

**KWAME NKURUMAH UNIVERSITY OF SCIENCE AND
TECHNOLOGY**

**COLLEGE OF SCIENCE
DEPARTMENT OF CHEMISTRY**

**HEAVY METAL POLLUTION IN SEDIMENTS AND WATER
FROM STREAMS WITHIN THE DAMANG MINE CONCESSION**

KNUST

**A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY
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IN PARTIAL FULFILMENT FOR THE AWARD OF MASTER OF
SCIENCE DEGREE (ENVIRONMENTAL CHEMISTRY)**

By

**THOMAS KWASI KYEREMATENG
B.SC (Hons) CHEMISTRY, DIPLOMA IN EDUCATION.**

MARCH, 2013

DECLARATION

I hereby declare that the experimental work described in this thesis is my own work towards the MSc and to the best of my knowledge; it contains no material previously published by another person or material which has been submitted for another degree of the university except where due acknowledgement has been made in the text.

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Thomas Kwasi Kyeremateng

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Date

KNUST

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Mr. Osei Akoto

.....

Date

(Supervisor)

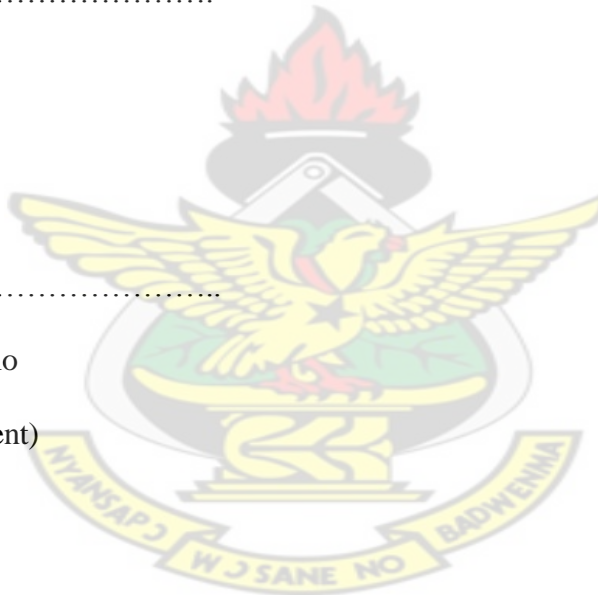
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Dr. R..B. Voegborlo

.....

Date

(Head of Department)



ABSTRACT

Impact of environment caused by elevated metals resulting from past or present mining and smelting activities can be observed in nearby receiving water bodies several decades after mine and smelter closure. There is a growing need for managing solid wastes from mining activities as well as water and sediment to assess the impact of mining on these ecosystems. In this study, concern of heavy metals, and Arsenic deposited in sediments and water from streams in the Damang Mine Concession was investigated. To evaluate the contamination levels in sediments and water, 15 water and sediment samples were collected from different sampling points and analysed for Arsenic, Calcium, Cadmium, Copper, Iron, Manganese, Lead and Zinc contents under laboratory conditions. Physicochemical properties like pH, conductivity, bulk density, organic matter, temperature, dissolved oxygen, alkalinity, total hardness and Sulphate were also measured from sediments and water samples respectively. By the investigation, the mean concentrations of heavy metals in water samples were 11.31 mg/L for As, 462.64 mg/L for Ca, 0.04 mg/L for Cd, 10.87 mg/L for Cu, 16919 mg/L for Fe, 101.89 mg/L for Mn, 115.36 mg/L for Pb, 14.62 mg/L for Zn. Similarly, the mean concentrations of heavy metals in sediments samples were 41.48 mg/Kg for As, 2063.40 mg/Kg for Ca, 0.03 mg/Kg for Cd, 27.85 mg/Kg for Cu, 56418 mg/Kg for Fe, 230.12 mg/Kg for Mn, 28.01 mg/Kg for Pb, 58.43 mg/Kg for Zn. In general, iron and calcium recorded the highest concentrations in both sediment and water samples, while copper and cadmium were the least concentrated metals in the samples. For heavy metal concentrations based on calculated Geoaccumulation Index, the sampling sites were categorized as unpolluted to moderately polluted with As, Cd, Cu, Mn, Pd and Zn, and for Ca and Fe the sites were categorized as very highly polluted.

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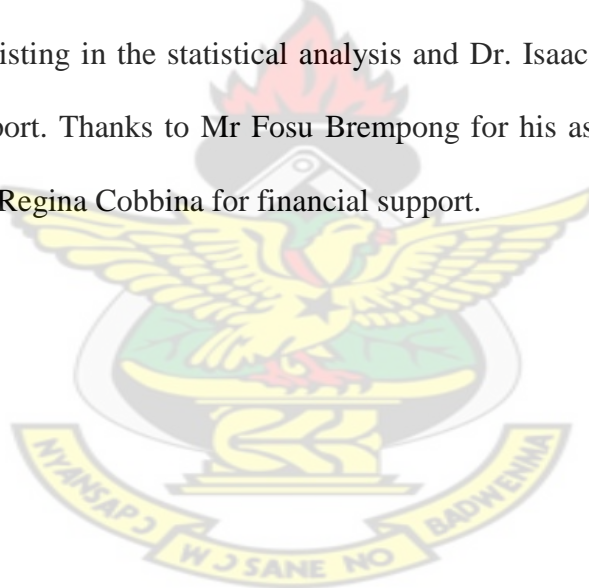


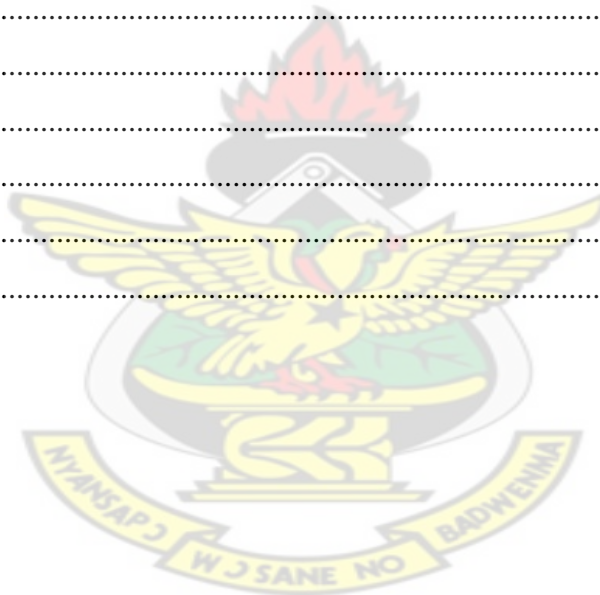
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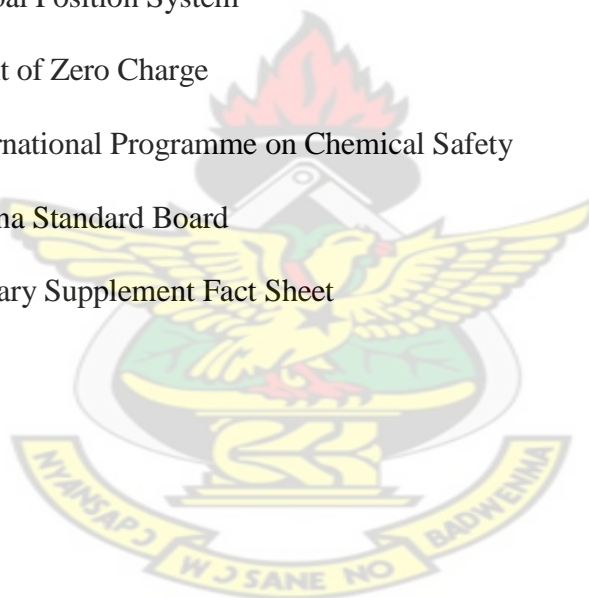
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ABBREVIATIONS

GEMS	Global Environmental Monitoring System
ARD	Acid Rock Drainage
UNEP	United Nation Environmental Program
WHO	World Health Organization
pH	Hydrogen Ion Concentration
DO	Dissolved Oxygen Concentration
USEPA	United State Environmental Protection Agency
SOM	Soil Organic Matter
HA	Humic Acids
FA	Fulvic Acids
DOM	Dissolved Organic Matter
BFD	Black Food Disease
ICARD	International Conference on Acid Rock Drainage
PVD	Peripheral Vascular Disease
NAPE	National Association of Physicians for the Environment
ER	Erythrocyte
ATSDR	Agency for Toxic Substances and Disease Registry
CIL	Carbon-in-Leach
AGL	Abosso Goldfields Limited
DO	Dissolved Oxygen
SGS	Societe Generale Souvenir
DDW	Double Distilled-Deionised Water
B.D.H	British Drug House
THD	Total Hardness

EC	Electrical Conductivity
OM	Organic Matter
USDA	United State Development Agency
EBT	Erichrome Black T
EDTA	Ethylenediammine tetra-acetic acid
FAU	Formation Attenuation Units
IOSHFC	International Occupational Safety and Health Information Centre
CSEM	Case Study in Environmental Medicine
Lsd	Least Standard Deviation
GPS	Global Position System
PZC	Point of Zero Charge
IPCS	International Programme on Chemical Safety
GSB	Ghana Standard Board
DSFS	Dietary Supplement Fact Sheet



CHAPTER ONE

INTRODUCTION

1.0 BACKGROUND

Heavy metals make significant contribution to environmental pollution from human activities such as mining, smelting, electroplating, energy and fuel production, power transmission, intensive agriculture, sludge dumping and military operations (Güven and Akıncı, 2008). Mining and smelting activities including grinding, concentration of the ores and disposal of tailings, along with mines and mill waste water, can cause heavy metal contaminations in the sediment environment (Vega *et al.*, 2004; Kemper and Sonwner, 2002; Mackenzic and Palford. 2002; Jung, 2001;). Large heavy metal content in tailings poses threat to nearby agriculture and stream water quality. Indeed, elevated levels of heavy metals have been reported in and around mines due to discharge and dispersion of mines wastes into nearby agricultural soil, food crops and stream systems (David, 2003; Hao *et al.*, 2003; Liu, 2003; Broun *et al.*, 2002). Eventually, heavy metals may pose health risk to the residents in the vicinity of mining areas.

Health related environmental monitoring is one of the four major components of the Global Environmental Monitoring Systems (GEMS), the others being climate, natural resources and oceans. The health related environmental programme includes global assessment of urban air quality, fresh water quality, soil, sediment and food contamination (Alary, 1998). Pollution of air, water, soil, sediment and food which may affect human health occurs in every country. Pollutants such as heavy metals vary in nature and so are the sources. Environmental contaminants by a single metal is rare since mineral ores often contain exploitable quantities of more than one elements and

invariably include trace amounts of several metallic minerals as associated inclusions (Robert and Johnson, 1978).

In this study, heavy metal pollution of sediments and streams which is caused by mining is being investigated within the catchment of the Damang mine area. Heavy metals refer to any metallic element that has a relative density greater than 4 g/cm^3 or 5 times greater than that of water (NCSU, 2006). Some heavy metals are also toxic or poisonous at low concentrations (Garbarino *et al.*, 1995; Nriagu, 1989). Examples of such heavy metals are Pb, Cd, Zn and Hg. They occur naturally in the environment but may also be introduced as a result of human (anthropogenic) activities (Anderson *et al.*, 1998).

Elevated levels of metal contaminants in and around mining areas, resulting from mining activities, are of major environmental concern (Marques *et al.*, 2001; Lottermoser *et al.*, 1999). Mining involves the removal, processing and disposal of large volumes of tailings and waste rock (Allan, 1997; Paktunc, 1999). Release of metals from mining activities occurs primarily through the formation of Acid Rock Drainage (ARD). The ARD is generated as a result of the oxidation of sulphide minerals (e.g. pyrite), which can occur in waste rock dumps, ore stock piles, tailing impoundments and open pits (Concas *et al.*, 2006; Sola *et al.*, 2004; ICARD, 1997; Salomons, 1995; Ferguson and Erickson, 1988). The ARD is characterized by low pH and often contain dissolved metals in toxic concentrations. The delivery of such acid effluents into streams and rivers can have significant environmental impact on sediment and water quality in downstream reservoirs (Sola *et al.*, 2004; Paktunc, 1999; Allan, 1997; Salomons, 1995). Increased concentrations of metals such as Cd, Cu, Pb and Hg in the sediments downstream of the mining sites can be harmful to aquatic life (Sola *et al.*, 2004; Müller *et al.*, 2000; Smith

and Kalch, 1999). Sediment is an essential, integral and dynamic part of aquatic environments. It functions as a final storage for heavy metals and other contaminants which can be hazardous to the aquatic environment (Salomons and Brils, 2004; Burton, 2002; Salomons, 1995; Förstner, 1990). Adverse effects of sediment-associated contaminants on sediment dwelling species have been intensively reported. Once associated with sediments, contaminants undergo various biogeochemical transformations. As long as the ecosystem remains undisturbed, most of the metals and other contaminants are strongly bound to sediments. However, the capacity of sediments to adsorb and retain contaminants depends on their composition.

