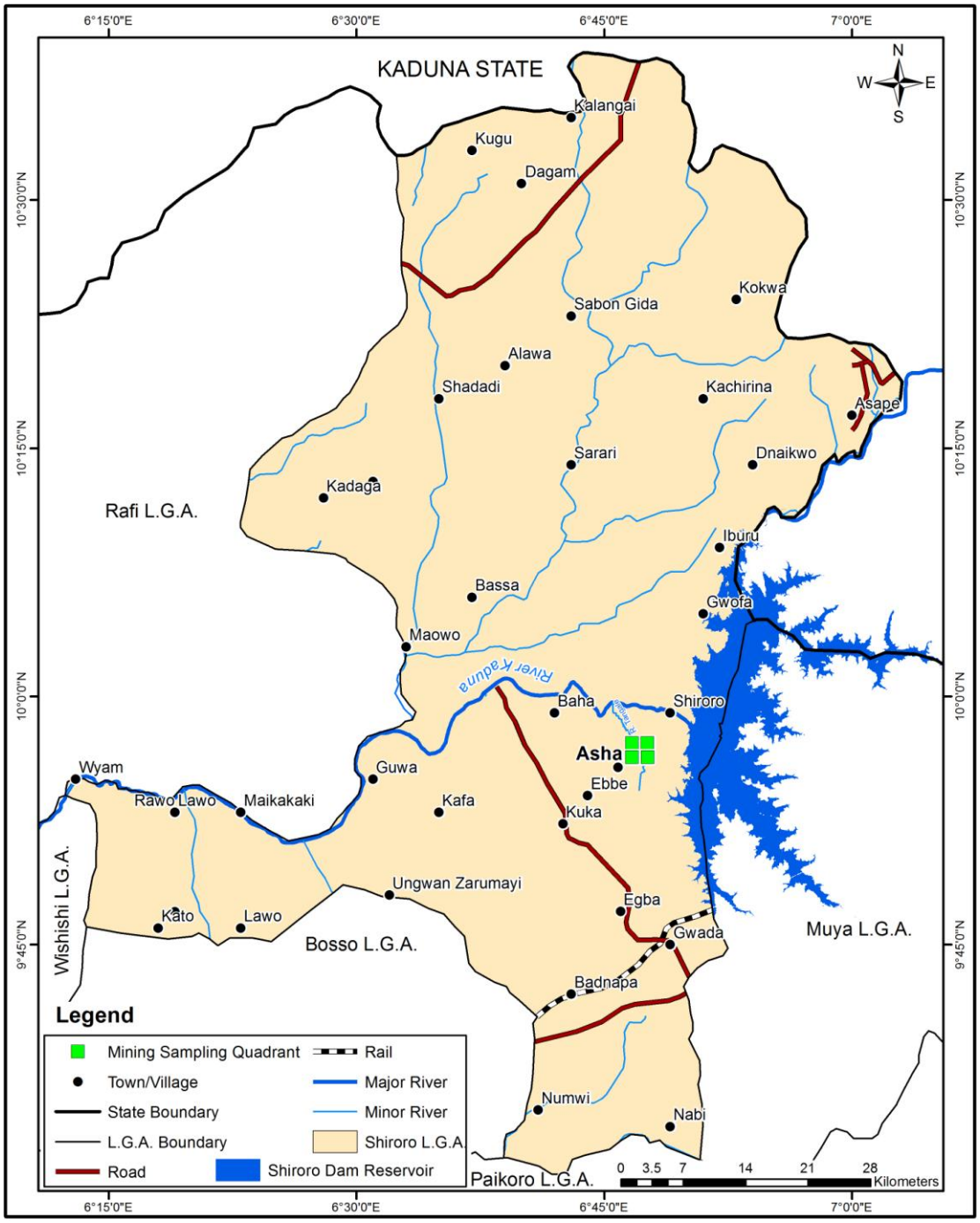
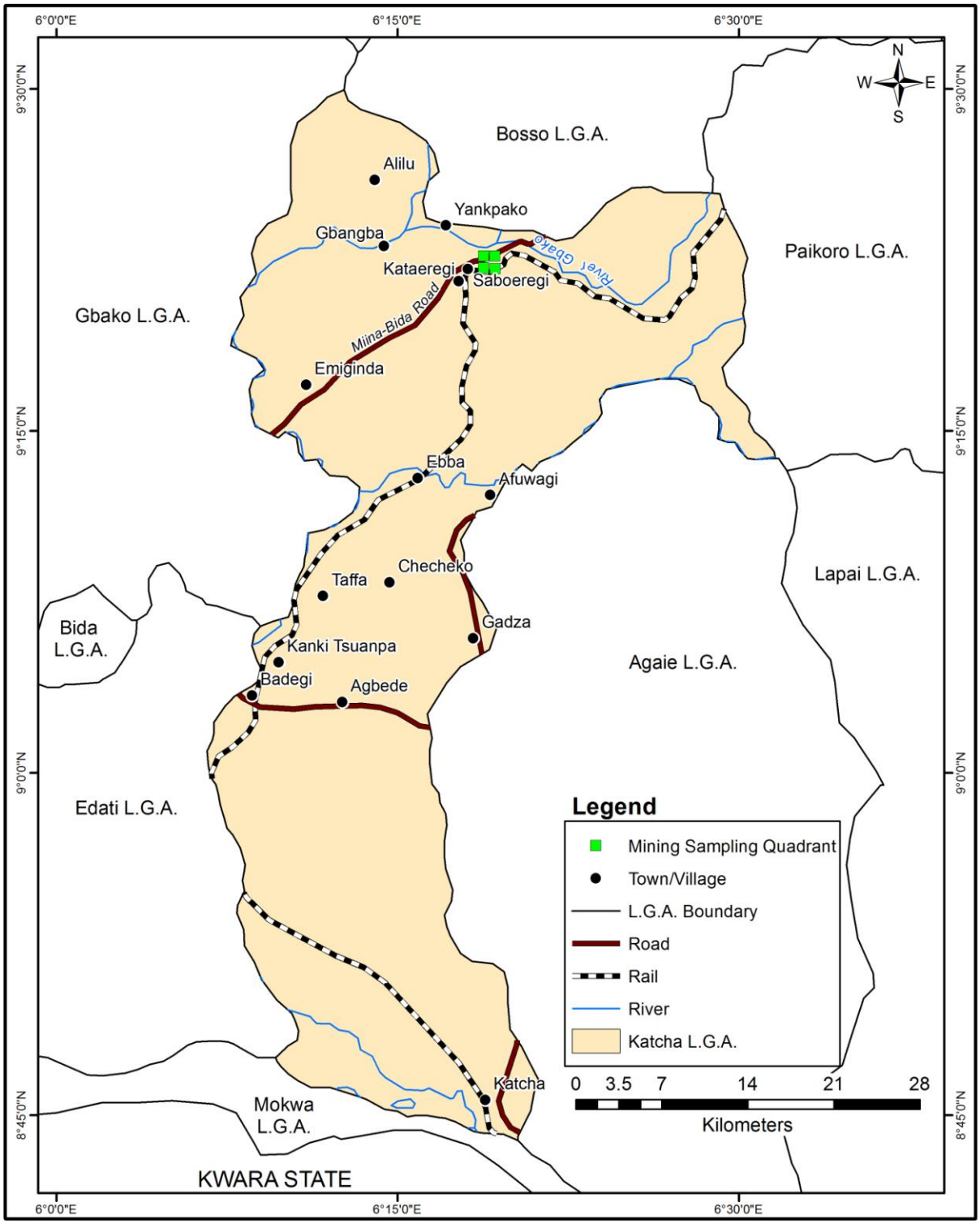


Figure 3.2: Map of a Part of Shiroro LGA showing Asha mining site

Source: Adapted and modified from the administrative map of Niger State, 2016.


6°0'0"E
6°15'0"E
6°30'0"E
9°30'0"N
9°15'0"N
9°0'0"N
8°45'0"N
N
W
E
S
Bosso L.G.A.
Alilu
Yankpako
Gbangba
Kataeregi
Saboeregi
River Gbako
Paikoro L.G.A.
Gbako L.G.A.
Miina-Bida Road
Emiginda
Ebba
Afuwagi
Taffa
Checheko
Lapai L.G.A.
Bida L.G.A.
Gadza
Kanki Tsuanpa
Agaie L.G.A.
Badegi
Agbede
Edati L.G.A.
Legend
Mining Sampling Quadrant
Town/Village
L.G.A. Boundary
Road
Rail
River
Katcha L.G.A.
Katcha
0 3.5 7 14 21 28
Kilometers
Mokwa L.G.A.
KWARA STATE

3.2.2 Chemicals and reagents

The chemicals and reagents used were of analytical grade, (BDH) and were used without further purification.

3.2.3 Determination of soil pH (Hendershot *et al*., 1993)

The pH of soil samples was measured using Grison MicropH 2000, pH meter. A portion (10 g) of 2 mm sieved air-dried soil samples was weighed into plastic containers and 20 cm^3 of distilled deionized water was added. The mixtures were stirred several times for 30 minutes. The soil suspensions were then allowed to stand for 30 minutes undisturbed. The electrode of the pH meter was then inserted into the settled suspension and the pH of soil measured. The pH meter was calibrated with standard buffers of pH solutions 4, 7 and 9 before use. The pH meter was rinsed with deionized distilled water for each soil sample in order to obtain the accurate result that is required.

3.2.4 Determination of particle size distribution (Agbenin, 1995)

Particle size distribution was determined by pulverizing 50g of the soil placed in a tall, slender jar (35cm height and 6cm diameter) to about a one –quarter full of soil. De-ionized water was added until the jar was three-quarter full. A teaspoon of powdered, non-foaming dishwasher detergent was added. The jar was shaken for 15 minutes to break the soil aggregates and allow the soil to settle according to particle sizes. The jar was kept undisturbed for three days. The soil particles that settled after 1 minute according to its size were marked on the jar depth of the sand. After 2 hours the level was marked on the jar the depth of the silt. After 3 days the level of clay was marked on the jar. The results were calculated by using equations 3.1 – 3.3.

$$\% \text{ Sand} = \frac{\text{Thickness of Sand}}{\text{Total Thickness}} \times 100 \qquad 3.1$$

$$\% \text{ Clay} = \frac{\text{Thickness of Clay}}{\text{Total Thickness}} \times 100 \qquad 3.2$$

$$\% \text{ Silt} = \frac{\text{Thickness of Silt}}{\text{Total Thickness}} \times 100 \qquad 3.3$$

3.2.5 Determination of organic matter in soil sample

(Dichromate Oxidation Method by Walkley-Black, 1937)

i. **Potassium dichromate (0.2 mol dm^{-3}):** $K_2Cr_2O_7$solution was prepared by dissolving 49.04 g of the compound in distilled water and made up to 1dm^3 in a standard volumetric flask.

ii. **Ferrous ammonium sulphate (0.4 mol dm^{-3}):**Ferrous ammonium sulphate (156.9 g) was dissolved in distilled water, 20 cm^3 conc $H_2SO_4$was added and shaken, then made up to 1 dm^3 with distilled water in a volumetric flask.

iii. **Sulphuric acid reagent:**Thereagent was prepared by adding 15 g of Ag_2SO_4 to 1 dm^3 conc.H_2SO_4.

iv. **Conc.Phosphoric acid (85 %):** This solution was prepared by adding 85 $cm^3$of phosphoric acidto 15 cm^3distilled water.

v. **Ferroin indicator: Phenanthroline ferrous sulphate (ferroin) indicator solution:** 1, 10 – (ortho)-phenanthroline (1.48 g) and $FeSO_4.7H_2O$ (0.70 g) were dissolved in 100 cm^3 distilled water.

Soil sample (1.0 g) was weighed into 250 cm^3 conical flask. Then 10 cm^3 of 0.2 $moldm^{-3}$ $K_2Cr_2O_7$ was added and the flask swirled gently to disperse the soil in solution. Concentrated H_2SO_4 (20 cm^3) was added quickly and then mixed thoroughly. The mixture was allowed to cool for 30 minutes after which 200 cm^3 of distilled water was added, followed by 10 cm^3 concentrated phosphoric acid and 2-3 drops of ferroin indicator. The solution was titrated against 0.4 $moldm^{-3}$ ferrous sulphate solution. A colour change from bluish green to brilliant green indicated the end point.

A blank titration was carried out using deionized water without the soil sample. The results for the organic matter were calculated using equation 3.4

$$\% \text{ OM} = \frac{10\,(B - S)}{ZB} \times \frac{12}{4000} \times \frac{1.72}{0.77} \times \frac{100}{1} \qquad 3.4$$

where B = titre value for blank, S = titre value for sample, Z = weight of soil sample used,1.72 = factor for organic matter from carbon, 0.77= Walkley recovery factor,

$\frac{12}{4000}$ = milliequivalent weight of carbon and 10 = conversion factor for units

Therefore:

$$\% \text{ OM} = \frac{(B - S)}{ZB} \times 6.7 \qquad 3.5$$

3.2.6 Determination of cation exchange capacity (CEC)

(Ammonium Acetate Saturation Method, Chapman, 1965)

Ammonium acetate (1moldm^{-3}): CH_3COONH_4 (77.08 g)was dissolved in distilled water and the pH was adjusted to 7.0 with NH_4OH and volume made up to 1 dm^3 in a volumetric flask.

i. **Ammonium chloride (1moldm^{-3}):** AR NH_4Cl (53.5 g) was dissolved in distilled water and adjusted to pH 7.0 with NH_4OH then made up to 1 dm^3 in a volumetric flask.

ii. **Ammonium chloride (0.2 moldm^{-3}):**NH_4Cl(1 mol dm^{-3},100 cm^3) was taken and made up to 500 cm^3 with distilled water in a volumetric flask.

iii. **Ammonium oxalate (10 %):** $(NH_4)_2C_2O_4.H_2O$ (10 g) was dissolved in distilled water and made up to 100 cm^3 in a volumetric flask.

iv. **Silver nitrate (0.1 moldm^{-3}):** $AgNO_3$(17.0 g) was dissolved in distilled water and made up to 1 dm^3 in a volumetric flask.

v. **Boric acid (2 %,w/v):** H_3BO_3 (2 g) was dissolved in distilled water and made up

to 100 cm^3 in a volumetric flask.

vi. **Sodium hydroxide (1 $moldm^{-3}$):** NaOH (40 g) was dissolved in distilled water and made up to 1 dm^3 in a volumetric flask.

vii. **Bromocresol green - methyl red mixed indicator:** Bromocresol green (0.099 g) and 0.066 g of methyl red were dissolved in 100 cm^3 of ethanol (99 %).

viii. **Standard H_2SO_4 solution (0.01 $moldm^{-3}$):** Concentrated H_2SO_4 (98 %, sp. gr 1.84,0.54 cm^3)was measured into 1 dm^3 volumetric flask containing some distilled water. After thorough shaking, the solution was made up to the mark with distilled water.

Soil sample (10 g) was weighed into a 500 cm^3 Erlenmeyer flask and 40 cm^3 of 1 $moldm^{-3}$ CH_3COONH_4 (pH 7.0) was added. The flask was shaken thoroughly and allowed to stand overnight. The soil was filtered under light suction using Buchner funnel with Whatman No. 42 filter paper. The soil was leached with more CH_3COONH_4 until test for calcium was negative in the filtrate. The calcium was tested by adding a few drops of 1 $moldm^{-3}$ NH_4Cl, 10 % $(NH_4)_2C_2O_4.H_2O$ and dilute NH_4OH to 10 cm^3 of the leachate in a test-tube, and heated to near boiling point. White precipitate indicated the presence of Ca.

The soil was leached four more times with 25 cm^3 of 1 $moldm^{-3}$ NH_4Cl and once with 25 cm^3 0.25 $moldm^{-3}$ NH_4Cl. Then 200 cm^3 of 99 % ethanol was used to wash out the electrolyte. The leachate was tested for chloride using 0.1 $moldm^{-3}$ $AgNO_3$ and when it was negligible, the soil was allowed to drain thoroughly.

The NH_4Cl leachate was transferred into 500 cm^3 distillation flask and 10 cm^3 of 1 $moldm^{-3}$ NaOH was added, and then distilled. The distillate (60 cm^3) was collected into 50 cm^3 of 2 % Boric acid solution in a 250 cm^3 Erlenmeyer flask and 10 drops of bromocresol green - methyl red indicator were added and then titrated with standard

0.01 moldm^{-3} H_2SO_4. The colour changed from bluish green through bluish purple to pink.

A blank distillation was carried out, without the soil extracts. Solution of 1 moldm^{-3} NH_4Cl (100 cm^3) was measured into a 500 cm^3 distillation flask containing 250 cm^3 distilled water, and 10 cm^3 of 1 moldm^{-3} NaOH was added then distilled. The distillate (60 cm^3) was collected into 50 cm^3 of 2 % Boric acid solution in a 250 cm^3 Erienmeyer flask and 10 drops of bromocresol green-methyl red indicator were added and then titrated with standard 0.01 moldm^{-3} H_2SO_4. The CEC of the samples were calculated using equation 3.6

$$\textbf{CEC (meq/100g)} = \frac{(T - B) \times C \times 100}{W} \qquad 3.6$$

whereT = the value for sample, B = blank, C = Concentration of acid used (moldm^{-3}) and W = Weight of soil sample used.

3.2.7 Determination of phosphate concentration in soil (Stannous chloride method) (APHA-AWWA-WPCF, 1985)

i. **Ammonium molybdate (0.13 moldm^{-3}):** $(NH_4)_6Mo_7O_{24}.4H_2O$ (25g) was dissolved in some distilled water in a 250 cm^3 volumetric flask and then made up to the mark.

ii. **Sulphuric acid solution (12.8 mol dm^{-3})**: Conc. H_2SO_4 (98 %, sp. gr. 1.84, 280 cm^3) was added carefully to 400 cm^3 distilled water and allowed to cool.

iii. **Molybdate Reagent:** The solutions prepared in (i) and (ii) abovewere mixed together in 1 dm^3 volumetric flask and then made up to the mark.

iv. **Stannous chloride reagent**: $SnCl_2.2H_2O$ (2.5 g) was dissolved in 100 cm^3 glycerol. The mixture was heated on water bath and stirred with glass rod to hasten dissolution.

v. **Standard phosphate Stock solution (100 mg/dm^3):** KH_2PO_4 (0.438 g) was

dissolved in distilled water and the solution was made up to 1 dm^3.

vi. **Working Phosphate standard solution (5 mg/dm^3):** The stock solution(5 cm^3) was taken into a 100 cm^3 volumetric flask and made up to the mark with distilled water.

Standard phosphorus solutions of 0 cm^3, 0.5 cm^3, 1.0 cm^3, 2.0 cm^3, 3.0 cm^3, 4.0 cm^3 and 5.0 cm^3 were pipetted into separate 50 cm^3 volumetric flasks and made up to the mark with distilled water. These solutions with concentrations of 0, 0.1, 0.2, 0.4, 0.6, 0.8and 1.00 mg/dm^3 respectively were taken in separate test-tubes thereafter, 4.0 cm^3 of molybdate reagent and 0.5 cm^3 of stannous chloride reagent were added and the solution was made up to the mark with distilled water.

The mixture was allowed to stand for 10 minutes for the blue colour to develop. The wavelength region of maximum absorbance λ_{max} of the coloured substance was determined from the absorption spectrum using HACH DR-2000 spectrophotometer. Absorbance of the various solutions of KH_2P0_4 were measured at λ_{max} and corrected with blank. The data was used to construct a calibration curve.

Aliquot (5 cm^3) of the soil extract was pipetted into a separate 25 cm^3 volumetric flask. Then distilled water was added followed by 4.0 cm^3 of molybdate reagent and 0.5 cm^3 of stannous chloride and then made up to the mark with distilled water .The mixtures were allowed to stand for 10 minutes for the colour to develop and the absorbance determined. The phosphate concentrations were calculated from the calibration curve using equation 3.7

$$PO_4\text{-P (mg/kg)} = \frac{\text{conc, of } PO4^{2-} \text{ x } 1000}{\text{weight of sample(g)}} \qquad 3.7$$

3.3 Determination of Physicochemical Properties of Water

3.3.1 Determination of pH (Chimuka *et al.*, 2005)

The pH meter (made manufacture by HANNA Company; Model No.111222) was switched on and calibrated with standard buffers of pH 4, 7, and 9.The pH meter probe was then immersed into the water sample**.** The water sample was stirred with pH meter probe gently and waited until the display on the pH meter was stabilized**.** The pH value was recorded accordingly after the reading had been stabilized**.** The pH meter probe was rinsed with distilled water after each determination. Triplicate determinations were carried out for each sample and the average recorded. Total number of eight samples per river in each season were taken. Therefore sixteen samples in all per season for the two rivers.

3.3.2 Determination of total solid dried (APHA, 1992)

Clean evaporating dishes were heated between 103 to 105 °C for 1hour. The dishes were cooled and stored in desiccators. They were weighed immediately before use.

The sample was well-mixed and 50 cm^3 was measured into a pre-weighed dish and evaporated to dryness on a steam bath and in a drying oven. During evaporation, the temperature was lowered to approximately 2 °C below boiling to prevent splattering. The evaporated sample was dried for 1hour in an oven at 103 to 105 °C and the dish was cooled in desiccator and weighed. Cycle of drying, cooling, desiccating, and weighing was repeated until a constant weight was obtained or until weight change is less than 4 % of previous weight. Duplicate determinations agree within 5% of their average. The calculation for total solid was carried out using equation 3.8

$$\text{Total solid (mg /dm}^3\text{)} = \frac{(A - B)1000}{\text{Sample Volume in cm}^3} \qquad 3.8$$

whereA = weight of dried residue + dish (mg) and B = weight of dish (mg)

3.3.3 Determination of total dissolved solids (APHA, 1992)

The TDS Meter (Model 50150 of HACH Company) was switched on the probe was immersed into distilled water and agitated. The reading displayed 0.00 mg/dm^3. The probe was removed and then immersed in the water sample, the result displayed was recorded. Triplicate determinations were made for each sample and the mean recorded.

3.3.4 Total suspended solid (APHA, 1992)

Total suspended solid was determined by difference between the total solid and total dissolved solid.

3.3.5 Determination of electrical conductivity (APHA, 1992)

The portable conductivity meter type MC. 3 EIL was used in determining the electrical conductivity. The cell was rinsed with the sample and the sample poured into the cell until it was up to the top at the edge of the bore. The selector switch was set to the appropriate range XI, X10, X100 or X1000 the "ON" key depressed and the conductivity was recorded.

3.3.6 Determination of chloride (AOAC, 1990)

i. **Potassium chromate indicator solution:** K_2CrO_4 (50 g) was dissolved in distilled water and a few drops of $AgNO_3$ solution was added until a definite red precipitate forms. This was allowed to stand for 12 hours, then filtered and diluted to 1dm^3 with distilled water.

ii. **Standard silver nitrate solution (0.014mol dm^{-3}):** $AgNO_3$ (2.377 g) was dissolved in distilled water and diluted to 1000 cm^3. This was standardized against NaCl and stored in a brown bottle.

iii. **Standard sodium chloride(0.0141 mol dm^{-3})**: NaCl (824.0 mg)dried at 140 °C was dissolved in distilled water and diluted to 1dm^3.

iv. **Aluminium hydroxide suspension:** Aluminium potassium sulphate ($AlK(SO_4)_2.12H_2O$)(125 g) was dissolved in 1 dm^3 distilled water.

v. **Phenolphthalein indicator solution:** Phenolphthalein (0.5 g) was dissolved in 50 % ethanol solution consisting of 50 cm^3 ethanol and 50 cm^3 water.

vi. **Sodium hydroxide(1 mol dm^{-3})**: Sodium hydroxide (40 g) was weighed into 400 cm^3 and dissolved with distilled water. The solution was transferred into 1$dm^3$of volumetric flask and made up to mark.

vii. **Sulphuric acid (1mol dm^{-3}):** Concentrated H_2SO_4 (98 % sp gr.1.84, 54 cm^3) was measured into 1 dm^3 measuring cylinder containing 700 cm^3 of distilled ice water and was made up to mark.

viii. **Hydrogen peroxide 30 % (V/V):** Hydrogen peroxide (30 cm^3) was diluted in 70 cm^3 of distilled water.

A 100 cm^3 of water sample was transferred into a conical flask.The samples were directly titrated in the pH range of 7 to 10. K_2CrO_4(1 cm^3) indicator solution was added and titrated with standard $AgNO_3$ titrant was standardized and reagent blank value was established by titration method outlined above. A blank of 0.3 cm^3 was used.Chloride concentrations in the water sample were calculated using equations 3.9 and 3.10

$$mgCl^-/dm^3 = \frac{(A - B)}{cm^3\ Sample} \times M \times 35450 \quad 3.9$$

whereA – Titre value (cm^3) for sample, B –titre value (cm^3) for blank and M - Molarity of $AgNO_3$

$$\text{mgNaCl} = \left(\frac{mgCl}{dm^3} \right) \times 1.65 \qquad 3.10$$

3.3.7 Determination of sulphide (Iodometric Method, APHA, 1992)

i. **Hydrochloric acid (6 mol dm^{-3})**: This was prepared by transferring 515.46 cm^3 of concentrated HCl (36% purity, sp.gr. 1.18) with distilled water and the solution was made up to 1dm^3.

ii. **Standard iodine solution (0.025 mol dm^{-3}):** KI (25g) was dissolved in distilled water and 3.3 g of iodine was added. After iodine had dissolved, the solution was diluted to1000 cm^3 and standardized with 0.025 mol dm^{-3} $Na_2S_2O_3$, using starch solution as indicator.

iii. **Standard sodium thiosulphate solution (0.025 mol dm^{-3}):** $Na_2S_2O_3.5H_2O$ (6.205 g) was dissolved in distilled water. NaOH (6 mol dm^{-3})(1.5 cm^3) was added and the solution diluted to 1000 cm^3. The solution was standardized with bi-iodate solution.

iv. **Starch solution (2 %, w/v):**Laboratory – grade (2 g) soluble starch was dissolved in 100 cm^3 hot distilled water and 0.2 g salicylic acid.

i. Exactly 3$cm^3$of iodine solution was measured and distilled water was added to bring the volume to 20 cm^3. HCl (6 mol dm^{-3})(2 cm^3) was added. Sample (200 cm^3) was pipeted into flask bydischarging sample under solution surface. As iodine colour disappears, more iodine was added to retainthe colour. It was back titrated with $Na_2S_2O_3$ solution adding a few drops of starch solution as end point was approached, this was continued until blue colour disappeared.

ii. Sulphide was precipitated with zinc and ZnS filtered out, the filter paper was returned with precipitate to original bottle and 100 cm^3 of water added.

iii. Iodine solution and HCl were then added and titrated as in (i) above. Sulphide concentration in water samples were calculated using equation 3.11 below

One milliliter of 0.025 mol dm^{-3} iodine solution reacts with 0.4 mg S^{2-}

$$\frac{mgS^{2-}}{dm^3} = \frac{(A \times B) - (C \times D) \times 16000}{cm^3 sample} \quad 3.11$$

where A = cm^3 of iodine solution, B = Molarity of iodine solution, C = cm^3 of $Na_2S_2O_3$ solution and D = Molarity of $Na_2S_2O_3$ solution

3.3.8 Determination of alkalinity (Indicator Method, APHA. 1992)

i. **Sulphuric acid (0.05 mol dm^{-3}):** Concentrated sulphuric acid (2.72 cm^3) was dissolved in distilled water and diluted to 1000 cm^3 with water.

ii. **Sodium carbornate solution(0.05 mol dm^{-3}):** This was prepared by dissolving 5.30 g anhydrous sodium carbonate in distilled water and diluting to 1 dm^3. It was used to standardize the sulphuric acid.

iii. **Phenolphthalein indicator:** Phenolphthalein (0.5 g) was dissolved in 50 % ethanol solution consisting of 50 cm^3 ethanol and 50 cm^3 water.

iv. **Methyl orange indicator:** Methyl orange (0.5 g) was dissolved in 400 cm^3 distilled water free of CO_2 in 1 dm^3 volumetric flask and made up to mark.

i. Phenolphthalein alkalinity (p-values).

Sample (100 cm^3) was titrated to phenolphthalein end point after removal of suspended matter by filtration using 0.01 mol dm^{-3} sulphuric acid.

ii. Methyl orange alkalinity (m- values)

The solution used above was titrated to methyl orange end point. The result for the alkalinity concentrations in the samples were calculated using equations 3.12 and 3.13

$$\text{p-value (mg/dm}^3\ CaCO_3) = \frac{a \times M \times 50{,}000}{cm^3 \text{of sample}} \quad 3.12$$

$$\text{m-value } (mg/dm^3\ CaCO_3) = \frac{b \times M \times 50{,}000}{cm^3 \text{of sample}} \qquad 3.13$$

where a = cm^3 of titrant required to reach the end point with phenolphthalein indicator and b = total titrant value to reach the second end point with methyl orange indicator.

3.3.9 Determination of biochemical oxygen demand (AOAC, 1990)

i. **Phosphate buffer solution:** KH_2PO_4(8.50 g), 21.75 g K_2HPO_4, 33.40 g $Na_2HPO_4.7H_2O$ and 1.7 g NH_4Cl were mixed in 500 cm^3 H_2O and made up to 1 dm^3. The pH was 7.2 without further adjustment.

ii. **Calcium chloride solution(0.25mol dm^{-3}):**Anhydrous$CaCl_2$(27.5 g) was dissolved in distilled water and diluted to 1 dm^3.

iii. **Ferric chloride solution (0.0009 mol dm^{-3}):** $FeCl_3.6H_2O$ (0.25 g) was dissolved in distilled water and diluted to 1 dm^3.

iv. **Alkaline iodide solution:** NaOH (125 g) was dissolved in 125 cm^3 of distilled water and 37.50 g of potassium iodide was added. The solution was kept hot until the iodide dissolved. This was labeled solution (a).

v. **Sodium azide solution:** NaN_3 (2.5 g) was dissolved in 10 cm^3 distilled water. This was labeled solution (b)

vi. **Alkaline iodide -azide solution:** this was prepared by mixing solutions (a) and (b) above and making it up to 250 cm^3.

vii. **Sodium thiosulphate solution:** (a) $Na_2S_2O_3.5H_2O$ (0.75 mol dm^{-3},46.54 g) was dissolved in 250 cm^3 of distilled water (b) A solution of 0.0375 mol dm^{-3} was prepared by diluting 50 $cm^3$of solution above to 1dm^3. This was standardized with potassium dichromate solution.

viii. **Magnesium Sulphate Solution(0.1 mol dm^{-3}):** $MgSO_4.7H_2O$ (22.5 g) was dissolved in distilled water and diluted to 1 dm^3.

ix. **Dilution Water:**To 1 dm^3 of distilled water was added in a bottle and 1cm^3/dm^3 each of phosphate buffer, $MgSO_4$, $CaCl_2$ and $FeCl_3$ solutions were added, before use, the bottles were placed in the incubator for 24 hours.

Water sample(3 cm^3) was diluted with dilution water and mixed well and make up to 600 cm^3 in a 1000 cm^3 graduated cylinder avoiding entrainment of air. The mixed solution was siphoned into two BOD bottles (300 cm^3 capacity each). One was incubated at 20 °C for 5 days while dissolved oxygen in the other was determined immediately as follows: $MnSO_4$ (0.15 mol dm^{-3}, 2 cm^3) was added followed by 2 cm^3 alkaline iodide-azide solution well below the surface of the sample. It was stoppered carefully and mixed by inverting it for 20 times. The precipitate was allowed to settle. After carefully removing the stopper, 2 cm^3 of conc. H_2SO_4 was added by running it down the neck of the bottle and mixed by gentle inversion. The contents of the bottle was decanted and 250 cm^3 measured into a 500 cm^3 conical flask and titrated with 0.0375 mol dm^{-3}sodium thiosulphate using starch as indicator. Equation 3.14 was used to calculate BOD values.