Sediments also function as a secondary source of pollution, when trapped contaminated particles are released into the water phase (Westrich and Forstner, 2005; Salomons and Brils, 2004; Eggleton and Thomas, 2004). This will occur as a result of change in physico-chemical and biotic variables such as pH, redox conditions, bacterial activities and natural or artificial re-suspension. This function of sediments has come into the focus of researchers in recent year (Westrich and Forstner, 2005; Salomons and Brils, 2004; Eggleton and Thomas, 2004).

In small quantities, certain heavy metals are nutritionally essential for a healthy life. They are sometimes referred to as trace elements (e.g., Fe, Cu, Mn and Zn). These elements, or some form of them, are commonly found naturally in foodstuffs, and in multivitamin products (IOSHFC, 1999). Trace elements become toxic when they are not metabolized by the body and accumulate in the soft tissues. Heavy metals may enter the human body through food, water, air, or absorption through the skin. Ingestion is the most common route of exposure in children (Roberts, 1999). Children may approach

toxic levels from the normal hand-to-mouth activity of children who come in contact with contaminated soil (Dupler, 2001).

1.1 STATEMENT OF PROBLEM

Water is unquestionably the most precious natural resource on earth and covers over 70% of the earth's surface. However, morbidity and mortality throughout the world resulting from water related diseases are significant and increasing. Diseases related to drinking contaminated water constitute a major burden on human health (WHO, 2006). Both anthropogenic pressures and natural processes account for degradation in sediments and surface water quality (Carpenter *et al*; 1998). In Ghana, contamination of sediments and surface water bodies has particularly been experienced in gold mining communities (Kuma, 2007; Obiri, 2007; Manu, 2004; Kuma and Young, 2004; Davis *et al*, 1994). Gold mining has played a significant role in the socio-economic life of Ghana for the past hundred to two hundred years (Akabzaa *et al*, 2005). However, gold mining in recent times has become unpopular as it is regarded as a significant source of heavy metal contamination in the environment owing to activities such as mineral exploration, ore transportation, smelting and refining of tailings and waste waters around mines (Essuman *et al*, 2007; Hanson *et al*, 2007; Obiri, 2007; Koku and Balfor, 2007).

Water is a major pathway through which toxic chemicals such as heavy metals affect plants, animals and humans. Gold mining generates a lot of chemicals and other mine wastes which cause various degrees of environmental damages and which constitute a threat to human health, plants, animals and the ecosystem. Heavy metal pollution from gold mining is difficult to control and unless eliminated or strictly contained in tailing pond, mining remains a major source from which heavy metal pollutants can spread into

water bodies and the environment. The long period of mining in the study area may have resulted in increased concentration of heavy metals and other pollutants in water bodies. For example, from 1947 and until 1992, mine effluents were discharged without restriction into water bodies, soil and air, thereby resulting in the degeneration of the environment (Carboo, 1997; Tsidzi, 1993). According to Amegbey and Adimado, 2003), there have been 11 officially reported cyanide spillages between 1989 and 2003 in the Tarkwa area. Recent accounts in the media about cyanide spillages as well as the release of other hazardous chemicals into water bodies from mining operations have necessitated assessment of levels of heavy metals in water bodies in the study area. Whereas cyanide species in water bodies are photo-degradable, heavy metals on the other hand are non-degradable in the environment.

1.2 Main Objective

The main objective of this project work is to assess the quality of sediments and water from streams within the Damang Mining Concession with respect to heavy metals contamination

1.2.1 Specific Objectives of the Research

To measure the levels of As, Ca and heavy metals (Cu, Cd, Pb, Zn, Fe and Mn) in sediment and water from streams within the Damang Mining Area.

To measure physicochemical properties of sediments and water samples of streams within the Damang Mine Area.

To use this information to assess the probable effects of the Damang Mine on the quality of sediment and water from streams within the concession.

1.3 JUSTIFICATION OF THE RESEARCH

Activities of mining have serious consequences on the environment. Mining has destroyed natural habitats, polluted air, soils, sediments, water, and has produced enormous amounts of waste that can have environmental impacts for decades after mine closure (UNEP/GPA, 2004). Until recently, environmental impacts were not given great importance by mining companies and few regulations were needed to be complied with. Although, environmental concerns are now increasingly being integrated in the planning and operations of mining, particularly in Ghana, mining operations need to be contained in order to meet current expectations of environmental responsibility (UNEP/GPA, 2004).

Determination of heavy metal in sediments and water from streams within the Damang Community is important. This information can be used to assess the probable effects of the Damang Mine on the quality of sediment and water from streams within the concession. This will lead to better understanding of the extent of pollution in the aquatic environment and its effect on human and other organisms that depend on these streams. The heavy metal data will provide information on the stream sediments and water quality in the area. In the course of mining, metal pollutants are released directly into soils in the vicinity of the mine or into the water bodies. Water bodies also receive their share of pollutants through effluents discharged into them. Uptake from contaminated soils and sediments, and deposition from the atmosphere onto plants surface are the sources of elevated levels of heavy metals on terrestrial plant growth in areas where mining is done(Othman., 2001; Fernadez *et al.*, 2000).

Heavy metals find their way into humans either by direct adsorptions via the air or drinking water, or food. An indispensable link in the food chain is plant and animal from which humans receive their greater allocation of heavy metals either directly or indirectly by feeding upon them. For these reasons, this project has chosen the sediments and water from streams within Damang mine area where inhabitants farm around the concession and sometimes drink from some of the streams when they visit their farms. It is hoped that data obtained in this work will be an invariable guidance for environmentalists and toxicologists, since it will help them make informed decisions in their areas of interest.

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CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy Metals and the Environment

Most heavy metals are found in minute quantities in all living things. Sometimes these elements serve specific physiological functions within the organisms, but in the majority of cases the elements can accumulate for no apparent reason in living organisms (Briggs and Calloway, 1984). It is known that 15 metals have a universal role in plants and animals nutrition (Ca, Cu, Fe, Mg, Mo, K, Na, Zn, Co, Se, B etc.).

One consequence of the build-up of abnormal concentrations of a particular element in the environment is that humans and animals may be adversely affected not only because of its toxic effect but because it may lessen the availability of other essential elements and hence produce in the victim symptoms of a deficiency disease (Furst, 1997). An example of the elemental imbalance is found in the effect of excess of Zn in animals. Effect of Zn toxicity is Fe deficiency anemia (Smith and Larson, 1949). The resulting anemia causes depression of Fe-containing enzymes. Another example of an elemental imbalance is the classical case of Cu deficiency in cattle caused by inordinately high Mo levels in food (Thornton *et al.*, 1960).

2.1.1 Heavy Metals in Sediments

Natural background levels of heavy metals exist in the majority of sediments due to mineral weathering and natural soil erosion. It is when man's activities accelerate these processes that the background levels are increased to levels that have detrimental effects on the environment (Singh *et al.*, 2004; Vega *et al.*, 1996). Sediments with low heavy metal concentrations are not necessarily "natural" just because the levels are indeed low.

They may represent a mixture of small quantities of pollutants diluted by a large amount of natural sediment with low heavy metal content (Herut *et al.*, 1993). Sediments are also complex mixtures of a number of solid phases that may include clays, silica, organic matter, carbonates and large bacterial populations. There are three possible mechanisms by which heavy metals may be taken up by sediments and suspended matter. These are:

1. Physicochemical adsorption from the water column.
2. Biological uptake by organic matter or organisms
3. Physical accumulation of metal enriched particulate matter by sedimentation.

Physicochemical adsorption direct from the water column takes place in many different ways. Physical adsorption usually occurs when particulate matter directly adsorbs heavy metals straight from the water. Chemical and biological adsorptions are more complicated as they are controlled by factors such as pH and oxidation (Fatma *et al.*, 2009; Levy *et al.*, 1992).

A number of studies have shown that metal ions are strongly adsorbed by solid organic matter. The structure and composition of humic substances can vary considerably depending upon its origin and can influence the results of sorption experiments. Organic matter has a very important influence on the distribution of heavy metals in aquatic systems. In addition uptake may be actively completed by bacteria and algae which results in sediment enrichment. Another important mechanism by which sediments may concentrate heavy metals is through sedimentation (Hart, 1982). Within the sediments, heavy metals can either be transformed to less soluble forms or they can move to living biota. There is also the possibility that they may be eluted into the watershed and

contribute to diffuse pollution in that area. Elevated levels can be promoted by oxidation of surface sediments due to periodic drying (Hanet *et al.*, 2001).

Long (1992) suggests that the oxidation-reduction potential and the concentration of sulphides in the sediments can strongly influence the concentration of heavy metals and their availability. Clark *et al.* (1998) explained that the redox potential of the sediment can affect metal trapping directly through change in the oxidation state of the ions that can form complexes with the metal. Calcium and Manganese ions influence the sorption of other heavy metals ions. For example, Cadmium and Manganese are normally present at concentrations many orders of magnitude higher than the other trace metals. They may, therefore, occupy most of the surface binding sites and leave little opportunity for binding of other metals even though they form less stable surface complexes. Tipping (1981) showed that twice as much natural fluvial (changeable) heavy metal material was sorbed to goethite (hydrated iron oxide sediment) when calcium and magnesium were present than were absent.

Benjamin and Leckie (1980), however, suggested that oxide surfaces may consist of groups of binding sites. The strength of binding between a given metal ion and the surface may vary from one site to another. At small sorption densities all types of sites are available in excess. Hart (1982) supports this view by reporting that at higher adsorption densities the availability of strong binding sites decrease in the apparent adsorption equilibrium constant. This seems to occur only when a few percent of all surface sites are occupied. Vertical sections of sediments can give detailed records of the historical level of contamination over time provided that the pollutants are persistent and the sediment stratum has not been seriously disturbed (Che, 1999).

Aquatic plants and animals depend on sediment for their supply of food, nitrogen and other mineral elements. Heavy metals such as Zn, Cu, Mo and Fe have structural functions in plants and animals. These elements are taken up by plants roots incorporated into plants tissues and subsequently pass into the bodies of animals (Palmer *et al.*, 1992). According to Casey and Hambridge (1980) entry of some of these metals into the food chain occur in areas of high degree of contamination, for example in mining areas. Cadmium which is toxic and usually accumulates in plant root and shoot, has reportedly caused havoc to people who consumed locally grown rice on Cadmium contaminated paddy fields (Clarkson *et al.*, 1984).

The important sediment characteristics influencing heavy metal binding are the clay content and mineralogy, content of Fe, Al and Mn oxides, organic matter quality and quantity, pH and concentration of other ions in sediment solution (Ross, 1994a; Gustafsson *et al.*, 2003). The minerals that dominate in the clay fraction in most sediments (i.e. secondary aluminosilicates or clay minerals) have a net charge due to electrical imbalances in the mineral structure and from dissociating surface groups (pH-dependent or variable charge) (Sposito, 1989). The charge properties of the clay fraction in a specific soil thus depend on the relative fraction of permanent versus variable charges and on pH. Even so, looking at the clay fraction as a metal binding component, it could be considered to be a negatively charged surface, which attracts metal cations, electrostatically (Papelis and Hayes, 1996; O'Day *et al.*, 1994a;).

The influence of Fe, Al and Mn-oxides on heavy metals binding is twofold. The oxides have a pH-dependent surface charge attracting ions but they are also a source of free Fe, Al and Mn ions. The free ions, Fe^{2+} and Al^{3+} in particular, act in competition with other

metal cations for binding sites on soil minerals and organic material (Tipping, 2002). At high pH, oxide adsorption may be important for metals such as Pb^{2+} . For heavy metals forming cations, Al-oxides in particular can also be considered as a source of a binding site blocker (Al^{3+}), which increases the solubility of the heavy metals (Fendoff *et al.*, 1994).