Each 1 cm^3 of 0.037 mol dm^{-3} $Na_2S_2O_3$ = 1 mg DO/ dm^3 when the entire bottle contents were titrated.

$$\text{BOD (mg/ cm}^3\text{)} = \frac{DO_1 - DO_2}{P} \qquad 3.14$$

whereDO_1 = initial DO before incubation, DO_2 = DO after incubation and P = % dilution used

3.3.10 Determination of chemical oxygen demand (AOAC, 1990)

i. **Reflux apparatus:** - Erlenmeyer (500 cm^3) flask with T joint connected to 30 cm (12^o) Allihn condenser.

ii. **Potassium dichromate standard solution – (a) 0.25 mol dm^{-3}:** $K_2Cr_2O_7$ (12.259

g) primary standard grade, previously dried for 2 hr at 103 ^{0}C was dissolved in distilled water and diluted to 1 dm^3. **(b) 0 .025 mol dm^{-3}:**A solution containing 100 cm^3 and 0.25mol dm^{-3} of$K_2Cr_2O_7$ was diluted to 1 dm^3 with distilled water.

iii. **Sulphuric acid reagent:** - Ag_2SO_4(23.5 g) was dissolved in 1000 cm^3 concentrated H_2SO_4. Dissolutionwas carried out in 2 days.

iv. **Ferrous ammonium sulphate standard solution – (a) 0.25 mol dm^{-3}:** $Fe(NH_4)_2(SO_4)_2$. $6H_2O$ (98g) was dissolved in distilled water, 20 cm^3 of H_2SO_4 was added and cooled, and diluted to 1 dm^3. This was standardized daily with 0.25 mol dm^{-3} $K_2Cr_2O_7$. (b) **0 .025 mol dm^{-3}**: A 100 cm^3 of 0.25 mol dm^{-3}from (iv) was diluted to 1 dm^3 with distilled water and standardized daily with 0.025 mol dm^{-3} $K_2Cr_2O_7$.

v. **Phenanthroline ferrous sulphate (ferroin) indicator solution:** 1,10 – (ortho)-phenanthroline (1.48 g) and 0.70 g $FeSO_4.7H_2O$ were dissolved in 100 cm^3 distilled water.

vi. **Standardization of Ferrous Solutions**

a. **Concentrated solution:** To 25 cm^3 of 0.25 mol dm^{-3} $K_2Cr_2O_7$ diluted to 250 cm^3 with distilled water was added 75 cm^3 H_2SO_4 and cooled. This was titrated with 0.25 mol dm^{-3} $Fe(NH_4)_2(SO_4)_2$ using 10 drops of ferroin indicator.

Molarity of $Fe(NH_4)_2(SO_4)_2$ = (cm^3 $K_2Cr_2O_7$ x molarity)/ cm^3 $Fe(NH_4)_2(SO_4)_2$

b. **Dilute solution:** H_2O (15 cm^3) was added to 10 cm^3 of 0.025 mol dm^{-3} $K_2Cr_2O_7$ followed by 20 cm^3 of H_2SO_4 and the solution cooled. This was titrated with 0.025 mol dm^{-3} $Fe(NH_4)_2(SO_4)_2$ using 1 drop of ferroin indicator. The bluegreen to reddish brown colour change was sharp. The molarity was calculated as in (a).

Several boiling chips and 1 g of $HgSO_4$ was placed in reflux condenser. 5 cm^3 of H_2SO_4 was added and swirled until $HgSO_4$ dissolved. This was placed in ice bath and

25 cm^3 0.25 mol dm^{-3} $K_2Cr_2O_7$ and 70 cm^3 H_2SO_4 -Ag_2SO_4 reagent were slowly added with swirling. While still in the bath, 50 cm^3 sample (or aliquot diluted to 50 cm^3) was added. The condenser was attached and refluxed for 2 hr.The condenser was cooled and washed down with 25 cm^3 distilled water. About 10 drops of ferroin indicator were added and excess $K_2Cr_2O_7$ was titrated with 0.25 mol dm^{-3} $Fe(NH_4)_2(SO_4)_2$ to sharp, reddish end point (Scm^3). Blank determination was performed with all reagents, including refluxing, on distilled water in place of sample and volume of $Fe(NH_4)_2(SO_4)_2$ required was determined (Bcm^3). Equation 3.15 was used to calculate COD of the water samples

$$\text{COD (mg/dm}^3\text{)} = \frac{(B-S) \times M \times 8000}{\text{Volume of sample (cm}^3\text{)}} \qquad 3.15$$

whereB = Titre value for blank,S = Titre value for sample,

M = Molarity of $Fe(NH_4)_2(SO_4)_2$ solution and 8000 = Factor for oxidizable organic matter oxygen equivalent.

3.3.11 Determination of colour (Visual comparison method) (APHA-AWWA-WPCF, 1985)

Water sample was filtered and 50 cm^3 was measured into one nessler tube, and the second tube contained 50 cm^3 of distilled water. These tubes were held on a metallic case. The colour of the sample was matched with the colours of the clear distilled water and the calibrated colour glass disks when viewed by looking toward a wide surface. Each disk was calibrated to correspond with the colours on the platinum – cobalt scale. Colour values were determined using equation 3.16

$$\text{Colour Units} = \frac{A \times 50}{V} \qquad 3.16$$

where A = estimated colour of the sample and V =volume of sample (cm^3)

3.3.12 Determination of turbidity (Nephelometric Method) (APHA, 1985)

i. **Stock Turbidity Suspension**

ii. **Solution** I: hydrazine sulphate $(NH_2)_2H_2SO_4$ (1 g) was dissolved in distilled water and made up to 100 cm^3 in a volumetric flask.

iii. **Solution II**: Hexamethylenetetramine $(CH_2)_6N_4$(10 g) was dissolved in distilled water and made up to 100 cm^3 in a volumetric flask.

A 5 cm^3 each of Solutions i and ii were mixed together in a 100 cm^3 volumetric flask and allowed to stand at 25 °C for 24 hours, then made up to mark to obtain the stock turbidity suspension.

iv. **Standard Turbidity Suspension**: The stock turbidity suspension (10 cm^3) was diluted with de-ionised water to 100 cm^3.

The turbidimeter, HACH 2100P was calibrated with the standard turbidity suspension. The sample was shaken thoroughly, and the air bubbles allowed to disappear before pouring into the sample tube. The turbidity was read directly from the turbidimeter. Water samples were diluted with one or more volumes of distilled water until the turbidity fell between 30 and 40 NTU. The turbidity of the original sample was computed from turbidity of dilute sample and the dilution factor.

$$\text{Turbidity (NTU)} = \frac{A \times (B + C)}{C} \qquad 3.17$$

where A = NTU found in dilute sample, B = Volume of dilution water cm^3 and

C = Sample volume taken for dilution (cm^3)

3.3.13 Determination of phosphate (HACH, 2000)

The programme number (490) for phosphate was entered; the wavelength was adjusted to 890 nm and in $mgdm^{-3}$ PO_4^{3-} was displayed. A blank of 25 cm^3 of deionized water was measured into the sample cell and placed into the cell holder. The light shield

was closed, the zero key pressed, and the reading displayed 0.00 $mgdm^{-3}$ PO_4^{3-}. The blank was replaced with 25 cm^3 of water sample on addition of one phosVer 3 phosphate pillow and allowed to stand for two minutes reaction period .The read/enter key was pressed and the reading displayed the value in them gdm^{-3} PO_4^{3-}.This procedure was repeated for all the water samples.

3.3.14 Determination of Nitrate (HACH, 2000)

The programme number (355) for nitrate was entered and the wavelength was adjusted to 500 nm and the unit $mgdm^{-3}$ NO_3^- was displayed. A blank of 25 cm^3 of deionized water was measured into the sample cell and placed into the cell holder. The light shield was closed, the zero key pressed, and the reading displayed 0.00 $mgdm^{-3}$ NO_3. The blank was replaced with 25 cm^3 of water sample on addition of one nitriVer 5 nitrate powder pillow and allowed to stand for one minute reaction period. The read/enter key was pressed and the reading displayed the value in the $mgdm^{-3}$ NO_3^-.This procedure was repeated for all the water samples.

3.3.15 Determination of dissolved oxygen (HACH, 2000)

The high range dissolved oxygen method was adopted using the Direct Reading 2000 Spectrophotometer. The programme number (445) for dissolved oxygen was entered and the wavelength was adjusted to 535 nm and the unit $mgdm^{-3}O_2$HRDO was displayed. A blank of 10 ml of deionized water was measured into the blue ampoule cap sample cell, without inverting the ampoule. The ampoule cap was immediately placed over the tip of the ampoule. The ampoule was shaken for 30 seconds the shift timer key was pressed to read the time for two minutes. This period enabled the degassed oxygen to redissolve and react. The AccuVac adaptor was placed into the cell holder. The light shield was closed and the display shown in $mgdm^{-3}O_2$HRDO. The blank was placed into

the cell holder and the zero key was pressed, and the reading displayed 0.00mgdm^{-3}O_2HRDO. The AccuVac ampoule was placed into the cell holder and the light shield was closed, after 30 seconds, the read/enter key was pressed and the reading displayed the value of the dissolved oxygen was recorded. Triplicate determinations were made for each sample and the mean recorded.

3.4 Determination of Au, Cd, Cu, Fe, Mn, Pb and Zn by Atomic Absorption Spectrophotometry

i. Nitric acid Analytical Reagent(69 %, sp. Gr. 1.42)

ii. Hydrochloric acid AR (37 % sp.Gr.1.18)

One gram of each of the soils and *Surghum bicolor* grains samples were digested separately with 10 cm^3 of aqua regia (a mixture of 3 parts concentrated HCl to 1 part concentrated HNO_3) on a hot plate in fume cupboard, until a clear solution was obtained. Water was added periodically to avoid drying up of the digest. To the hot solution, 30 cm^3 of water was then added and filtered through Whatman No.42 filter paper into a 50 cm^3 standard volumetric flask and then made up to the mark (Kisku *et al*., 2000), the analyses were done in triplicate.

3.5 Modified Tessier's Sequential Extraction (Masa *et al.*, 2013)

i. **Magnesium nitrate (1 mol dm^{-3}):** $Mg(NO_3)_2.6H_2O$ (64.10 g) was dissolved and made up to 250 cm^{3}withdeionizeddistilled water.

iii. **Ammonium acetate (1 mol dm^{-3}):** CH_3COONH_4 (77.08 g) was dissolved and made up to 1dm^3 with deionized distilled water.

iv. **Hydroxyl ammonium chloride (0.1 mol dm^{-3}):** $HONH_3Cl$ (64.49 g) was dissolved and made up to 1 dm^3 with deionized distilled water.

v. **Nitric acid (0.02 mol dm^{-3}):** An amount of 1.29 cm^3 conc. HNO_3 (69 %, sp Gr.1.42) was pipetted into 1dm^3 volumetric flask containing 10 cm^{3}of

deionizeddistilled water, shaken and made up to mark.

vi. **Hydrogen peroxide (30 %,V/V):** Hydrogen peroxide (30 cm^3) was diluted in 70 cm^3 of deionized distilled water.

vii. **Aqua regia:** HCl was mixed with conc. HNO_3 in the ratio 3:1 ($HCl:HNO_3$).

The water soluble fraction (F1): Air dried soil sample (1 g) was weighed into a 60 cm^3 capacity polythene container, 10 cm^3 of deionized distilled water was added and shaken for 1 hr. The soil colloids was then centrifuged with Baird % TatLock autobench centrifuging machine at 4000 rpm for 20 min. The supernatant was decanted and filtered through Whatman No.42 filter paper into 50 cm^3 volumetric flask, then made up to the mark with deionized distilled water.

The exchangeable fraction (F2): To the residual soil sample from F1, 10 cm^3 of 1 mol dm^{-3} $MgNO_3$ was added and shaken for 2 hrs, then treated as in F1.

The fraction bound to carbonates (F3): The residual soil sample from F2, 10 cm^3 of 1 mol dm^{-3} CH_3COONH_4 was added to it, the pH was adjusted to 5 and shaken for 5 hrs. This was again treated as above.

The fraction bound to Fe and Mn oxides (F4): $NH_2OH.HCl$(0.1mol dm^{-3}) (20 cm^3) was added to residual soil sample from F3; the pH was adjusted to 2 and shaken for 12 hrs. This was again treated as above.

The fraction bound to organic matter (F5): To the residual soil sample from F4, 3 cm^3 of 0.02 mol dm^{-3} HNO_3 and 5 cm^3 of 30 % H_2O_2 was added and heated for 3 hrs 85 ^0C, followed by adding 15 cm^3 of 1 mol dm^{-3} NH_4OAc and shaken for 30 min. This was again treated as above.

The final residual fraction (F6): The residual soil sample from F5 was digested with 10 cm^3 of aqua regia. The clear solution was filtered through Whatman No.42 filter paper into 50 cm^3 volumetric flask, and then made up to the mark with water.

The concentration of heavy metals was determined by Atomic absorption spectrophotometry (AAS) (Manufacturer: Varian; Model No.AA240FS), for each fractionation sequence. The final fractional recovery of the metals was calculated by comparing the sum of their concentrations in all six fractions with their pseudototal concentration (assessed by aqua regia digestion) in the corresponding soil.

3.6 Preparation of Calibration Curves

Stock Solutions

Cadmium solution (1000 mg/dm^3): $CdSO_4.H_2O$ (2.02g) was dissolved in deionizeddistilled water and made up to 1 dm^3 in a volumetric flask.

Copper Solution (1000 mg/dm^3):$Cu(NO_3)_2.3H_2O$ (3.798 g) was dissolved in deionizeddistilled water and made up to 1 dm^3 in a volumetric flask.

Iron Solution (1000 mg/dm^3): ($FeCl_3.6H_2O$) (4.844 g) was dissolved in deionizeddistilled water and made up to 1 dm^3 in a volumetric flask.

Lead Solution (1000 mg/dm^3): $Pb(NO_3)_2$ (1.590 g)was dissolved in deionizeddistilled water and made up to 1 dm^3 in a volumetric flask.

Manganese Solution (1000 mg/dm^3): $MnCl_24H_2O$ (3.600 g) was dissolved in 50 cm^3 conc. HCI and made up to 1d m^3 in a volumetric flaskwith deionizeddistilled water.

Zinc Solution (1000 mg/dm^3): ZnO (1.245 g) was dissolved in 5 cm^3deionized distilled water and 25 $cm^3$of 5 $moldm^{-3}$ HCI and the solution made up to 1 dm^3 in a volumetric flask with deionizeddistilled water.

For each metal, five working standards were prepared by serial dilution using stock solution. The working standard solutions were aspirated into the flame and their absorbance recorded. A calibration curve was prepared by plotting absorbance against concentrations.

The digested sample solutions were aspirated into the flame and the absorbance values recorded. The metal concentration was calculated from the calibration curve. The instrumental conditions used are as in Table 3.1.

3.7 Quality Assurance for Metal Analysis (Spiking Experiment)

Validation of the technique for the metal determination on digested soil, water and *Sorghum bicolor* grain sample was conducted. This was done by spiking the pre-digested samples with multi-element standard solution (0.5 mg/dm^3 of Au, Cd, Cu, Fe, Mn, Pb and Zn) as reported by Awofolu (2005)

3.7.1 Preparation of 0.5 mg/dm^3 multi-element standard solution (MESS) (Awofolu, 2005)

$Cd(NO_3)_2.4H_2O$: $Cd(NO_3)_2.4H_2O$ (0.0014 g) was dissolved in 2 cm^3 of 2 mol dm^{-3} HNO_3 in a beaker and then quantitatively transferred into a 1 dm^3 standard volumetric flask.

Similarly 0.0126 g of $CuSO_4$, 0.0008 g of $Pb(NO_3)_2$, 0.0220 g of $ZnSO_4.7H_2O$, 0.0011 g of $MnCl_2$, 0.0025 g of $Fe(SO_4)_2.7H_2O$ and 0.5 mg liquid gold were directly transferred into the above 1 dm^3 standard volumetric flask.and made up to the mark with deionized distilled water

3.7.2 Spiking experiment

Multi-element standard (30 cm^3) was pipetted to spike water, soil and plant samples.These were digested as in section 3.4 and their metal concentrations determined by AAS at intrusmental conditions given in Table 3.1. The concentration of metals in

the spiked and their corresponding unspiked samples were used to calculate the percentage recovery in order to validate the method.

Calculation:

Amount of metal used to spike a sample $=\frac{\text{vol of MESS used x conc.of metal in MESS(mg/L)}}{1000}$ =Xmg 3.18

Amount of metal in spiked sample $=\frac{\text{vol.of digest spiked x conc.(mg/L)}}{1000}$=Ymg 3.19

Amount of metal in unspiked sample$=\frac{\text{vol.of digest of unspiked x conc.(mg/L)}}{1000}$ =Zmg 3.20

Recovered amount of metal used in a spike sample =Y-Z 3.21

$$\% \text{ Recovery} = \frac{Y-Z}{X} \times 100$$ 3.22

Table 3.1: Instrumental conditions for AAS determination of metals with model No: AA240FS (Company: Varian) Atomic Absorption Spectrometer

Element	Wavelength (nm)	Slit Width (nm)	Flame type	Fuel flow rate L/Min
Au	242.8	1.0	Air/C_2H_2	13.50/2.00
Cd	228.8	0.5	Air/C_2H_2	13.50/2.00
Cu	324.8	0.5	Air/C_2H_2	13.50/2.00
Fe	248.3	0.2	Air/C_2H_2	13.50/2.00
Pb	217.0	0.5	Air/C_2H_2	13.50/2.00
Mn	279.5	0.2	Air/C_2H_2	13.50/2.00
Zn	213.9	0.5	Air/C_2H_2	13.50/2.00

3.8 Statistical Analysis

All treatments in this experiment were in triplicates. Descriptive statistics, correlation analysis and one way analysis of variance (ANOVA) were calculated using Microsoft Office Excel 2007. The parameters of the descriptive statistics that were considered include: maximum, minimum, mean, and standard deviation.The correlation coefficient was used to determine the relationship between several properties of the data from the different sites. The equation for the correlation coefficient is:

$$Correl(X,Y) = \frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2}} \qquad 3.23$$

where $\bar{x}$ and $\bar{y}$ are the sample means.

3.9 Indices and Methods for the Assessment of Soil Contamination

In an attempt to understand the pattern of metal contamination in this study area, useful tools including pollution indices such as; i) Geo-accumulation Index (Igeo) and ii) Enrichment Factor (EF) were used to analyze heavy metals concentration in soil.

(I) Geo-Accumulation Index (Igeo)(Muller, 1969)

Igeo is mathematically expressed as: $Igeo = \log 2Cn/1.5Bn$ 3.24

where Cn is the concentration of element in the soil, Bn is the geochemical background value. The factor 1.5 is incorporated in the relationship to account for possible variation in background data due to lithogenic effect. The geo index scale consists of seven grades (0 –6) ranging from unpolluted to highly polluted (Table 3.2).

Table 3.2: Igeo classes with respect to soil quality (Muller, 1969)

Class	Value	Soil Quality
0	Igeo < 0	Practically unpolluted
1	0< Igeo < 1	unpolluted to moderately unpolluted
2	1< Igeo < 2	Moderately polluted
3	2< Igeo < 3	Moderately to heavily polluted
4	3< Igeo < 4	Heavily polluted
5	4< Igeo < 5	Heavily to extremely polluted
6	5< Igeo < 6	Extremely polluted

(II) Enrichment Factor

As proposed by Kisku, (2000) Enrichment factor (EF) was employed to assess the degree of contamination in soil of the study area.

$$\text{Enrichment factor} = \frac{\text{concentration of metal in soil}}{\text{concentration of metal in soil at control site}} \qquad 3.25$$

Table 3.3: Categories of EF (Sutherland, 2000)

EF	Category
EF < 1	Background concentration
EF > 1 < 2	Depletion to minimal enrichment
EF > 2 < 5	Moderate enrichment
EF > 5 < 20	Significant enrichment
EF > 20 < 40	Very high enrichment
EF > 40	Extremely high Enrichment

CHAPTER FOUR

4.0 RESULTS

4.1 Physico-chemical Parameters and Concentration of Heavy Metals in Rivers Gbako and Tangale Waters

4.1.1 Physico-chemical parameters of water

The results of the descriptive statistics for physico-chemical parameters of Rivers Gbako and Tangale waters in the study areas are presented in Tables 4.1and 4.2 respectively.

i. pH

The results obtained for pH are presented in Table 4.1 for both rainy and dry seasons for River Gbako Water. The pH ranged from 6.83 to 7.54 for the rainy season and from 6.93 to 7.66 for the dry season which shows slight variation at various sampling points throughout the study period. Mean pH of 7.21 ± 0.22 and 7.21 ± 0.25 were obtained throughout for the rainy and dry seasons respectively. Control sampling point recorded mean pH of 6.8 ± 0.13 and 7.17 ± 0.06 for the rainy and dry seasons respectively.

Results of pH value obtained for River Tangale during rainy and dry seasons are presented in Tables 4.2. The pH value ranged from 6.45 to 7.63 for the rainy season and from 7.02 to 7.30 for the dry season. These values show slight variation at various sampling points throughout the study period. Mean pH of 6.80 ± 0.38 and 7.15 ± 0.10 were obtained throughout for the rainy and dry seasons respectively. Control sampling point recorded mean pH of 7.63 ± 0.03 and 6.83 ± 1.42 for the rainy and dry seasons respectively.

ii. Turbidity

The result of the turbidity of the water sample analysed over the period of study are presented in Tables 4.1 and 4.2 for Rivers Gbako water and Tangale.

River Gbako turbidity values ranged between 1.06 NTU and 779.67 NTU with mean of 151.39 ± 268.21 NTU for the rainy season while the value ranged between 0.98 NTU and 48.73 NTU for dry season with mean of 11.58 ± 15.96. Control sampling points recorded mean turbidity of 9.40 ± 0.65 NTU and 1.53 ± 0.49 NTU for rainy and dry seasons respectively.

For River Tangale water samples turbidity values obtained ranged between 35.30 NTU and 829 NTU with mean of 242.71 ± 289.52 NTU for the rainy season. While in dry season the turbidity value obtained ranged from 6.07 NTU to 732.00 NTU with mean of 337.15 ± 286.32 NTU. Control values were mean of 151 ± 0.00 NTU and 9.40 ± 0.53 NTU for rainy and dry seasons respectively.

iii. Total Dissolved Solids

The results obtained for Total dissolved solids (TDS) ranged between 35.33 mg/dm^3 and 399.33 mg/dm^3 with the mean of 158.79 ± 133.57 mg/dm^3during the rainy season for River Gbako sample water. In the dry season, TDS values ranged between 138.33 mg/dm^3 and 673.33 mg/dm^3 with the mean value of 392.29 ± 182.78 mg/dm^3 (Table 4.1).The control points recorded mean of 58.7.00 ± 9.82 mg/dm^3 and 139.00 ± 6.93 mg/dm^3 for dry and rainy seasons respectively.

In the River Tangale water samples, the TDS values obtained ranged between 15.67 $mg/dm^3$and 102.00 mg/dm^3 with mean and its standard deviation of 57.84 ± 30.86 mg/dm^3 for the rainy season. During the dry season the TDS values obtained ranged between 66.67 mg/dm^3 and 238.67 mg/dm^3 with mean of 184.79 ± 55.30 mg/dm^3.The

control points recorded mean of 73 ± 0.00 mg/dm^3 and 58.67 ± 2.36 mg/dm^3 for dry and rainy seasons respectively (Table 4.2).

Table 4.1: Descriptive statistics of physicochemical parameters of River Gbako at Saboeregi mining site

	Rainy Season		Control Rainy Season		Dry Season		Control Dry Season	
Parameter	Mean	STD	Mean	STD	Mean	STD	Mean	STD
pH	7.21	0.22	6.8	0.13	7.21	0.25	7.17	0.06
Turbidity (NTU)	151.39	268.21	9.4	0.65	11.58	15.96	1.53	0.49
TDS (mg/dm^3)	158.79	133.57	58.7	9.82	392.29	182.78	139	6.93
Conductivity (µS/cm)	226.04	185.54	102.7	1.16	598.08	286.29	207	8.49
DO mg/dm^3	6.21	0.97	6.3	0.01	6.09	1.12	6.70	0.02
Chloride (mg/dm^3)	13.08	5.57	8.7	1.53	32.38	24.43	13	1.63
TA (mg/ dm^3)	88.58	67.74	75.7	3.79	140.33	45.37	64.33	2.62
Sulphide (mg/ dm^3)	0.39	0.18	0.6	0.01	0.49	0.24	0.43	0.01
Colour (Pt-Co)	5149.5	5913.31	467.0	28.58	655.25	731.54	74	3.27
SS (mg/dm^3)	633.25	1039.45	67.7	3.79	105.67	101.25	9.33	0.47
TS (mg/dm^3)	916.59	1019.87	142.7	24.01	502.83	265.21	148.33	5.44
BOD mg/dm^3	18.59	11.6	6.0	0.00	22.83	14.63	16.67	0.94
COD mg/dm^3	46.67	28.69	16.0	0.00	57.08	36.30	41.33	1.89
Nitrate (mg/dm^3)	48.31	56.68	15.8	0.29	24.92	21.89	5.43	0.19
Phosphate (mg/dm^3)	16.18	16.97	8.4	0.06	8.95	5.64	4.43	0.19

TDS = Total Dissolved Solids, DO = Dissolved Oxygen, TA= Total Alkalinity, SS=Suspended Solid, TS=Total Solid, BOD= Biochemical Oxygen Demand, COD= Chemical Oxygen Demand

Table 4.2: Descriptive statistics of physicochemical parameters of River Tangale at Asha mining site

	Rainy Season		Control Rainy Season		Dry Season		Control Dry Season	
Parameter	Mean	STD	Mean	STD	Mean	STD	Mean	STD
Ph	6.8	0.38	7.63	0.03	7.15	0.1	6.83	1.42
Turbidity (NTU)	242.71	289.52	151	0.00	337.15	286.32	9.4	0.53
TDS(mg/dm^3)	57.84	30.86	73	0.00	184.79	55.30	58.67	2.36
Conductivity (µS/cm)	86.06	46.42	111.3	0.42	275.66	83.02	102.67	0.94
DO mg/dm^3	7.38	1.02	7.52	0.05	7.28	0.38	6.32	0.01
Chloride (mg/dm^3)	9.22	4.69	5.39	0.09	15.05	7.07	8.67	1.25
TA (mg/dm3)	115.8	49.79	87.75	0.00	186.24	67.61	75.67	3.09
Sulphide (mg/dm^3)	0.23	0.27	0.07	0.00	0.13	0.08	0.55	0.01
Colour (Pt-Co)	7758.04	14077.52	1223.33	2.36	1995.42	2838.2	467	23.34
SS (mg/dm^3)	580.67	1115.85	47.33	1.25	91.92	89.97	67.67	4.97
TS (mg/dm^3)	639.79	1092.81	120.33	1.25	272.62	68.03	142.67	19.6
BOD mg/dm^3	11.71	14.55	12.33	0.47	2.33	4.34	6	0.00
COD mgdm^3	30.13	34.17	32.67	0.47	6.13	11.35	16	0.00
Nitrate (mg/dm^3)	291.85	461.05	56.37	0.28	152.48	226.23	15.77	0.23
Phosphate (mg/dm^3)	76.91	135.21	8.07	0.09	22.77	14.40	8.37	0.05

TDS = Total Dissolved Solids, DO -Dissolved Oxygen, TA= Total Alkalinity, SS=Suspended Solid, TS=Total Solid, BOD= Biochemical Oxygen Demand, COD= Chemical Oxygen Demand

iv. Electrical Conductivity

The result of the electrical conductivity of the water sample analysed over the period of study are presented in Tables 4.1 and 4.2 for Rivers Gbako and Tangale respectively. For River Gbako electrical conductivity values ranged between 53.33 µS/cm and 597.7 µS/cm with mean value of 226.04 ± 185.54 µS/cm for the rainy season. Conductivity value obtained ranged between 207.00 µS/cm and 1008.00 µS/cm for dry season with mean of 598.08 ± 286.29 µS/cm. The control sampling points recorded mean of 102.7 ± 1.16 µS/cm and 207 ± 8.49 µS/cm for dry and rainy seasons respectively.

For River Tangale water samples electrical conductivity value obtained ranged between 22.77 µS/cm and 151.97 µS/cm with mean and standard deviation of 86.06 ± 46.42 µS/cm for the rainy season (Table 4.2). While in dry season the electrical conductivity value obtained ranged between 97.97 µS/cm and 357.33 µS/cm with mean of 275.66 ± 83.02 µS/cm. The control sampling points recorded mean of 111.3 ± 0.42µS/cm *and* 102.67± 0.94µS/cmfor rainy and dry seasons respectively.

v. Dissolved Oxygen

The results for the DO content of the sampled water analysed over the period of study are presented in Tables 4.1 and 4.2 for Rivers Gbako and Tangale respectively. River Gbako waters during rainy season recorded DO values ranging between 4.42 mg/dm^3 and 7.21 mg/dm^3 with mean value of 6.21 ± 0.97 mg/dm^3. DO values between 3.75 mg/dm^3 and 7.43 mg/dm^3 were obtained for dry season with mean of 6.09 ± 1.12 mg/dm^3. Control sampling point recorded mean of 6.3 ± 0.01 mg/dm^3 and 6.70 ± 0.02 mg/dm^3 for rainy and dry seasons respectively.

For River Tangale water samples, the DO value obtained ranged between 5.94 $mg/dm^3$and 9.52 mg/dm^3 with mean and standard deviation of 7.38 ± 1.02 mg/dm^3 for

the rainy season (Table 4.2). While in dry season the DO value obtained ranged between 6.67 mg/dm^3 and 7.61 mg/dm^3 with mean of 7.28 ± 0.38 mg/dm^3. Control sampling point recorded mean of 7.52 ± 0.05 mg/dm^3 and 6.32 ± 0.01 mg/dm^3 for rainy and dry seasons respectively.

vi. Chloride

The results for chloride content of the water in all sampling points in Rivers Gbako and Tangale for both rainy and dry seasons are presented in Tables 4.1 and 4.2 respectively. The value ranged from 7.33 mg/dm^3 to 22.33 mg/dm^{3}with mean value of 13.08 ± 5.57 mg/dm^3 for River Gbako. Chloride content value ranged from 7.33 mg/dm^3 to 64.67 mg/dm^3 in the dry season with mean value of 32.38 ± 24.43 mg/dm^3. Control sampling points recorded mean of 8.7 ± 1.53 mg/dm^3 and 13.00 ± 1.63 mg/dm^3 for rainy and dry seasons respectively.

However, in River Tangale, chloride content of the sampled water ranged from 5.34 mg/dm^3 to 17.01 mg/dm^3 with mean and standard deviation of 9.22 ± 4.69 mg/dm^3 for rainy season (Table 4.2). The level of chloride during the dry season ranged between 6.55 mg/dm^3 and 26.92 mg/dm^3. Mean chloride content of the water over the period of investigation was 15.05 ± 7.07 mg/dm^3. Control sampling points recorded mean of 5.39 ± 0.09 mg/dm^3 and 8.67 ± 1.25 mg/dm^3 for rainy and dry seasons respectively.

vii. Total Alkalinity

The results of the alkalinity content of the water sample analysed over the period of investigation are presented in Tables 4.1 and 4.2 for Rivers Gbako and Tangale respectively. The range of values obtained for alkalinity content was between 9.00 mg/dm^3 and 229.00 mg/dm^3 with the mean value of 88.58 ± 67.74 mg/dm^3 for the rainy season for River Gbako.

The dry season results of the alkalinity of the water sample throughout the period of study ranged from 64.33 to 184.00 mg/dm^3 with mean and standard deviation of 140.33 ± 45.37 mg/dm^3, while the control sampling points recorded mean of 75.7 ± 3.79 mg/dm^3 and 64.33 ± 2.62 mg/dm^3 for rainy and dry seasons respectively.

River Tangale alkalinity content ranged from 52.98 mg/dm^3 to 215.17 mg/dm^3 with mean and standard deviation of 115.80 ± 49.79 mg/dm^3 for rainy season (Table 4.2). The level of alkalinity content during the dry season ranged between 78.00 mg/dm^3 and 312.00 mg/dm^3.Whereas the mean alkanility content of the water over the period of investigation was 186.24 ± 67.61 mg/dm^3 and the control sampling points recorded mean of 87.75 ± 0.00 mg/dm^3 and 75.67 ± 3.09 mg/dm^3 for rainy and dry seasons respectively.

viii. Sulphide

The results of the sulphide content of the water sample analysed over the period of investigation are presented in Tables 4.1 and 4.2 for Rivers Gbako and Tangale respectively. The range of values obtained for sulphide content was between 0.14 and 0.65 mg/dm^3, with mean of 0.39 ± 0.18 mg/dm^3 in the rainy season for River Gbako.

The dry season results of the sulphide content of the water sample throughout the period of study ranged from 0.16 mg/dm^3 to 0.86 mg/dm^3 with mean and standard deviation of 0.49 ± 0.24 mg/dm^3.The control sampling points recorded mean of 0.6 ± 0.01 mg/dm^3 and 0.43 ± 0.01 mg/dm^3 for River Gbakoin the rainy and dry seasons respectively.