Soil organic matter (SOM) is a complex mixture of different organic compounds with a detailed composition not fully understood, but some properties important for heavy metal adsorption, desorption and solubility are well known (Braddy and Weil, 2008). SOM consists of large molecules which are traditionally divided into humin, humic acids (HA) and fulvic acids (FA). Humic acids have a molecular weight of 2000 to 10000 $gmol^{-1}$ and fulvic acids, 500 $gmol^{-1}$ to 2000 $gmol^{-1}$. In the organic molecules these charges are localized to specific sites or chemical groups with specific binding properties. The binding properties for a single site also very much depend on the chemical 'surroundings', electropotential and steric factors (Soil Science Society of America, 2010).

Metal ion binding to HA and FA groups is generally very strong, especially for di- or trivalent ion, and ion capable of covalent binding. There are only a limited number of sites for strong or specific binding and their relative importance for the binding of a specific metal is very much dependent on the total concentration of the metal. The strong binding of metal ions to SOM does not necessarily mean that the metals are insoluble. Some of the lower molecular weight dissolved organic matter (DOM) bind metals and as carrier that makes the metals even more 'soluble'. The total effect of SOM on metal solubility depends on the relative amount of DOM, which in turn depends on other

sediment factors such as pH and total ion strength (Bergkvist *et al.*, 1989; Strickland *et al.*, 1979; Bloomfield *et al.*, 1976).

2.1.2 Heavy Metals in Water

Natural water contains some amount of heavy metals which are dependent on the geochemistry of the soil, topography, climate and land use. If the land use involves urbanization, contaminated effluents from industries are discharged into water bodies and the levels of metals ions into waters may be increased considerably. There is also the likelihood of introducing new ones which may be foreign to a water body through leaching from rocks or fallout from the air (Moss, 1980; Craft *et al.*, 2006).

Every heavy metal has a specific physiological functions in living organisms, thus the level and the type of heavy metals in a water body will have some effect on the biota and users of the water. The most important ones are Zn, Cu, Pb, Cd, Ni, Hg and Cr. Traces of some of these metals are essential for the growth of plants and animals (Crallay, 1972). For example, Fe, Zn, Mn, Co, Mo, Cr, Sn are said to be essential for life (Underwood, 1977). These essential metals are useful within varying limits depending on the organisms. Below the limits deficiency occurs and they may result in defects, but above the limits, the metals are toxic and hence fatal to organisms. For example, Zn is regarded as being nontoxic to mammals but has a lethal threshold of 570 mg/L (Underwood, 1977; Biney *et al.*, 1994). The essential metals usually form parts of the enzyme systems of organisms, or their presence in the cell induces catalytic reaction.

Heavy metals cause chronic poisoning in fish and other aquatic mammals. It is the ionic forms which produce the immediate fish kills. Baumann *et al.*, (1991) reported that the

brown bullhead (*Inclahirus nebulusus*) has been shown to accumulate Cr to concentrations more than 2600 times that found in the stream. This accumulation may be due to ingestion of macro invertebrates. Thus the diet of fish has some bearing on their heavy metal accumulation (Underwood, 1987).

One important factor which varies the concentration of metals in water is the influence of water bound to sediments. The heavy metals loading of sediments often reaches such high levels that sudden desorption would increase heavy metals levels in water (Underwood, 1987). The study of metal pollutants in sediments can be used to investigate possible pollution in stream waters (Mason, 1981). The toxicity of various compounds in a stream will affect the quality of the water, especially by factors like dissolved oxygen concentration (DO), water hardness, temperature and pH. For example, the toxicity of Cd increases with reduction in pH and it also increases with temperature (Ellis, 1993). Different species of aquatic organisms are affected by toxic compounds and much depends on their stage of development. For example, Mason (1981) reported that the larval stages of fish are more strongly affected by pollutants than the adult fish.

Odei (1987) made a comparative study of some heavy metal in lake Bosomtwe and Barekese and reported that mercury concentration in sediments in Barekese was four times higher than in Bosomtwe, while tilapia from Bosomtwe had mercury levels twice higher than tilapia of the same size from Barekese. Biney (1991) also made comparative study of trace metals concentration in fillet and whole body of tilapia species and noted high concentration in whole body analyzed including all organs, some of which have the capacity to accumulate heavy metals and other toxic substances. Heavy metals can also be toxic to most microorganisms at specific concentrations (Morgan and Lackey, 1991).

The heavy metals may block the enzyme system or interfere with some essential cellular metabolite of bacteria and protozoa.

2.1.3 Metal Toxicity

Heavy metals are stable, nondegradable and thus become potential environmental contaminants to plants and animals. They tend to accumulate in soils and sediments (Palmer *et al.*, 1992). Many organisms are able to regulate the metal concentration in their tissues (Palmer *et al.*, 1992). Fish and crustacean can excrete essential metals such as Cu, Zn and Fe that are present in excess (Adamson *et al.*, 1984). Research has shown that aquatic plants and bivalves are not able to successfully regulate metal uptake. Thus, they tend to suffer from metal accumulation in polluted environment. In estuarine systems, bivalve often serves as biomonitor organisms in areas of suspected pollution of heavy metals (Kennish, 1992). In comparison to fresh water and invertebrates, aquatic plants are equally less sensitive to metals such as Hg, Cu, Pb and Zn (Duffus, 2002).

The ability of fish and invertebrates to absorb metals is largely dependent on the physical and chemical characteristics of the metal (Kennish, 1992; USEPA, 1987). Studies have revealed that these metals enter the aquatic organisms through free ion that are absorbed through respiratory surfaces, body surfaces which are readily diffused into the blood stream. Hutchison (1983) has shown that Al is a key factor in causing deaths to fishes in lakes waters at pH levels below 5.0.

Plants and animals depend on soil and sediments for the supply of food, nitrogen and other mineral elements. Therefore, their internal biochemistry and associated composition is a reflection of the soil or the sediment in which they live. Trace elements

such as Zn, Cu, Mo, and Fe have structural functions in plants and animals. The composition of plants and animals is also influenced by a wide range of non-essential trace elements in the soil such as Sb, Cd, Hg and Pb. These elements are taken by plants roots incorporated into plants tissues and subsequently passed onto the bodies of animals, although they have no known biochemical or structural functions in the plants (Palmer *et al.*, 1992). According to Casey and Hambridge (1980), entry of some of these metals into the food chain may occur in mining areas where there is high degree of metal contamination.

The environmental risk arising from potentially toxic metals in sediments depends on the bioavailability and the mobility of the metal, factors that are only partly related to the total amount of the metal in sediments. Risk assessment of metal-contaminated sediment or sites also has to include evaluation of metal binding and solubility in the actual sediment (Ozmen *et al.*, 2004). Heavy metals bound in sediments are either incorporated as a building blocks in the solid mineral material or are attached to the surface of sediment particles. If a heavy metal is one of the cations in a solid compound it could be the solid fraction that regulates the sediment solution concentration, but more commonly it is the surface-bound fraction that interacts directly with the sediment solution (Camouso *et al.*, 1995). Heavy metals from an external source trapped in a soil are primarily bound to the surface of sediment particles and the surface-bound fraction could also most easily be released to the environment (Hyde, 2003).

Some of the symptoms of heavy metal toxicity are: Chronic pain throughout the muscles and tendons or any soft tissues of the body. Chronic malaise include general feeling of discomfort, fatigue, and illness, brain fog-state of forgetfulness and confusion. Chronic

infections include Candida, gastrointestinal complaints, such as diarrhea, constipation, bloating, gas, heartburn, and indigestion, food allergies, dizziness, migraines and/or headaches, visual disturbance mood swings, depression, and/or anxiety, nervous system malfunctions-burning extremities, tingling, paralysis, and/or an electrifying feeling throughout the body (Duruibe *et al.*, 2007).

2.2 CHARACTERISTICS OF ARSENIC AND METALS THAT HAVE BEEN SELECTED FOR THIS WORK

2.2.1 Arsenic

Arsenic is a metalloid widely distributed in the earth's crust and present at an average concentration of 2 mg/Kg. The metallic form is brittle, tarnishes and when heated it rapidly oxidizes to arsenic trioxide, which has a garlic odour. The non metallic form is less reactive but dissolves when heated with strong oxidizing acids and alkalis (Duran *et al.*, 2005). Arsenic is released into the atmosphere through natural and anthropogenic sources. Naturally, arsenic is released from volcanoes and by microorganisms (ATSDR, 1998). Anthropogenic sources of arsenic in the environment are released from smelting of non-ferrous metals, burning of fossil fuel, use of arsenical pesticides and wood preservatives (Jung *et al.*, 2002).

Most arsenic is found in conjunction with sulfur in minerals such as arsenopyrite (AsFeS), realgar, orpiment and enargite. Arsenic is not mined but it is a by-product from refining of ores of other metals, such as Cu and Pb (Boyle and Jonasson, 1973). Arsenic compounds are used in making special types of glass, as a wood preservative and, lately, in the semiconductor galliumarsenide, which has the ability to convert electric current to laser light. Arsenic pentoxide (As_2O_5) and arsenic trioxide (As_2O_3) are used as additives

in alloys with copper and lead. Arsenic and As_2O_3 are used in the manufacture of low-melting glass (OSHA, 2004; WHO, 2001). Fowler's solution, 1% potassium arsenite solution, was used as a general tonic for treating leukemia, psoriasis and asthma. Fowler's solution was not withdrawn from the U.S market until the 1950s (Cuzick *et al.*, 1992). As_2O_3 has been used for the treatment of acute promyelocytic leukaemia (Soignet *et al.*, 1998). Soluble inorganic arsenic is acutely toxic, and ingestion of large doses leads to gastrointestinal symptoms, disturbances of cardiovascular and nervous system functions, and eventually death. In survivors, bone marrow depression, haemolysis, hepatomegaly, melanosis, polyneuropathy and encephalopathy may be observed (Gregus *et al.*, 2000).

Long-term exposure to arsenic in drinking-water is casually related to increased risks of cancer in the skin, lungs, bladder and kidney, as well as other skin changes such as hyperkeratosis and pigmentation changes. Increased risks of lung and bladder cancer and arsenic-associated skin lesions have been reported to be associated with ingestion of drinking water at concentrations of 50 μg arsenic/litre (Smith *et al.*, 2000). Chronic arsenic exposure in Taiwan has been shown to cause Blackfoot disease (BFD), a severe form of peripheral vascular disease (PVD) which leads to gangrenous changes. This disease has not been documented in other parts of the world, and the findings in Taiwan may depend upon other contributing factors. However, there is good evidence from studies in several countries that arsenic exposure causes other forms of PVD. Acute inhalation exposure of workers to high levels of arsenic dust or fumes has resulted in gastrointestinal effects, such as nausea, diarrhea and abdominal pain, while acute exposure of workers to inorganic arsenic has resulted in central peripheral nervous disorders (ASTDR, 1998).

2.2.2 Calcium

Calcium is never found in free-state naturally but occurs in the form of minerals such as limestone (CaCO_3) and fluorite (CaF_2) (Pauling, 1970). Calcium is essential for plants and animals. The main sources of calcium are the dairy products such as milk and cheese, nuts, some green vegetables like spinach, and cauliflower, beans, lentils and eggshell (Schaafsma and Beelen, 1999; Schaafsma *et al.*, 2002; Rovensky *et al.*, 2003).

The metal is used in aluminium alloys for bearings, as a helper in the bismuth removal from lead, as well as in controlling graphitic carbon in melted iron. It is also used as a deoxidizer in the manufacture of many steels; as a reducing agent in the preparation of metals as chromium, thorium, zirconium and uranium, and as separating material for gaseous mixtures of nitrogen and argon. Calcium is used as an alloying agent in the production of aluminium, beryllium, copper, lead and magnesium alloys. It is also used in making cements and mortar that are used in buildings (Lide, 2005). Calcium is used in the production of many products including glass, batteries, and steel. It also combines readily with many other elements to form compounds such as calcium carbonate, calcium tungstate (CaWO_4) and calcium stearate are used for a variety of buildings purposes (Lide, 2005).