River Tangale sulphide content ranged from 0.07 mg/dm^3 to 0.84 mg/dm^3 with mean of 0.23 ± 0.27 mg/dm^3 for rainy season (Table 4.2). The level of sulphide content during the dry season ranged between 0.03 mg/dm^3 to 0.23 mg/dm^3. Whereas the mean

sulphide content of the water over the period of investigation was 0.13 ± 0.08 mg/dm^3. The control sampling points recorded mean of 0.07 ± 0.00 mg/dm^3 and 0.55 ± 0.01 mg/dm^3 for rainy and dry seasons respectively.

ix. Colour

The results obtained for colour are presented in Table 4.1 for both rainy and dry seasons for River Gbako. The colour ranged from 201.00 pt.co to 13033.00 pt.co for the rainy season and from 48.00 pt.co to 1701.7 pt.co in the dry season. Mean colour content of 5149.5 ± 5913.31 pt.co and 655.25 ± 731.54 pt.co were obtained throughout in the rainy and dry seasons respectively. The control sampling points recorded mean of 467.0 ± 28.58 mg/dm^3 and 74.00 ± 3.27 mg/dm^3 for rainy and dry seasons respectively.

The results obtained for Colour for River Tangale Water are presented in Table 4.2 for both rainy and dry seasons. The Colour ranged from 81.33 pt.co to 36746.67 pt.co for the rainy season and from 62.00 pt.co to 6659.33 pt.co for the dry season which shows slight variation at various sampling points throughout the study period. Mean Colour of 7758.04 ± 14077.52 pt.co and 1995.42 ± 2838.82 pt.co were obtained throughout for the rainy and dry seasons respectively. The control sampling points recorded mean of 1223.33 ± 2.36 pt.co and 467.00 ± 23.34 pt.cofor rainy and dry seasons respectively.

x. Suspended Solid

The results of the suspended solid content of the water samples analysed over the period of investigation are presented in Tables 4.1 and 4.2 for Rivers Gbako and Tangale respectively. The range of values obtained for suspended solid content was between 10.30 and 2636.00 mg/dm^3, while mean was 633.25 ± 1039.45 mg/dm^3 for the rainy season at River Gbako.

The dry season results of the suspended solid content of the water sample ranged from 9.33 mg/dm^3 to 270.33 mg/dm^3 with mean and standard deviation of 105.67 ± 101.25 mg/dm^3. The control sampling points recorded mean of 67.7 ± 3.79 mg/dm^3 and 9.33 ± 0.47 mg/dm^3 for rainy and dry seasons respectively.

Suspended solid value obtained ranged from 13.00 mg/dm^3 to 3122.00 mg/dm^3 with mean of 580.67 ± 1115.85 mg/dm^3 for rainy season in river Tangale (Table 4.2). The level of suspended solid content during the dry season ranged between 0.33 mg/dm^3 and 238.67 mg/dm^3.Whereas the mean of suspended solid content of the water over the period of investigation was 91.92 ± 89.97 mg/dm^3.The control sampling points recorded 47.33 ± 1.25 mg/dm^3 and 67.67 ± 4.97 mg/dm^3 for rainy and dry seasons respectively.

xi. Total Solid

The results of the total solid content of the water sample analysed over the period of investigation are presented in Tables 4.1 and 4.2 for Rivers Gbako and Tangale respectively. The range of values obtained for total solid content was between 105.67 mg/dm^3 and 2672.00 mg/dm^3, while mean was 916.59.± 1019.87 mg/dm^3 for the rainy season in River Gbako.

The dry season results of the total solid content of the water sample ranged from 148.3 mg/dm^3 to 812.33 mg/dm^3 with mean of 502.83 ± 265.21 mg/dm^3. The control sampling points recorded 142.7 ± 24.01 mg/dm^3 and 148.33 ± 5.44 mg/dm^3 at River Gbako for rainy and dry seasons respectively.

Total solid content ranged from 42.67 mg/dm^3 to 3136.67 mg/dm^3 with mean of 639.79±1092.81 mg/dm^3 for rainy season in River Tangale. The level of total solid content during the dry season ranged from 164.00 mg/dm^3 to 373.33 mg/dm^3 with the

mean of 272.62± 68.03 mg/dm^3. The control sampling points recorded 120.33 ± 1.25 mg/dm^3 and 142.67 ± 19.6 mg/dm^3 for rainy and dry seasons respectively.

xii. Biochemical Oxygen Demand

The results of the BOD of the water sample analysed over the period of investigation are presented in Tables 4.1 and 4.2 for Rivers Gbako and Tangale respectively. The range of values obtained for BOD was between 6.00 mg/dm^3 and 38.67 mg/dm^3, with mean of 18.59 ± 11.60 mg/dm^3 for the rainy season in River Gbako.

The dry season results of the BOD of the water sample throughout the period of study ranged from 0.00 mg/dm^3 to 42.67 mg/dm^3 with mean of 22.83±14.63 mg/dm^3. The control sampling points recorded BOD values of 6.0 ± 0.00 mg/dm^3 and 16.67 ± 0.94 mg/dm^3 for rainy and dry seasons respectively at River Gbako.

BOD ranged from 0.00 mg/dm^3 to 37.67 mg/dm^3 with mean of 11.71 ± 14.55 mg/dm^3 for rainy season in River Tangale were recorded. The level of BOD during the dry season ranged between 0.00 mg/dm^3 and 10.00 mg/dm^3, with the mean BOD of 2.33 ± 4.34 mg/dm^3. The control sampling points recorded BOD values of 12.33 ± 0.47 mg/dm^3 and 6.0 ± 0.00 mg/dm^3 for rainy and dry seasons respectively.

xiii. Chemical Oxygen Demand

The results obtained for COD are presented in Tables 4.1 for both rainy and dry seasons for River Gbako water. The COD ranged from 16.00 to 96.00 mg/dm^3 for the rainy season and from 1.00 mg/dm^3 to 107.00 mg/dm^3 for the dry season which shows slight variation at various sampling points throughout the study period. Mean COD of 46.67 ± 28.69 mg/dm^3 and 57.08 ± 36.30 mg/dm^3 were obtained for the rainy and dry seasons respectively. The control sampling points recorded COD values of 16.0 ± 0.00 mg/dm^3 and 41.33 ± 1.89 mg/dm^3 for rainy and dry seasons respectively.

The results obtained for COD for River Tangale Water are presented in Table 4.2 for both rainy and dry seasons. The COD ranged from 0.00 mg/dm^3 to 93.67 mg/dm^3 for the rainy season and from 0.00 mg/dm^3 to 25.33 mg/dm^3 for the dry season which shows slight variation at various sampling points throughout the study period. Mean COD of 30.13 ± 34.17 mg/dm^3 and 6.13 ± 11.35 mg/dm^3 were obtained for the rainy and dry season's respectively.The control sampling points recorded COD values of 32.67 ± 0.47 mg/dm^3 and 16.00 ± 0.00 mg/dm^3 for rainy and dry seasons respectively

xiv. Nitrate

The results obtained for nitrate are presented in Table 4.1 for both rainy and dry seasons for River Gbako. Nitrate content ranged from 9.80 mg/dm^3 to 155.20 mg/dm^3 for rainy season and from 5.43 mg/dm^3 to 61.57 mg/dm^3 for dry season. Mean nitrate values of 48.31 ± 56.68 mg/dm^3 and 24.92 ± 21.89 mg/dm^3 were obtained for the rainy and dry seasons respectively. The control sampling points recorded nitrate values of 15.8 ± 0.29 mg/dm^3 and 5.43 ± 0.19 mg/dm^3 for rainy and dry seasons respectively.

The results obtained for nitrate for River Tangale are presented in Table 4.2 for both rainy and dry seasons. The nitrate levels ranged from 12.70 mg/dm^3 to 1248.87 mg/dm^3 for the rainy season and from 10.76 mg/dm^3 to 700.46 mg/dm^3 for the dry season. Mean nitrate of 291.85 ± 461.05 mg/dm^3 and 152.48 ± 226.23 mg/dm^3 were obtained for the rainy and dry seasons respectively. The control sampling points recorded nitrate values of 56.37 ± 0.28 mg/dm^3 and 15.77 ± 0.23 mg/dm^3 for rainy and dry seasons respectively.

xv. Phosphate

The results obtained for phosphate are presented in Table 4.1 for both rainy and dry seasons for River Gbako Water. The phosphate levels ranged from 4.40 mg/dm^3 to 50.10 mg/dm^3 for the rainy season and from 4.07 mg/dm^3 to 20.56 mg/dm^3 for the dry

season. Mean phosphate of 16.18 ± 16.97 mg/dm^3 and 8.95 ± 5.64 mg/dm^3 were obtained for the rainy and dry seasons respectively. The control sampling points recorded phosphate mean values of 8.4 ± 0.06 mg/dm^3 and 4.43 ± 0.19 mg/dm^3 for rainy and dry seasons respectively.

The results obtained for phosphate content for River Tangale Water are presented in Table 4.2 for both rainy and dry seasons. The phosphate content ranged from 1.37 mg/dm^3 to 354.90 mg/dm^3 for the rainy season and from 1.52 mg/dm^3 to 47.50 mg/dm^3 for the dry season. Slight variations in the results were observed at various sampling points throughout the study period. Mean phosphate of 76.91 ± 135.21 mg/dm^3 and 22.77 ± 14.40 mg/dm^3 were obtained for the rainy and dry seasons respectively. The control sampling points recorded phosphate mean values of 8.07 ± 0.09 mg/dm^3 and 8.37 ± 0.05 mg/dm^3 for rainy and dry seasons respectively.

4.1.2 Heavy metals in surface water of Rivers Gbako and Tangale

The results of the total heavy metal content in surface water of Rivers Gbako and Tangale are presented in Tables 4.3 and 4.4 respectively.

i. Gold

Au concentration ranges from 26.9 mg/dm^{3}to 29.8 mg/dm^3 and 4.1 mg/dm^3 to 6.4 mg/dm^3 during rainy and dry seasons respectively.

Mean gold (Au) concentration of 27.9 ± 0.02 mg/dm^3 and 5.39 ± 0.02 mg/dm^3 were obtained respectively for rainy and dry seasons for River Gbako surface water. The mean concentrations obtained for the control were 27.7 ± 0.01 mg/dm^3 and 4.8 ± 0.03 mg/dm^3 for rainy and dry season (Table 4.3).

The concentration ranges from 25.4 mg/dm^3 to 28.4 mg/dm^3 and from 2.7 mg/dm^3 to 5.3 mg/dm^3 for rainy and dry seasons respectively.The results obtained for

the surface water of River Tangale were similar to those for River Gbako with mean values of 26.9 ± 0.01 mg/dm^3 and 3.41 ± 0.02 mg/dm^3 respectively for rainy and dry seasons. The mean concentrations obtained for the control were 27.5 ± 0.00 mg/dm^3 and 60.2 ± 0.03 mg/dm^3 for rainy and dry season (Table 4.4).

ii. Cadmium

Cd concentration ranges from 2.0 mg/dm^3 to 43.1 mg/dm^3 and from below detection limit (BDL) to 7.0 mg/dm^3 for rainy and dry seasons respectively.The mean cadmium (Ca) concentration of 10.5 ± 0.04 mg/dm^3 was obtained for River Gbako surface water during rainy season, whereas 2.76 ± 0.02 mg/dm^3 (Tables 4.3) was obtained during the dry seaason. The mean concentrations obtained for the control were 18.1 ± 0.02 mg/dm^3 and 3.0 ± 0.0 mg/dm^3 for both rainy and dry seasons (Table 4.3).

Mean concentration value of 3.5 ± 0.04 mg/dm^3 was obtained for River Tangale surface water during rainy season, whereas during the dry season the values obtainedwere below detection limit (Table 4.4). The mean concentration obtained for the control was 2.6 ± 0.06 mg/dm^3 for rainy only, dry season recorded values below detection limit (Table 4.4). Mean values obtained during dry season were quite low when compared to the values obtained during rainy season.

iii. Copper

The total copper content obtained ranged from 18.7 mg/dm^3 to 249.0 mg/dm^3 and 5.0 mg/dm^3 to 33.7 mg/dm^3 with mean values of 23.86 ± 0.02 mg/dm^3 and 14.26 ± 0.02 mg/dm^3 respectively for rainy and dry seasons for River Gbako surface water. The control sampling points recorded 18.2 ± 0.01 mg/dm^3 and 5.9 ± 0.01 mg/dm^3 for rainy and dry seasons respectively (Table 4.3).

Whereas the result of total Cu contents ranged from 17.8 mg/dm^3 to 813.10 mg/dm^3 and from 5.30 to 39.70mg/dm^3 with mean values of 140.90 ± 0.03 mg/dm^3 and 20.04 ± 0.03 mg/dm^3 respectively for rainy and dry seasons for River Tangale surface

Table 4.3: Mean concentration of heavy metals (mg/dm^3) in surface water of River Gbako (rainy and dry seasons)

Sample	Au	Cd	Cu	Fe	Mn	Pb	Zn
			Rainy Season				
1	27.4 ±0.02	3.8±0.03	18.7 ±0.02	220.8±0.04	318.5±0.22	22.2 ±0.07	229.24±0.39
2	27.4±0.01	13.1±0.17	19.0 ±0.02	104.5 ±0.13	16.4 ±0.06	29.9 ±0.02	697.61±0.08
3	29.8±0.02	43.1±0.01	24.0 ±0.03	66.3 ±0.05	30.1 ±0.07	25.5±0.12	300.3±0.03
4	26.9±0.05	2.4 ±0.01	22.7 ±0.01	37.0 ±0.04	14.6 ±0.05	21.3±0.02	248.71±0.10
5	27.2±0.02	2.0±0.02	21.8 ±0.02	273.5±0.06	373.6±0.09	26.9±0.05	176.7±0.04
6	27.9±0.01	3.2±0.04	35.9 ±0.01	106.9 ±0.55	57.8 ±0.08	27.1 ±0.04	175.03±0.10
7	28.7±0.00	5.9±0.01	24.9 ±0.05	432.7 ±0.15	779.3 ±0.08	28.7±0.08	383.99±0.26
Mean	27.9±0.02	10.5±0.06	23.9±0.01	177.4±0.18	227.2±0.06	25.09±0.04	315.9 ± 0.13
Control	27.7±0.01	18.1±0.02	18.2±0.01	85.0 ±0.11	22.0 ±0.05	28.0±0.03	301.54±0.09
			Dry Season				
1	5.2±0.01	4.0 ±0.04	10.1 ±0.03	276.9±0.03	71.1 ±0.10	62.8 ±0.02	83.6±0.06
2	5.3±0.02	BDL	5.0 ±0.01	269.9 ±0.06	22.6 ±0.04	61.7 ±0.01	63.33±0.05
3	6.1±0.02	BDL	13.8 ±0.01	71.5 ±0.04	64.9 ±0.13	49.9 ±0.07	113.07±0.09
4	4.1±0.02	3.3±0.06	5.2 ±0.02	23.44±0.04	5.4 ±0.10	88.4±0.02	149.1±0.08
5	6.0±0.02	7.0±0.03	5.7±0.02	540.0 ±0.04	61.5±0.05	76.6±0.03	11.66±0.08
6	4.6±0.02	BDL	26.3 ±0.04	2.9 ±0.02	0.8 ±0.07	51.9±0.06	81.08±0.07
7	6.4±0.01	5.0±0.03	33.7±0.04	10.3±0.07	113.0±0.13	57.4±0.03	51.0±0.03
Mean	5.4±0.01	2.7±0.02	14.2 ± 0.01	170.7± 0.02	48.5±0.04	64.17 ± 0.02	79.0 ± 0.02
Control	4.8 ±0.03	3.0±0.02	5.9 ±0.01	198.2 ±0.07	5.1 ±0.02	66.3±0.05	107.71±0.15
WHO		5	30	20	5	10	90

Table 4.4: Mean concentration of heavy metals (mg/dm^3) in surface water of River Tangale (rainy and dry seasons)

Sample	Au	Cd	Cu	Fe	Mn	Pb	Zn
				Rainy Season			
1	26.7 ±0.01	2.9±0.04	21.8±0.00	89.8±0.04	13.2±0.05	27.8 ±0.05	207.88±0.03
2	28.4±0.02	2.7±0.03	19.3 ±0.02	53.4 ±0.01	4.7 ±0.05	23.1±0.03	161.84±0.07
3	27.2±0.01	2.6±0.04	36.1±0.03	10717.1 ± 0.6	58.6±0.06	25.9 ±0.05	236.26±0.02
4	27.2±0.02	2.2±0.03	52.7 ±0.03	9909.0± 0.4	49.7±0.02	22.2±0.03	254.25±0.11
5	25.8±0.03	2.7±0.04	25.5±0.01	271.9 ± 0.1	24.8±0.2	29.6 ±0.02	184.81±0.06
6	27.6±0.02	2.2±0.04	17.8 ±0.03	111.2±0.04	7.8 ±0.03	26.2±0.02	90.18±0.07
7	25.4±0.00	9.3±0.04	81.3±0.07	175.1 ±0.11	17.0±0.06	27.5 ±0.10	753.51±0.05
Mean	26.9±0.01	3.5± 0.01	36.4 ±0.02	3046.8±0.22	25.1±0.06	26.0±0.02	269.8±0.03
Control	27.5±0.03	2.6 ±0.06	16.9 ±0.03	123.7 ±0.06	5.6 ±0.05	24.4 ±0.03	248.90±0.12
				Dry Season			
1	2.7±0.03	BDL	6.3±0.01	531.3±0.14	8.3±0.02	64.8±0.07	142.78±0.05
2	4.2±0.00	BDL	33.8±0.03	301.6±0.14	2.6±0.01	66.4±0.04	138.4±0.04
3	3.5±0.02	BDL	8.2 ±0.01	4902.9±0.06	60.6±0.06	56.0±0.02	70.76±0.05
4	5.3±0.02	BDL	37.6±0.03	8628.3±0.05	50.0±0.03	65.6±0.05	116.2±0.24
5	4.4±0.02	BDL	39.7±0.04	5290.8±0.10	189.7±0.13	62.3±0.02	140.7±0.04
6	3.5±0.01	BDL	9.4 ±0.03	246.0±0.03	1.6±0.01	49.2±0.07	26.0±0.02
7	2.9±0.01	BDL	5.3±0.04	26.4±0.03	20.51±0.08	65.3±0.08	116.8±0.06
Mean	3.4±0.01	BDL	20.0± 0.01	2846.8 ± 0.05	47.6 ± 0.04	61.4 ± 0.02	107.4±0.08
Control	2.7±0.01	BDL	3.8±0.02	61.48±0.03	60.2 ±0.03	52.6±0.12	100.3±0.06
WHO		5	30	20	5	10	90

water (Table 4.4).The control sampling points recorded mean concentrations of 16.9 ± 0.03 mg/dm^3 and 3.8 ± 0.02 mg/dm^3 for rainy and dry seasons respectively (Table 4.4).

iv. Iron

The ironcontent ranged from 37.00 mg/dm^3 to 432.7 mg/dm^3 and 2.90 mg/dm^{3}to 540.0 mg/dm^3 with mean values of 177.39 ± 0.15 mg/dm^3 and 170.71 ± 0.04 mg/dm^3 respectively for rainy and dry seasons for River Gbako surface water. Mean concentrations of 85.0 ± 0.11 mg/dm^3 and 198.2 ± 0.07 mg/dm^3 were recorded the control sampling points for rainy and dry seasons respectively (Table 4.3).

The total Fe contents ranged from 53.40 mg/dm^3 to 10717.1 mg/dm^3 and from 26.40 mg/dm^3 to 8628.30 mg/dm^3 with mean of 3046.8 ± 0.19 mg/dm^3 and 2846.76 ± 0.08 mg/dm^3 respectively for rainy and dry seasons for River Tangale surface water. However, 123.7 ± 0.06 mg/dm^3 and 61.48 ± 0.03 mg/dm^3 were recorded for the control points for the two seasons (Table 4.4).

v. Manganese

The manganese contents ranged from 14.60 mg/dm^3 to 779.30 mg/dm^3 and from 5.4 mg/dm^3 to 113.00 mg/dm^3 with mean values of 227.19 ± 0.15 mg/dm^3 and 48.47 ± 0.09 mg/dm^3 respectively for rainy and dry seasons for River Gbako surface water. The control sampling points recorded values of 22.00 ± 0.05 mg/dm^{3}and 5.1 ± 0.02 mg/dm^3 for rainy and dry seasons respectively (Table 4.3).

Whilst the result of total Mn contents ranged from 4.70 mg/dm^3 to 58.60 mg/dm^3 and 1.60 mg/dm^3 to 189.70 mg/dm^3 with mean values of 25.1 ± 0.04 mg/dm^3 and 47.62 ± 0.49 mg/dm^3 respectively for rainy and dry seasons for River Tangale surface water . The concentrations at control points were 5.6 ± 0.05 mg/dm^3 and 60.2 ± 0.03 mg/dm^3 for the two seasons respectively (Table 4.4).

vi. Lead

The leadcontent ranged from 21.30 mg/dm^3 to 29.90 mg/dm^3 and 49.90 mg/dm^3 to 88.40 mg/dm^3 with mean of 26.2 ± 3.05 mg/dm^3 and 64.38 ± 12.84 mg/dm^3 respectively for rainy and dry seasons for River Gbako surface water. The control sampling points recorded concentrations of 28.0 ± 0.03 mg/dm^3 and 66.3 ± 0.05 mg/dm^3 for rainy and dry seasons respectively (Table 4.3).

However the result of total Pb contents for River Tangale surface water ranged from 22.2 mg/dm^3 to 29.6 mg/dm^3 and 49.2 mg/dm^3 to 66.40 mg/dm^3 with mean values of 26.0 ± 0.04 mg/dm^3 and 61.37 ± 0.05 mg/dm^3 respectively for rainy and dry seasons. The control sampling points recorded concentrations of 24.4 ± 0.03 mg/dm^3 and 52.6 ± 0.12 mg/dm^3 for rainy and dry seasons respectively (Table 4.4).

vii. Zinc

Zn content in River Gbako surface water during rainy and dry seasons ranged from 175.03 mg/dm^3 to 697.61 mg/dm^{3}and 0.51mg/dm^3 to149.10 mg/dm^3 with mean values of 315.94 ± 0.14 mg/dm^3 and 71.76 ± 0.07 mg/dm^3 respectively for rainy and dry seasons for River .The control sampling points recorded concentrations of 301.54 ± 0.09 mg/dm^3 and 107.71 ± 0.15 mg/dm^3 for rainy and dry seasons respectively (Table 4.3).

The result of total Zn contents ranged from 90.18 mg/dm^3 to 753.51 mg/dm^{3}and from 2.6 mg/dm^3 and 142.78 mg/dm^3 with mean values of 269.8 ± 0.06 mg/dm^3 and 104.03 ± 0.07 mg/dm^3 respectively for rainy and dry seasons for River Tangale surface water. The concentrations at control points were 248.90 ± 0.12 mg/dm^3 and100.3 ± 0.06 mg/dm^{3}for the two seasons respectively (Table 4.4).

4.2 Soil Physico-chemical Characteristics of the Mining Sites

The results for soil characteristics of Asha and Saboeregi mining sites are presented in Tables 4.5.The pH values ranged from 4.05 to 5.35 and 5.04 to 6.68 with

mean values of 4.92 ± 0.37 and 5.74 ± 0.51 respectively for rainy and dry seasons for Asha mining site. The result obtained for pH values ranged from 3.93 to 6.27 and 4.81 to 5.94 with mean values of 5.21 ± 0.62 and 5.28 ± 0.25 respectively for rainy and dry seasons for Saboeregi mining site. Soil organic carbon concentration ranged from 0.36 to 2.96 and 0.37 to 2.22 with mean values of 1.70 ± 0.66 and 1.32 ± 0.51respectively for rainy and dry seasons for Asha mining site. The result obtained for the soil organic carbon concentration values ranged from 0.12 to 3.75 and 0.68 to 3.13 with mean values of 2.15 ± 1.02 and 1.85 ± 0.69 respectively for rainy and dry seasons for Saboeregi mining site. The soil organic matter concentration ranged from 0.63 to 5.10 and 0.63 to 3.83 with mean values of 3.01 ± 1.11 and 2.25 ± 0.90 respectively for rainy and dry seasons for Asha mining site. The results obtained for soil organic matter concentration of Saboeregi mining site ranged from 0.22 to 6.91 and 1.17 to 5.40 with mean values of 3.73 ± 1.81 and 3.21 ± 1.20 for rainy and dry seasons.

The result of the available phosphorus content for Asha mining site ranged from 26.80 to 30.50 mg/dm^{3}and 1.19 mg/dm^3 to 15.83 mg/dm^3 with mean values of 28.54 ± 1.17 mg/dm^3 and 3.30 ± 3.33 mg/dm^3 respectively for rainy and dry seasons. The result obtained for soil organic matter concentration ranged from 26.60 mg/dm^3 to 76.90 mg/dm^3 and1.08 mg/dm^3 to 29.26 mg/dm^3 with mean values of 31.3 ± 11.51 mg/dm^3 and 7.30 ± 9.01 mg/dm^{3}respectively for rainy and dry seasons for Saboeregi mining site. The cation exchange capacity ranged from 2.84 meq/100g to 16.98 meq/100g and 4.84 meq/100g to 26.50 meq/100g with mean and standard deviation values of 6.82 ± 4.28 meq/100g and 11.95 ± 5.45 meq/100g respectively for rainy and dry seasons for Asha mining site.The result obtained for soil organic matter concentration values ranged from 3.64 meq/100g to 22.01 meq/100g and 4.77 meq/100g to 36.23 meq/100g with mean and

Table 4.5: Descriptive statistics of soil characteristics for Asha and Saboeregi sites at different seasons

Parameter		Asha		Saboeregi		Control	
	Season	Mean	STD	Mean	STD	Mean	STD
pH		4.92	0.37	5.21	0.62	6.4	0.21
O.C (%)	**Rainy**	1.7	0.66	2.15	1.02	1.3	0.14
O.M (%)		3.01	1.11	3.73	1.81	2.3	0.23
A.P (mg/kg)		28.54	1.17	31.3	11.51	81	10.57
CEC (Cmol/Kg)		6.82	4.28	8.6	4.81	12	3.94
pH		5.74	0.51	5.28	0.25	6.38	0.21
O.C (%)	**Dry**	1.32	0.51	1.85	0.69	1.33	0.13
O.M (%)		2.25	0.9	3.21	1.2	2.29	0.23
A.P (mg/kg)		3.3	3.33	7.3	9.01	93.16	6.55
CEC (Cmol/Kg)		11.95	5.45	25.39	9.52	12	3.73

O.C = organic carbon, O.M. = organic matter A.P. = available phosphate and
CEC= cation exchange capacity

standard deviation values of 8.60 ± 4.81 meq/100g and 25.39 ± 9.52 meq/100g respectively for rainy and dry seasons for Saboeregi mining site. The sand value results obtained for both mining sites revealed that the soils were very sandy.

4.2.1 Soil textural class of the mining sites

The result for soil texture of Asha and Saboeregi mining sites is presented in Figures 4.1 to 4.2 and Appendix III. The sand values were with mean and standard deviation of 63.67 ± 6.17% and 59.21 ± 8.55% respectively for rainy and dry seasons for Asha mining site. Whereas the result obtained for sand values were with mean and standard deviation values of 62.46 ± 8.09% and 54.17 ± 6.11% respectively for rainy and dry seasons for Saboeregi mining site.

Silt values were with mean and standard deviation values of 17.00 ± 4.83% and 23.20 ± 7.00 respectively for rainy and dry seasons for Asha mining site. The results obtained for silt were mean and standard deviation values of 15.33 ± 5.82% and 13.52 ± 4.90% respectively for rainy and dry seasons for Saboeregi mining site. Clay content were with mean and standard deviation values of 19.84 ± 8.21 % and 17.59 ± 2.25 % respectively for rainy and dry seasons for Asha mining site. The result obtained for clay content has mean and standard deviation values of 15.33 ± 5.82 % and 13.52 ± 4.90 % respectively for rainy and dry seasons for Saboeregi mining site.

4.2.2 Heavy metals in soils of the mining sites

The mean concentrations range of the heavy metals from the soils of the mining sites of Asha, Saboeregi and the control site are presented in Tables 4.6 and 4.7.

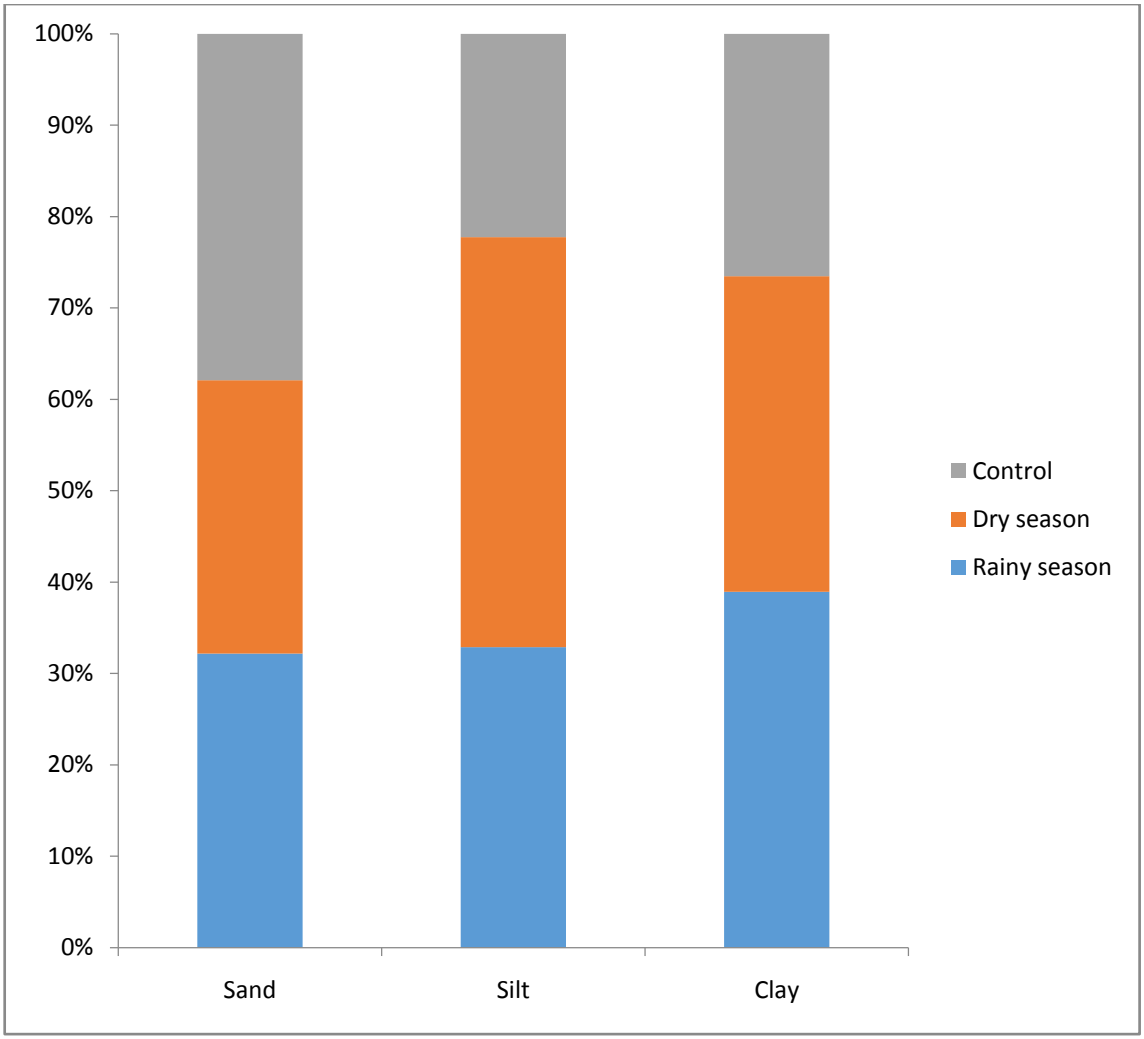


Fig. 4.1: Soil textural class for Asha mining site

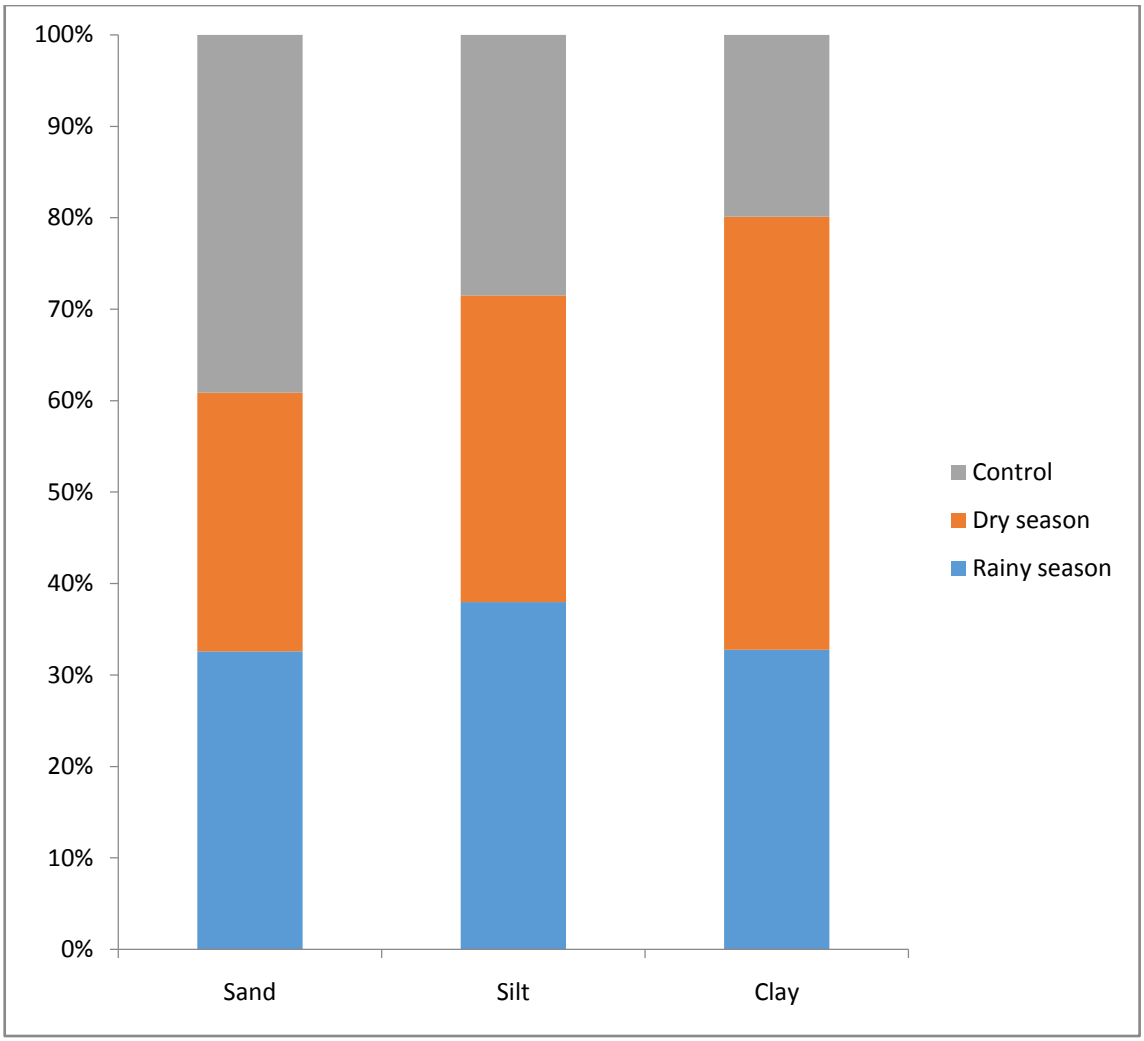


Fig.4.2: Textural class for Saboeregi mining site

Gold

Au mean concentration ranged from 12.4 ± 0.09 to 18.47 ± 0.03 mg/kg and 5.47 ± 0.01 to 7.60 ± 0.02 mg/kg respectively for rainy and dry seasons for Asha mining site. Mean values of 27.8 ± 1.01 mg/kg was obtained at the control site.