Evidence suggests that humans need a daily intake of 1,000 milligrams of calcium in order to preserve the osseous mass in normal conditions. This is both for man and pre-menopausal women. The recommended daily intake rises to 1,500 for menopausal woman. Calcium works together with magnesium to create new osseous mass. (Combs, 2006; Weaver, 2002). The National Osteoporosis Foundation says, 'Calcium plays an important role in building stronger, denser bones early in life and keeping bones stronger

and healthy later in life.’ Approximately 99 % of the body’s calcium is stored in the bones and teeth (Dietary Supplement Fact Sheet, 2011).

Long-term calcium deficiency can lead to rickets and poor blood clotting and in the case of menopausal women, it can lead to osteoporosis, impaired kidney function and decrease absorption of other minerals (FNB, 1997; Ross *et al.*, 2011). Several sources suggest a correlation between high calcium intake and prostate cancer (Giovannucci *et al.*, 1998). High calcium intake or high calcium absorption was previously thought to contribute to the development of kidney stones. However, a high calcium intake has been associated with a lower risk for kidney stones in more recent research (Bihl and Meyers, 2001; Hall *et al.*, 2001; Curhan *et al.*, 1993).

Calcium oxide is used in high intensity light arcs (lime light) for its unusual spectral characteristics and as dehydrating industrial agent. The metallurgic industry extensively uses the oxide during the reduction of ferrous alloys. The oxide is an excellent absorbent for carbon dioxide, because it produces carbonate, which is very insoluble, and is widely used to make cement. It is also used in the manufacture of glass (Lide, 2005). Calcium chloride (CaCl_2) is used as a drying agent. It is also used as a more effective and less corrosive substitute for common salt (NaCl) for melting ice on roads in the winter. Calcium hypochlorite, (Ca(OCl)_2) is used as a bleach. Calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ and calcium cyanamide, Ca(CN)_2 are used in the production of fertilizers. Dehydrated calcium sulphate is the mineral gypsum, constitutes the bigger portion of Portland concrete, and has been used to reduce the alkalinity of soils. Heating gypsum at high temperatures produces a calcium sulphate hemihydrate, which is sold with the commercial name as Parisian stucco (Founie, 2005, Gavett, 2003).

2.2.3 Cadmium

Cadmium is chemically similar to Zn and occurs naturally with Zn and Pb in sulphide ores, and is also present in various types of rocks as carbonates, hydroxides, chlorides and sulphates (Holleman *et al.*, 1985). Unlike other metals, cadmium is resistant to corrosion and as a result it is used as a protective layer when deposited on other metals. It is insoluble in water and is not flammable, however, in its powdered form it may burn and release toxic fumes (CSEM, 2011). Cadmium has variable oxidation states, its mobility and effects on the ecosystem depends to a great extent on the oxidation state.

Naturally cadmium is released into water bodies through weathering of rocks and into air through forest fires and volcanoes. Cadmium is found in small quantities in air, water and soil. It can be released into the air when household or industrial waste, coal or oil is burned (Hutton, 1986). Cadmium also can be released from mining activities, car exhaust, metal processing industries, battery and paint manufacturing, and waste hauling and disposal activities. Once cadmium is in the air, it does not break down and spreads with the wind and settles onto the soil or surface water as dust (MINEO, 2000).

Cadmium is used mainly in Ni-Cd batteries, pigments (Bauxbaum and Pfaff, 2005), coatings (Smith *et al.*, 1999), plating, and as stabilizers for plastics. Cadmium has the ability to absorb neutrons, so it is used as a barrier to control nuclear fission (Friberg, 1986; Scoullos *et al.*, 2001). Cadmium oxide is used in black and white television phosphors whilst the blue and green phosphors are used for colour television picture tubes (Ching-Hwa and Hsi, 2001). Cadmium sulphide is used as a photoconductive surface coating for photocopier drums (Miller and Mullin, 1991).

Human uptake of cadmium takes place mainly through food. An exposure to significantly higher cadmium levels occurs when people smoke cigarette (CSEM, 2011). Inhalation of cadmium can severely damage the lungs leading to death (Hayes, 2007). Cadmium is first transported to the liver through the blood after uptake where it bonds to proteins to form complexes that are transported to the kidneys. Cadmium accumulates in kidneys, where it damages filtering mechanisms. This causes the excretion of essential proteins and sugars from the body. Other health effects that can be caused by cadmium are: Diarrhoea, stomach pains and severe vomiting. Cadmium can also damage the central nervous system, immune system and cause psychological disorders (Sapna *et al.*, 2009; Lane and Morel, 2000).

Cadmium in soils can be extremely dangerous, because it can be taken up by plants easily. Soils that are acidic enhance cadmium uptake by plants. This can lead to bioaccumulation in animals that depend upon the plants. Earthworms and other essential soil organisms are extremely susceptible to cadmium poisoning. They can die at very low concentrations and this has negative consequences for the soil structure (Odei, 1987). In aquatic ecosystems cadmium can bioaccumulate in mussels, oysters, shrimps, lobsters and fishes. The susceptibility to cadmium can vary greatly between aquatic organisms.

2.2.4 Copper

Copper occurs naturally in many minerals and as an uncombined metal. The three most important sources of copper are chalcocite (Cu_2S), chalcopyrite (CuFeS_2), and malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (ATSDR, 1990). Human activities that contribute to the release of Cu into the environment include industrial, agriculture, mining, wood production and phosphate fertilizer production. Copper enters the air, mainly through the combustion of

fossil fuels and remain there for a long period of time, before it settles when it rains and end up mainly in soils (Gaetke *et al.*, 2003). Copper is often found near mines, industrial settings, landfills and waste disposals. Most copper compounds settle and are bound to either water sediment or soil particles. Usually water-soluble copper compounds occur in the environment after release through application in agriculture.

Most copper is used for electrical equipment, construction, such as roofing and plumbing, industrial machinery such as heat exchangers and alloys. Copper alloys such as bronze and brass, are used to make guns and cannons, and are known as gun metal (Emsley, 2011). Copper has a number of important functions in the human body. It is essential for the normal growth and development of human fetuses, infants, and children (Ralph and McArdle, 2001). As a component of cuproenzymes, copper is involved in key redox reactions in essential metabolic processes such as mitochondrial respiration and synthesis of melanin (WHO, 1998). Copper is incorporated into a variety of proteins and metalloenzymes which perform essential metabolic functions. Copper is involved in the formation of red blood cells, the absorption and utilization of iron, the metabolism of cholesterol and glucose, and the synthesis and release of life-sustaining proteins and enzymes (Stern and Bonnie, 2010). Although humans can handle proportionally large concentrations of copper, too much copper can cause eminent health problems including hypotension, melaena, coma, jaundice, and gastrointestinal distress (Casarett and Doull, 1996). Individuals with glucose-6-phosphate deficiency may be at increased risk of hematologic effects of copper.

Chronic effects of copper exposure can damage the liver and kidneys (ARD-EHP, 2005). Mammals have efficient mechanisms to regulate copper stored such that they are

generally protected from excess dietary copper levels (ARD-EHP, 2005). Acute exposure to copper can cause irritation of the nose, mouth and eyes. It causes headaches, stomach aches, dizziness, vomiting and diarrhoea. High uptakes of copper may cause liver and kidney damage and even death. Industrial exposure to copper fumes, dusts, or mists may result in metal fume fever with atrophic changes in nasal mucous membranes

Copper does not break down in the environment but accumulates in plants and animals when it is found in soils. On copper-rich soils only a limited number of plants survive because the excess copper inhibit the activities of microorganisms and earthworms and slows down the decomposition of organic matter (Wuana and Okieimen, 2011). When the soils of farmland are polluted with copper, animals will absorb concentrations that are damaging to their health. Mainly sheep suffer a great deal from copper poisoning, because the effects of copper are manifested at fairly low concentrations (Wuana and Okieimen, 2011).

2. 2.5 Iron

Iron occurs in concentrated deposits mainly as haematite (Fe_2O_3), spathic (FeCO_3), and magnetite (Fe_3O_4) ores. It sometimes occurs as a free metal, occasionally as fragments of iron or iron–nickel meteorites. Iron rusts in dump air and dissolves readily in dilute acids. Iron is chemically active and forms two major series of chemical compounds, the bivalent iron (II), or ferrous compounds and the trivalent iron (III), or ferric, compounds (Carol, 2002).

Iron is strongly magnetic and is the basis for steel and cast iron. Steel is used for buildings, bridges, ships, car bodies, and tools. Stainless steel is used for car parts,

kitchen sinks, and cutlery. In electrical equipment iron is used in permanent magnets and electromagnets, and forms the cores of transformers and magnetic amplifiers. Iron (II) oxides are used as pigments in paints and plastics. Various iron salts are used as coagulants in water treatments (Croot, *et al.*, 2004).

In rural areas, iron levels in air are about 50-90 $\mu\text{g}/\text{m}^3$, at urban sites, levels are 1.3 mg/m^3 . Concentration up to 12 mg/m^3 has been reported in vicinity of Fe and steel producing plants (WHO, 1992). In surface water, Fe is generally found in its precipitated ferric forms, but in deeper layers of some water reservoir or in ground water, it is found in a reduced dissolved form (Fe^{2+}) or often in chelated form. The state of Fe in water depends on the pH and the redox potential. Iron in the +2 state (Fe^{+2}), can be changed to a precipitated form FeCO_3 or $\text{Fe}(\text{OH})_3$ by either increasing the oxidation potential, the pH or both (McDonald, 2010).

Iron is an essential element in living organisms. In the human body, iron is an essential component of haemoglobin (Durupt, 2000; DGA, 2005). The daily requirement of Fe depends on age, sex, physiological status and Fe bioavailability and ranges from 200-250 mg/kg of body weight (Wander, 2008; Allen and Myers, 2006). A deficiency in the diet causes anaemia. Chronic Fe overload results primarily from a genetic disorder characterized by Fe absorption and from diseases that require transfusion (Wander, 2008). Iron may cause conjunctivitis, choroiditis, and retinitis if in contact with the tissues and remains there. Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis and may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens (Trumbo, 2001).

2.2.6 Manganese

Manganese occurs principally as pyrolusite (MnO_2), and also occurs to a lesser extent as rhodochrosite (MnCO_3) (NAS, 1989). In surface water, manganese occur both in dissolved and suspended forms. Manganese can be absorbed onto soil/sediment to an extent depending on the organic matter content and cation exchange capacity of the sediment. The concentration of Mn in lakes and streams around the world ranges from 0.001 to about 0.6 mg/kg. Higher levels in aerobic waters are usually associated with industrial pollution (Petrus and Warchol, 2005; IPCS, 2002).

Manganese is an essential element in plants and animal cells because of its catalytic role in the chemical processes within cells of living organisms (WHO, 1984). Although manganese is necessary for human survival, it is also toxic when too high concentrations are present in a human body. The uptake of manganese by humans mainly takes place through food, such as spinach, tea and herbs. Grains and rice, soya beans, eggs, nuts, olive oil, green beans and oysters contain high concentrations of manganese. Adults consume between 2 and 20 mg/day in a diet, but the average Mn nutrient requirement for normal physiological function is estimated to be 2-5 mg for adults. Infants consume 2.5-25 g/Kg of body weight/day during the first six months of life (Bouchard *et al.*, 2010). Mn intake from drinking water is lower than that from food.

Manganese is a key component of some low-cost stainless steel formulations and certain widely used aluminium alloys. Manganese dioxide is also used as a catalyst, batteries, applied in fertilizers and ceramics, and fireworks. Manganese carbonate (MnCO_3) is the starting material for making other manganese compounds. Manganese is used to

decolorize glass and make violet coloured glass. Potassium permanganate is an oxidant for cleaning, bleaching and used as a disinfectant (WHO, 1992).

Manganese-deficiency in animals impairs growth, skeletal abnormalities, reproductive defects, ataxia of the newborn and defects in lipid and carbohydrate metabolism (ATSDR, 2000). Manganese-deficient can also cause fatness, glucose intolerance, blood clotting, skin problems, lowered cholesterol levels, changes of hair colour and neurological symptoms. Manganese can also cause Parkinson disease, lungs embolism and bronchitis. When men are exposed to manganese for a longer period of time they may become impotent (Cersosimo and Koller, 2007).

Chronic Manganese poisoning resulting from prolonged inhalation of dust and fume cause damage to the central nervous system, which may result in permanent disability. Symptoms include languor, sleepiness, weakness, emotional disturbances, spastic gait, recurring leg cramps, and paralysis. A high incidence of pneumonia and other upper respiratory infections has been found in workers exposed to dust or fume of manganese compounds (Underwood, 1977).