The results obtained for the Saboeregi mining site the range were 19.5 ± 0.02 to 22.37 ± 0.02 mg/kg and from 1.43 ± 0.16 to 5.8 ± 0.01 mg/kg respectively for both rainy and dry seasons and 27.8 ± 1.01 mg/kg of Au was obtained at the control site.

Cadmium

The mean concentration of cadmium (Cd) was 2.83 ± 0.11 mg/kg at Asha mining site during rainy season, whereas during the dry season the value obtained was 1.12 ± 0.02 mg/kg .Cd content ranged from 1.8 ± 10.00 to 4.81 ± 0.21 mg/kg and BDLto 2.90 ± 0.02 mg/kg respectively for rainy and dry seasons for Asha mining site.(Table 4.6).

Mean concentration values of 8.66 ± 0.01 mg/kg and 0.33 ± 0.0 mg/kg were obtained at Saboeregi mining site during rainy and dry seasons respectively. At Saboeregi site Cd concentration ranged from BDL to 17.36 ± 0.01 mg/kg and BDLto 0.80 ± 0.02 mg/kg respectively for rainy and dry seasons.(Table 4.7).Mean values of 3.4 ± 1.39 mg/kg was obtained at the control site.

Copper

The value of the mean copper concentration of 27.07 ± 0.04 mg/kg was obtained for Asha mining site during rainy season, whereas during the dry season the values obtained were 36.02 ± 0.18 mg/kg. Cu concentration ranged from 21.21 ±0.03 to 47.53 ± 0.02 mg/kg and 27.96± 0.26to 45.8 ± 0.22mg/kg respectively for rainy and dry seasons. (Table 4.6).

Mean concentration values of 52.17 ± 0.03 mg/kg and 37.59 ± 0.12 mg/kg was obtained for Saboeregi mining site during rainy and dry seasons respectivelyCu concentration ranged from 16.16 ± 0.01 to 88.54 ± 0.03 mg/kg and 29.17 ± 0.08to 53.88 ± 0.13 mg/kg respectively for rainy and dry seasons(Table 4.7), with mean value of 17.6 ± 0.6 mg/kg at the control site.

Iron

The mean concentration of 12866 ± 0.026 mg/kg was obtained at Asha mining site during rainy season, whereas during the dry season the values obtained gave a mean of 202.86 ± 0.024.Fe concentration ranged from 3656.66 ± 0.05 to 24423.03 ± 0.1 mg/kg and 177.06 ± 0.03to 251.54 ± 0.08 mg/kg respectively for rainy and dry seasons Asha site. (Table 4.6).

At SaboeregiFe concentration ranged from 5358.00 ± 0.07 to 49898.56 ± 0.19 mg/kg and 124.06.08 ± 0.03to 343.18 ± 0.2 mg/kg respectively for rainy and dry seasons.Mean concentration values of 28931.51 ± 0.056 mg/kg and 229.09 ± 0.13 were obtained at Saboeregi mining site during rainy and dry seasons respectively (Table 4.7). Mean values of 3577.0 ± 12.11 mg/kg was obtained at the control site.

Manganese

Manganese mean concentration of 313.22 ± 1.527 mg/kg with range between 199.18 ± 3.12 and 454.47 ± 0.01 mg/kg were recorded at the Asha mining site during rainy season, whereas in the dry season the mean concentration obtained was 24.14 ± 0.008 mg/kg with range between 22.84 ± 0.05 and 25.32 ± 0.04 mg/kg (Table 4.6).

Mean concentration of 631.09 ± 0.044 mg/kg and 17.1 ± 0.056 were obtained at Saboeregi mining site during rainy and dry seasons respectively.Mn concentration

ranged from 225.00 ± 0.04 to 955.74 ± 0.09 mg/kg and 12.53 ± 0.06to 20.76 ± 0.18 mg/kg

Table 4.6: The mean concentrations (mg/kg) of heavy metals in soils of Asha mining site

Quadrant		Au	Cd	Cu	Fe	Mn	Pb	Zn
Rainy	1	13.78±0.11	4.81±0.21	21.21±0.03	7954.16±0.06	199.18±3.12	15.24±0.05	154.58±0.08
	2	12.4±0.09	1.8±10	27.79±0.02	15433.28±0.1	377.28±0.09	10.43±0.03	114.52±0.06
	3	17.7±0.07	2.4±0.03	11.74±0.1	3656.66±0.05	221.96±0.1	11.96±0.03	73.06±0.02
	4	18.47±0.03	2.3±0.01	47.53±0.02	24423.03±0.1	454.47±0.01	10.43±0.03	96.55±0.08
	Mean	15.59±0.034	2.83±0.09	27.07±0.038	12866±0.026	313.22±1.527	12.02±.0.01	109.68±0.03
Dry	1	7.6±0.02	1.58±0.06	45.8±0.22	251.54±0.08	25.32±0.04	28.83±0.06	86.8±0.32
	2	5.62±0.01	2.9±0.02	27.96±0.26	203.0±0.04	22.84±0.05	32.98±0.04	91.66±0.1
	3	6.46±0.02	BDL	30.66±0.22	179.82±0.03	23.72±0.04	28.86±0.4	302.18±0.65
	4	5.47±0.01	BDL	39.67±0.01	177.06±0.03	24.67±0.03	35.46±0.06	85.76±0.25
	Mean	6.63± 0.006	1.12±0.028	36.02±0.113	202.86±0.024	24.14±0.008	31.53±0.17	141.61±0.23
	Control	27.8±1.01	3.4±1.39	17.6±0.61	3577.0±12.11	129.8±2.8	10.6±1.89	63.3±2.8

Table 4.7: The mean concentrations (mg/kg) of heavy metals in soils of Saboeregi mining site

	Quadrant	Au	Cd	Cu	Fe	Mn	Pb	Zn
Rainy	1	19.84±0.01	BDL	88.54±0.03	49898.56 ± 0.19	955.74 ± 0.09	16.24 ± 0.03	119.6 ± 0.09
	2	19.5±0.02	17.36±0.01	72.72±0.03	44977.24 ± 0.08	886.28 ± 0.04	13.92 ± 0.03	132.52 ± 0.1
	3	20.72±0.03	2.08±0.01	31.26±0.02	15492.22 ± 0.08	457.34 ± 0.13	15.02 ± 0.03	119.83 ± 0.33
	4	22.37±0.02	15.21±0.01	16.16±0.01	5358.00±0.07	225.00 ± 0.04	15.5 ± 0.02	74.28 ± 0.14
	Mean	20.61±0.008	8.66±0.01	52.17±0.009	28931.51±0.056	631.09 ± 0.044	359.69 ± 0.005	111.56 ± 0.112
Dry	1	1.44±0.23	BDL	35.42±0.14	343.18±0.2	20.4 ± 0.18	18.22±0.22	85.92 ± 0.18
	2	2.54±0.06	0.5±0.02	31.88±0.13	224.5±0.18	14.7 ± 0.15	37.75±0.19	90.45 ± 3.70
	3	1.43±0.16	0.8±0.02	53.88±0.13	224.6±0.06	20.76 ± 0.18	26.84±0.15	91.09 ± 0.31
	4	5.8±0.01	BDL	29.17±0.08	124.06±0.08	12.53 ± 0.06	33.53±0.07	102.36 ± 0.05
	Mean	2.8±0.098	0.33±0	37.59±0.027	229.09±0.070	17.10±0.056	29.09±0.065	92.46±1.763
	Control	27.8±1.01	3.4±1.39	17.6±0.61	3577.0±12.11	129.8±2.8	25.6±1.89	63.3±2.8

respectively for rainy and dry seasons. (Table 4.7). Mean value of 129.8 ± 2.8 mg/kg was obtained at the control site.

Lead

Mean lead concentration of 12.2 ± 0.01 mg/kg was obtained for Asha mining site during rainy season while 31.53 ± 0.17 mg/kg was obtained in the dry season. The range for the rainy and dry seasons were from 10.43 ± 0.03 to 15.24 ± 0.05 mg/kg and from 28.83 ± 0.06 mg/kg to 35.46 ± 0.06 mg/kg respectively (Table 4.6). Mean concentration values of 631.09 ± 0.08 mg/kg and 29.09 ± 0.16 were obtained for Saboeregi mining site during rainy and dry seasons respectively (Table 4.7). At the control site mean value of 10.6 ± 1.89 mg/kg Pb was obtained.

Zinc

Zn content of 109.68 ± 0.03 mg/kg was obtained for Asha mining site during rainy season and 141.61 ± 0.23 mg/kg for the dry season.The range for the rainy and dry seasons were from 73.06 ± 0.02 to 154.58 ± 0.08 mg/kg and from 85.76 ± 0.25 mg/kg to 302.18 ± 0.65 mg/kg respectively (Table 4.6). Mean concentration values of 111.56 ± 0.112 mg/kg and 92.46 ± 1.763 was recorded for Saboeregi mining site during rainy and dry seasons, respectively.Zn range for the rainy and dry seasons were from 74.28 ± 0.14 to 132.52 ± 0.1 mg/kg and from 85.92 ± 0.18 mg/kg to 102.36 ± 0.05 mg/kg respectively (Table 4.7). Control site recorded mean values of 63.3 ± 2.8 mg/kg.

4.3 Mean Heavy Metals Concentration in the *Sorghumbicolor* grains Cultivated in the Mining Vicinity

The results of the mean concentration for Au, Cd, Cu, Fe, Mn, Pb, and Zn contents in the *Sorghum* grains harvested from the mining vicinity and the control sites are presented in Table 4. 8. The Au contents in *Sorghum bicolor* grains ranged from

1.48 to 2.16 mg/kg with mean of 1.74 ± 0.07 mg/kg for Asha site while that of Saboeregi site

Table 4.8: Heavy metals concentration(mg/kg) in S*orghum* bicolor grains

	Asha site		Saboeregi site		Control site
Metal	Mean ± STD	Range	Mean ± STD	Range	Mean ± STD
Au	1.74±0.07	1.48-2.16	2.01±0.01	1.13- 2.80	1.34 ± 0.01
Cd	0.2±0.02	BDL-0.8	0.03±0.02	BDL-0.10	BDL
Cu	9.01±0.02	6.43-14.28	6.09±0.11	3.66-9.90	7.64 ± 0.02
Fe	1674.85±0.06	156.8-5830.26	2299.36±0.08	112.13-8605.33	322.29±0.00
Mn	48.38±0.34	13.6-152.7	62.82±0.34	24.85-122.26	18.99±0.00
Pb	29.28±0.17	26.8-33.35	35.56± 0.05	33.84-37.90	41.66±0.00
Zn	65.21±0.03	45.71-83.75	19.04±0.05	1.41-82.90	29.48±0.00

ranged from 1.13 to 2.80 mg/kg with mean of 2.01 ± 0.02 mg/kg (Table 4.8). The mean for the control site was 1.34 ± 0.01 mg/kg.

The Cd contents in *Sorghum bicolor* grains ranged from below detection limit to 0.8 mg/kg with mean of 0.2 ± 0.06 mg/kg for Asha site while that of Saboeregi site ranged from below detection limit to 0.1 mg/kg with mean of 0.03 ± 0.01 mg/kg (Table 4.8). The mean for the control site was below detection limit.

The Cu contents in *Sorghum bicolor* grains ranged from 6.43 to 14.28 mg/kg with mean of 9.01 ± 0.02 mg/kg for Asha site while that of Saboeregi site ranged from 3.66 to 9.9 mg/kg with mean of 6.09 ± 0.11 mg/kg (Table 4.8). The mean for the control site was 7.64 ± 0.02 mg/kg.

Values obtained for Fe in *Sorghum bicolor* grains ranged from 156.8 to 5830.26 mg/kg with mean of 1674.85 ± 0.06 mg/kg for Asha site while that of Saboeregi site ranged from 112.13 to 8605.33 mg/kg with mean of 2299.36 ± 0.08 mg/kg (Table 4.8).

Mean value obtained for the control site was 322.29 ± 0.00 mg/kg.

Mn levels in *Sorghum bicolor* grains ranged from 13.6 to 152.7 mg/kg with mean of 48.38 ± 0.34 mg/kg for Asha site while that of Saboeregi site ranged from 24.85 to 122.26 mg/kg with mean of 62.82 ± 0.34 mg/kg (Table 4.8). The mean for the control site was 18.99 ± 0.00 mg/kg.

Pb levels in *Sorghum bicolor* grains ranged from 26.8 to 33.35 mg/kg with mean of 29.28 ± 0.17 mg/kg for Asha site while that of Saboeregi site ranged from 33.84 to 37.9 mg/kg with mean of 35.56 ± 0.05 mg/kg (Table 4.8). The mean for the control site was 41.66 ± 0.00 mg/kg.

Zn in *Sorghum* grains ranged from 45.71 to 83.75 mg/kg with mean of 62.21 ± 0.03 mg/kg for Asha site while that of Saboeregi site ranged from 6.36 to 30.47 mg/kg

with mean of 19.04 ± 0.05 mg/kg (Tables 4.8). The mean for the control site was 29.48 ± 0.00 mg/kg.

4.3 Correlation Analysis

4.3.1 Pearson's correlation coefficients between the physico-chemical parameters and heavy metals in the waters from the study sites

The results in Tables 4.9 to 4.12 showed correlation between the physico-chemical parameters, whereas Tables 4.13 to 4.16 the correlations between the heavy metals in the waters of rivers Gbako and Tangale where the mining activities were conducted in rainy and dry seasons.

The result from Gbako waters showed that conductivity was positively correlated with TDS and chloride. DO was negatively correlated with TDS and conductivity. Alkalinity was positively with TDS, conductivity and chloride negatively correlated with DO.Total solid was positively correlated with turbidity, colour and suspended solid. COD showed perfect correlation with BOD at (r = 1). Nitrate was positively correlated with pH, turbidity and colour. Phosphate showed positive correlation with turbidity and nitrate.

The result for River Tangale waters showed that conductivity was perfectively correlated with TDS (r = 1). Chloride was positively correlated with turbidity. Total alkalinity and sulphide were positively correlated with turbidity and chloride. Colour, suspended solid and total solid were positively correlated with turbidity, chloride and sulphide. BOD was positively correlated with pH and DO. COD was positively correlated with turbidity, sulphide colour suspended solid and total solid. Nitrate was positively correlated with turbidity, chloride, sulphide and colour suspended solid, total solid and COD. Phosphate was positively correlated with turbidity, chloride, sulphide, colour, suspended solid, total solid, COD and nitrate.

Table 4.9: Pearson's correlation coefficients between physico-chemical parameters in waters from River Gbako rainy season

	pH	Turbidity	TDS	Conductivity	Dissolved Oxygen	Chloride	Total Alkalinity	Sulphide	Colour	Suspended Solid	Total Solid	Biochemical Oxygen Demand	Chemical Oxygen Demand	Nitrate	Phosphate
Ph	1														
Turbidity	.499	1													
TDS	.242	-.347	1												
Conductivity	.221	-.357	.984**	1											
Dissolved Oxygen	-.408	.036	-.747*	-.729*	1										
Chloride	.549	.065	.853**	.814*	-.900**	1									
Alkalinity	.085	-.455	.948**	.974**	-.767*	.771*	1								
Sulphide	-.051	.025	-.062	-.171	-.304	.240	-.083	1							
Colour	.667	.657	.056	-.058	-.386	.507	-.148	.561	1						
Susp. Solid	.273	.740*	.016	-.083	-.137	.292	-.192	.242	.744*	1					
Total Solid	.536	.771*	.076	-.028	-.300	.461	-.143	.373	.924**	.937**	1				
BOD	.306	.144	.228	.283	-.043	.047	.177	-.845**	-.193	.081	-.009	1			
COD	.294	.139	.228	.285	-.036	.042	.180	-.853**	-.206	.076	-.018	1.000**	1		
Nitrate	.745*	.762*	-.314	-.328	-.144	.188	-.386	.298	.743*	.349	.591	-.145	-.156	1	
Phosphate	.548	.930**	-.548	-.550	.142	-.099	-.624	.084	.622	.515	.618	.035	.028	.892**	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed)

Table 4.10: Pearson's correlation coefficients between physico-chemical parameters in waters from River Gbako dry season

	pH	Turbidity	TDS	Conductivity	Dissolved Oxygen	Chloride	Total Alkalinity	Sulphide	Colour	Suspended Solid	Total Solid	Biochemical Oxygen Demand	Chemical Oxygen Demand	Nitrate	Phosphate
pH	1														
Turbidity	-.200	1													
TDS	-.501	.570	1												
Conductivity	-.519	.547	.993**	1											
DO	.752*	-.240	-.724*	-.684	1										
Chloride	-.592	.729*	.927**	.930**	-.700	1									
T. Alkalinity	.420	-.057	.112	.036	-.046	-.180	1								
Sulphide	-.105	.243	.587	.550	-.430	.464	.169	1							
Colour	-.354	.798*	.519	.559	-.129	.704	-.331	-.104	1						
Susp. Solid	-.550	.712*	.797*	.838**	-.439	.907**	-.316	.179	.903**	1					
Total Solid	-.526	.641	.973**	.984**	-.650	.961**	-.029	.432	.685	910**	1				
BOD	-.916**	.432	.796*	.810*	-.825*	.853**	-.313	.323	.525	.777*	.816*	1			
COD	-.916**	.426	.798*	.812*	-.829*	.851**	-.304	.330	.517	.772*	.816*	1.000**	1		
Nitrate	-.334	.642	.872**	.819*	-.736*	.826*	.237	.686	.304	.546	.793*	.624	.626	1	
Phosphate	-.439	.407	.797*	.733*	-.901**	.731*	.306	.610	.142	.421	.695	.639	.644	.895**	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed)

Table 4.11: Pearson's correlation coefficients between physico-chemical parameters in waters from River Tangale rainy season

	pH	Turbidity	TDS	Conductivity	Dissolved Oxygen	Chloride	Total Alkalinity	Sulphide	Colour	Suspended Solid	Total Solid	Biochemical Oxygen Demand	Chemical Oxygen Demand	Nitrate	Phosphate
pH	1														
Turbidity	-.407	1													
TDS	.565	-.676	1												
Conductivity	.581	-.671	1.000**	1											
DO	.853**	-.578	.357	.371	1										
Chloride	-.490	.834**	-.493	-.494	-.684	1									
T. Alkalinity	-.343	.879**	-.284	-.282	-.688	.822*	1								
Sulphide	-.525	.759*	-.712*	-.711*	-.460	.852**	.550	1							
Colour	-.501	.862**	-.757*	-.754*	-.489	.883**	.652	.982**	1						
Suspend. Solid	-.489	.754*	-.716*	-.714*	-.422	.848**	.535	.998**	.983**	1					
Total Solid	-.484	.750*	-.702	-.700	-.421	.850**	.538	.998**	.981**	1.000**	1				
BOD	.870**	-.103	.175	.196	.838**	-.307	-.208	-.211	-.159	-.165	-.164	1			
COD	-.312	.807*	-.746*	-.738*	-.258	.698	.559	.888**	.916**	.896**	.892**	.061	1		
Nitrate	-.509	.856**	-.739*	-.736*	-.499	.887**	.656	.986**	.999**	.985**	.984**	-.176	.914**	1	
Phosphate	-.526	.857**	-.779*	-.777*	-.500	.878**	.639	.981**	.999**	.981**	.979**	-.177	.913**	.997**	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed)

Table 4.12: Pearson's correlation coefficients between physico-chemical parameters in waters from River Tangale dry season

	pH	Turbidity	TDS	Conductivity	Dissolved Oxygen	Chloride	Total Alkalinity	Sulphide	Colour	Suspended Solid	Total Solid	Biochemical Oxygen Demand	Chemical Oxygen Demand	Nitrate	Phosphate
pH	1														
Turbidity	-.468	1													
TDS	-.151	-.156	1												
Conductivity	-.152	-.155	1.000**	1											
Dissolved Oxygen	.305	-.246	-.089	-.087	1										
Chloride	-.224	-.088	.679	.674	-.455	1									
Total Alkalinity	.082	-.220	.599	.605	.428	-.160	1								
Sulphide	.218	.143	-.247	-.244	-.141	-.469	.145	1							
Colour	-.266	.743*	.014	.012	-.283	-.098	-.066	.057	1						
Suspended Solid	-.415	.699	-.709*	-.709*	.007	-.494	-.499	.042	.512	1					
Total Solid	-.149	.039	-.863**	-.865**	-.034	-.486	-.647	.219	-.074	.663	1				
B OD	-.222	-.297	-.425	-.424	.169	-.530	.004	.371	-.259	.247	.714*	1			
COD	-.223	-.312	-.391	-.389	.179	-.523	.044	.374	-.265	.217	.683	.999**	1		
Nitrate	-.250	.696	.120	.119	-.630	.184	-.194	.442	.744*	.255	-.073	-.239	-.245	1	
Phosphate	-.419	.061	-.302	-.296	.346	-.187	-.064	-.145	-.512	.309	.332	.319	.312	-.506	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed)

Table 4.13: Pearson's correlation coefficients between heavy metals in waters from River Gbako rainy season

	Au	Cd	Cu	Fe	Mn	Pb	Zm
Au	1						
Cd	-.178	1					
Cu	.366	-.167	1				
Fe	.053	-.225	.234	1			
Mn	.150	-.283	.840**	.177	1		
Pb	.241	.494	.334	.228	.170	1	
Zn	.039	.917**	.137	-.341	-.084	.557	1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed)

Table 4.14: Pearson's correlation coefficients between heavy metals in waters from River Gbako dry season

	Au	Cd	Cu	Fe	Mn	Pb	Zm
Au	1						
Cd	.290	1					
Cu	.359	-.055	1				
Fe	-.002	.276	-.225	1			
Mn	.867**	.475	.453	.284	1		
Pb	-.437	.552	-.595	.016	-.279	1	
Zn	-.727*	-.506	-.442	-.025	-.652	.216	1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed)

Table 4.15: Pearson's correlation coefficients between heavy metals in waters from River Tangale rainy season

	Au	Cd	Cu	Fe	Mn	Pb	Zm
Au	1						
Cd	-.665	1					
Cu	-.654	.992**	1				
Fe	.131	-.252	-.177	1			
Mn	-.146	-.137	-.073	.949**	1		
Pb	-.081	.173	.226	.123	.160	1	
Zn	-.667	.965**	.970**	-.064	.034	.175	1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed)

Table 4.16: Pearson's correlation coefficients between heavy metals in waters from River Tangale dry season

	Au	Cd	Cu	Fe	Mn	Pb	Zm
Au	1						
Cd	.[a]	.[a]					
Cu	.913**	.[a]	1				
Fe	.792*	.[a]	.625	1			
Mn	.339	.[a]	.479	.527	1		
Pb	.349	.[a]	.500	.237	.023	1	
Zn	.143	.[a]	.419	.137	.292	.845**	1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).
a. Cannot be computed because at least one of the variables is constant.

On the other hand in Gbako waters heavy metal correlation were noticed between Mn and Cu (r = 0.840) and also between Zn and Cd (r = 0.917) the correlation was significant at (P < 0.01) in the rainy season. Dry season showed that Mn and Au were positively correlated (r = 0.867) however, Zn showed negative correlation with Au (r = 0.727) and significant at (P < 0.05).

Tangale waters showed that Cu was positively correlated with Cd (r = 0.972). Mn was positively correlated with Fe while Zn was positively correlated with Cd and Cu and significant (P < 0.01) in the rainy season. In the dry season Tangale waters showed positive correltion between Cu and Au, Fe and Au, Zn and Pb

4.3.2 Pearson's correlation coefficients between soil physico-chemical characteristics and metals in soils at Asha and Saboeregi mining sites rainy and dry seasons

In Tables 4.17 to 4.20 Pearson correlation coefficients was used to understand the relationship between different physico-chemical parameters and heavy metals concentrations. There exist very strong significant positive correlations between organic matter (OM) and organic carbon (OC); Au and P; Mn and P; Pb and P with r values 0.980; 0.842; 0.752 and 0.764 respectively significant at (P < 0.05). The pH was negativelycorrelated with P, Au and Mn with r values -0.672; -0.561; -0.518; in the rainy season. However, in dry season strong positive correlations were also noticed between OM and OC; Au and P; Au and CEC; Au and Mn; Fe and Cu; Mn and Fe significant at (P< 0.05), the remaining correlations were either moderate or weak with r values between 0.348 and 0.684; at Asha site (Tables 4.17 and 4.18).

At Saboeregi site a strong positive correlation between OM and OC; Au and P; Fe and Cu; Mn and Au; Mn and Fe was observed in the study. Conversely strong but negative correlations were seen between Au and CEC; Pb and Au all at significant

levels of ($p < 0.05$). It was also observed that there were moderate and weak positive correlations

Table 4:17: Pearson's correlation coefficients between soil physico-chemical characteristics and metals in soils at Asha mining site rainy season

	PH	OC	OM	P	CEC	Au	Cd	Cu	Fe	Mn	Pb	Zn
PH	1											
OC	-0.030	1										
OM	-0.092	0.980**	1									
P	-0.672**	0.296	0.338	1								
CEC	0.302	0.361*	0.327	-0.491*	1							
Au	-0.561**	0.272	0.301	0.842**	-0.454**	1						
Cd	-0.060	0.136	0.140	0.257	-0.203	0.192	1					
Cu	-0.112	-0.025	0.090	-0.076	-0.018	-0.393*	0.095	1				
Fe	-0.277	0.345*	0.391*	0.519**	-0.009	0.023	-0.062	0.165	1			
Mn	-0.518**	0.217	0.243	0.752**	-0.214	0.091	-0.161	0.142	0.594	1		
Pb	0.615**	-0.193	-0.218	-0.764**	0.269	-0.259	0.464**	-0.222	-0.569	-0.142	1	
Zn	-0.307	-0.068	0.029	0.225	-0.219	-0.049	-0.134	0.190	0.155	0.561**	0.497**	1

* = Significant at 0.05
** = Significant at 0.01

Table 4.18: Pearson's correlation coefficients between soil physico-chemical characteristics and metals in soils at Asha mining site dry season

	PH	OC	OM	P	CEC	Au	Cd	Cu	Fe	Mn	Pb	Zn
PH	1											
OC	-.061	1										
OM	-.056	.999**	1									
P	.107	.059	.059	1								
CEC	.198	-.009	-.003	-.561**	1							
Au	-.133	.180	.183	.763**	-.753**	1						
Cd	.055	-.036	-.039	.146	-.185	.263	1					
Cu	.258	.473**	.481**	.244	-.161	.262	-.104	1				
Fe	.222	.397*	.400*	.555**	-.437**	.567**	-.050	.774**	1			
Mn	.115	.286	.287	.541**	-.514**	.731**	.046	.684**	.780**	1		
Pb	-.009	-.205	-.197	-.661**	.670**	-.833**	-.155	-.381*	-.603**	-.664**	1	
Zn	.160	.406*	.400*	.251	-.114	.207	.344*	.356*	.422*	.348*	-.124	1

* = Significant at 0.05

** = Significant at 0.01

Table 4.19: Pearson's correlation coefficients between soil physico-chemical properties and metals in soils at Saboeregi mining site rainy season

	PH	OC	OM	P	CEC	Au	Cd	Cu	Fe	Mn	Pb	Zn
PH	1											
OC	-0.061	1										
OM	-0.056	0.999**	1									
P	0.107	0.059	0.059	1								
CEC	0.198	-0.009	-0.003	0.561**	1							
Au	-0.133	0.180	0.183	0.763**	-0.753**	1						
Cd	0.055	-0.036	-0.039	0.146	-0.185	0.263	1					
Cu	0.258	0.473**	0.481**	0.244	-0.161	0.262	-0.104	1				
Fe	0.222	0.397*	0.400*	0.555**	-0.437**	0.567**	-0.050	0.774**	1			
Mn	0.115	0.286	0.287	0.541**	-0.514**	0.731**	0.046	0.684**	0.780**	1		
Pb	-0.009	-0.205	-0.197	-0.661**	0.670**	-0.833**	-0.155	-0.381*	-0.603**	-0.664**	1	
Zn	0.160	0.406*	0.400*	0.251	-0.114	0.207	0.344*	0.356*	0.422*	0.348*	-0.124	1

* = Significant at 0.05

** = Significant at 0.01

Table 4.20: Pearson's correlation coefficients between soil physico-chemical characteristics and metals in soils Saboeregi mining site dry season

	PH	OC	OM	P	CEC	Au	Cd	Cu	Fe	Mn	Pb	Zn
PH	1											
OC	-.061	1										
OM	-.056	.999**	1									
P	.107	.059	.059	1								
CEC	.198	-.009	-.003	-.561**	1							
Au	.329	.036	.053	.183	.519*	1						
Cd	.402	.008	.017	.821**	.129	.704**	1					
Cu	.299	-.004	-.010	.992**	-.205	.247	.853**	1				
Fe	.157	-.179	-.186	-.157	-.179	.054	-.123	-.112	1			
Mn	-.103	-.064	-.072	-.084	-.288	-.279	-.243	-.079	.502*	1		
Pb	-.364	-.035	-.050	-.188	-.532*	-.961**	-.685**	-.240	-.021	.284	1	
Zn	.363	-.002	.000	.895**	-.120	.478	.924**	.926**	-.016	-.089	-.435	1

* = Significant at 0.05

** = Significant at 0.01

between CEC and P; Cu and OC; Cu and OM; Fe and P; Fe and Au; Mn and P; at significant levels of ($P < 0.05$). There are also records of weak positive correlation between Zn and OC; Zn and OM; Zn and Cd; Zn and Cu; Zn and Fe; Zn and Mn significant at ($P < 0.01$) (Table 4.19).