Humans absorb manganese in the air through industrial activities and burning of fossil fuels, and also through surface water, groundwater and sewage water. Manganese enters the soils through the application of pesticides (ATSDR, 2000). Highly toxic concentrations or deficiencies of manganese in soils can cause swelling of cell walls, withering of leaves and brown spots on leaves (Owen, 2007)

2.2.7 Lead

Lead in the environment is derived from either natural or anthropogenic sources. Natural sources of lead include geological weathering of Pb bearing rocks such as galena (PbS) and volcanic emissions. Smelting and mining are some of the anthropogenic sources of lead. Anthropogenic inputs greatly exceed those of natural sources (Rosenman, *et al.*, 1998). Atmospheric lead concentrations of 50.0 $\mu\text{g}/\text{m}^3$ have been found in remote areas. Background levels of lead in soil range from 10 to 70 mg/Kg and a mean level near roadways of 138 mg/kg have been reported (NAPE, 1993). The natural concentration of lead in surface water has been estimated to be 0.2 $\mu\text{g}/\text{L}$.

The primary use of lead is in the manufacture of batteries (USEPA, 2006). Lead is also used in the production of lead sheet, solder, and pipes, and in, ammunition, cable covering, and other products. Tetraethyl lead was used in gasoline to increase the octane rating until lead additives were phased out and eventually banned from use in on-road gasoline (Schnass *et al.*, 2004; Pino *et al.*, 2004). Areas in the vicinity of lead mine and smelter are subject to high level of air emissions. Airborne lead can be deposited on soil and water, thus reaching humans through the food chain and in drinking water.

Lead is very toxic and can cause irreversible neurologic damage, renal diseases and reproductive toxicity in humans. Major adverse impacts on public health can be divided into four categories: Brain and nervous system damage, and particularly mental development impairment in Children; Reproductive system interference including effects such as premature infant and low births; Circulatory system damage such as O_2 absorption decrease and increase in blood pressure; and Kidneys malfunctioning (Pearge and Mitchell, 1993). Human studies are inconclusive regarding lead exposure and

increased cancer risk. Animal studies have reported kidney tumors in rats and mice exposed to lead via the oral route (USEPA, 2004).

The most sensitive target of Pb poisoning is the nervous system. In children, neurologic deficits have been documented at exposure levels once thought to cause no harmful effects. Exposure to Pb can have a wide range of effects on a child's development and behaviour. Even when exposed to small amounts of lead levels, children may appear inattentive, hyperactive and irritable. Children with greater lead levels may also have problems with learning and reading, delayed growth and hearing loss. At high levels, lead can cause permanent brain damage and even death (ATSDR, 2007).

Acute high-level lead poisoning has been associated with hemolytic anemia. In chronic lead poisoning, lead induces anemia by diminishing red blood cell survival (ATSDR, 1992) and has a direct nephropathy effect on the kidney. There is also evidence of an association between lead exposure and hypertension (Laveille *et al.*, 1991). Lead in humans resembles calcium in deposition and transport which accounts for the high concentration of Pb in the skeletal compartments (Patrick, 2006).

2.2.8 Zinc

Zinc occurs naturally in a number of ores, the principal ones are the carbonates and sulphides. It occurs in air, water and soil, but most is added during industrial activities, such as mining, coal and waste combustion and steel processing (Tolcin, 2011). Soils that are heavily contaminated with zinc are found in areas where zinc had been mined or refined, or where sewage sludge from industrial areas has been used as fertilizer. Levels of Zn in excess of 500 mg/kg in soil interfere with the ability of plants to absorb other

essential metals, such as Fe and Mn (Emsley, 2001). The natural Zn content of soil is estimated to be 1-300 mg/kg (IMFNB, 2001).

Zinc is used principally for galvanizing steel. It is also important in the preparation of certain alloys. It is used in batteries and for roofing and gutters in building construction (Bounoughaz *et al.*, 2003; Whatman and Brown, 2008). Zinc oxide is used as a white pigment in paints, and as an activator in the rubber industry (Emsley, 2001). It is also used in plastics, cosmetics, photocopier paper, wallpaper, printing inks (Zhang, 1996). In rubber production, zinc act as a catalyst during manufacture and as a heat disperser for the rubber and acts to protect its polymers from ultraviolet radiation industry (Emsley, 2001). Zinc metal is believed to possess anti-oxidant properties, which protect against premature aging of the skin and muscles of the body and also helps speed up the healing process after an injury (Milbury and Richer, 2008; WHO, 1992).

Although Zn is an essential requirement for good health, excess absorption of zinc suppresses copper and iron absorption (Fosmire, 1990). The free zinc ion in solution is highlytoxic to plants, invertebrate and fish (Milbury and Richer, 2008; Muysen *et al.*, 2006; Eisler, 1993). Vomiting usually occurs after consumption of more than 500 mg of zinc sulphate (Moore and Ramomoorthy, 1984). Mass poisoning has been reported following the drinking of acidic beverage kept in galvanized container: vomiting, fever, nausea, stomach cramps and diarrhea occurred 3-13 hour after ingestion. When people absorb too little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores (Ring and Gabriel, 2000; Ibs and Ring, 2003). Zinc-deficiencies can even cause birth defects (WHO, 1992). Although humans can handle proportionally large concentrations of zinc, too much of zinc can damage the

pancreas and disturb the protein metabolism, and cause arteriosclerosis (Castillo *et al.*, 2000). Some fish can accumulate zinc in their bodies, when they live in zinc-contaminated waterways. When zinc enters the bodies of these fish it is able to bio magnify up the food chain. Zinc has direct effect on the life of fish and other aquatic life, for example, zinc induces coagulation of muscles in blue gills and coughing occurs in order to free the gills of mucus (Adzaku, 1987).

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CHAPTER THREE

MATERIALS AND METHODS

3.1 Description of Study Area and Sampling Sites

Damang Gold Mine (“Damang”) is operated by Abosso Goldfields Limited (AGL) and is located in south-western Ghana at latitude 5°11’N and longitude 1°57’W. Damang is located 40 km north of Tarkwa (Barnes *et al.*, 2004).

The environs of Damang are characterized by gentle rolling hills incised by an extensive drainage network with low lying swamp areas. A tropical climate with temperature ranging between 21°C and 32°C and is characterized by two distinct rainy seasons from March-July and September-November. The average annual rainfall is about 2,030 mm. Extensive subsistence farming occurs throughout the area with cocoa, plantain, pineapple, cassava, maize, yam, oil palm and coffee being the principal crops. The natural forest vegetation in the area has been degraded as a result of farming, lumbering and mining to secondary forest, scrub and cleared land (Barnes *et al.*, 2004).

Small scale gold mining activities in the area dates back to the late 19th Century, but the most significant operation on the Damang lease area comprised the abandoned Abosso Mine which is an exploited Blanket conglomerates to a depth of approximately 850 m. It operated from 1882 until 1956 with a recorded production of about 2.7 million oz of gold from ore with an average grade of 9.8 g/t. Other underground mines to the north, particularly Adjah Bippo and Cinnamon Bippo which produced significant quantities of gold between 1882 and 1918, were incorporated into the Abosso Mine holdings after 1920 (Barnes *et al.*, 2004).

The Damang orebodies are located within the Tarkwaian System which forms a significant portion of the stratigraphy of the Ashanti Belt in southwest Ghana. The Ashanti Belt is a north-easterly striking, broadly synclinal structure made up of Lower Proterozoic sediments and volcanics underlain by the metavolcanics and metasediments of the Birimian System. Damang Mine contains mineralization hosted within Tarkwaian palaeoplacer deposits, present as individual tabular quartz pebble conglomerate units (reefs) interlaminated within quartzites and argillaceous sandstone units. Palaeoplacer mineralization has been traced from the Damang main pit (in the North) approximately 35 km to the Abooso Deeps area, in the southern part of the Damang Mineral Lease Area. Abooso Deeps is situated on the western limb of the Damang Antiform and was a major producer of gold until the 1950s. The Damang Extension Project (“DEP”) consists of four separate project areas, namely the Rex and Amoanda areas that host hydrothermal mineralization and the Tomento North and Tomento South areas that host Tarkwaian palaeoplacer mineralization present as quartz pebble conglomerates. Rex is located to the east of the Chida South pit, south of Amoanda which is located south of the Tomento North and Tomento East project areas (Figure 3.1). Despite the apparent differences within the geological construction of the two mineralization styles (namely palaeoplacer and hydrothermal mineralization) the geological modelling and following geostatistical modelling follow very similar routes (Barnes *et al.*, 2004).

Damang is hosted within a north-north-westerly plunging antiform developed within Tarkwaian rocks and is located approximately 50 km northeast of Tarkwa. The antiformal closure plunges shallowly to the north, whereas the eastern and western limbs of the antiform dip steeply (40-50 degrees) to the east and west respectively. The main Damang Pit is located close to the closure of the antiform, whereas the Kwesie-Lima

deposit is located within the eastern limb and the Damang Extension Project areas are all located within the western limb of the antiformal structure.

The mine has multiple open pits, surface stockpiles source and a carbon-in-leach (CIL) plant as shown in Fig. 3.1 below. Damang is adequately resourced with the appropriate levels of technically qualified and experienced personnel in production and related support functions. Damang mine employs 500 permanent and 1276 contract staff. The population of Damang Township is approximately 3,000 (Barnes *et al.*, 2004).

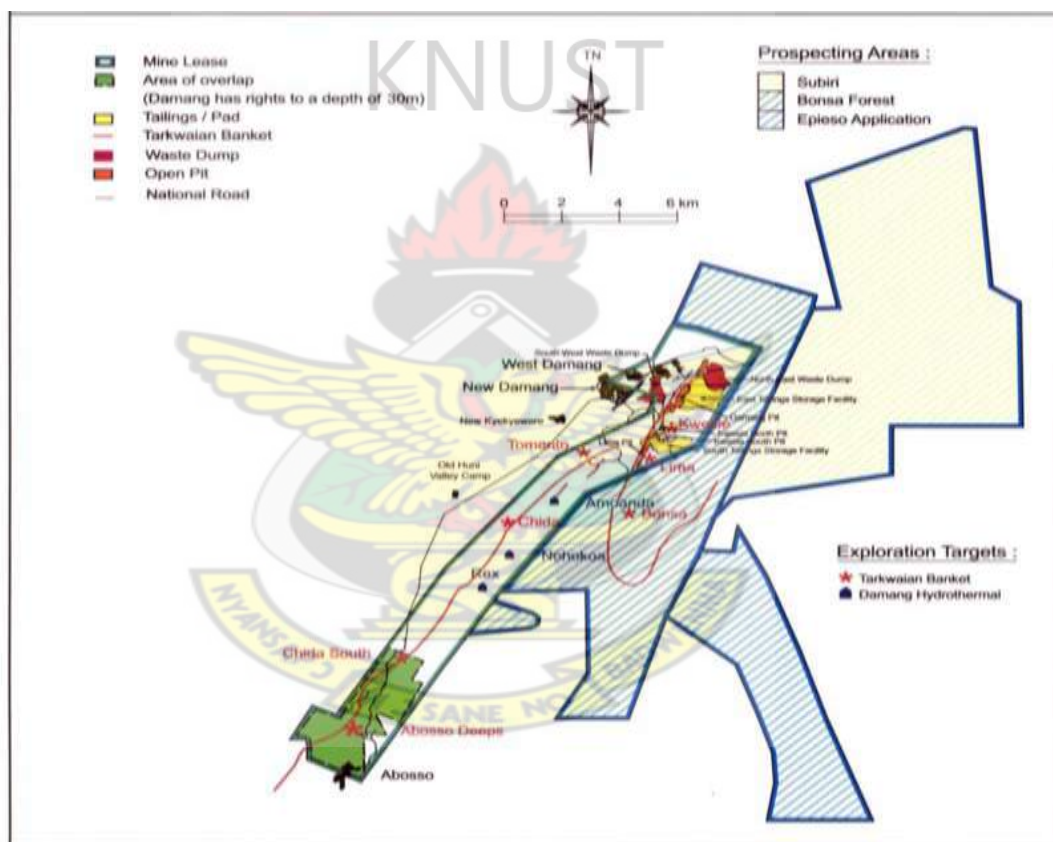


Fig. 3.1 Damang Gold Mine: Plan showing Mine Infrastructure and Open Pits

3.2 Sampling and Samples Preparation

A map of the study area shown in Fig3.2 was visited and sampling points were selected with the assistance of a staff from Abosso Goldfields Limited (AGL) Environmental

Department. Sediments and water samples were collected from 15 different locations within Damang mine concession (Table: 3.1).