Dry season record at Saboeregi show very strong positive correlations between OM and OC; Cd and P; Cd and Au; Cu and P; Cu and Au; Zn and P; Zn and Cd; Zn and Cu with r values 0.999; 0.821; 0.704; 0.992; 0.853; 0.895; 0.924; 0.926 respectively all significant at ($P < 0.05$), while moderate positive correlations were seen between CEC and Au; Mn and Fe with r values 0.519 and 0.502 respectively at significant levels ($P < 0.01$). A strong negative correlation is noticed between Pb and Au with r value of 0.961 significant at ($P < 0.05$), while moderate negative correlations were seen between CEC and P; Pb and CEC; Pb and Cd with r values 0.561; 0.532 and 0.685 respectively at significant levels ($P < 0.05$) (Table 4.20).between clay and sand; Pb and Au with r values 0.821 and 0.961 respectively significant at ($P < 0.05$) (Table 4.20).

4.3.3 Pearson's correlation coefficients between soil metal concentrations and metal concentrations in *Sorghum bicolor* grains at themining sites

Correlation studies between the soil heavy metals and heavy metals in the *Sorghum bicolor* grains from the two mining sites (Tables 4.21 and 4.22) indicated that at Asha site, strong positive correlation existed between Mn soil and Fe soil similarly between Cd soil and Cd *Sorghum*, other positive but moderate correlations were seen between Zn soil and Cd soil, Zn soil and Cu soil; Cd *Sorghum* and Zn soil; Mn Sorghum and Fe *Sorghum*.

Moreover at the Saboeregi mining site there were strong and moderate positive correlations among the metals in the soil such as between Cu soil and Au; Fe soil and Au soil; Fe soil and Cu soil; Mn soil and Au soil; Mn soil and Cd soil.

Table 4.21: Pearson's correlation coefficient between heavy metal concentrations in soil and metal concentrations in *Sorghum*bicolor at Ashasite

	AuSoil	CdSoil	CuSoil	FeSoil	MnSoil	PbSoil	ZnSoil	Ausorghurn	Cdsorghurn	Cusorghurn	Fesorghurn	Mnsorghurn	Pbsorghurn	Znsorghurn
Au Soil	1													
Cd Soil	.007	1												
Cu Soil	.111	-.040	1											
Fe Soil	-.114	.018	.351	1										
Mn Soil	-.138	-.185	.216	.719**	1									
Pb Soil	.195	.129	-.065	-.418	-.424	1								
Zn Soil	.016	.534*	.543*	.050	.061	-.059	1							
Ausorghurn	-.118	-.041	.274	.019	.221	-.057	.059	1						
Cdsorghurn	.011	.971**	-.075	-.026	-.186	.041	.536*	.090	1					
Cusorghurn	-.277	-.163	.345	-.092	.216	-.151	.401	.019	-.159	1				
Fesorghurn	-.321	-.082	.130	-.051	-.284	.359	-.053	-.113	-.092	.210	1			
Mnsorghurn	.240	-.267	.042	.082	.188	.384	-.278	.198	-.238	.074	.340	1		
Pbsorghurn	.044	-.393	.302	.407	.234	-.222	-.029	-.134	-.362	.273	.506*	.280	1	
Znsorghurn	-.124	-.176	.306	-.186	.187	-.023	.372	.030	-.179	.942**	.032	.110	.159	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table 4.22: Pearson's correlation coefficient between heavy metal concentrations in soil and metal concentrations in *Sorghum* bicolor at Saboeregi site

	AuSoil	CdSoil	CuSoil	FeSoil	MnSoil	PbSoil	ZnSoil	Ausorghurn	Cdsorghurn	Cusorghurn	Fesorghurn	Mnsorghurn	Pbsorghurn	Znsorghurn
Au Soil	1													
Cd Soil	.590*	1												
Cu Soil	.925**	.688**	1											
Fe Soil	.837**	.695**	.982**	1										
Mn Soil	.967**	.746**	.977**	.928**	1									
Pb Soil	.958**	.377	.789**	.663**	.853**	1								
Zn Soil	.987**	.710**	.940**	.865**	.989**	.909**	1							
Ausorghurn	-.103	-.110	-.091	-.081	-.108	-.089	-.113	1						
Cdsorghurn	-.108	-.069	-.097	-.086	-.103	-.105	-.107	.106	1					
Cusorghurn	.022	.110	.032	.035	.045	-.004	.043	.171	.064	1				
Fesorghurn	-.105	-.058	-.092	-.080	-.098	-.106	-.101	.057	-.060	.900**	1			
Mnsorghurn	.453	.393	.573*	.601**	.522*	.334	.471*	.309	-.161	.170	-.131	1		
Pbsorghurn	-.176	-.106	-.118	-.081	-.158	-.187	-.181	-.217	-.171	-.199	-.109	-.182	1	
Znsorghurn	.516*	.297	.432	.366	.482*	.517*	.510*	.031	.373	.033	-.221	.257	-.481*	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

4.3.4 Pearson's correlation coefficients between soil, river water and *Sorghum* bicolor grains metal concentrations at the mining sites

The results of the correlation studies between the soil heavy metals and heavy metals in rivers Gbako and Tangale from the two mining sites presented in Tables 4.23 to 4.28 indicated that at Saboeregi site strong positive correlation existed between Mn river water and Cu river water; Zn river water and Cd river water; Fe river water and Cd soil; Cd soil and Fe river; Fe soil and Cu soil. Similarly strong negative correlation was also seen between Mn soil and Cu river water (Table 4.23).

In the dry season at Saboeregi site strong positive correlation existed between Mn river water and Au river water; Cd soil and Cu river water; Cu soil and Au river water,Cu soil and Mn river; Fe soil and Pb river water; Mn soil and Cu soil. Negative correlation was observed between Zn river water and Au river water (Table 4.24).

At the Asha site positive and significant correlations were observed between Cu river water and Cd river water; Mn river water and Fe river water; Zn river water and Cd river water; Cu soil and Mn river water; Fe soil and Cd river water similarly negative correlations also existed between Au soil and Cd river water.

The results for Saboeregi site showed Au water was positively correlated with Fe*Sorghum bicolor* grain(r = 0.9672) and negatively with Zn *Sorghum bicolor* grain (r = 0.9035). Cd water had positive, moderate correlation with Fe *Sorghum bicolor* grain (r=0.5531) however,it has negative correlations with Zn (r = 0.6960) and Cu *Sorghum bicolor* grain (r = 0.5550). Cu water showed strong positive correlation with Cu(r = 0.9508) and Fe *Sorghum bicolor* grain (r= 0.9537). Pb in water had positive correlation with Zn (r = 0.9919) but negatively with Fe (r = 0.9654) in *Sorghumbicolor* grains (Table 4.25).

Table 4.23: Pearson's correlation coefficient between heavy metal concentrations in Gbako River and metals in Saboeregi mining soils rainy season

	Au River	Cd River	Cu River	Fe River	Mn River	Pb River	Zn River	Au Soil	Cd Soil	Cu Soil	Fe Soil	Mn Soil	Pb Soil	Zn Soil
Au River	1													
Cd River	-.178	1												
Cu River	.366	-.167	1											
Fe River	.053	-.225	.234	1										
Mn River	.150	-.283	.840**	.177	1									
Pb River	.241	.494	.334	.228	.170	1								
Zn River	.039	.917**	.137	-.341	-.084	.557	1							
Au Soil	.066	-.261	.172	-.282	.421	-.576	-.148	1						
Cd Soil	.011	-.150	-.077	.923**	-.211	.119	-.331	-.425	1					
Cu Soil	-.077	.064	-.320	-.229	-.004	-.567	-.109	.512	-.222	1				
Fe Soil	.141	-.032	.206	-.349	.398	-.319	-.003	.393	-.488	.757*	1			
Mn Soil	-.074	-.330	-.746*	-.142	-.576	-.275	-.541	-.331	.077	.153	-.060	1		
Pb Soil	-.314	-.342	-.295	-.155	-.078	-.347	-.341	.452	-.126	-.170	-.495	.150	1	
Zn Soil	.329	.178	.198	.549	.158	.055	.142	.339	.483	.255	-.030	-.503	-.104	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 4.24: Pearson's correlation coefficient between heavy metal concentrations in Gbako River and metals in Saboeregi mining soils dry season

	Au River	Cd River	Cu River	Fe River	Mn River	Pb River	Zn River	Au Soil	Cd Soil	Cu Soil	Fe Soil	Mn Soil	Pb Soil	Zn Soil
Au River	1													
Cd River	.290	1												
Cu River	.359	-.055	1											
Fe River	-.002	.276	-.225	1										
Mn River	.867**	.475	.453	.284	1									
Pb River	-.437	.552	-.595	.016	-.279	1								
Zn River	-.727*	-.506	-.442	-.025	-.652	.216	1							
Au Soil	.506	.523	.344	-.475	.330	-.011	-.640	1						
Cd Soil	.546	.342	.755*	-.204	.696	-.220	-.607	.567	1					
Cu Soil	.859**	.236	.048	.211	.809*	-.294	-.472	.249	.434	1				
Fe Soil	-.552	.034	-.242	-.256	-.333	.712*	.539	-.316	-.088	-.429	1			
Mn Soil	.667	.517	-.185	.390	.637	-.043	-.503	.380	.283	.851**	-.520	1		
Pb Soil	.062	-.222	.383	.552	.212	-.488	-.198	-.488	-.044	-.077	-.323	-.211	1	
Zn Soil	.180	.067	.148	.144	.114	-.089	-.441	-.113	-.158	-.157	-.157	-.242	.662	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 4.25: Pearson's correlation coefficient between heavy metal concentrations in Tangale River and metals in Asha mining soils rainy season

	Au River	Cd River	Cu River	Fe River	Mn River	Pb River	Zn River	Au Soil	Cd Soil	Cu Soil	F Soil	Mn Soil	Pb Soil	Zn Soil
Au River	1													
Cd River	-.665	1												
Cu River	-.654	.992**	1											
Fe River	.131	-.252	-.177	1										
Mn River	-.146	-.137	-.073	.949**	1									
Pb River	-.747*	.314	.253	-.414	-.132	1								
Zn River	-.667	.965**	.970**	-.064	.034	.190	1							
Au Soil	.677	-.905**	-.905**	.164	.081	-.239	-.942**	1						
Cd Soil	.595	-.148	-.186	-.203	-.328	-.444	-.231	.396	1					
Cu Soil	-.041	-.332	-.316	.725*	.823*	.097	-.238	.413	-.130	1				
Fe Soil	-.368	.820*	.845**	.108	.152	.114	.778*	-.648	-.075	-.033	1			
Mn Soil	-.640	.754*	.748*	-.369	-.212	.495	.692	-.597	-.298	-.138	.583	1		
Pb Soil	.548	-.705	-.763*	-.109	-.230	-.123	-.680	.510	.070	.017	-.720*	-.547	1	
Zn Soil	.121	-.124	-.173	.038	.126	.153	-.195	.466	.560	.579	.025	.092	-.027	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table 4.26: Pearson's correlation coefficient between heavy metal concentrations in Tangale River and metals in Asha mining soils dry season

	Au River	Cd River	Cu River	Fe River	Mn River	Pb River	Zn River	Au Soil	Cd Soil	Cu Soil	Fe Soil	Mn Soil	Pb Soil	Zn Soil
Au River	1													
Cd River	.327	1												
Cu River	.913**	.550	1											
Fe River	.792*	.340	.625	1										
Mn River	.339	.915**	.479	.527	1									
Pb River	.349	.122	.500	.237	.023	1								
Zn River	.143	.316	.419	.137	.292	.845**	1							
Au Soil	-.328	-.336	-.266	-.293	-.199	-.259	.035	1						
Cd Soil	-.337	-.434	-.535	-.238	-.374	-.822*	-.759*	.248	1					
Cu Soil	.422	-.096	.288	.368	-.004	-.289	-.300	.544	.309	1				
Fe Soil	.716*	.375	.670	.774*	.450	.295	.300	-.396	-.094	.114	1			
Mn Soil	.648	.024	.434	.584	.131	-.358	-.444	.182	.359	.890**	.389	1		
Pb Soil	-.471	-.316	-.521	-.381	-.225	-.696	-.417	.330	.846**	.019	-.027	.054	1	
Zn Soil	.255	.271	.348	-.272	-.023	-.190	-.336	-.177	.021	.175	-.183	.248	-.125	1

**. Correlation is significant at the 0.01 level (2-tailed).

Table 4.27:Pearson's correlation coefficient between heavy metal concentrations in River Gbako and metal concentrations in *Sorghum*bicolor at Saboeregi site

	Au River	Cd River	Cu River	Fe River	Mn River	Pb River	Zn River	Au Sorghum	Cd Sorghum	Cu Sorghum	Fe Sorghum	Mn Sorghum	Pb Sorghum	Au
Au River	1.0000													
Cd River	-0.6573	1.0000												
Cu River	0.7711	-0.1730	1.0000											
Fe River	0.2508	0.0164	-0.1289	1.0000										
Mn River	0.7441	0.0143	0.8759	0.3344	1.0000									
Pb River	-0.9896	0.6118	-0.7245	-0.3863	-0.7689	1.0000								
Zn River	-0.4966	0.3354	0.0192	-0.9355	-0.3497	0.6072	1.0000							
Au Sorghum	0.3977	0.0501	0.1152	0.9672	0.5608	-0.5247	-0.9035	1.0000						
Cd Sorghum	0.1014	-0.5721	-0.5550	0.5531	-0.3826	-0.1644	-0.6960	0.3649	1.0000					
Cu Sorghum	0.6879	-0.2692	0.9508	-0.4105	0.6834	-0.6015	0.2549	-0.1863	-0.5957	1.0000				
Fe Sorghum	0.8074	-0.4088	0.9537	-0.2908	0.7165	-0.7312	0.0935	-0.0769	-0.4436	0.9828	1.0000			
Mn Sorghum	-0.2985	0.8324	-0.0599	0.5458	0.3356	0.1923	-0.2283	0.5950	-0.2692	-0.3050	-0.3573	1.0000		
Pb Sorghum	-0.4719	0.2254	-0.0138	-0.9654	-0.4142	0.5900	0.9919	-0.9504	-0.6149	0.2462	0.0971	-0.3435	1.0000	
Zn Sorghum	0.6009	0.0613	0.4929	0.7857	0.8443	-0.6958	-0.7442	0.9168	0.0383	0.2034	0.2868	0.5641	-0.8080	

Table 4.28: Pearson's correlation coefficient between heavy metal concentrations in River Tangale and metal concentrations in *Sorghum* bicolor at Asha site

	Au River	*Cu* River	*Fe* River	*Mn* River	*Pb* River	*Zn* River	*AuSorghum*	*CdSorghum*	*CuSorghum*	*FeSorghum*	*MnSorghum*	*PbSorghum*	*ZnSorghum*
Au River	1.000												
Cu River	0.911	1.000											
Fe River	0.702	0.354	1.000										
Mn River	0.347	-0.064	0.855	1.000									
Pb River	0.329	0.623	-0.221	-0.695	1.000								
Zn River	-0.065	0.290	-0.545	-0.892	0.920	1.000							
Au*Sorghum*	-0.508	-0.491	-0.165	-0.255	0.233	0.427	1.000						
Cd*Sorghum*	-0.741	-0.613	-0.514	-0.504	0.220	0.521	0.928	1.000					
Cu*Sorghum*	-0.057	0.329	-0.744	-0.815	0.511	0.596	-0.352	-0.060	1.000				
Fe*Sorghum*	-0.745	-0.598	-0.551	-0.544	0.245	0.550	0.913	0.999	-0.012	1.000			
Mn*Sorghum*	-0.741	-0.613	-0.514	-0.504	0.220	0.521	0.928	1.000	-0.060	0.999	1.000		
Pb*Sorghum*	0.646	0.407	0.864	0.530	0.197	-0.089	0.236	-0.137	-0.677	-0.170	-0.137	1.000	
Zn*Sorghum*	-0.424	-0.127	-0.843	-0.623	0.010	0.221	-0.385	-0.017	0.850	0.025	-0.017	-0.957	1.000

Asha site showed Cd water negatively correlation with Au *Sorghum bicolor* grain (r = 0.7410), whereas Cu water was negatively correlated with Fe (r=0.7440) and Mn *Sorghum bicolor* grain (r =0.8150). Fe water correlated positively with Zn (r = 0.550) but negatively with Au *Sorghum bicolor* grain (r = 0.7450). Similarly, Mn and Pb water correlated positively with Zn *Sorghum bicolor* grain (r = 0.5210) and Fe (r = 0.864) respectively. Zn water also showed negative correlation with Fe *Sorghum bicolor* grain (r = 0.8430) (Table 4.26).

4.4 Heavy Metal Speciation in Asha and Saboeregi Mining Sites

The result of heavy metal distribution in the different fractions in the mining soils at Asha and Saboeregi Mining Sites are presented in Figures 4.3 to 4.6 and in appendix IV to VII. The results are as summarized below:

i. Gold

At Asha mining site rainy season recorded carbonate bound fraction (F3) 17.83% > Fe-Mn oxide bound fraction (F4)17.76% > residual fraction (F6)17.28% > organic matter bound fraction (F5) 17% > exchangeable fraction (F2) 16.85% > water soluble fraction (F1) 13.28%.

Dry season record is therefore of order: residual fraction (F6) 24.3% > exchangeable fraction (F2)17.91% > organic matter bound fraction (F5) 15.87% > water soluble fraction (F1) 14.74% > Fe- Mn oxide bound fraction (F4) 14.24% > carbonate bound fraction (F3) 12.94% (Fig.4.3 and 4.4).

At Saboeregi mining site gold distribution is as follows

Rainy season: carbonate bound fraction (F3) 17.79% > exchangeable fraction (F2) 17.44% >Fe- Mn oxide bound fraction (F4) 17.29% > organic matter bound (F5) 17.1% > residual fraction (F6) 16.12% > water soluble fraction (F1) 14.26%.

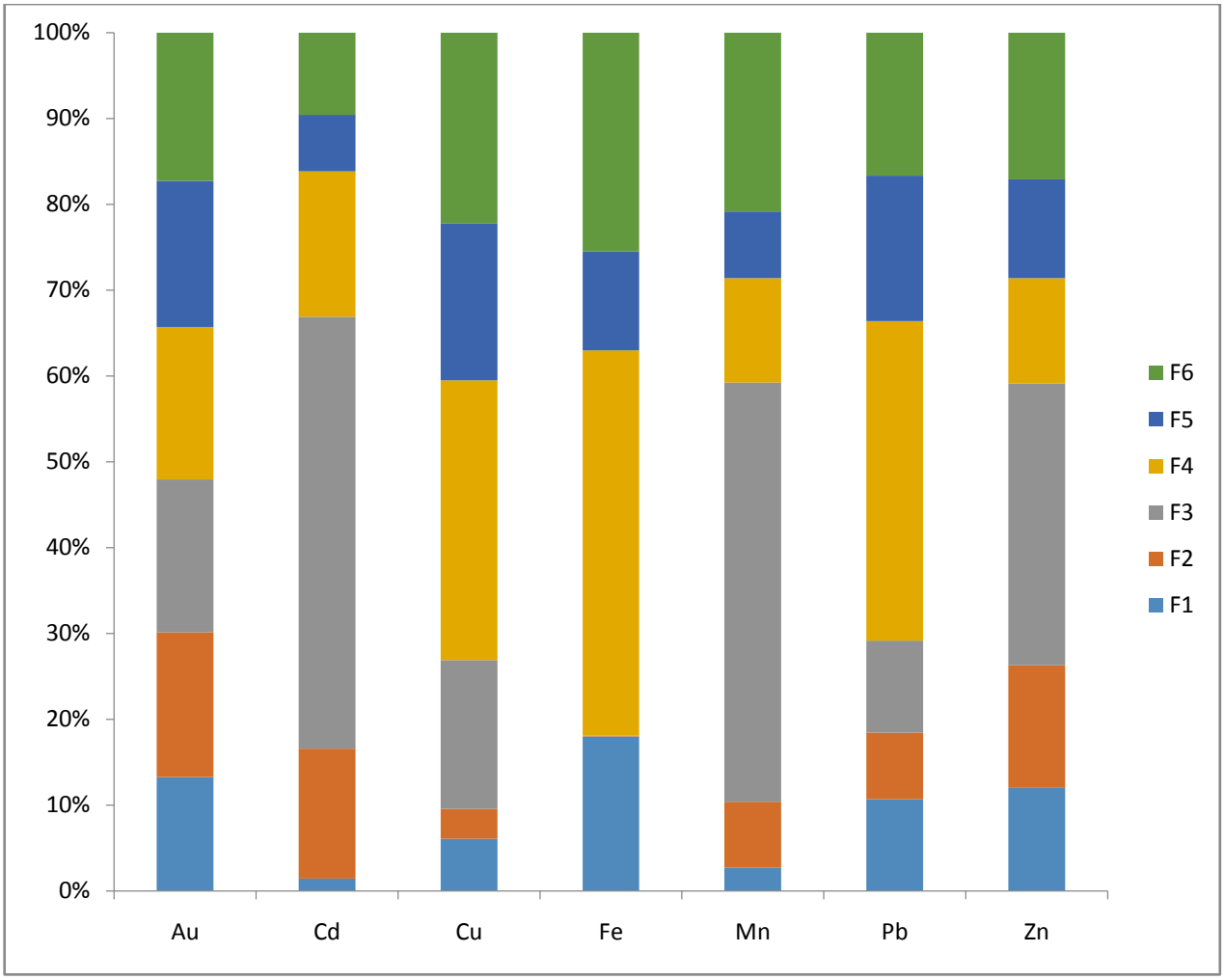


Fig. 4.3: Relative percentage distribution of heavy metals among six fractions (F1-F6) for rainy season at Asha site

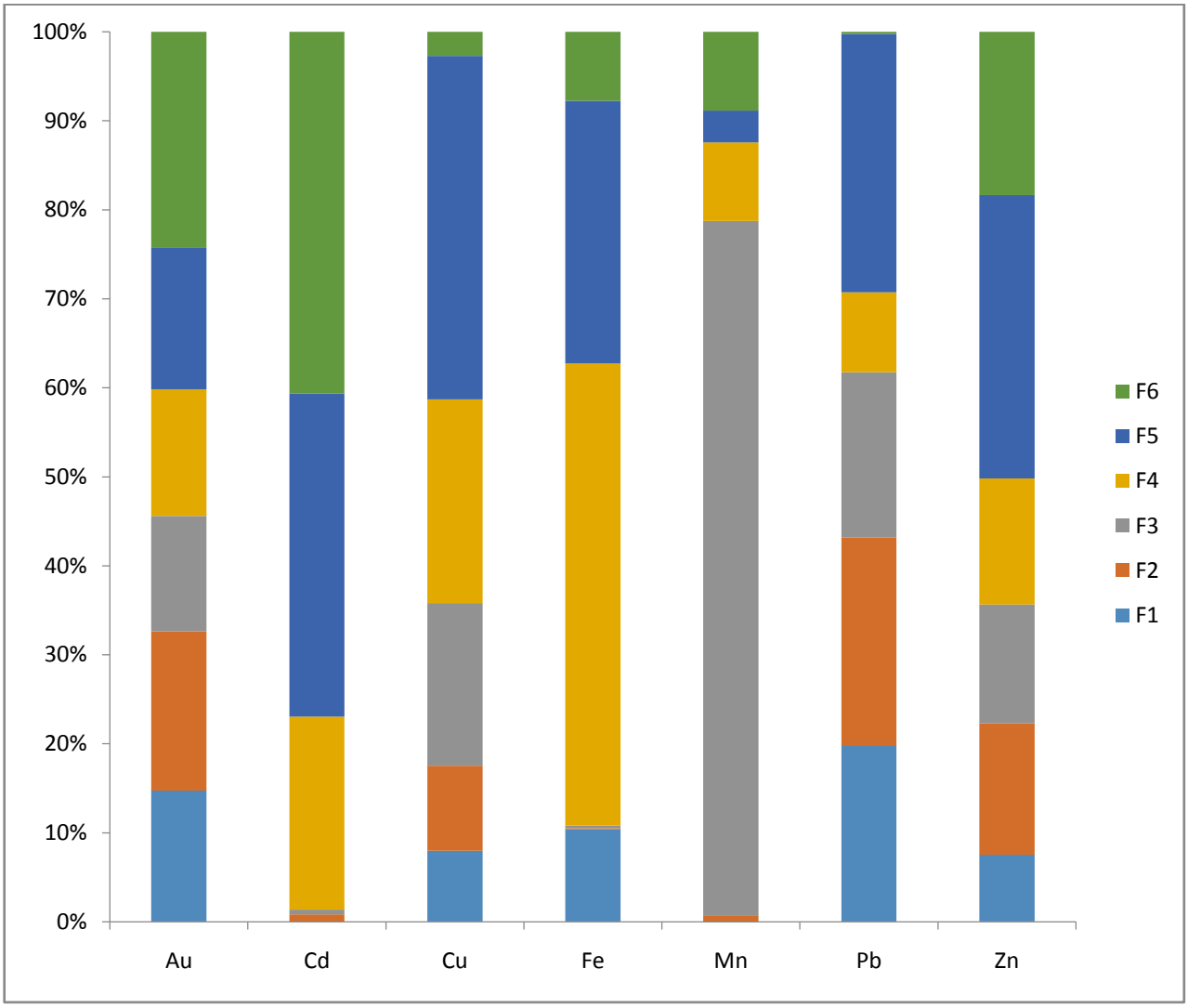


Fig. 4.4: Relative percentage distribution of heavy metals among six fractions (F1-F6) for dry season at Asha site

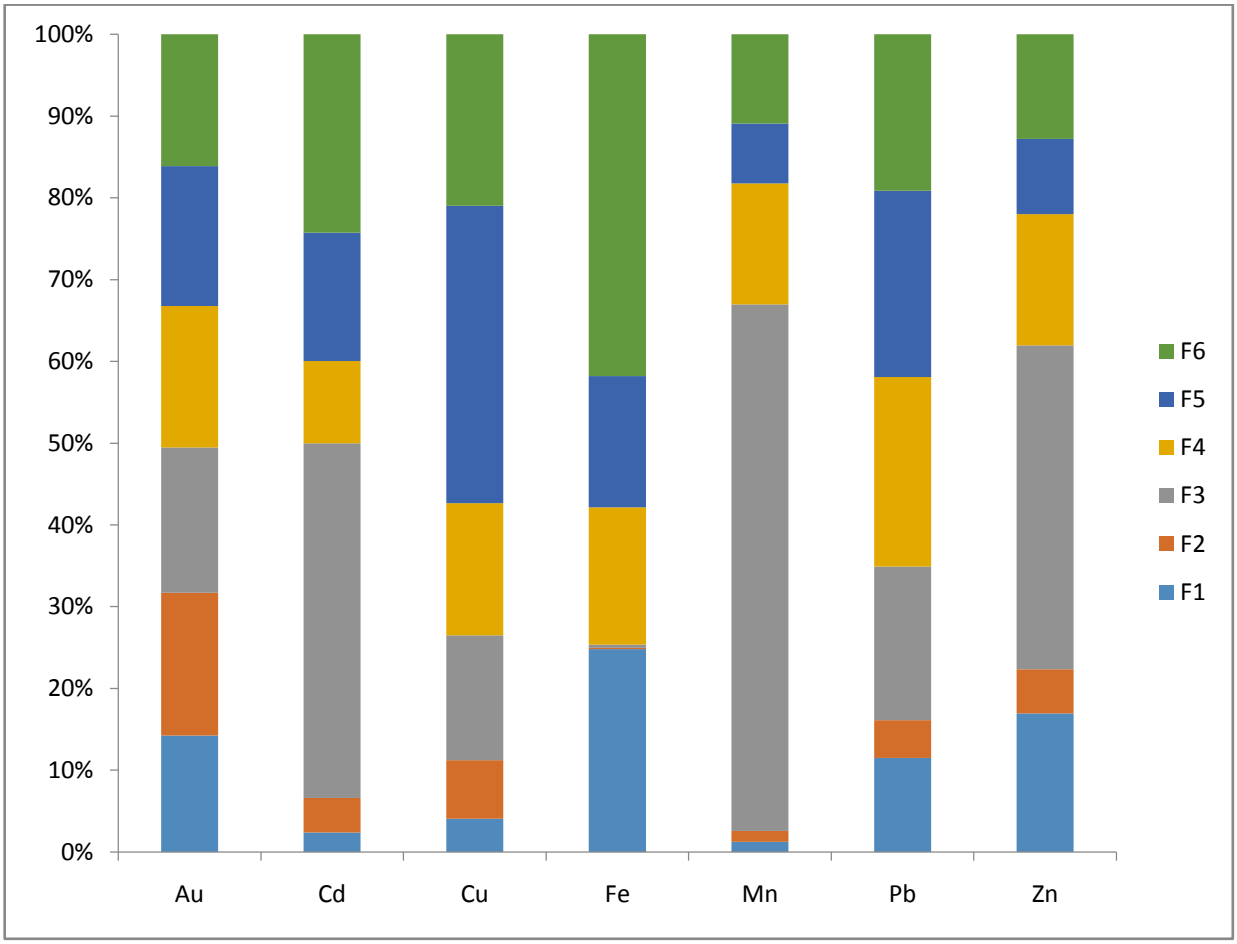


Fig. 4.5: **Relative percentage distribution of heavy metals among six fractions (F1-F6) for rainy season at Saboeregi site**

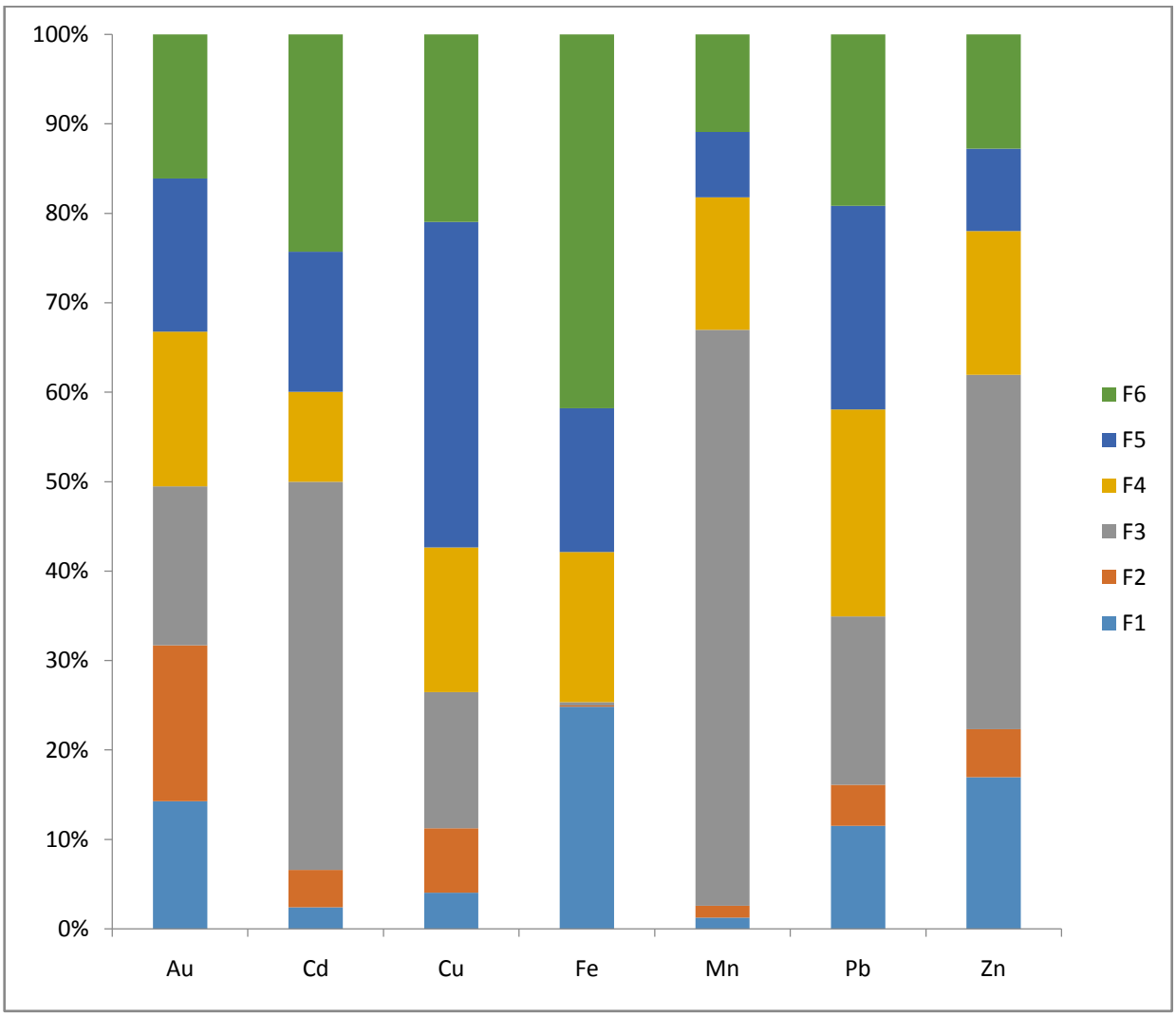


Fig. 4.6: **Relative percentage distribution of heavy metals among six fractions (F1-F6) for dry season at Saboeregi site**

Dry season: residual fraction (F6) 27.88% > organic matter bound (F5) 23.99% > exchangeable fraction (F2) 15.67% > Fe- Mn oxide bound fraction (F4) 14.04% > carbonate bound fraction (F3) 9.31% > water soluble fraction (F1) 9.11% (Fig.4.5 and 4.6).

ii. Cadmium

At Asha mining site rainy season record is as given carbonate bound fraction (F3) 50.33% > Fe- Mn oxide bound fraction (F4) 16.93% > exchangeable fraction(F2)15.13% > residual fraction (F6) 9.56% > organic matter bound (F5) 6.6% > water soluble fraction (F1) 1.45%.