To obtain accurate results, sampling bottles were soaked in 2.0 M nitric acid solution overnight. The bottles were thoroughly flushed with distilled water and finally with de-ionized water and then dried in a drying cabinet. Triplicate water samples were taken at each sample location to ensure consistency and reliability of data. Water samples for physicochemical and heavy metal analyses were collected in 1L plastic bottles, acidified with concentrated nitric acid and were stored in refrigerator. Separate portions of the water samples were collected and the Dissolved Oxygen (DO), Temperature, conductivity and pH were determined on site.

Triplicate sediment samples were also collected from each sampling site using a push-tube core device and kept in polythene bags. The sediment samples were taken to the S.G.S. laboratory at the mine site, emptied from their containers and spread on polythene bags, and air dried. The dried samples were passed through 2 mm mesh to remove stones and plant fragments. They were homogenized and part of each sample was removed and kept in small paper sample bags for physicochemical analysis. The remainder were dried at 105 °C in an oven, then pulverized to fine powder and passed through a 75 µm mesh sieve. The particles less than 200 mesh (< 75 µm) in the sediments samples, which were representative of true sediments, were used for analysis.

SAMPLE IDENTITY	FULL MEANING OF SAMPLE ID	GPS
ABU-1	Abumang River-Upstream	N0628630 E0611520
ABO-STR	Abosso Stream	N0617526 E0594349
ABU-PT	Abumang Pond at the Process Water Plant	N0627705 E0610604
AME-05	Amoanda East Stream No.5	N0624090 E0605150
AYAS-1	Ayansu River-Upstream	N0630061 E0611009
B-SUMP	Bismark Sump	N0627901 E0609573
KWA-1	Kwakronkron River-Upstream	N0627159 E0610797
MDD-2	Mine Diversion Drain Downstream	N0629067 E0608918
MWD	Mine Water Dam	N0628196 E0610336
NKR-1	Nkranka River-Upstream	N0626300 E0609398
TAM-1	Tamang River-Upstream	N0626379 E0609007
TAM-2	Tamang River Floodway Crossing	N0628566 E0608019
TOM-3	Tomento Bamboo Area Upstream	N0624597 E0606052
REX-D1	Rex-Upstream No.1	N0628577 E0607272
REX-U2	Rex-Upstream No.2	N0620975 E0598993

Table 3.1: Identity Sampling Point location with their GPS Readings.

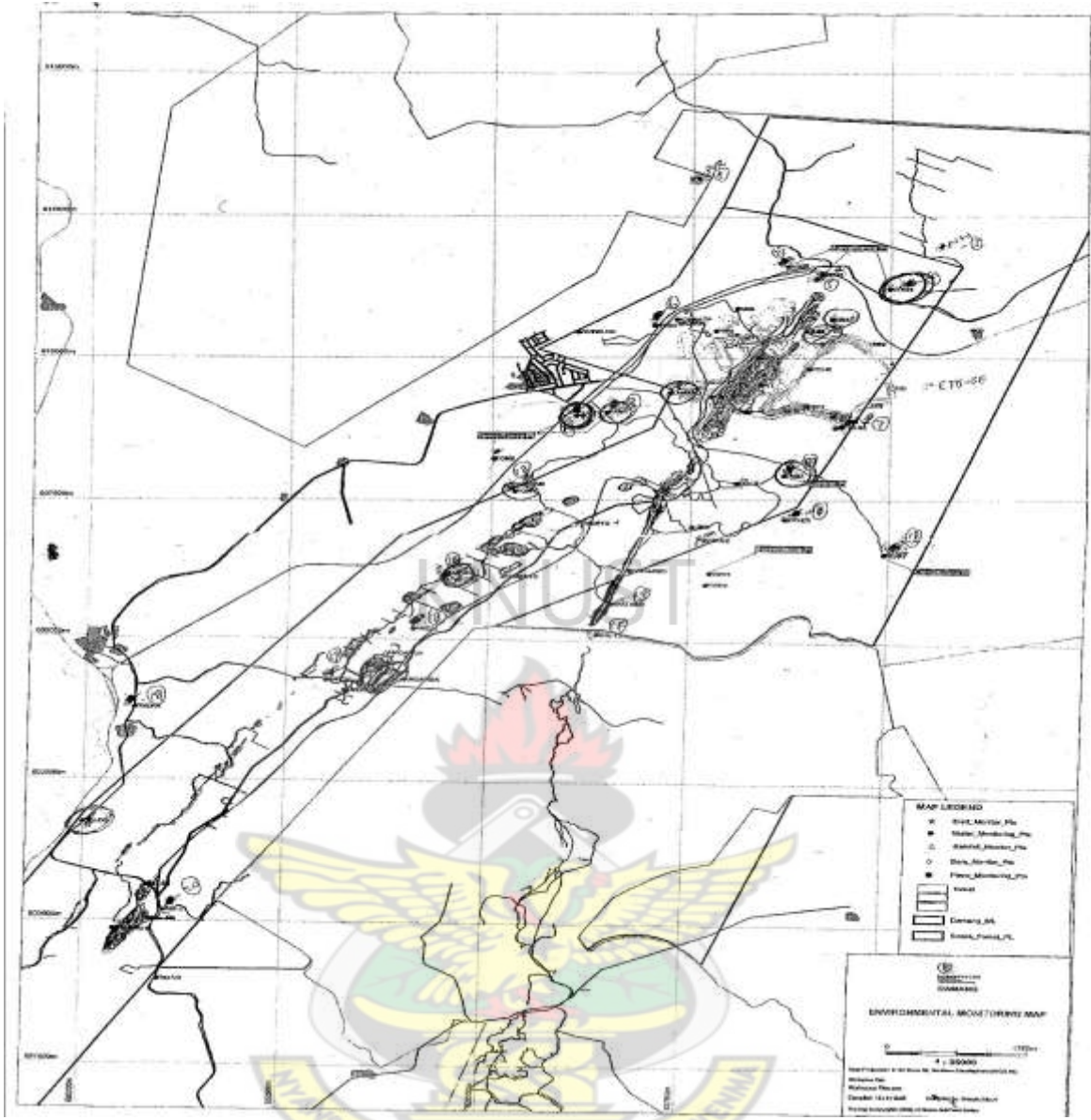


Figure 3.2 Map of Environmental Monitoring Area

3.3 Chemicals and Equipment

Analytical reagent grade chemicals from B.D.H. and Philip Harris Chemicals, and Double Distilled Water (DDW) were used to prepare all solutions, unless stated otherwise. Stock solutions containing 1000 mg/L of analyte were prepared from trioxonitrate (V) salts of As, Ca, Cd, Cu, Fe, Mn, Pd and Zn. Working standard solutions were prepared in 2.0 M HNO₃ by appropriate dilutions of the stock solutions. Blank determinations were run by using the same reagents, in equal quantities as described in the analytical procedure throughout the experiment.

3.3.1 Chemicals

1. Concentrated AnalAR Trioxonitrate (V) acid (70% W/V) (Philip Harris Chemicals)
2. Concentrated AnalAR Tetraoxosulphate(VI) acid (98% W/V) (Philip Harris Chemicals)
3. Concentrated Hydrochloric acid (37%) (B.D.H)
4. Hydrogen peroxide (B.D.H.)
6. Ammonium Acetate (B.D.H.)
7. Ethanoic acid (97 %) (B.D.H.)

3.3.2 Equipment /Apparatus

1. Pulverizing Machine
2. Oven
3. pH meter (corning Incorporated, corning NY, 14831, USA)
4. Conductivity meter (Hanna Instruments, HI 9032)
5. Wagtech Photometer
6. Turbidity meter (Hanna Instrument LP2000)
7. Flame Atomic Absorption Spectrometer (Varian SpectrAA-55/110)

3.4 Parameters Measured

3.4.1 Determination of Heavy Metals in Water Samples

20.0 ml of concentrated HNO₃ was added to 250 ml of the water samples in a conical flask. The mixture was digested at 60 °C until the volume was reduced to about 5ml. The mixture was then filtered into 50 ml volumetric flask, diluted to the mark with distilled water and stored in the polythene bottles at 4 °C for the elemental analysis. The elemental analysis was done using a Flame Atomic Absorption Spectrometer, Varian Spectr-55/110.

3.4.2 Determination of Physicochemical Properties of Water Samples.

3.4.2.1 pH

The pH was measured on site using the pH meter (corning incorporated, corning NY, 14831, USA). The pH meter was calibrated with buffer solutions of pH of 4.01, 7.00 and 11.00. The standardized pH meter was then rinsed with distilled water and wiped with tissue paper, after which it was immersed in the water sample and allowed to stabilize. The pH of the sample appeared digitally.

3.4.2.2 Dissolved Oxygen

Dissolved Oxygen was measured using Hanna instruments dissolved oxygen meter. The electrode was immersed in the water sample and the reading was taken after the reading became stable.

3.4.2.3 Electrical Conductivity

This parameter was also measured at the sampling sites by using Microprocessor Conductivity Meter LF323/set. The instrument was first calibrated using potassium

chloride solution as provided in the set. The measuring electrodes were first immersed into distilled water, wiped with tissue paper and were then immersed into the samples. The instrument was allowed to stabilize and the conductivity values were read directly.

3.4.2.4 Temperature

The temperatures of the water samples were determined on site as soon as the samples were collected. This was done with a digital thermometer. The thermometer was rinsed thoroughly with distilled water. A clean dry beaker was taken and it was rinsed with distilled water and then with some of the sample of which temperature was to be determined. Some of the sample was poured into the beaker. The thermometer was immersed completely in the sample in the beaker. Some time was allowed for equilibrium to be established. This was achieved when the signals become steady and Readings was then taken.

3.4.2.5 Total Hardness in Water by Titration

50.0 ml of the sample was pipette into a 250 ml conical flask. 1.0 ml ammonia buffer solution was added to the contents of the conical flask. Two (2) drops of Erichrome Black T (EBT) Indicator was then added. The content of the conical flask was titrated against a standard EDTA solution (0.01 M) until the end point colour changed from wine-red to blue. The titre volume of the EDTA was recorded. The Total Hardness was calculated as:

$$\text{Total Hardness as CaCO}_3 \text{ content (mg/l)} = \frac{v \times E (\text{CaCO}_3) \times 1000}{\text{Sample volume}}$$

Where $E (\text{CaCO}_3) = 20 \times 1 \text{ mg } (\text{CaCO}_3)$

3.4.2.6 Total Dissolved Solids by Gravimetric Method

100.0 ml of the filtrate sample was measured into a weighed evaporating dish and evaporated to dryness on a water bath. The residue left after evaporation was dried in an oven for 1 hour at 105°C, cooled in a dessicator and then weighed to constant weight. Total dissolved solid is then calculated from the equation below.

$$\text{Total Dissolved Solids (TDS)} = \frac{\text{Weight of dried sample + dish} - \text{Weight of Dish}}{\text{Volume of Sample (ml)} \times 10}$$

3.4.2.7 Turbidity

Attenuation Radiation Method (Direct Reading) was used. When a wavelength of 860 nm was dialled, the display quickly showed: Zero sample. 25.0 ml of de-ionized water (the blank) was poured into a sample cell, placed into the cell holder and the light shield was closed. The instrument was zeroed by pressing the zero button to display zero (0). FAU TURBIDITY. 25.0 ml of sample was poured into another sample cell and was immediately placed into the cell holder. The read button was pressed and the value was displayed in Formazin Attenuation Units (FAU). The Turbidity value was determined using the DREL/2010 Spectrophotometer, HACH Company, 1999.

3.4.3 Principles of operations of the Photometer.

The Wagtech Photometer was used to analyze the water samples for Alkalinity, Sulphate, Nitrate, Nitrite and Fluoride. In all the parameters analyzed the required wavelength which gave a maximum percentage Transmittance was selected on the photometer for each parameter.

3.4.3.1 Alkalinity

The sample was stirred and immediately poured into a sample cell. One Alkaphot tablet was crushed and mixed with the sample until it dissolved. Another sample cell was filled

with distilled water to serve as a blank. Wavelength 570 nm was selected on the photometer. The blank was placed into the cell holder and the instrument was zeroed by pressing the zero button. The prepared sample was placed into the cell holder and the Photometer reading was taken. The alkalinity calibration chart was used to determine the actual alkalinity in mg/L.

3.4.3.2 Sulphate

The sample was stirred and an aliquot poured into a sample cell to the 10.0 ml mark. One Sulphate tablet containing 20.0 mg BaCl_2 was crushed and mixed with the sample in the test tube to dissolve. The solution turned milky which indicated the presence of sulphate in the sample. The solution was allowed to stand for 5 minutes and then stirred again to ensure uniform mixture. The wavelength of 520 nm was selected on the Photometer. The prepared sample was placed in the cell holder and the read bottom was pressed to display the absorbance. The Sulphate calibration chart was consulted to determine the Sulphate concentration in mg/L.

3.4.3.3 Nitrate

The sample was stirred and poured into a Nitrate tube to the 20.0 ml mark. One level spoonful of Nitratest powder and one Nitratest tablet was added to sample in the tube. The screw cap was replaced and the tube was shaken well for one minute. The tube was then allowed to stand for one minute and then gently inverted three times to aid flocculation. The screw was removed and the top of the tube was wiped off with tissue paper. The clear solution was decanted into a sample cell, filled to the 10 ml mark. One Niticol tablet was crushed and added to the mixture in the tube to dissolve. The solution was allowed to stand for ten minutes for the colour to develop. Wavelength 570 nm was

selected on the photometer. The reading was taken on the photometer after pressing the read bottom. The Nitatest calibration chart was used to determine the Nitrate concentration in mg/l.

3.4.3.4 Nitrite

Using the measuring syringe, 1 ml of the sample was taken and transferred into a test tube and made up to 10 ml mark with distilled water. One Nitriphot tablet was crushed and added to the sample in the tube to dissolve. The screw cap was replaced immediately. The mixture was allowed to stand for five minute to enable the colour to develop fully. The prepared sample was placed in the cell holder. The photometer reading was displayed as mg/l NaNO_2 .

3.4.3.5 Fluoride

The sample tube was filled with the water sample to the 10 ml mark. One Fluoride No.1 tablet was crushed and added to the sample to dissolve. One Fluoride No. 2 tablet was also crushed and added to the resulting solution to dissolve. The mixture was allowed to stand for 5 minutes for full colour to develop. Wavelength 570 nm was selected on the photometer. The prepared sample was placed into the cell holder. The photometer reading was taken. Fluoride concentration was read.

3.5 Determination of Heavy Metals in Sediment Samples

3.000 g of each of the sediment samples was weighed into separate 250 ml glass beaker (tall type) and 28 ml of aqua regia (HCl (37%) and HNO_3 (70%)) in the ratio 3:1 were added to each beaker. The samples were digested on hot plate at $110\text{ }^\circ\text{C}$ for 3 hr. After evaporating to near dryness, the samples were diluted with 20 ml of 2% (V/V HNO_3).

The mixtures were then filtered through whatman No. 42 filter paper into separate 100 ml volumetric flask. Each sample was diluted to the mark with deionized water and then stored in polyethene bottles at 4°C for elemental analysis using Flame Atomic Absorption Spectrometer, Varian Spectr-55/110.

3.6 Determination of Physicochemical Properties of Sediment Samples

3.6.1 pH

The pH meter was first standardized by immersing the electrodes into a buffer solution of pH of 4.01 and 11.0. 10.0g of the sediment sample was placed into a 50 ml beaker and 20 ml of water was added. The sediment was allowed to absorb the water without stirring and then stirred thoroughly for 10 minutes with a glass rod. The suspension was stirred for 30 minutes, allowed to settle and the pH was recorded using the calibrated pH meter.

3.6.2 Electrical Conductivity

Electrical Conductivity is a measure of the ionic transport in a solution between the anode and the cathode. The Electrical Conductivity of sediment is considered to be a measurement of the dissolved salt in a solution. 40.0 g of sediment sample was placed in a 250 ml Erlenmeyer flask, and 80 ml of distilled water was added, stoppered and shaken on a reciprocating shaker for 1 hour. The mixture was filtered through a Whatman No. 1 filter paper. The conductivity electrode was washed with distilled water, and rinsed with standard potassium chloride solution. The Electrical Conductivity electrode was dipped into the sediment extract, and the digital display was the Electrical Conductivity of the sediment sample recorded.

3.6.3 Organic Matter Content

Loss in weight on ignition which is a direct measure of the organic matter was the method used. 10.0 g of the sediment sample was weighed into an ashing vessel. The vessel with sediment was dried in an oven at 105 °C for 4 hours, removed and placed in a dessicator. After cooling, the vessel and content was reweighed to the nearest 0.01 g (W_1), and then placed into a muffle furnace at a temperature of 400 °C, for 4 hours. The ashing vessel was removed from the muffle furnace cooled in a dry atmosphere and weighed again to the nearest 0.01 g (W_2).

$$\text{The percentage of (OM) is} = \frac{W_1 - W_2}{W_1} \times 100$$

Where:

W_1 is the weight of sediment at 105 °C

W_2 is the weight of sediment at 400 °C

3.6.4 Bulk Density

Soil bulk density is a measure of how dense and tightly packed a sample of soil is. It is determined by measuring the mass of dry sediment per unit volume (g/ml). A metal can was carefully filled to the brim with a sediment sample and then weighed without the lid. The sample was then dried in an oven at 105 °C after which it was removed from the oven and the weight of the sample and its container determined and recorded. The sample was sieved through a 2 mm mesh by carefully pressing the dry sample through the mesh onto a paper beneath the mesh. The rocky sediment remained on top of the mesh. To measure the volume the can was filled to the brim with water and then poured into a graduated cylinder. The weight of the rocks was measured and recorded. Exactly 30 ml of water was poured into a 100 ml graduated cylinder the rocks were carefully

placed in the cylinder. The level of the water after all the rocks had been added was recorded. The net increase in volume was recorded as the volume of the rocks.

Calculation:

$$\text{bulk density (g/ml)} = \frac{\text{weight of sediment (g)} - \text{weight of rocks (g)}}{\text{volume of sediment (ml)} - \text{volume of rocks (ml)}}$$

3.6.5 Sediment Texture

50.0 g of sediment sample was put into a 500 ml heat resistance (105°C) screw lid bottle calibrated at 250 ml. 125.0 ml of water was added and the mixture was swirled to wet the sediment thoroughly. 2.0 g of sodium hexametaphosphate was added and made up to 250 ml mark with water. The mixture was shaken from end to end for 18 hours and was transferred to a 1000 ml sedimentation cylinder, and water washings from the bottle were added to make up to the 1000 ml mark. The cylinder was placed in a water bath to maintain a constant temperature. A blank was prepared by dissolving 2.0g of sodium hexametaphosphate in water in a cylinder, and made up to the mark with water. The blank was placed in the same tank with the sample. The cylinders were allowed to equilibrate for 30 minutes. The sample in the cylinder was mixed vigorously with a plunger, and a stop clock was started at the moment the plunger was removed. The Bouyoucos hydrometer readings for the sample and the blank were recorded at 40 sec and 5 hours and the temperature of tank was also recorded.

Calculations

$$40 \text{ sec (correction)} = 2 (40 \text{ sec reading} - 40 \text{ sec blank} + T)$$

$$5 \text{ hr (correction)} = 2 (5 \text{ hr reading} - 5 \text{ hr blank} + T)$$

Where;

T = temperature corrections: For every °C above 20 °C (d), T= 0.3 × d; for every °C below 20°C (d), T =-0.3 × d.

% sand = 100- 40 sec (correction).

% silt = 40 sec (correction) – 5 hr (correction).

% clay = 5 hr (correction).

For; sand = 2 mm – 0.6 mm; silt = 0.6 mm – 0.002 mm; clay =< 0.002 mm (ref).

The two dimensional chart for assigning USDA soil texture classification (from Booker Tropical Soil Manual) was used. The "soil-texture triangle" was used to plot the type of soil (i.e. sandy loam, silty clay, etc.) via percentages of textures (Esguerra and Landsberger, 1994).

3.7 Analysis of Data

Data obtained were subjected to Analysis of Variance (ANOVA) using Statistex 9 Statistical Package. Descriptive Statistics were also performed on the analysed means. Differences between means were determined using Least Standard Deviation (lsd) at 5 % (p= 0.05).

The geoaccumulation index (I_{geo}) introduced by Muller (1969) was also used to assess metal pollution in soils. It is express as:

$$I_{geo} = \text{Log}_2 \left(\frac{C_n}{1.5B_n} \right)$$

Where C_n is the measured concentration of the examined metal in the sediment and B_n is the geochemical background concentration of the same metal. Factor 1.5 is the background matrix correction factor due to lithogenic effect. The index of

geoaccumulation includes seven grades (0-6) ranging from unpolluted to very highly polluted as shown in Table 3.2 below

(Igeo) Value	Igeo Class	Pollution Intensity
0 - 0	< 0	Unpolluted
0 - 1	< 1	Unpolluted to moderately polluted
1 - 2	< 2	Moderately polluted
2 - 3	< 3	Moderately to highly polluted
3 - 4	< 4	Highly polluted
4 - 5	< 5	Highly polluted very highly polluted
5 - 6	>5	Very highly polluted

Table 3.2 Goeaccumulation Index in relation to pollution extent.



CHAPTER FOUR

RESULTS AND DISCUSSION

4.1.0 Results of analysis of Physicochemical Parameters of Water from the various Sampling Sites

Statistical analysis of physicochemical parameters of water from the various water samples are presented in Appendix IV and the raw data with the recommended values from WHO are presented in Appendix V

4.1.1 Temperature

Temperature ranged from a minimum of 22.57 ± 1.15 °C in the sample from TOM-3 to a maximum of 30.67 ± 1.15 °C in the sample from MWD as shown in Figure 4.1.1. The temperature range is influenced by atmospheric ambient temperature of 27 °C at the sampling sites. This does not give any significant indication to pollution.

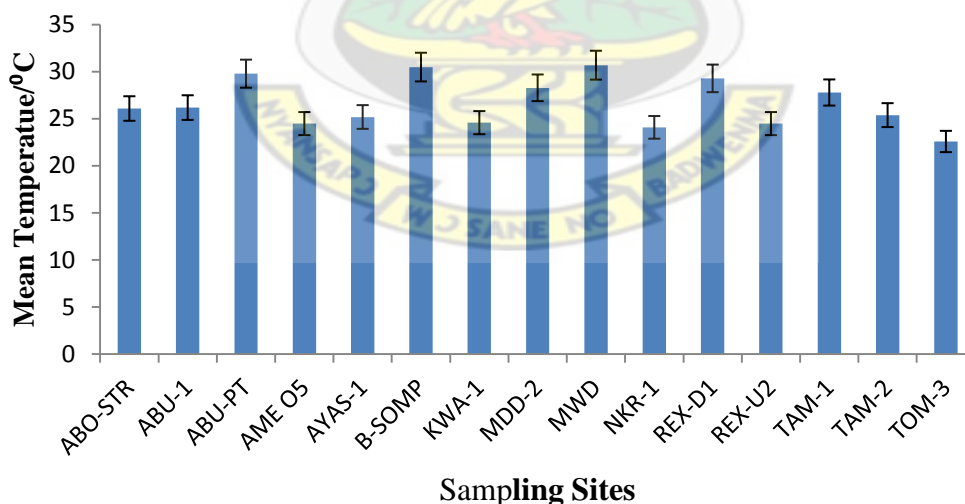


Figure 4.1.1 Mean Temperature of water samples from the streams

4.1.2 pH

Figure 4.1.2 below shows that, the mean pH values range for the entire water samples from the streams were higher than WHO level (6.5-8.5) mg/L for drinking water. This indicates that the water was slightly alkaline with sample from TAM-2 stream recording a minimum pH value of 7.27 ± 1.15 . The highest value of 9.17 ± 1.15 recorded at ABU-PT stream may due to the overflow of water from the tailings water into the stream. The tailings water has high pH as a result of addition of CaCO_3 in gold extraction processes at the process plant and it is recirculated into the plant.