In the dry season Cd is distributed thus residual fraction (F6) 40.64% >organic matter bound (F5) 36.3% > Fe- Mn oxide bound fraction (F4) 21.7% >exchangeable fraction (F2) 0.82% >carbonate bound fraction (F3) 0.54% >water soluble fraction (F1) below detection limit (Fig.4.3 and 4.4).

At Saboeregi mining site rainy season record is as given carbonate bound fraction (F3) 43.4% >residual fraction (F6) 24.28% >organic matter bound (F5) 15.69%> Fe- Mn oxide bound fraction (F4) 10.03% >exchangeable fraction (F2) 4.2% >water soluble fraction (F1) 2.4%.

Dry season: residual fraction (F6) 34.87% > organic matter bound (F5) 31.84% > Fe- Mn oxide bound fraction (F4) 22.51% > carbonate bound fraction (F3) 9.22% > exchangeable fraction (F2) 1.45% > water soluble fraction (F1) 0.11% (Fig.4.5 and 4.6).

Copper

At Asha mining site rainy season record is as given Fe-Mn oxide bound fraction (F4) 32.59% > residual fraction (F6) 22.21% > organic matter bound (F5) 18.31%

>carbonate bound fraction (F3) 17.31% > water soluble fraction (F1) 6.08% > exchangeable fraction (F2) 3.5%.

In the dry season Cu is distributed thus organic matter bound (F5) 38.58% > Fe-Mn oxide bound fraction (F4) 22.9% > carbonate bound fraction (F3) 18.28% > exchangeable fraction (F2) 9.56% > water soluble fraction (F1) 7.97 % > residual fraction (F6) 2.71% (Fig.4.3 and 4.4).

At Saboeregi mining site rainy season record is as given organic matter bound (F5) 36.38% > residual fraction (F6) 20.97% > Fe- Mn oxide bound fraction (F4) 16.17% > carbonate bound fraction (F3) 15.23% > exchangeable fraction (F2) 7.19% > water soluble fraction (F1) 4.06%

Dry season record is thus organic matter bound (F5) 42.35% > Fe- Mn oxide bound fraction (F4) 16.23% > residual fraction (F6) 15.76% > carbonate bound fraction (F3) 13.06% > water soluble fraction (F1) 7.25% > exchangeable fraction (F2) 5.35% (Fig.4.5 and 4. 6).

Iron

At Asha mining site rainy season record is as given Fe-Mn oxide bound fraction (F4) 44.86% > residual fraction (F6) 25.47% > water soluble fraction (F1) 17.96%>organic matter bound (F5) 11.54% >carbonate bound fraction (F3) 0.1% > exchangeable fraction (F2) 0.07%.

In the dry season Fe is distributed thus Fe-Mn oxide bound fraction (F4) 51.91% > organic matter bound (F5) 29.5% > water soluble fraction (F1) 10.38 % > residual fraction (F6) 7.75%. > carbonate bound fraction (F3) 0.3% > exchangeable fraction (F2) 0.16% (Fig.4.3 and 4.4)

At Saboeregi mining site rainy season record is as given residual fraction (F6) 41.81% > water soluble fraction (F1) 24.83% > Fe-Mn oxide bound fraction (F4) 16.8% > organic matter bound (F5) 16.04% > carbonate bound fraction (F3) 0.39% > exchangeable fraction (F2) 0.13%

Dry season record is thus Fe-Mn oxide bound fraction (F4) 42.21% > water soluble fraction (F1) 25.68% > organic matter bound (F5) 20.76% > residual fraction (F6) 11.3% > carbonate bound fraction (F3) 0.05% > exchangeable fraction (F2) 0% (Fig.4.5 and 4. 6).

Manganese

At Asha mining site rainy season record is as given carbonate bound fraction (F3) 48.85% > residual fraction (F6) 20.84% >Fe- Mn oxide bound fraction (F4) 12.15% >organic matter bound (F5) 7.77% >exchangeable fraction (F2) 7.65%> water soluble fraction (F1) 2.74%.

In the dry season Mn is distributed thus carbonate bound fraction (F3) 78% >residual fraction (F6) 8.86% > Fe-Mn oxide bound fraction (F4) 8.81% >organic matter bound (F5) 3.58% > exchangeable fraction (F2) 0.74% > water soluble fraction (F1) 0.01% (Fig.4.3 and 4.4)

At Saboeregi mining site rainy season record is as given carbonate bound fraction (F3) 64.39% >Fe-Mn oxide bound fraction (F4) 14.82% >residual fraction (F6) 10,91% >organic matter bound (F5) 7.31% >exchangeable fraction (F2) 1.32% >water soluble fraction (F1) 1.25% Saboeregi sites (Rainy season)

In the dry season Mn is distributed thus carbonate bound fraction (F3) 96.44% > residual fraction (F6) 1.45% > organic matter bound (F5) 1.24% > Fe- Mn oxide bound

fraction (F4) 0.72% > exchangeable fraction (F2) 0.15% > water soluble fraction (F1) 0 % (Fig.4.5 and 4.6).

Lead

At Asha mining site rainy season record is as given Fe-Mn oxide bound fraction (F4) 37.25% > organic matter bound (F5) 16.94% > residual fraction (F6)16.64% > carbonate bound fraction (F3) 10.7% > water soluble fraction (F1) 10.68% > exchangeable fraction (F2) 7.79%.

In the dry season Pb is distributed thus organic matter bound (F5) 29.04% > exchangeable fraction (F2) 23.43% > water soluble fraction (F1) 19.75 % > carbonate bound fraction (F3) 18.55% > Fe- Mn oxide bound fraction (F4) 9% > residual fraction (F6) 0.23% (Fig.4.3 and 4.4).

Rainy season record of Saboeregi mining site is given as Fe-Mn oxide bound fraction (F4) 23.15% > organic matter bound (F5) 22.78% > residual fraction (F6) 19.15% > carbonate bound fraction (F3) 18.81% > water soluble fraction (F1) 11.52% > exchangeable fraction (F2) 4.59%

In the dry season Pb is distributed thus exchangeable fraction (F2) 36.93% > water soluble fraction (F1) 34.39% Fe-Mn oxide bound fraction (F4) 11.73% > carbonate bound fraction (F3) 10% > organic matter bound (F5) 4.12% > residual fraction (F6) 2.83% (Fig. 4.5 and 4.6).

Zinc

At Asha mining site the rainy season distribution was carbonate bound fraction (F3) 32.83% > residual fraction (F6)17.08% > exchangeable fraction (F2) 14.27% > Fe-Mn oxide bound fraction (F4) 12.29% > water soluble fraction (F1) 12.03% > organic matter bound (F5)11.5%.

In the dry season Pb is distributed thus organic matter bound (F5) 31.85% > residual fraction (F6) 18.35% > exchangeable fraction (F2) 14.79% > Fe- Mn oxide bound fraction (F4) 14.16% > carbonate bound fraction (F3) 13.33% > water soluble fraction (F1) 7.52 % (Fig.4.3 and 4.4).

At Saboeregi mining site rainy season the distribution of Zn is of the following order carbonate bound fraction (F3) 39.6% > water soluble fraction (F1) 16.95% > Fe-Mn oxide bound fraction (F4) 16.07% > residual fraction (F6) 12.78% > organic matter bound (F5) 9.21% > exchangeable fraction (F2) 5.39% .

In the dry season Zn distribution is of the order organic matter bound (F5) 38.2% > residual fraction (F6) 24.03% > carbonate bound fraction (F3) 14.44% > Fe-Mn oxide bound fraction (F4) 11.78% >exchangeable fraction (F2) 10.81% > water soluble fraction (F1) 0.74% (Fig.4.5 and 4.6).

4.5 Pollution Indices in the Study Sites

4.5.1 Pollution degree based on Igeo

The calculated results of Igeo of heavy metals in the soil of Asha and Saboeregi mining sites are presented in Tables 4.29 and 4.30.The Igeo mean values at Asha site for the heavy metals are Au (2.44); Cd (1.27); Cu (2.55); Fe (7.43); Mn(4.41); Pb (2.32) and Zn (3.66) in the rainy season while the mean values for dry season are Au (2.07); Cd (0.05);Cu (2.62); Fe (5.84); Mn (3.32); Pb (2.73) and Zn (3.55) (Table 4.29).

Saboeregi mining site has Igeo mean values of 2.58; 1.25; 2.82; 7.88; 4.77; 2.41 and 3.69 for Au; Cd; Cu; Fe; Mn; Pb and Zn respectively during rainy season while the mean values for dry season are 1.59; -0.64; 2.65; 5.76; 3.20; 2.75 and 3..59 for Au; Cd; Cu; Fe Mn; Pb and Zn respectively during dry season (Table 4.29).

4.5.2 Pollution degree based on enrichment factor

The calculated results of Enrichment Factor of heavy metals in the soil at Asha and Saboeregi mining sites are presented in Table 4.30 .The Enrichment Factor mean values at Asha site for the heavy metals are Au (0.32); Cd (1.43);Cu (1.01); Fe (1.83); Mn (1.34); Pb (0.28) and Zn (1.00) in the rainy season while the mean values for dry season are Au (0.17); Cd (0.11); Cu (1.50); Fe (0.06); Mn (0.14); Pb (0.93) and Zn (1.00) (Table 4.30). Saboeregi mining site has Pollution Index mean values of 0.4; 1.27; 1.75; 4.83; 2.85; 0.32 and 1.00 for Au; Cd; Cu; Fe; Mn; Pb and Zn respectively in the rainy season while the mean values for dry season has 0.09;0.00; 1.56; 9.82; 0.75; 1.34 and 3.72 for Au; Cd; Cu; Fe Mn; Pb and Zn respectively (Table 4.30).

Table 4.29: Geo accumulation index of heavy metals in mining soils

	Asha				Saboeregi			
Heavy Metal	Rainy	Soil quality	Dry	Soil quality	Rainy	Soil quality	Dry	Soil quality
Au	2.44	Moderately to heavily polluted	2.07	Moderately to heavily polluted	2.58	Moderately to heavily polluted	1.59	Moderately polluted
Cd	1.27	Moderately polluted	0.05	Unpolluted to moderately unpolluted	1.25	Moderately polluted	-0.64	Practically unpolluted
Cu	2.55	Moderately to heavily polluted	2.62	Moderately to heavily polluted	2.82	Moderately to heavily polluted	2.65	Moderately to heavily polluted
Fe	7.43	Extremely polluted	5.84	Extremely polluted	7.88	Extremely polluted	5.76	Extremely polluted
Mn	4.41	Heavily polluted	3.32	Heavily polluted	4.77	Heavily polluted	3.2	Heavily polluted
Pb	2.32	Moderately to heavily polluted	2.73	Moderately to heavily polluted	2.41	Moderately to heavily polluted	2.75	Moderately to heavily polluted
Zn	3.66	Heavily polluted	3.55	Heavily polluted	3.69	Heavily polluted	3.59	Heavily polluted

Table 4.30: Enrichment factor of heavy metals in mining soils

	Asha				Saboeregi			
Heavy Metal	Rainy	Soil quality	Dry	Soil quality	Rainy	Soil quality	Dry	Soil quality
Au	0.2	Backgroung concentration	0.02	Backgroung concentration	0.74	Backgroung concentration	0.1	Backgroung concentration
Cd	0.8	Backgroung concentration	0.33	Backgroung concentration	2.5	Moderate enrichment	0.1	Backgroung concentration
Cu	1.5	Depletion to minimal enrichment	2.0	Depletion to minimal enrichment	3.0	Moderate enrichment	2.1	Moderate enrichment
Fe	3.6	Moderate enrichment	0.06	Backgroung concentration	8.1	Significant enrichment	0.1	Backgroung concentration
Mn	2.4	Moderate enrichment	0.2	Backgroung concentration	5.0	Significant enrichment	0.1	Backgroung concentration
Pb	1.1	Depletion to minimal enrichment	3.0	Moderate enrichment	14.1	Significant enrichment	1.1	Depletion to minimal enrichment
Zn	1.7	Depletion to minimal enrichment	2.2	Moderate enrichment	1.8	Depletion to minimal enrichment	1.5	Depletion to minimal enrichment

CHAPTER FIVE

5.0 DISCUSSION OF RESULTS

5.1 Physico-chemical Parameters and concentration of Heavy metals in Rivers Gbako and Tangale Waters

5.1.1 Physico-chemical Parameters of Water

i. pH

Low standard deviation was noticed in the result (Tables 4.1 and 4.2) which indicates that the spatial distribution of the pH values do not vary remarkably. The slight variation observed throughout the sampling points may possibly be due to the differences in the release and composition of mining pollutants in the water. The pH values recorded for Rivers Gbako and Tangale during rainy season were observed to be slightly lower than those recorded during the dry season suggesting possible acidity. This implied that during rainy season rainfall dissolves CO_2 in the atmosphere to form carbonic which in turn increase the acidity of the water (Ocheri and Ahola, 2010). Schafer *et al*., (2009) and Ayantobo *et al*., (2014) in previous studies reported that low pH in surface and groundwater may be due to natural geochemical and biochemical processes within the aquifers. This also possibly may have been effect of dissolution of acid associated with discharges from mining and processing facilities which finds its way into rivers Tangale and Gbako (Jason *et al*., 2001). The overall results for pH indicated that, the river water was within the acceptable range of 6.5 to 8.5 pH values given by WHO (2007) and SON (2007) and therefore, the rivers did not seem to be affected by mining activities with respect to pH at the time the study was conducted. This was corroborated with the results obtained in the upstream which were almostsimilar to that of downstream.

ii. Turbidity

The maximum values of turbidity obtained for the two Rivers (Gbako and Tangale) under investigation were 779.67 NTU and 829 NTU for Rivers Gbako and Tangale respectively (Tables 4.1 and 4.2).The results therefore revealed that both Rivers were highly turbid particularly in the rainy season and are well above values in the upstream and the permissible limit of 5 NTU (WHO, 2008). Elevated turbidity values in this study is in consonate with the findings of Younger and Wolkersdorfer (2004) which state that increased turbidity in surrounding water bodies are among the common impacts of mining. Earlier reports by Schafer *et al*., (2009) and Sousa *et al*., (2011) attributed this to the lack of erosion management and control measures at mining operation sites.

iii. Total dissolved solid

The values of TDS obtained were significantly higher in Gbako River when compared to the values recorded in Tangale River (Tables 4.1 and 4.2). This may have resulted from the differences in the geology of the drainage, atmospheric precipitation and the water balance (evaporation– precipitation) between the two rivers (Phyllis *et al*., 2007; Kunz *et al*., 2013). According to Karikari and Ansa-Asare (2006), the quality of water with TDS level less than 600 mg/dm^3 is generally considered to be good compared to those with TDS above 1,200 mg/dm^3. The low values obtained for the two rivers when compared with WHO permissible limit of 1200 mg/dm^3 indicate that TDS values of these waters could not be a problem. The results obtained were noticed to be lower in the upstream when compared to the values recorded in the downstream for the two rivers. This occurrence might be as a result of absence or low human activity upstream with respect to progressive increase downstream, inaddition to the impact of mining (Pórcel and de León-Gómez, 2013).

iv. Electrical Conductivity

This is an important parameter of water quality. The conductivity values recorded in Gbako River for both seasons downstream were observed to be higher than the values in the upstream (control site) (Table 4.1). The high values ranging from 207.33 µS/cm to 1008.00 µS/cm observed in Gbako River indicating higher amounts of dissolved ions in Gbako River. Generally, the mining activities at this study site was moreprominent.The elevated conductivity content may be due to the weathering of sulphide-bearing rocks, which might have been facilitated by the on-going mining activities (Marcovecchio *et al.*, 2007; Ayantobo *et al*., 2013). Similarly industrial discharges, mine waste, sewage and agricultural runoff can also raise conductivity of surface water (WHO, 1998).

The conductivity values for River Tangale were low when compared to the conductivity values of 111.30 µS/cm in the upstream (Table 4.2). Similar observations were made by Nkuli (2008) in a study on theeffects of mining activities at Bulyanhulu gold mine (BGM) on the water quality of Bulyanhulu River: Shinyanga - Tanzania. The researcher opined that this could be attributed to low sulphate and heavy metal concentrations due to poor seepage from the waste rock dump.

Generally the results were found to be within recommended values for drinking water quality for potable water of 2500 µS/cm and 1000 µS/cm by (WHO 1988) and (SON, 2007) respectively. However, conductivity values that exceeded 1500 µS/cm around the mine site, can have negative effects on the freshwater ecosystems, particularly on biota with low tolerance to salts (Zalizniak *et al.*, 2006).

v. Dissolved Oxygen

The values obtained for river Gbako were within the WHO permissible limit of 6.00 mg/dm^3. However, it was noticed that DO values obtained for River Tangale were

slightly above WHO permissible limit of 6.00 mg/dm^3 which implies that River Gbako has higher degree of freshness and higher tendency for the survival of aquatic organisms than River Tangale. The results obtained from the two rivers when compared to the upstream results revealed that the means were almost the same indicating that mining activities may not have impacted much on the DO of the studied water bodies. The descriptive statistics for the result reveals that the dissolved oxygen content was distributed with slight variation as seen from low standard deviation obtained (Tables 4.1 and 4.2).

vi. Chloride

Higher chloride level mean of 32.38 mg/dm^3 was recorded for River Gbako during dry season while that for River Tangale was 15.05 mg/dm^3. The results were also observed to be higher when compared with those obtained at the upstreams of the studied rivers. Elevated chloride concentrations indicate high degree of organic pollution in addition to mining activities (Chatterjee, *et al*., 2002).

However, low chloride levels were recorded for the rivers during rainy season (Tables 4.1 and 4.2). The low chloride levels in raining season might be due to river dilution by the stream flow (IDNR, 2007).

All chloride values for both Rivers (Gbako and Tangale) throughout the period of investigation were generally lower than the upper limit of 600 mg/dm^3 and 250 mg/dm^3 set by WHO and SON respectively for drinking water. The amount of chloride levels in these water bodies may not constitute health hazard to human beings and hence safe for irrigation purposes (Yisa, 2004). However, chloride levels above 140 mg/dm^3 are considered to be toxic for plants (Flood, 1996).

The descriptive statistics for the results reveals that the spatial distribution of chloride content of these water bodies varied remarkably at different sampling points as at the time of study (Tables 4.1 and 4.2).

vii. Alkalinity

The alkalinity value recorded for River Gbako varied widely as depicted by wide range of values recorded (9 mg/dm^3 to 229 mg/dm^{3}and 64.33mg/dm^3 to 184 mg/dm^3) during the period of study (Table 4.1). Alkalinity values obtained at the two studied rivers were also noticed to be higher when compared to the upstreams values. The observed range of alkalinity values obtained in this study are well above the range of 0-50 mg/dm^3 alkalinity prescribed by FEPA (1991) for discharge into rivers which implies that these water bodies may have problems associated with alkalinity.

viii. Sulphide

Tangale water recorded very wide range of sulphide content in contrast to Gbako waters. The high variation of sulphide level in water of these two rivers may be due to some geological differences. The result of the sulphide content values obtained in upstreams were relatively higher when compared to the values obtained in the downstream.The high sulphide content observed in this study may lead to suppressed growth and development, iron chlorosis, leaf necrosis, suppressed flowering, black and flaccid root decay and even the death of the whole plant (Van der wells *et al*., 2007b). The result of the study also revealed that sulphide content values were above SON (2007) upper limit of 0.01mg/dm^3 for potable drinking water. However, it was reported that sulphide levels of the order of 8-10 mg/dm^{3}can cause high fish mortality (Yisa, 2004). It is therefore pertinent to note that sulphide levels in this study for both rivers

may not be considered dangerous with respect to irrigation but may be unfit as potable drinking water.

ix. Colour

Higher colour intensities were recorded in rainy season when compared to the values in dry season (Tables 4.1 and 4.2). This observation was in contrast to earlier report on pollution studies of soil and water by Benjamin (2014) that the colour was higher during dry season than rainy season due to high volume of water during rainy. In addition, it was noticed that higher colour intensities were consistently recorded downstream when compared to the values recorded upstream of the studied rivers. Higher colour intensities may have been contributions from mining activities. The results recorded in this study revealed that colour intensities are well above WHO recommended value of 15 pt.co. The implication of this result is that highly coloured water has significant effects on aquatic plants and algal growth. According to United States Department of the Interior/United States Geological Survey (2016) report, light is very critical for the growth of aquatic plants and coloured water can limit the penetration of light. Thus, a highly coloured body of water could not sustain aquatic life which could lead to the term impairment of the ecosystem.

x. Suspended Solid

The result obtained revealed low levels of suspended solid in the upstreams when compared to the values downstream of the two studied rivers .The higher values recorded downstream may be associated with some anthropogenic activities such as mining and agricultural activities taking place around the river sites. It was generally noticed that the values for suspended solid during rainy season was higher than in the dry season. This may be connected to the volume of materials found during rainy season whilst during dry season they settled at the river bed. From the results, it can be inferred that suspended solid values obtained during the period of investigation for both rivers were above WHO standard of suspended solid (50.00 mg/dm^3) for drinking water.

The level of suspended solid content shows very strong positive correlation with sulphide, colour and chloride levels of the sampled water within the study period. Strong linear correlations observed above between individuals pairs of parameters indicates that they are of similar origin, usually connected with human activities in this case mining (Agnieszka*et al*., 2014).

xi. Total Solid

Total solid (TS) values recorded in the rainy season were observed to be higher than the values in the dry season.TS values in the downstreams for the studied rivers were consistently higher than the values obtained in the upstreams (Table 4.1 and 4.2). Elevated TS values observed downstreams may be associated to the waste discharged in addition to other pollutants into the river possibly from mining activities.

xii. Biochemical Oxygen Demand

The result revealed low BOD values in the upstream when compared to the downstream values for River Gbako. However, reverse was the case in River Tangale. The former occurence may be attributed to mining and other activities such as agriculture however, the latter may be as a result of low input of these activities.

BOD means values of 11.71 ± 14.55 mg/dm^3 and 2.33 ± 4.34 mg/dm^3 respectively recorded for rainy and dry season from River Tangale is in consonance with earlier report given by Ezekiel *et al*., (2011). They reported that BOD values are usually higher in rainy season than dry season.

Generally BOD values recorded from both rivers in this study were below the health desirable limits of 100 mg/dm^3 recommended standard for domestic uses set by World Health Organization. Rivers with low BOD have low nutrient levels indicating high dissolved oxygen. Unpolluted natural waters are expected to have BOD values of 5

mg/dm^{3}or less. The result recorded in this study therefore reveals that both rivers are fairly polluted.

xiii. Chemical Oxygen Demand

Chemical Oxygen Demand (COD) test measures the total organic carbon, with the exception of certain aromatics such as benzene which are not completely oxidized in the reaction. COD is an indicator of organic pollution, which is caused by the inflow of domestic, livestock and industrial waste that contains elevated levels of organic pollutants. The introduction of undesirable substances into the river has negative effects on the quality of the water causing some harm to aquatic life, especially fish and other aquatic organisms (Yisa, 2004; Benjamin, 2014). The record reported for both rivers indicates slight variation of COD values at various sampling points throughout the study period. Low COD values were recorded for River Gbako in the upstream when compared to the downstream values which could be an indicator of contributions from anthropogenic activities such as mining taking place around the river site. Higher COD values were recorded for River Tangale in the upstream when compared to the downstream values which is in contrast to the observations made for the River Gbako. The range of COD value obtained in this study was between 16 mg/dm^3 and 96 mg/dm^3; 1 mg/dm^3 and 107 mg/dm^3 for rainy and dry seasons respectively for Gbako River. Tangale River recorded a range of 0 mg/dm^3 to 93.67 mg/dm^3 and 0 mg/dm^3 to 25.33 mg/dm^3 for rainy and dry seasons respectively. Other authors' studies have reported higher range values between 18.52 and 248.50 mg/dm^3 (Igbhinosa and Okoh, 2009). Low COD values recorded in this study may be indicative of low rate of oxidation in these water bodies. COD content of these water bodies were within the WHO (2007) acceptable limits of 120 mg/dm^3.

xiv. Nitrate

The findings of this research revealed that nitrate levels in the water samples were found to be higher during rainy than dry season, also upstream values were noticed to be lower when compared to the values downstream (Tables 4.1 and 4.2). The elevated nitrates in mine water reflects the effects of mining activities which include blasting, mine pitting and rock waste storage which expose the rock materials to water. It is also reported that some of the detonating agents used in mining commonly contain ammonium nitrate, calcium nitrate or sodium nitrate (Huisman *et al*., 2006; Zaitsev *et al*., 2008). Unlike the solid particles and other particulate-bound elements including metals, dissolved nitrates cannot simply settle out from the water but may need specific technology such as nano-flitration or reverse osmosis to remove it (Malaiyandi *et al*., 1981).

Results for nitrate levels were observed to be above 45.00 mg/dm^3 maximum permissible limits acceptable by WHO and SON. Discharge or overspill of nitrates rich water, especially in large quantities and high frequencies, could disrupt the integrity of the surrounding natural aquatic ecosystems (Matthaei *et al.*, 2010; Wagenhoff *et al*., 2012). Nitrates in mine waters continue to pose challenges because elevated nitrates are toxic to biota and can create eutrophication which poses a serious threat to freshwater ecosystems (Kunz *et al*., 2013). The adverse effects of chronically elevated nitrate on freshwater macroinvertebrates and macrophytes have been widely studied (Soucek and Kennedy, 2005; Camargo and Alonso, 2006).

It can therefore imply that nitrate associated adverse health effects in humans and other living organisms may be prevalent in River Tangale water because of higher nitrate levels and hence the water may not be safe for drinking.

xv. Phosphate

Comparing the values of phosphate concentration obtained in this study with that of upstream values with mean of 8.4 mg/dm^3 revealed this study has recorded elevated phosphate values in water samples (Tables 4.1 and 4.2). Elevated Phosphate level can be related to the weathering of calcium-bearing minerals which may be largely facilitated by mining activities in the area (Singh *et al*., 2008).

High concentrations of phosphate could also indicate the presence of pollution and are largely responsible for eutrophication conditions in water bodies (Taiwo *et al*., 2010; DebRoy *et al*., 2012).

5. 1.2 Heavy metals in surface water of Rivers Gbako and Tangale

i. Gold

The results obtained for gold levels in the downstream in this study revealed that the values were almost similar to gold levels at the upstream (Tables 4.3 and 4.4). This is an indication that the on going anthropogenic activities may not reflect much on these water bodies with respect to gold. However, the effect of gold mine activities on surface water quality (rivers) have been investigated by a number of researchers in many parts of the world; they generally acknowledge water quality deterioration due to the discharge of partially or untreated mine effluents, and/or accidental discharges, which can change the chemistry of water (McKinnon, 2002 ; Kaye, 2005).

The Central Rand goldfield of the Witwatersrand Basin, South Africa has been one of the most important gold mining areas in the world. It is, however, replete with gold mine tailings which have contributed significantly to water pollution as a result of acid mine drainage. Water quality is affected mainly by mine tailings and spillages, especially from active slimes dams, reprocessed tailings, as well as from footprints left behind after reprocessing.

ii. Cadmium

Cadmium levels in water surfaces of rivers Gbako and Tangale ranged from below detection limits for the two rivers especially during dry season to 43.10 ± 0.01 mg/dm^3 during rainy season (Tables 4.3 and 4.4). The study revealed that Cd concentrations in water surface at both seasons were higher than the permissible limit of 0.05 mg/dm^3 in drinking water by the World Health Organization (WHO, 2007) and 0.03 mg/dm^3 by Nigerian standard for drinking water quality (SON, 2007). Previous studies on water quality trends in the Takwa gold mining district in Ghana show maximum levels in surface water were less than 0.05 mg/dm^3 (Yem *et al*., 2013). A similar study conducted in artisanal gold mining communities within the Kibi traditional area, Ghana, reported levels of cadmium in river water at Apapam, Bunso, Kibi-Deaf, and Obronikrom as 0.006, 0.008, 0.008, and 0.010 mg/dm^3, respectively (Asamoah-Boateng, 2009). Earlier study in Nangodi catchment reported Cd concentrations that ranged from below detection limit to 0.223 mg/dm^3 (Cobbina *et al*.,2012) and in Datuku, Cd concentrations ranged from below detection limits to 1.700 mg/dm^3 (Cobbina *et al*., 2013a).

Higher level of cadmium in this study especially in the rainy season may be associated with the anthropogenic activities in addition to mining that may expose cadmium metal sources during dry season when mining activities was at its peak. The exposed cadmium metal sources may gradually release cadmium metal during rainy season and drained into the river. Another possible source could be associated with geological nature and long term refuse dump left standing by the river bank, when it rains cadmium metal associated materials may be released into the rivers thereby increasing its concentration in the river.

The observed cadmium values show that water quality in the study area is questionable and unfit for human consumption. Literature survey shows that heavy metals at mining sites can leach and carried by acidic water downstream.They can be acted upon by bacterial and methylated to yield organic forms, such as dimethylcadmium. These organic forms have been reported to be very toxic and adversely affect water qualities by seepage to pollute surface and underground water sources (Duruibe *et al*., 2007). Cadmium when ingested by humans accumulates in the intestine; liver and kidney where it has a long biological life of 20-30 years (WHO, 1999).The health effect of chronic exposure of cadmium include proximal tubular and osteomalacia diseases. Long term exposure is associated with renal dysfunction. High exposure can lead to obstructive lung diseases and has been linked to lung cancer. Cadmium may also cause bone defects in humans and animals (Odoh *et al.,* 2016).

It is noteworthy that river Gbako is a major source of water for its inhabitants used for drinking, livestock watering, irrigation and other possible uses. The level of cadmium in river Gbako at the time of study may be detrimental to the health of its inhabitants especially during rainy season.

iii. Copper

The result recorded indicated that copper was detected in all the sampling points with variation without any definite pattern (Tables 4.3 and 4.4). All the water samples analyzed contain copper above WHO permissible limits of 0.05 mg/dm^3. Comparing the values of copper concentration obtained in the mine site (downstream mine) with that of upstream mine water (Table 4.3 and 4.4); it can be concluded that, the study recorded elevated copper values in downstream mine water samples. High concentrations of copper could indicate the presence of pollution and are largely responsible for eutrophication conditions in water bodies (Taiwo *et al*., 2012).

The present findings show much higher values than the concentrations of copper reported in a previous study conducted in the Indus River, Pakistan (5.0 mg/dm^3) and Mississippi River, USA (4.0 mg/dm^3) (Ayantobo, *et al*., 2014).The elevated copper levels may possibly be attributed to the anthropogenic activities of the miners, making discharges of copper metal associated materials into the rivers.

The concentration levels for copper in water for use by the aquatic ecosystem ranges from 0.3 mg/dm^3 to 0.8 mg/dm^3 and irrigation requires copper concentration range of 0 mg/dm^3 to 0.2 mg/dm^3. These limits were exceeded in the river and therefore will make the river unsuitable for the maintenance of the aquatic ecosystem and irrigation (Yisa, 2004). Copper is both an essential nutrient and a drinking water contaminant. Its compounds are naturally present in the earth crust. Much of the copper that enter environmental waters are associated to particulate matter. Copper is a natural constituent of soil and will be transported into streams and water ways in runoff either due to natural weathering or anthropogenic soil disturbances. 68% of releases of copper are estimated to derive from these processes (ATSDR, 2000). The inhabitants of these communities are peasant farmers and engage in irrigation and other agricultural practices. The level of copper is therefore a problem.

iv. Iron

The result of iron levels recorded in this study (Tables 4.3 and 4.4) is higher when compared to similar study by Nkuli (2008) on river water samples with concentration range of 0.1 to 7.2 mg/dm^3.The elevated iron values measured in this study may be attributed to anthropogenic sources (land use activities) coupled with inputs from mining activities at the study site (Nkuli, 2008). The results of iron levels recorded from studied rivers do not follow a particular pattern downstream however, at certain sampling points it showed increasing values from upstream to downstream mine

while at other sampling points decrease in values were noticed downstream. This variation observed could possibly be due to the geological nature of the area, anthropogenic sources (land use activities and artisanals) (Shuttle, 2005).

The results of iron concentration recorded from all sampling points showed that they were above 0.3 mg/dm^3 WHO permissible limit for iron in water. The implication of this high iron concentration is that the water from the river may have taste and other aesthetic problems (Yisa, 2004). Similarly this water will not be suitable for livestock watering because it exceeded the WHO limit of 0 mg/dm^3 to 10 mg/dm^3 (DWAF,1996).

v. Manganese

Manganese levels recorded were noticed to be lower in the upstream when compared to the values recorded in the downstream for the two rivers (Tables 4.3 and 4.4). This could be attributed to the impact of mining activities along the downstream of the rivers.

Surface water bodies investigated in this study had Mn concentrations (0.08 to 779.3 mg/dm^3) above the WHO and SON guideline values of 5 mg/dm^3 and 0.2 mg/dm^3 (Ugwu *et al*., 2012). The high Mn concentration level (779.3 mg/dm^3) observed in Gbako River in the rainy season, this could be due to effect of dissolution of rocks with natural content of manganese, due to the action of rainfall in addition to anthropogenic sources such as effluent discharges and acid-mine drainage from mining activities (Singh *et al*., 2008; Maria, *et al*.,2012).

Manganese concentrations above 0.1 mg/dm^3 can impact an undesirable taste to drinking water. Effects from manganese are primarily to the central nervous system (Bada *et al*., 2012). The WHO standard for the aquatic ecosystem and irrigation uses are 0.18 mg/dm^3 and 0.2 mg/dm^3 respectively (DWAF, 1996). These limits for manganese

were exceeded in the rivers therefore manganese will pose health challenge if the rivers will be used as aquatic ecosystem and irrigation. Manganese is known to block calcium channels and with chronic exposures results in CNS dopamine depletion, which duplicates almost all the symptomlogy of Parkinson's disease (Odoh *et al*., 2016).

vi. Lead

The Pb values in this study revealed clear excedencies relative to the permissible limit of 1.5 mg/dm^3 set by the WHO. Previous studies also show maximum levels in surface water to be < 0.05 mg/dm^3 (Yem *et al*., 2013). The result indicated that lead concentrations were also higher than those reported by Asamoah-Boateng (2009) and Cobbina, (2013b) from surface waters samples in Newmont Ghana gold mining concession areas (0 to 2.710 mg/dm^3) and Tinga surface water (below detection limits to 0.188 mg/dm^3) respectively. The high content of Pb in the stream could be due to weathering, dissolution and leaching of lead from waste rocks dumps and minerals containing lead (Maria *et al*., 2012).

vii. Zinc

The result in this study indicated higher mean Zn values downstream when compared to upstream values in the rainy seasons for the two rivers. The result was also noticed to be above 90 mg/dm^3 WHO (1998) permissible limit for zinc in water (Tables 4.3 and 4.4). The findings in this study are in consonance with earlier studies by Kahatano *et al*., (1995) that reported high levels of Zn in streams and rivers of Lake Victoria Gold Fields in Tanzania. However it is in contrast to the studies conducted by Asamoah-Boateng, (2009) and Cobbina, (2013a) that reported low Zn concentrations from surface water samples in Newmont Ghana gold mining concession areas (0 to 0.190 mg/dm^3) and Datuku in Nangodi catchment (below detection limits to 0.013 mg/dm^3) respectively.

High values of Zn concentrations noticed in this study could be related to anthropogenic sources including mining activities, elevated Zn can also arise from seepage of groundwater into mining pits, mineralisation / leaching from pit walls, burden, waste rocks, tailings, etc (Akcil and Koldas, 2006; Ugwu *et al.*, 2012).

Although the species diversity or impact of aquatic system was not studied it is i mportant to note that the study found high levels of Zn at all points downstream the rivers Gbako and Tangale especially in the rainy seasons, which could affect the aquatic and human health that depend on the river. The impacts of Zn on human health include fainting, nausea and stomach disorder. However, a few sampling points were noted for low Zn values in the dry season when compared to WHO guidelines (1998) of drinking water quality. The reason for Zn being low probably was due to low inputs from mine or anthropogenic sources.

5.2 Soil Physico-Chemical Characteristics of Asha and Saboeregi Mining Sites

The result showed that pH values recorded at Asha and Saboeregi indicate that these soils are weakly acidic. The results at the control sites in both seasons were close to neutral (Table 4.5). In a study carried out by Jung (2001) in soil around the Imcheon Au- Ag mine in Korea pH values of the soil were reported to be strongly acidic to neutral (pH 1.9 to 7.4) . However, in contrast the pH values of the soil of the artisanal gold mining reported by Ali *et al.*, (2017) in a study carried out in Sudan were neutral to alkaline with pH 7.46 to 8.8. From these facts, the pH values of the soil are strongly dependent on the mining studied in each research.The pH of soil serves as a guide in the determination of the ability of the soil to be used as a medium for growing plants.

In the present study, the organic carbon content in soil samples varied from 0.12% to 3.75% in Asha and Saboeregi mining sites. The result obtained from the two mining sites favouarably compared with previous study conducted by Sayar *et*

al.,(2015) on mining soils of Raniganj in India with a range which varied from 0.29% to 2.05%. The results also indicate slightly higher organic carbon levels at the mining sites when compared to the organic carbon levels at the control site especially in the rainy season (Table 4.5). Elevated organic carbon levels at the mining sites may be related to the anthropogenic activities such as agriculture and mining coupled with presence of higher amount of humic substances which was absent in the control site.The organic carbon in Asha site which were found to be low, this may be due to lack of several microbes, low humification, rate, lack of weeds in the sampling sites, whereas high organic carbon recorded at Saboeregi site may be due to higher amount of humic substances present in the soil samples from decomposition of garbage wastes dumped on the soil and also due to addition of domestic wastes (Sayar *et al*., 2015). The amount of soil organic carbon (SOC) depends on soil texture, climate, vegetation and historical and current land use/management. Soil texture affects Soil Organic Carbon (SOC) because of the stabilizing properties that clay has on organic matter (Sayar et al., 2015). Organic carbon levels greater than 0.8% is rated as good quality of soil (Saxena 1987), while a level of organic carbon greater than 0.75% indicates good fertility (Ghosh *et al.*, 1983). The results of organic carbon at the study site shows that the soils are of good quality.

Organic matter content varied considerably across the study site (Table 4.5). The organic matter of soil in the Saboeregi site recorded slightly higher values when compared to Control sites at both seasons. The slightly elevated organic matter may be attributed to low input from mining activities in addition to the decomposition of garbage wastes dumped on the soil and also due to addition of domestic wastes found at the study site which was absent at the control site. It was also noticed that organic matter of soil in the studied areas with average values of 3.01% and 3.73% at Asha and

Saboeregi respectively were higher when compared to 1.76% reported by Sayar *et al*., (2015) in a study carried out on mining soils of Raniganj in India. Higher organic matter observed in this study may be attributed to higher amount of humic substances present in the soil samples from decomposition of garbage wastes dumped on the soil and also due to addition of domestic wastes. Organic matter chelates or binds nutrients, preventing them from becoming permanently unavailable to plants. It also encourages the development of plant roots, besides improving aggregation, preventing erosion and increases the rate of pesticides decomposition in the soil (Fagbote and Olanipekun, 2011).

The phosphate content of the soil samples at the study sites in both seasons were lower when compared to mean of 81.00 mg/kg and 93.16 mg/kg in the rainy and dry seasons respectively at the Control site (Table 4.5).This result is in agreement with findings of Mrinal (2004) who reported lower presence of P in coal mine soil. Phosphate level obtained from the two study sites in the rainy season (Table 4.5) were generally observed to be above 10 mg/dm^3 limit Guideline for soil by FEPA (1991). The present study is in conformity with findings of Narayanan and Devarajan (2012) who shows that the concentration of phosphorus (11 and 14.66 mg/kg) from mine soil were higher than the permissible limit. High phosphate levels recorded at the two sites in the rainy season might be due to slightly alkaline nature of soil and addition of commercial fertilizers used for cultivation of crops (Sayar *et al*., 2015).

The result of the cation exchange capacity was observed to be higher at Asha mining site when compared to the values obtained at the control site while at Saboeregi site the result was reversed (Table 4.5). However, lower mean C.E.C. values were observed in the rainy season when compared to the result obtained in dry season from both study sites. The lower C.E.C. values observed at Saboeregi site and may possibly

be attributed to wash out process during rains or leaching thereby decreasing the topsoil C.E.C. content of the study area (Odoh, 2011).The result of the cation exchange capacity also generally indicates a noticeable variation throughout the sampling sites over the period of study as seen from high standard deviation (Table 4.5). The result obtained in this study is in contrast to findings of Sayar *et al*., (2015) that reported higher range of 120 to 527 Cmol/kg. This observation may be attributed to differences in geological, climatic coupled with other factors such as pH between the sites (Alloway, 1995; Brady and Weil, 2002).The results therefore reflects low input from mining activities.

5.2.1 Soil textural class of the mining site

The result of soil particle size distribution in this study as presented in figures 4.1 and 4.2 was dominated by high percentage values of sand fractions. The high mean percentage values of sand fractions could be attributed to rate of deposition of particles and soil type in each study site (Agbenin, 1995). The result also reveals that Asha soil texture is sandy loam and that of Saboeregi is sandy clay loam.The result reported by Ali *et al.,* (2017) and Solongo *et al*., (2016) on previous studies conducted on artsanal gold mining in Sudan and Mongolia was mostly sand and silt respectively. These results therefore revealed that the texture of the soil is dependent on the mining studied in each research (Solongo *et al*., 2016).

5.2.2 Heavy metals concentrations in soils of Asha and Saboeregi Mining Sites

i. Gold

The result of the study showed that control site recorded a much higher mean Au concentration value of 27.8 ± 1.01 mg/kg when compared to the values recorded at the mining sites (Tables 4.6 and 4.7). This is in contrast to the studies conducted by Adetoyinbo *et al.,* (2011) on the concentration of major elements in the soil samples

collected from five locations in the mining areas of Itagunmodi Osun state Nigeria and three locations outside the mining which shows that the concentrations of the elements were higher within the mining site than outside mining site.The result also revealed that higher mean Au concentrations were consistently recorded in the rainy season when compared to the values in the dry season.This seasonal variation could be due to effect of dissolution of rocks with natural content of gold as a result of rainfall (Maria, *et al*., 2012). Health challenges associated with gold miners are the following among others, bacterial and viral diseases, noise-induced hearing loss, lung cancer, eye jaundice and chrisiasis (darkening) and central headache (Ronald, 2003).

ii. Cadmium

The results shown in Tables 4.6 and 4.7 indicate that Cd concentration values were generally low when compared to other metals in the study area. The result in this study is in conformity with previous studies carried out by Cabala *et al*., (2004);Cabala and Teper (2007) and Cabala *et al*., (2008) which recorded a very low concentration ratio for Cd relatively to other metals. The researchers reported that zinc, lead and cadmium most often occurred in the ratio of 100:25:1. Low Cd values generally recorded in this study may be attributed to the fact that Cd is very mobile and because it is weakly sorbed and is not retained in soils through cation exchange (Sparks, 2005). On the average cadmium concentration values recorded in the two study sites were within the critical level of 3-5.00 mg/kg Cd in soil (Kabata-Pendias and Pendias, 1992). Conversely Chopin and Alloway, (2007) reported high concentrations values of Cd (1811.66 & 1246.66 and 911.53, 728.33 mg/kg) in summer and rainy season of waste dump of magnesite and bauxite mines. He stated that the major source of these heavy metal contaminations were from metalliferous mining and smelting, metallurgical industries waste disposal sites and agricultural fertilizers.

iii. Copper

Overall mean concentrations of copper at the mining sites were higher than that of control and the WHO acceptable limit of 30 mg/kg for world soils hence suggesting the pollution of the sites due to copper. This high level of copper concentration may be associated with the activities of the minners as well as the environmental factors. The minners through their open earth surface activity in an attempt to excavate their metals of interest exhumed other materials thereby making them available at topsoil level. Copper is an essential element for plants and animals. Critical concentration in plants is in between 20-100 mg/kg. Phytotoxicity can occur if copper concentration in plants is higher than 20 mg/kg dry weight (Nikki, 2016).

iv. Iron

Iron mean concentrations in the study sites ranged from 124.06 ± 0.08 mg/kg to 49898.56 ± 0.19 mg/kg the highest iron concentration occurred at Saboeregi mining sites in the rainy season. The control recorded 3577.0 ± 12.11 mg/kg. Iron concentrations observed in the soils of the studied sites were highly varied as seen on Tables 4.6 and 4.7.

The high variation in the iron concentration as is in the case with other metals may be connected with the occurrence of metalliferous minerals whose accumulations depend on natural factors such as geological structure and erosion of shallow ore-bearing iron formations and anthropogenic factors such as mining (Chopin and Alloway, 2007).

In summary, the iron concentration at the various sampling points from the study sites were found to be high including the control site. The elevated values measured at the sampling points were attributed to anthropogenic sources (land use activities) with low inputs from mining activities. This observation is in agreement with Niger State

Geographic Information System (NIGIS, 2013) which stated that iron is one of the abundant mineral resources in the state

The values of mean concentration of Fe recorded from the study sites were observed to be higher than the permissible limit of 1500 mg/kg recommended by European Union (EU).

Analysis of variance (ANOVA) showed that there was significant strong positive correlation between Fe in soil and Au, Cd and Cu in soil at Saboeregi site, thus according to Angelovicova and Fazekasova (2014) these metals may have originated from same source and suggest interaction between Fe, Au and Cd in soil.

v. Manganese

The result reported from the two study sites showed that manganese mean concentration varied widely when compared to the control site (Tables 4.6 and 4.7). The high variation may be connected to the occurrence of metalliferous minerals whose accumulations depend on natural and anthropogenic factors. These factors may include geologic structure and erosion of shallow ore-bearing Triassic formations; mining as well as processing of metal ores (Baran *et al*., 2014). The result also indicated that manganese content observed in this study was generally higher than the ones reported by Odoh (2011) and Omoniyi *et al.,* (2016) as 10.59 ± 5.17 mg/kg to 42.60 ± 23.80 mg/kg and 170.00 mg/kg to 205.20 mg/kg Mn in soils respectively. Elevated manganese values reported in this study collaborate well with the findings of Dara, (1993) and Singh *et al*.,(2008) they reported that manganese may be found in most soils since it is one of the essential elements and can also be attributed to anthropogenic sources such as discharges from mining activities. Manganese health implication is known to block calcium channels and with chronic intoxication result in central nervous system (CNS) dopamine depletion. This latter condition duplicates almost all the symptomology of

Parkinson's disease (Ndinannyi, 2013). The result in this study was lower than the European Union Standards (EU, 2002) of about 2000 mg/kg. The level of manganese therefore may not cause much problem to the soils as at the time of study.

vi. Lead

The result showed that the overall Pb mean concentrations from the two study sites are higher than that of control site (Tables 4.6 and 4.7) and the critical value of 10 mg/kg documented by Alloway (1990). This therefore implied that Pb concentrations in the two study sites have reached critical levels of pollution which may have resulted from mining extract activities. This could have negative consequence on the soils of the study area. The soil in the study area may therefore not be fit for agricultural activities it is used for among other uses. Conversely, other authors like Cabała and Teper, (2007) and Cabała *et al*., (2008) have reported much higher lead concentrations up to 3,614 mg/kg and 5,000 mg/kg when compared to the values in the present study. They have shown that soils in areas of ore mining and metallurgy are characterized by very high concentrations of lead and other metals such as zinc and cadmium. Statistical analysis of variance (ANOVA) showed strong positive correlations between Pb and Au, Pb and Cu, Pb and Fe, Pb and Mn. This result suggested that these metals came from the same pollution source and their formations were possibly caused by natural production or anthropogenic activities such as mining (Bodie and Paul 2015).

vii. Zinc

Zn contents of the studied soil presented in Tables 4.6 and 4.7 indicated that the soils from Asha and Saboeregi mining sites recorded higher Zn contents when compared to the values recorded at the control site. High values of Zn concentrations noticed in the mining site in contrast to control site could be related to anthropogenic sources including mining activities which may have resulted from the over-burden, waste rocks and tailings (Akcil and Koldas, 2006; Ugwu *et al.*, 2012).

However, the levels of Zn in the soil were generally below the European Union Standards of 300 mg/kg (European Union, 2002).This finding may suggest that Zn impact

on the health of inhabitants in the study area may not be prominent.

5.3 Mean Heavy Metals Concentration in the *Sorghum* bicolorgrains cultivated in the Mining Vicinity

The results of heavy metal concentrations in *Sorghum bicolor* grains harvested from the farm lands located in the mining vicinities and the control site are presented in Table 4.8 and appendices i and ii.

The result showed Au mean content in *Sorghum bicolor* grain samples harvested from the mining sites were above 1.34 mg/kg recorded from *Sorghum* grains harvested from control site. This is in agreement with the studies conducted by Adetoyinbo *et al.,* (2011) which shows that the concentrations of the elements were higher within the mining site than outside mining site.This is an indication that mining activities may have impacted on the soils at the study sites.The result also indicated that Au concentrations were found in *Sorghum bicolor* grain samples in varying levels with those samples from Saboeregi mining site slightly higher. Higher gold levels found at Saboeregi mining site when compared to Asha site could be attributed to geological differences between the two sites and may lead to the reduction in the growth of this crop plant at Saboeregi site ((Jayakumar *et al*., 2013).

The result revealed that only *Sorghum bicolor* grain samples harvested from two of the four sampling points of Asha and Saboeregi mining sites recorded Cd content as shown in Table 4.8 and appendices i and ii . It is also pertinent to note that earlier in this study the results for soil metal concentration (Tables 4.6 and 4.7) showed that some levels of cadmium concentrations were only observed in the aforementioned sampling

points at Asha and Saboeregi mining sites. This finding suggests interaction between Cd in the soil and in the *Sorghum bicolor* grains samples harvested from the same location. This finding is further affirmed by high positive correlation that existed between Cd in the *Sorghum bicolor* grain and Cd in the soil (Table 4.22). This finding is further corroborated with studies by Kachenko *et al.* (2004).This result depict despite low concentration of Cd in soil samples Cd is still found present in the *Sorghumbicolor* grains. The accumulation of Cd in *Sorghumbicolor* grains confirms the research results of Brian (2005) that Cd is one of the elements that are intensively accumulated in plant bodies. The WHO (1996) permissible limit of 0.02 mg/kg in crops was exceeded at the two mining sites. This uptake of Cd is of special interest as Cd is considered one of the most toxic crop contaminants (Mendoza-Cozatl *et al*., 2008) thus the *Sorghum bicolor* grains harvested at studied sites may not be safe for consumption.

On the whole the result from the two mining sites revealed *that Sorghum bicolor* grains showed copper content above 7.64 ± 0.02 mg/kg (control site). Higher copper concentrations noticed at Asha site and Saboeregi sites when compared to the control site may be attributed to anthropogenic activities, such as mining taking place in the two sites. The result recorded from the two sites were below tolerance limit of 10 mg/kg by WHO (1996) in crops. This implies that copper content levels in the *Sorghum bicolor* grains harvested from the two studied sites could not pose immediate health problem however if accumulated over time it may become a problem.

The result revealed that copper levels in *Sorghum bicolor* grains harvested at Asha mining site with range (6.43 to 14.28 mg/kg) were higher than those obtained from control site. Copper levels at Saboeregi mining site were lower than the levels at control site (Table 4.8).The high copper concentrations noticed at Asha site when compared to control site may be attributed to anthropogenic activities such as mining and other

agricultural inputs at the mining site which were absent from the controls. Whereas the differences in the two sites may be attributed to geological differences such as pH and other soil properties (Venditti *et al*., 2000). The result also showed that copper levels in *Sorghum bicolor* grains harvested from the study sites were lower than the permissible limit of 10 mg/kg by WHO (1996) in crops.This implies that copper content in the *Sorghum bicolor* grains could not pose immediate health problem however if accumulated over time it may become problem.

Analysis of variance (ANOVA) showed that there was significant strong positive correlation between Cu in *sorghum* grains and Au and Cd in the *sorghum* grains thus according to Angelovicova and Fazekasova (2014) these metals may have originated from same source and suggest interaction between Cu, Au and Cd in both sorghum and soil.

The results shown in Table 4.8 and appendix I revealed that iron content recorded in *Sorghum bicolor* grains from the study sites do not follow a particular trend hence highly varied. However, higher Fe values appears to be in *Sorghum bicolor* grains harvested from Asha site this probably may be attributed to the fact that higher iron concentrations were reported at Asha site especially in the rainy season. The results also indicated that of all the heavy metals under study, *Sorghum bicolor* grains absorbed and accumulated iron more than other metals. The Fe content in *Sorghum bicolor* grains recorded values was above 322.29 ± 0.02 mg/kg recorded from *Sorghum bicolor* grains harvested from control site and above tolerance limit 28.3 mg/kg by WHO (2007). It is worth mentioning that, at higher concentrations of these metals, reductions in plant growth have been recorded (Jayakumar *et al.*, 2013).

The result shown in Table 4.8 indicates that Mn mean levels of 62.82 ± 0.34 mg/kg recorded in *Sorghum bicolor* grains from Saboeregi site was higher than those

recorded (48.38 ± 0.34 mg/kg) at Asha site. This result is not surprising as there were higher concentrations of Mn recorded in Saboeregi site than at Asha site, this result is affirmedby the result of the analysis of variance (ANOVA) that showed positive correlation between Mn in *Sorghum bicolor* grains and Mn in soil, which suggests some levels of interaction between each other. Mn content recorded in *Sorghum bicolor* grains from the study sites and control were below tolerance limit of 300 mg/kg WHO (1996). Hence Mn levels in the *Sorghum bicolor* grains may not be of immediate harm to man and animals but could if accumulated over time.

The result revealed that Pb content in *Sorghum bicolor* grains from the two study sites were below 41.66 ± 0.00 mg/kg recorded from *Sorghum bicolor* grains harvested from control site but above tolerance limit of 2.00 mg/kg by WHO (1996).This implies that lead content levels in the *Sorghum bicolor* grains could be harmful to man if accumulated over time through the food chain.

Pb mean content found in the *Sorghum bicolor* grains harvested from Saboeregi site were higher when compared to the *Sorghum bicolor* grains from Asha site (Table 4.8). Higher Pb levels found at Saboeregi mining site when compared to Asha site could be attributed to geological differences between the two sites and may lead to the reduction in the growth of this crop plant at Saboeregi site where the absorption is prominant (Jayakumar *et al.*, 2013).

The result of zinc content found in *Sorghum bicolor* grains from Asha mining site (Table 4.8) revealed that Zn concentration in *Sorghum bicolor* grains varied widely in levels in the soil .This could be attributed to the background Zn present in the soil (Omoniyi *et al.*, 2016).This was evident by the concentrations of Zn noticed in the *Sorghum bicolor* grains harvested at different sampling locations. Zinc content in *Sorghumbicolor* grains was 65.21 ± 0.03 mg/kg and 19.04 ± 0.05 mg/kg (Table 4.8)

that grew on soils with 141.61 ± 0.33 mg/kg and 92.46 ± 1.06 mg/kg (Tables 4.6 and 4.7) at Asha and Saboeregi sites respectively. Pearson correlation analysis established that Zn concentrations in the plants were positively correlated with Zn concentrations in the soil ($r = 0.510$, $P < 0.01$). Similarly, positive correlations were also noticed between zinc *Sorghum* and Mn soil, zinc *Sorghum* and Pb soil, however, the relation between concentrations of Mn in the soil was weak ($r = 0.482$) (Table 4.23). Zinc levels in *Sorghum bicolor* grains was above 29.48 ± 0.00 mg/kg recorded for *Sorghum bicolor* grains harvested from control site and above tolerance limit of 20 mg/kg by WHO (1996). Higher levels of these metals have been reported to reduce plant growth and protein content (Jayakumar *et al.*, 2013)

It was generally observed that the concentration trend of the heavy metals in the *Sorghum bicolor* grains from Asha site is of the following order Fe > Mn > Zn > Pb > Cu > Au > Cd and that of Saboeregi was Fe > Mn > Pb > Zn > Cu > Au > Cd . These differences noticed in the order reported at the sites might be attributed to differences in soil properties considering the two different locations involved (Antwi-Agyei *et al.,* 2009)

5.4 Pearson's Correlation Coefficients Analysis between Physico-Chemical Parameters, Soil, River Water and *Sorghum* bicolor grains Metal Concentrations at the Mining Sites

There exists a significant strong positive correlation between organic matter (OM)and organic carbon (OC), Au and P, Mn and P, Mn and Fe with r values 0.980, 0.842, 0.752 and 0.789 respectively all at significant level of $P < 0.05$. This observation favourably compared with previous study carried out by Sun, *et al.,* (2012) on Heavy Metals' Spatial Distribution Characteristics in a Copper Mining Area of Zhejiang Province. They reported that a strong correlation occurred between As-Cu, As-Zn, As-Ni, As-Pb, Cu- Zn, Cu- Ni, Cu-Pb, Zn- Ni, Zn-Pb, Ni-Pb and iterated that this indicates

that all these elements may have a same source mainly from anthropogenic mining relevant activities.

The result shows that decrease in pH in the soil can increase the available P, Au and Mn. These results are in agreement with the earlier report by Tripathi and Misra, (2012) the results of their work show that pH was negatively correlated with water holding capacity, bulk density, Fe and Ni at significant level ($P < 0.05$).

The result also shows that Mn and Fe had strong positive correlation significant at ($P < 0.05$, $r = 0.789$). Strong correlation between individual pairs of heavy metal indicates that they are of similar origin, usually connected with human activities and particularly mining as is the case in this study (Agnieszka, *et al*., 2014). There is no significant correlation found between the textural class with respect to other heavy metals.

A strongly positive correlation between OM and OC; Au and P; Fe and Cu; Mn and Au; Mn and Fe was observed in the study. The result observed here may be due to their geochemical connections and sources of origin (Guo, *et al*., 2012). Conversely strong but negative correlations are seen between Au and CEC; Au and Pb all at significant levels of ($P < 0.05$). This implies that increase in Au concentration may possibly reduce the availability of the aforementioned parameters (Tripathi and Misra, 2010). It is also observed that there are moderate and weak positive correlations between CEC and P; Cu and OC; Cu and OM; Fe and P; Fe and Au; Mn and P at significant levels of ($P < 0.05$). There is also records of weak positive correlation between Zn and OC; Zn and OM; Zn and Cd; Zn and Cu; Zn and Fe; Zn and Mn significant at ($P < 0.01$).

The results also showed strong positive correlations between Au water and Fe *Sorghum bicolor* grain, Cu water and Cu *Sorghum bicolor* grain, Cu water and Zn *Sorghum bicolor* grain,Mn water and Zn *Sorghum bicolor* grain, Pb water and Fe *Sorghum bicolor* grain. Negative correlations were also observed between Au water and Zn *Sorghum bicolor* grain, Cd water and Zn,Cu, Au and Mn *Sorghum bicolor* grain, Zn water and Fe *Sorghum bicolor* grain.

Generally the results no significant correlation coeffiecient between any pair of metals (Tables 4.27 and 4.28).

5.5 Heavy Metal Speciation in Asha and Saboeregi Mining Sites

The result of heavy metal distribution in the different chemical fractions in the mining soils at Asha and Saboeregi Mining Sites.

i. Gold

Au showed similar pattern of distribution among the fractions at both Asha and Saboeregi mining sites during rainy season (Figures 4.3 to 4.6). The result of this study revealed that Au was mostly associated with carbonate fraction. This indicates that carbonate phase provided more binding phase for Au metal than any other phase. This implies that Au is in long-term mobile phase in the mining sites and therefore would not readily move into the environment for any possible health implication.

ii. Cadmium

For Cd comparison of figures 4.3 and 4.4 showed that water soluble fraction (F1) is the lowest ranging from below detection limit to 2.4% (Fig. 4.3). This is contrary to the earlier report in a study on Assessment of Heavy Metals in Mining Tailing Around Boroo and Zuunkharao Gold Mining Areas of Mongolia by Solongo *et al*.,(2016). They reported thatCd was extracted in the mobile phase. This implied that

Cd would easily move to the environment and have health risk on living organisms. This study showed Carbonate bound fraction was the most predominate with 50.33% and 43.4% (Fig. 4.3) for Asha and Saboeregi mining sites respectively during rainy season, indicating Cd in the long-term mobile phase.

Dry season recorded highest amount of 40.64% and 34.87% in the residual fraction for Asha and Saboeregi sites respectively (Fig. 4.4). This result corroborates well with studies carried out by Tahar and Keltoum (2014) where the result of their studies of sequential speciation showed that Cd is predominantly present in the residual phase (F6) by a relative weight ratio of 85%. High content of Cd in the residual fraction during dry season was probably due to high association or retention ability of the mineral's structure such as detrital silicates (Ogunfowokan *et al.,* 2013). The results in the rainy season at Asha site (Fig. 4.3) indicate that about 16.58% of Cd is bound to the short-term mobile fraction (F1 and F2). The long-term mobile fraction (F3, F4 and F5) contains 73.86% of the total metal. However, the immobilized fraction (F6) has about 9.56%, whereas in dry season Asha soils contains relatively very low value of 0.82% bound to short-term mobile fraction (F1 and F2).The long-term mobile fraction (F3,F4 and F5) contains 58.54% while the immobilized fraction (F6) has about 40.64%.

Similar results were also obtained for Saboeregi soils (Figs. 4.5 and 4.6). The rainy season results show that 6.6% was bound to the short-term mobile fraction (F1 and F2). The long-term mobile fraction (F3, F4 and F5) contains 69.12% while the immobilized fraction (F6) has 24.28%. The dry season results show that 1.56% was bound to the short-term mobile fraction (F1 and F2). The long-term mobile fraction (F3, F4 and F5) contains 45.57% while the immobilized fraction (F6) has 34.87%.

The high association of Cd in immobilized fraction in both mining sites during rainy season indicates that Cd may not be readily available to the environment.

iii. Copper

Organic fraction (F5) is the most prevalent phase for Cu with 36.38% in Saboeregi soils in the rainy season (Fig. 4.5); dry season recorded 38.58% and 42.35% for Asha and Saboeregi soils respectively (Fig. 4.6). The high percentage of Cu in the organic bound fraction may be attributed to the fact that it is characterized by high complex constant organic matter thus according to Barkouch and Pineau (2015), Cu may be said to be bound to labile organic matter such as lipids, proteins and carbohydrates. The results also indicate that organic fraction provided more binding site than any other phase. This is followed by iron-manganese oxide bound fraction (F4) with values 32.59% and 16.17% for Asha and Saboeregi soils during rainy season while dry season recorded 22.9% and 16.23%.

On the average percentage of total Cu associated with different geochemical fraction in Asha during rainy is of the order : iron-manganese oxide (F4) > residual fraction (F6) > organic fraction bound (F5) > carbonate fraction bound (F3) > water soluble fraction(F1) > exchangeable fraction (F2) while that of dry season is of the order : organic fraction bound (F5) > iron-manganese oxide (F4) > residual fraction (F6) > carbonate fraction bound (F3) > water soluble fraction (F1) > exchangeable fraction (F2).

On the other hand Saboeregi mining site is of the order : organic fraction bound (F5) > residual fraction (F6) > iron-manganese oxide (F4) > carbonate fraction bound (F3) > exchangeable fraction (F2) > water soluble fraction(F1) for rainy season and that of dry season is organic fraction bound (F5) > iron-manganese oxide (F4) > residual fraction (F6) > carbonate fraction bound (F3) > exchangeable fraction (F2) > water soluble fraction(F1) (Figs. 4.5 and 4.6).

iv. Iron

The distribution of iron in both sites was mostly associated with iron-manganese oxide bound fraction (F4) except at Saboeregi site during rainy with residual (F6) value of 41.81%. At Asha during rainy season iron-manganese oxide bound fraction (F4) value of 44.86% was recorded, while 51.91% and 42.21% were recorded for Asha and Saboeregi in dry season respectively. The high percentage of Fe in iron-manganese oxide bound fraction (F4) may be due to high association or retention ability of the mineral (Ogunfowokan *et al.,* 2013).

Iron distribution in exchangeable and carbonate phases are very low as seen in the values below (F2) 0.07% and (F3) 0.1% for Asha while Saboeregi site recorded (F2) 0.13 and (F3) 0.39 during rainy season. Dry season result recorded distribution values as (F2) 0.16% and (F3) 0.05%). This result indicates that exchangeable fraction (F2) phase and carbonate fraction bound (F3) phase were the lowest binding phases and hence has the least affinity for iron-manganese oxide (F4). Similarly this could also be as a result of large adsorption surface area of iron- manganese oxides/hydroxides (Yisa *et al.*, 2006).

v. Manganese

Mn distribution in the studied soils followed similar order for both Asha and Saboeregi sites throughout the two seasons (Figs. 4.3 to 4.6). The distribution follows the order given below: carbonate fraction bound (F3) > residual fraction (F6) > iron-manganese oxide (F4) > organic fraction bound (F5) > exchangeable fraction (F2) > water soluble fraction (F1). The highest percentage Mn distribution occurred at carbonate bound fraction (F3) phase with 48.85% and 64.39% for Asha and Saboeregi sites respectively during dry season. The lowest distribution occurred in water soluble fraction (F1) phase with 2.74% and 1.25% at Asha and Saboeregi sites during rainy season, while dry season recorded 0.01% and 0.15%. The result indicates that carbonate

bound fraction (F3) provided highest binding phase for Mn while water soluble phase provided the lowest binding phase (Yisa *et al*., 2006).Low amount of Mn extracted from the bio-available fraction, indicates that the soil mining samples contained Mn in immobile state.

vi. Lead

The analysis of the results of Pb distribution in (Figures 4.3 to 4.6) shows that iron- manganese oxide bound fraction (F4) is the highest with 37.25% and 23.15% for Asha and Saboeregi sites respectively during rainy season. However, dry season distribution shows that exchangeable bound fraction (F2) is the highest with 23.43% and 36.93% for Asha and Saboeregi soils respectively. The very high levels of the exchangeable bound fraction (F2) suggest that Pb possibly co-precipitated (Zaranyika and Chirinda, 2011). The distribution is characterized by a strong dominance (43.9%) and (41.96%) of Pb bound to long term mobile fraction (F3, F4 and F5) for Asha and Saboeregi soils during dry season .The short term mobile fraction represents about 16.11% to 18.47% while the immobilized fraction(F6) is 16.64% and 11.15% for Asha and Saboeregi soils respectively during rainy season. The dry season recorded 18.35% and 24.03% for Asha and Saboeregi soils respectively for the same fraction. The study therefore revealed that Pb in the mining sites would not be readily made available to the environment because of its strong dominance in long-term phase in the rainy season.

vii. Zinc

Zinc distribution in the studied soils is almost the same as in the case of other metals. The carbonate fraction (F3) is the most prevalent for Zn with 32.83% and 39.6% respectively for Asha and Saboeregi soils during rainy season (Figs. 4.3 and 4.4). On the other hand dry season distribution shows that organic matter fraction (F5) predominates with 31.85% and 38.2% for Asha and Saboeregi soils respectively. The high content of

Zn in the organic matter fraction is probably due to either high retention capability of organic matter like humic acids and fulvic acids (Belzile *et al.*, 2004).This result is in contrast to the one reported by Ogunfowokan *et al*., (2013) where Zn was found to be associated with low organic fraction. The Zn component is associated with water soluble fraction (F1) with 12.03% and 16.95% and Fe-Mn oxide fraction (F4) with 12.03% and 16.07% for Asha and Saboeregi respectively during rainy season.

5.6 Pollution Degree Indices in the Study Sites

5.6.1 Pollution degree based on Igeo

According to the Muller scale (Muller, 1969), the calculated results of Igeo values (Table 4.29) indicate that Fe (7.88) can be considered as an extreme pollutant at the two study sites because its Igeo mean lies in the seventh class (I >7), indicating extreme contamination of the soils in the two study sites by these elements. The contamination noticed in the study site possibly might have been attributed to some anthropogenic activities such as mining. Excess iron up take is a serious problem in developed and meat eating countries and it increases the risk of cancer (Monisha *et al.,* (2014). Soils at the study sites with Mn (I > 4.41) can be considered as heavily to extremely polluted in the rainy season but in dry season the soils are heavily polluted (I > 3.2) (Table 4.29). Zn has (I > 3.5) throughout the two seasons for the two study sites and so the soils are said to be heavily polluted with Zn. Cu and Au on the other hand could be said to have moderately to heavily polluted the soils at the two sites in both seasons. The pollution of soils by these heavy metals may have been facilitated by anthropogenic activities which include mining. Heavy metals in soils may be absorbed by shallow rooted plants or washed into surface water, from where they may contaminate the food chain (Eludoyin *et al*., (2017). Long term exposure and bioaccumulation of some of these metals, including Pb and Zn have been linked with inhibition of blood cells formation and brain damage in children (World Health Organisation, 2010).

The results indicate thatsoils at Asha site are unpolluted with Cd (I = 0.05). The order of contribution of various heavy metals at both mining sites on the basis of Igeo follow: Fe > Mn > Zn >Cu > Pb > Au > Cd. It also shows that the two study sites are polluted with Fe and Mn (Table 4.29)

5.6.2 Pollution degree based on enrichment factor

Enrichment factor (EF) is an essential part of geochemical studies in distinguishing heavy metals that originated from human activities and those from natural weathering (Praveena *et al.*, 2010). Table 4.30 present EF values of the investigated metals. The results revealed that mean values of EF were less than 2 for Au and Cd, indicating nonexistence to minimal enrichment by these metals in the soils (Sutherland, 2000), however Cd recorded an exceptional EF value of 2.5 at Saboeregi site in the rainy season. It was further revealed that Mn, Zn have mean EF of 2.85 and 3.72 at Saboeregi site during rainy and dry season respectively. The above obtained result with mean EF value greater than 2 suggests that these soils were moderately enriched with these metals as a result of anthropogenic inputs (especially mining activities) during this period (Hernandez *et al*., 2003). However, the mean EF values of 14.1, 8.1 and 5.0 for Pb, Fe and Mn were the highest obtained at Saboeregi site during rainy season indicating that these soils were significantly enriched with Pb, Fe and Mn.These high enrichment factors would be defining as main mineral compositions of these mining areas. The mean EF values for Mn, Zn, Fe and Pb varies from depletion to minimal through to significant enrichment, which reiterates the close association between pollution of these soils in Pb, Mn, Fe and Zn (Ekengele *et al*., 2016).The mean EF of the metals decrease as follows: Pb > Zn > Fe > Cu > Mn > Cd > Au at Asha mining site and Pb > Fe > Cu = Mn > Zn > Cd > Au at Saboeregi mining site. The result of high EF values for Pb and Zn favourably compared with previous study conducted by Ali *et al*., (2017) on soils of artisanal gold mining in Sudan. The researchers opined that the high EF values in Pb and Zn indicate contributions of anthropogenic sources, which are showing mining soil samples enriched during gold extraction processes.

CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

6.1 Summary

The results indicated that the soils at Asha mining site were sandy loam while those of Saboeregi were sandy clay loam in texture and showed Saboeregi soils had better structural stability and water holding capacity.The soils of the two sites were weakly acidic. The concentrations of the metals (Au, Cd, Cu, Fe, Mn, Pb and Zn) in the soils from the mining sites were higher than the corresponding values from the control site, and also higher than the recommended limits given by Joint Food and Agriculture Organization and World Health Organization (FAO/WHO). The Igeo Pollution Index showed that soils at the two study sites (i.e Asha and Saboeregi) were extremely polluted with Fe ($I > 7$). Mn ($I > 4.41$) extremely to heavily polluted in the rainy season for the two sites. Zn polluted the two sites heavily while Cu and Au pollution were considered moderate. The concentrations of the metals (Au, Cd, Cu, Fe, Mn, Pb and Zn) in the *Sorghum* grains harvested from the mining sites were higher than the corresponding values from the control site with exception of Cd and Pb, and also higher than the recommended limits given by Joint Food and Agriculture Organization and World Health Organization (FAO/WHO) with the exception of Cu and Mn.

The result of the research work on environmental assessement on pollution caused by mining activities indicated that of the fifteen physical and chemical properties of waters from rivers Gbako and Tangale studied, eight of the properties (turbidity,alkalinity, sulphide, colour, suspended solid, nitrate, phosphate and total solid) exceeded the acceptable WHO standard limits for surface waters while four of the properties (total dissolved solid,electrical conductivity, chloride and biochemical

oxygen demand) were found to be below the acceptable WHO standard limits for surface waters and the remaining three properties (pH, dissolved oxygen and chemical oxygen demand) were within the acceptable WHO standard limits for surface waters during the period of study.

The distribution of heavy metals in water surfaces of rivers Gbako and Tangale indicates anthropogenic activities in the sites as an important factor contributing to increased metals (Au, Cd, Cu, Fe, Mn, Pb and Zn) concentration in the water. Heavy metal levels were higher than the values obtained for control experiments except for Cd and Pb and also higher than the recommended limits given by Joint Food and Agriculture Organization and World Health Organization (FAO/WHO).

6.2 Conclusion

Based on the field, laboratory and statistical analyses of the data, the following conclusions were made:

The concentrations of Cu, Fe, Mn, Pb and Zn at Asha and Saboeregi sites were higher than the control site which implies that the mining activities on these soils have contributed significantly to the heavy metals contamination of the soils and can be of health risk since crops are planted on the nearby farmlands.

The Cd, Fe, Pb and Zn content of *Sorghum bicolor* grain from the two study sites were of range 0.02 to 0.8, 156.8 to 8605.33, 26.80 to 37.90 and 1.41 to 82.90 mg/kg respectively. These concentrations are above tolerance limits of 0.5, 28.3, 2 and 20 mg/kg respectively set by WHO and hence the consumption of *Sorghum bicolor* grain may pose health challenge to the public.

Majority of the heavy metals (Au, Cd, Mn, and Zn) were mostly found in the carbonate bound fraction which implied that they are in long term mobile state, hence

may not be readily available to the crops.

Significant relationship existed between Cu water and Cd soil; Au water and Cu soil; Mn water and Cu soil; Cd soil and Cd *Sorghum bicolor* grain, Zn soil andCd *Sorghum bicolor* grain. However, the relationship that existed between Au water and Fe *Sorghum bicolor* grain; Cu water and Cu *Sorghum bicolor* grain; Cu water and Zn *Sorghum bicolor* grain; Mn water and Zn *Sorghum bicolor* grain was not significant.

6.3 Recommendations

In the light of the above the following recommendations are drawn:

i. The study has revealed that some levels of River Gbako and Tangale as well as soils within the study area were polluted. This resulted from the mining activities taking place in the study area. However, phytoremediation research can be carried out by future reseachers to clean up the area.

ii. The study was limited to the assessment of soil, water and plant crops. To provide a more comprehensive understanding of the pollution status of the mining areas, future research that can focus on gases, more crop plants and animals.

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APPENDICES

APPENDIX I: Heavy metal concentrations (mg/kg) in S*orghum* grains in Asha site

Quadrant	Au	Cd	Cu	Fe	Mn	Pb	Zn
1	2.16±0.01	0.8±0.06	8.68±0.02	5830.26±0.09	152.7±0.08	28.7±0.04	64.82±0.05
2	1.48±0.02	BDL	14.28±0.02	447.168±0.01	13.6±0.12	26.8±0.04	83.75±0.06
3	1.58±0.02	BDL	6.65±0.02	265.18±0.05	13.6±0.05	28.28±0.03	66.55±0.02
4	1.75±0.02	BDL	6.43±0.02	156.8±0.09	13.6±0.09	33.35±0.06	45.71
Control	1.340.01	0±0.02	7.64±0.02	322.29±0.06	18.99±0.00	41.66±0.00	29.48
WHO		0.2	10	28.3	300	2	20

APPENDIX II: Heavy metal concentrations (mg/kg) in S*orghum* grains in Saboeregi site

Quadrant	Au	Cd	Cu	Fe	Mn	Pb	Zn
1	2.8±0.02	BDL	5.98±0.02	255.85±0.09	122.26±0.10	34.3±0.04	30.47±0.05
2	2.42±0.02	0.10±0.02	3.66±0.02	224.14±0.06	45.88±0.1	33.84±0.04	19.61±0.02
3	1.70±0.02	BDL	9.9±0.02	8605.33±0.06	24.85±0.11	36.2±0.04	19.73±0.02
4	1.13±0.01	BDL	4.8±.0.2	112.13±0.10	58.3±0.12	37.9±0.06	6.36±0.10
control	1.34±0.01	0.00±0.02	7.64±0.02	322.29±0.00	18.99±0.00	41.66±0.00	29.48±0.00
Who		0.2	10	28.3	300	2	20

APPENDIX III: Descriptive statistics of soil textural class for Asha and Saboeregi sites at different seasons

Parameter	Season	Asha		Saboeregi		Control	
		Mean	STD	Mean	STD	Mean	STD
Sand (%)	Rainy	63.67	6.17	62.46	8.09	75.0	12.88
Silt (%)	Rainy	17.00	4.83	15.33	5.82	11.5	9.00
Clay (%)	Rainy	19.84	8.21	22.23	9.20	13.5	0.00
Sand (%)	Dry	59.21	8.55	54.17	6.11	81.80	13.01
Silt (%)	Dry	23.20	7.00	13.52	4.90	5.56	1.00
Clay (%)	Dry	17.59	2.25	32.14	5.74	12.64	0.00

APPENDIX IV: Speciation result for Asha mining site rainy season

		F1	F2	F3	F4	F5	F6	Sum
Au	Mean	11.96	15.17	16.05	15.99	15.31	15.55	90.03
	%	13.28	16.85	17.83	17.76	17	17.28	100
	Minimum	10.95	14.35	15.15	14.7	9.3	11.4	
	maximum	13.05	16.15	16.85	17.15	16.6	16.5	
	Std. Dev.	0.61	0.52	0.46	0.66	1.59	1.12	
Cd	Mean	0.24	2.5	8.32	2.8	1.09	1.58	16.53
	%	1.45	15.13	50.33	16.93	6.6	9.56	100
	Minimum	0	0	0.85	0.55	0.6	0.42	
	maximum	4.05	30.9	8.32	15.65	2.4	5.9	
	Std. Dev.	0.95	7.2	15.93	22.16	0.53	1.54	
Cu	Mean	1.81	1.04	5.15	9.7	5.45	6.61	29.76
	%	6.08	3.5	17.31	32.59	18.31	22.21	100
	Minimum	0.17	0.16	0.41	4.85	5.15	6	
	maximum	2.9	3.5	17.35	21.3	6.05	8.65	
	Std. Dev.	4.82	0.76	3.46	4.34	0.27	0.22	
Fe	Mean	227.98	0.86	1.3	569.65	146.47	323.39	1269.65
	%	17.96	0.07	0.1	44.86	11.54	25.47	100
	Minimum	0	0	0	0.25	0.14	0.34	
	maximum	1181.9	8.6	10.95	7856.6	390.2	2119.5	
	Std. Dev.	288.35	2.19	3.06	1821.8	94.51	477.2	
Mn	Mean	3.83	10.67	68.2	16.96	10.85	29.1	139.61
	%	2.74	7.65	48.85	12.15	7.77	20.84	100
	Minimum	1.1	1.1	12.1	2.72	2.5	3.75	
	maximum	16.76	41.5	160.05	35.35	17.85	134.16	
	Std. Dev.	4.44	13.22	41.27	9.58	4.23	37.29	
Pb	Mean	8.54	6.23	8.55	29.79	13.55	13.31	79.97
	%	10.68	7.79	10.7	37.25	16.94	16.64	100
	Minimum	5.65	3.6	0	3.9	0.01	0.01	
	maximum	28	10.7	59	158.25	47.4	22.8	
	Std. Dev.	4.97	1.99	13.51	33.91	10.23	5.17	
Zn	Mean	13.6	16.13	37.12	13.9	13	19.31	113.06
	%	12.03	14.27	32.83	12.29	11.5	17.08	100
	Minimum	2.35	0.38	3.32	3.81	3.88	12.18	
	maximum	24.82	34.7	135.52	37.51	68.25	37.79	
	Std. Dev.	5.77	9.38	35.59	10.16	16.78	6.68	

APPENDIX V: Speciation result for Asha mining site dry season

		F1	F2	F3	F4	F5	F6	Sum
Au	Mean	3.53	4.29	3.1	3.41	3.8	5.82	23.95
	%	14.74	17.91	12.94	14.24	15.87	24.3	100
	Minimum	1.95	1.25	2.65	2.5	2.65	5.3	
	maximum	19	32.95	3.75	4.6	4.75	6.3	
	Std. Dev.	3.89	7.19	0.35	0.48	0.59	0.3	
Cd	Mean	BDL	0.12	0.08	3.2	5.35	5.99	14.74
	%	NIL	0.82	0.54	21.7	36.3	40.64	100
	Minimum	NIL	BDL	BDL	2.75	5	0.6	
	maximum	NIL	2.27	1.5	3.55	5.6	9.95	
	Std. Dev.	NIL	0.12	0.35	0.23	0.18	1.3	
Cu	Mean	1.5	1.8	3.44	4.31	7.26	0.51	18.82
	%	7.97	9.56	18.28	22.9	38.58	2.71	100
	Minimum	1.3	1.6	1.85	2.55	BDL	BDL	
	maximum	1.75	2.05	5.85	6.9	30.9	3.2	
	Std. Dev.	0.12	0.15	1.33	1.12	9.55	0.89	
Fe	Mean	79.86	1.23	2.28	399.41	226.92	59.59	769.29
	%	10.38	0.16	0.3	51.91	29.5	7.75	100
	Minimum	5.15	BDL	BDL	30.15	BDL	BDL	
	maximum	193.6	3.6	19.25	1976.9	696.8	364.15	
	Std. Dev.	53.62	1.1	5.87	462.19	203.7	119.18	
Mn	Mean	0.02	1.03	108.49	12.26	4.98	12.32	139.1
	%	0.01	0.74	78	8.81	3.58	8.86	100
	Minimum	BDL	BDL	8.3	0.2	0.5	BDL	
	maximum	0.15	5.35	218.3	45.9	23.85	205	
	Std. Dev.	0.03	1.53	59.48	12.39	5.28	48.13	
Pb	Mean	26.84	31.85	25.2	12.14	39.52	0.32	135.87
	%	19.75	23.43	18.55	9	29.04	0.23	100
	Minimum	2	3.1	0.55	7.9	3.7	0	
	maximum	23.35	71.85	35.05	15.55	550	3.6	
	Std. Dev.	30.9	12.19	12.69	2.05	128.25	0.88	
Zn	Mean	2.64	5.19	4.68	4.97	11.18	6.44	35.1
	%	7.52	14.79	13.33	14.16	31.85	18.35	100
	Minimum	0	0.3	3.19	2.64	3.93	2.47	
	maximum	46.68	8.75	7.1	12.87	59.81	21	
	Std. Dev.	11	2.3	1.18	2.38	13.81	4.84	

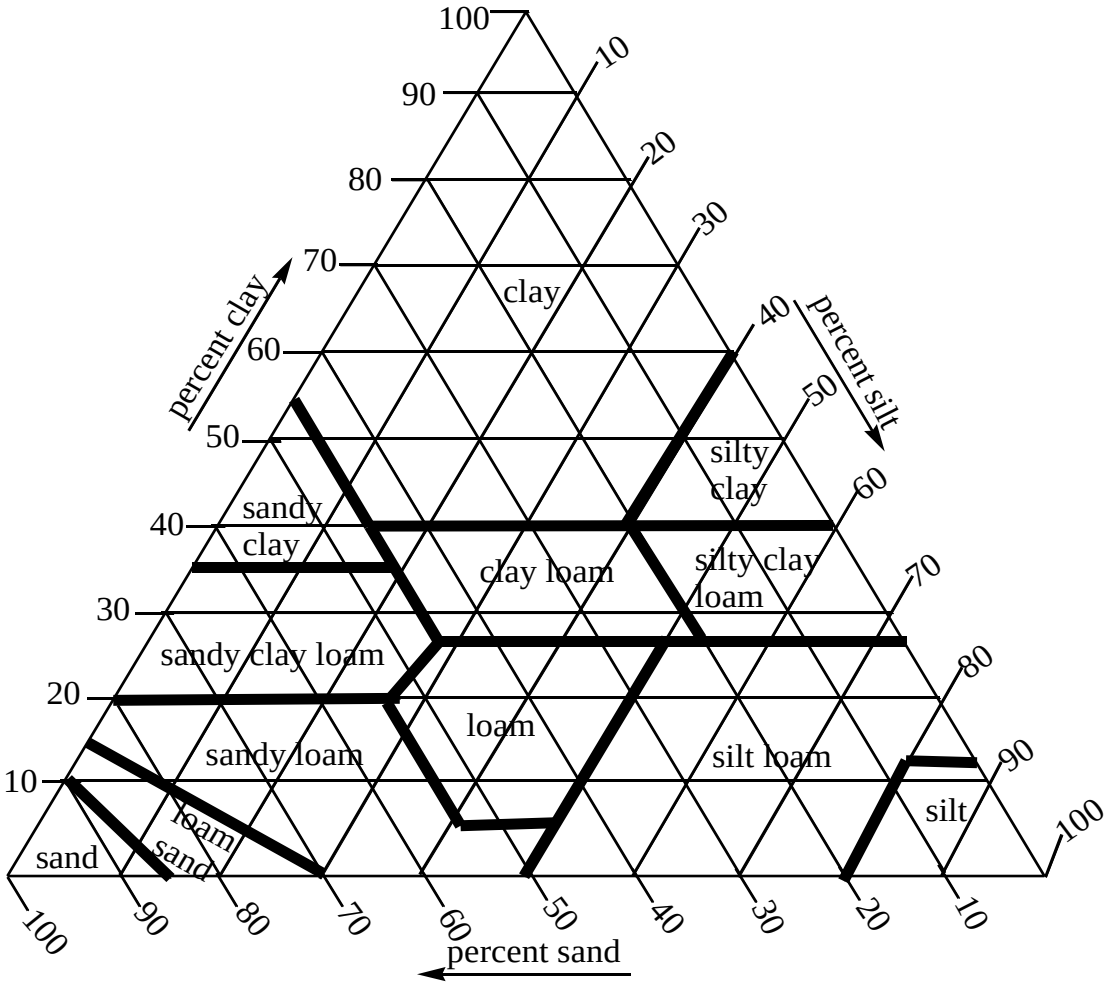
APPENDIX VI: Speciation result for Saboeregi mining site rainy season

		F1	F2	F3	F4	F5	F6	Sum
Au	Mean	13.07	15.98	16.3	15.84	15.66	14.78	91.63
	%	14.26	17.44	17.79	17.29	17.1	16.12	100
	Minimum	12.3	15.4	15.2	15.3	15.05	12.9	
	maximum	14.3	16.35	17.4	16.6	16.4	17.75	
	Std. Dev.	0.7	0.23	0.69	0.37	0.34	1.04	
Cd	Mean	0.28	0.49	5.06	1.17	1.83	2.83	11.66
	%	2.4	4.2	43.4	10.03	15.69	24.28	100
	Minimum	0	0	0.75	0.65	0.7	0.95	
	maximum	3.6	1.3	49.6	2	10.05	19.45	
	Std. Dev.	0.83	0.33	11.43	0.41	2.39	4.88	
Cu	Mean	1.25	2.21	4.68	4.97	11.18	6.44	30.73
	%	4.06	7.19	15.23	16.17	36.38	20.97	100
	Minimum	0	0.95	3.19	2.64	3.93	2.47	
	maximum	3.5	4.95	7.1	12.87	59.81	21	
	Std. Dev.	0.92	0.86	1.18	2.38	13.81	4.84	
Fe	Mean	277.36	1.49	4.32	187.65	179.21	466.94	1116.97
	%	24.83	0.13	0.39	16.8	16.04	41.81	100
	Minimum	0.55	0	0	42.54	82.4	4.1	
	maximum	618.85	7.75	34	664	475.55	4251.6	
	Std. Dev.	184.04	2.71	8.01	174.79	101.49	960.27	
Mn	Mean	2.42	2.56	125.15	28.8	14.21	21.23	194.37
	%	1.25	1.32	64.39	14.82	7.31	10.91	100
	Minimum	1.8	1.25	7.9	3.1	4.5	2.4	
	maximum	4.8	9	241.95	78.05	33.05	39.05	
	Std. Dev.	0.69	2.43	67.85	23.95	8.74	10.46	
Pb	Mean	8.76	3.49	14.31	17.61	17.33	14.56	76.06
	%	11.52	4.59	18.81	23.15	22.78	19.15	100
	Minimum	5.55	0	4.65	5	8.85	1.4	
	maximum	15.15	5.1	38.95	53.15	40.9	28.7	
	Std. Dev.	1.87	1.24	9.94	14.19	9.43	6.78	
Zn	Mean	18.5	5.88	43.21	17.54	10.05	13.94	109.12
	%	16.95	5.39	39.6	16.07	9.21	12.78	100
	Minimum	8.24	0.35	2.73	4.54	4.8	0.03	
	maximum	45.09	37.4	424.93	45.4	44.38	21.29	
	Std. Dev.	11.31	10.29	96	11.5	9.29	5.64	

APPENDIX VII: Speciation result for Saboeregi mining site dry season

		F1	F2	F3	F4	F5	F6	Sum
Au	Mean	1.85	3.18	1.89	2.85	4.87	5.66	20.3
	%	9.11	15.67	9.31	14.04	23.99	27.88	100
	Minimum	1.05	2.25	1.15	2	4.4	4.05	
	maximum	3.05	3.9	2.75	3.85	5.65	6.75	
	Std. Dev.	0.55	0.44	0.48	0.59	0.35	.0.61	
Cd	Mean	0.02	0.26	1.65	4.03	5.7	6.24	17.9
	%	0.11	1.45	9.22	22.51	31.84	34.87	100
	Minimum	0	0	0	3.5	5.5	5.6	
	maximum	0.4	0.45	3	4.8	5.95	6.55	
	Std. Dev.	0.09	0.16	0.89	0.44	0.13	0.22	
Cu	Mean	2.31	1.89	4.16	5.17	13.13	5.2	31.86
	%	7.25	5.35	13.06	16.23	42.35	15.76	100
	Minimum	1.2	1.75	2.05	1.15	1.1	0	
	maximum	11.7	2.5	10.35	19.7	71.85	20.8	
	Std. Dev.	2.35	0.19	1.88	4.11	21.78	7.32	
Fe	Mean	209.97	0	0.39	345.08	169.72	92.36	817.52
	%	25.68	0	0.05	42.21	20.76	11.3	100
	Minimum	50.5	0	0	17.5	0.28	0	
	maximum	448.2	0	2.6	1146.25	340.95	340.55	
	Std. Dev.	115.7	0	0.87	327.37	96.34	112.87	
Mn	Mean	0	0.59	378.24	2.84	4.87	5.66	392.2
	%	0	0.15	96.44	0.72	1.24	1.45	100
	Minimum	0	0	9.29	2	4.4	4.05	
	maximum	0	4.3	899.8	3.85	5.65	6.75	
	Std. Dev.	0	1.04	311.71	0.59	0.35	0.61	
Pb	Mean	27.87	29.93	8.11	9.51	3.34	2.29	81.05
	%	34.39	36.93	10	11.73	4.12	2.83	100
	Minimum	0.71	5.33	1.75	6.06	0	0	
	maximum	32.6	33.3	10.25	16.7	6	8	
	Std. Dev.	6.92	6.31	2.34	2.31	1.57	2.03	
Zn	Mean	0.36	5.28	7.05	5.75	18.65	11.735	48.825
	%	0.74	10.81	14.44	11.78	38.2	24.03	100
	Minimum	0	0.99	3.71	2.38	3.5	2.84	
	maximum	2.3	8.45	26.38	15.46	124.96	49.72	
	Std. Dev.	0.59	1.89	5.49	3.17	30.88	11.09	

APPENDIX VIII: Texture triangle



APPENDIX IX:Descriptive statistics of physicochemical parameters of river gbako at saboeregi mining site

		Parameters																	
	Description	pH	Turbidity (NTU)	TDS (mg/L)	Conductivity (µS/cm)	Dissolved Oxygen (mg/L)	Chloride (mg/L)	Total Alkalinity (mg/L)	Sulphide (mg/L)	Colour (Pt-Co)	Suspended Solid (mg/L)	Total Solid (mg/L)	Bicarbonate (mg/L)	Biochemical Oxygen Demand	Chemical Oxygen Demand	Nitrate (mg/L)	Nitrate as Nitrogen (mg/L)	Phosphate (mg/L)	Phosphorus (mg/L)
RAINY SEASON	Maximum	7.54	779.67	399.33	597.67	7.21	22.33	229.00	0.65	13033.00	2636.33	2671.67	229.00	38.67	96.00	155.20	254.49	50.10	34.30
	Minimum	6.83	1.06	35.33	53.33	4.42	7.33	9.00	0.14	201.00	10.30	105.67	9.00	6.00	16.00	9.80	2.18	4.40	1.39
	Mean	7.20	151.39	158.79	226.04	6.21	13.08	88.58	0.39	5149.46	633.25	916.59	88.46	18.59	46.67	48.31	38.33	16.18	9.12
	STD	0.22	268.21	133.57	185.54	0.97	5.57	67.74	0.18	5913.31	1039.45	1019.87	67.73	11.60	28.69	56.68	87.74	16.97	11.53
DRY SEASON	Maximum	7.66	48.73	673.33	1008.00	7.43	64.67	184.00	0.86	1701.67	270.33	812.33	186.00	42.67	107.00	61.57	13.71	20.56	6.70
	Minimum	6.93	0.98	138.33	207.00	3.75	7.33	64.33	0.16	48.00	9.33	148.33	64.00	0.00	1.00	5.43	1.21	4.07	1.30
	Mean	7.21	11.58	392.29	598.08	6.09	32.38	140.33	0.49	655.25	105.67	502.83	142.92	22.83	57.08	24.92	5.58	8.95	2.84
	STD	0.25	15.96	182.78	286.29	1.12	24.43	45.37	0.24	731.54	101.25	265.21	47.78	14.63	36.30	21.89	4.91	5.64	1.89

APPENDIX X:Descriptive statistics of physicochemical parameters of river tangali at asha minning site

		Parameters																	
	Description	**pH**	**Turbidity (NTU)**	**TDS (mg/L)**	**Conductivity (µS/cm)**	**Dissolved Oxygen (mg/L)**	**Chloride (mg/L)**	**Total Alkalinity (mg/L)**	**Sulphide (mg/L)**	**Colour (Pt-Co)**	**Suspended Solid (mg/L)**	**Total Solid (mg/L)**	**Bicarbonate (mg/L)**	**Biochemical Oxygen Demand**	**Chemical Oxygen Demand**	**Nitrate (mg/L)**	**Nitrate as Nitrogen (mg/L)**	**Phosphate (mg/L)**	**Phosphorus (mg/L)**
RAINY SEASON	Maximum	7.63	829.00	102.00	151.97	9.52	17.01	215.17	0.84	36746.67	3122.00	3136.67	215.67	37.67	93.67	1248.87	282.07	354.90	7209.00
	Minimum	6.45	35.30	15.67	22.77	5.94	5.34	52.98	0.07	81.33	13.00	42.67	53.33	0.00	0.00	12.70	2.55	1.37	0.49
	Mean	6.80	242.71	57.84	86.06	7.38	9.22	115.80	0.23	7758.04	580.67	639.79	115.71	11.71	30.13	291.85	65.99	76.91	916.97
	STD	0.38	289.52	30.86	46.42	1.02	4.69	49.79	0.27	14077.52	1115.85	1092.81	49.68	14.55	34.17	461.05	104.13	135.21	2542.67
DRY SEASON	Maximum	7.30	732.00	238.67	357.33	7.61	26.92	312.00	0.23	6659.33	238.67	373.33	312.00	10.00	25.33	700.46	100.37	47.50	14.73
	Minimum	7.02	6.07	66.67	97.97	6.67	6.55	78.00	0.03	62.00	0.33	164.00	78.00	0.00	0.00	10.76	2.60	1.52	0.50
	Mean	7.15	337.15	184.79	275.66	7.28	15.05	186.24	0.13	1995.42	91.92	272.62	186.25	2.33	6.13	152.48	27.30	22.77	6.37
	STD	0.10	286.32	55.30	83.02	0.38	7.07	67.61	0.08	2838.82	89.97	68.03	67.61	4.34	11.35	226.23	31.37	14.40	5.04