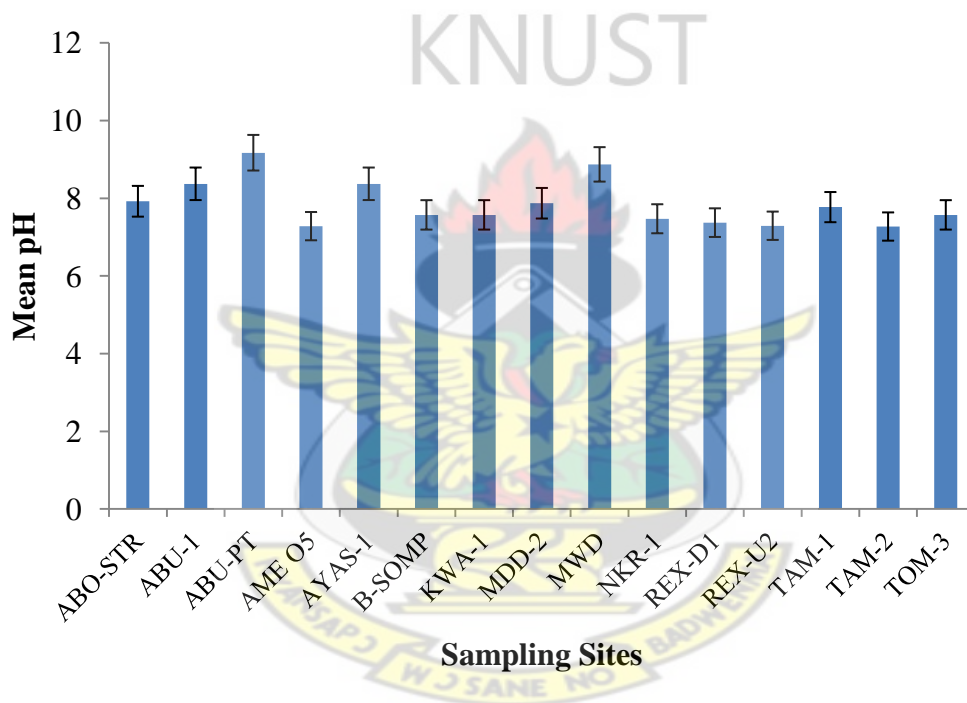


Figure 4.1.2 Mean pH of water samples from the streams

4.1.3 Dissolved Oxygen (DO)

As shown in Figure 4.1.3 below, the minimum recorded value of DO was 1.77 ± 1.15 mg/L at AME-05 and KWA-1 streams while B-SUMP recorded a maximum of 7.27 ± 1.15 mg/L. Dissolved Oxygen affects chemical and biological processes occurring in water bodies. Its optimum level is therefore important for the maintenance of life within the streams. According to Todd (1970), DO concentration of 5 mg/L and above

are recommended for maintaining life in water. DO concentrations in unpolluted water are normally about 8-10 mg/L at 25 °C. These values indicate that the water from all the streams apart from ABU-PT, B-SUMP, MWD, TAM-1 and TAM-2 are not suitable for supporting all forms of aquatic life since the concentrations of DO are lower than 5 mg/L. Water from ABU-PT, B-SUMP, MWD, TAM-1 and TAM-2 can support aquatic life but are unfit for drinking because the concentrations of DO from these streams are above 5 mg/L but lower than 8 mg/L.

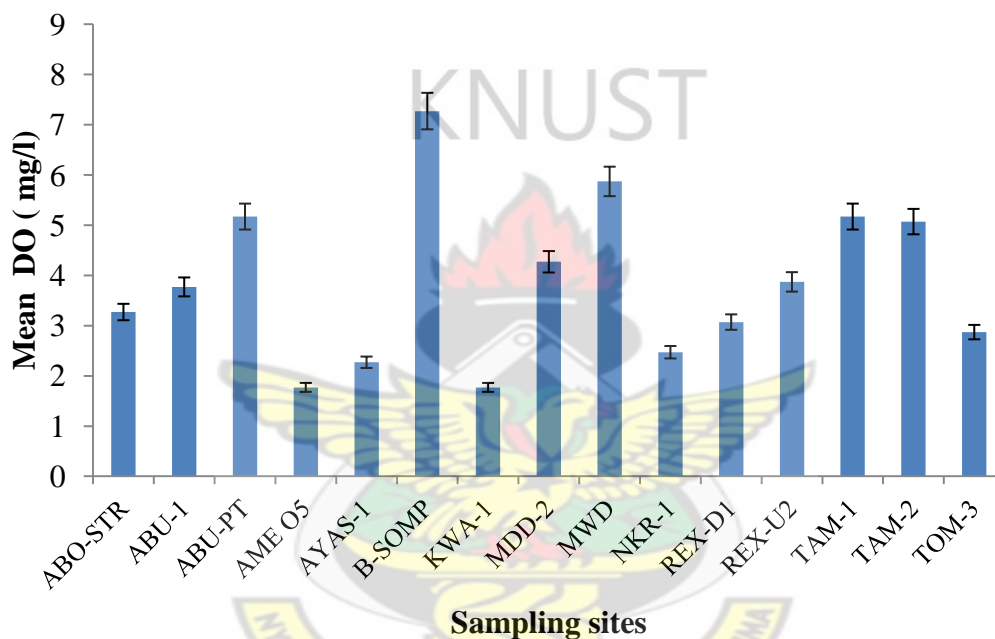


Figure 4.1.3 Mean Dissolved Oxygen of water samples from the streams

4.1.4 Electrical Conductivity (EC)

The mean electrical conductivity (EC) of most of the water samples analyzed were below the WHO recommended value of 700 $\mu\text{s}/\text{cm}$ (Figure 4.1.4). However B-SUMP, MDD-2 and MWD recorded high values of 970.7, 980.7 and 899.3 $\mu\text{s}/\text{cm}$ respectively. The effluent from the processing plant is discharged into B-SUMP and this might have accounted for its high EC value. While that of MDD-2, and MWD possibly resulted from leachate from the waste dumpsite.

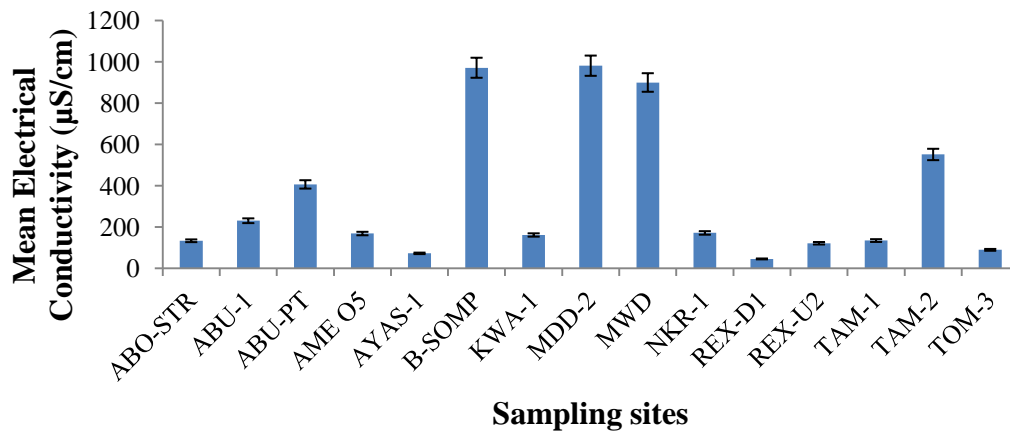


Figure 4.1.4 Mean Electrical Conductivity of water samples from the streams

4.1.5 Alkalinity

Figure 4.1.5 below shows the mean Alkalinity in the water samples from the streams. Alkalinity levels were below the detection limit in all the water samples except that from B-SUMP and MDD-2 streams. Alkalinity value of 90.67 ± 1.15 mg/L recorded from B-SUMP was below the WHO recommended limit of 400 mg/L for drinking water (WHO, 2006). High alkalinity value of 700.67 ± 1.15 mg/L was recorded from MDD-2 stream. This value is far above the WHO limit and makes it difficult for the water to be neutralized by acids.

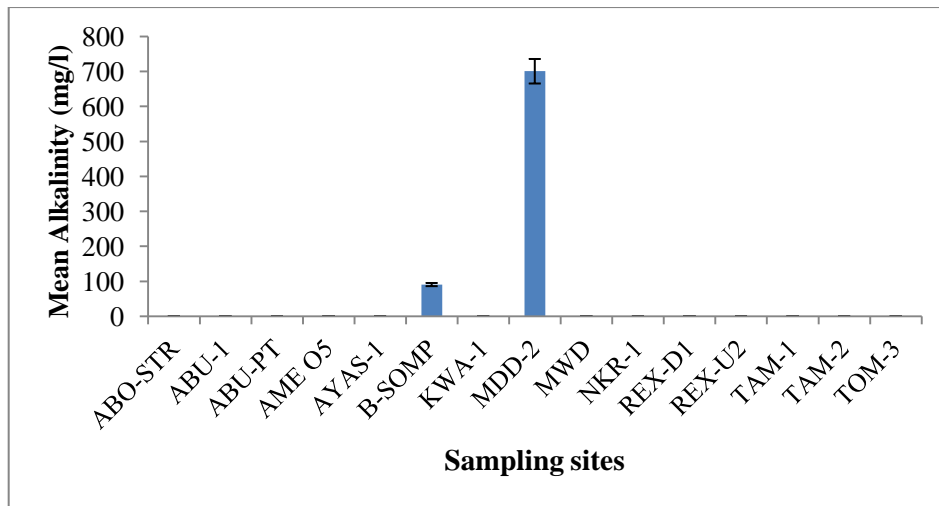


Figure 4.1.5 Mean Alkalinity of water samples from the streams

4.1.6 Total Hardness (TH)

The levels of total hardness of the water samples from the various streams shown in Figure 4.2.6 were lower than WHO recommended levels of 500 mg/L for drinking water. The hardness of water is generally due to the presence of Ca and Mg in the water. The presence of Ca in hard water is important in building stronger and denser bones in early life and keeping bones stronger and healthy later in life (Dietary Supplement Fact Sheet, 2011). Hard water has the effect of reducing the toxicity of some metals such as Pb, Zn and Cu. Soft water may corrode Pb pipes, while hard water may result in scale deposits in the pipes.

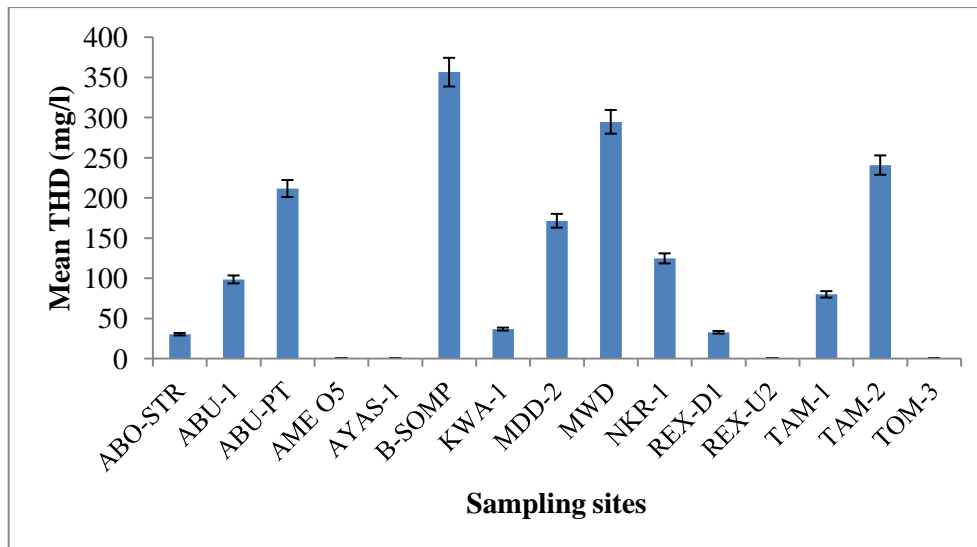


Figure 4.1.6 Mean Total Hardness of water samples from the streams

4.1.7 Sulphate

Figure 4.1.7 shows the mean sulphate concentrations in the water samples from the stream samples. Sulphate is one of the least toxic anions and WHO does not recommend any guideline value for drinking high concentrations in drinking water and WHO therefore suggest that health authorities should be notified when it concentrations in drinking water exceed 500 mg/L (UNEP/WHO, 1996). The water samples from AYAS-1 and REX-D1 streams recorded the maximum sulphate concentration of 22.7 mg/L while B-SUMP and TAM-1 recorded the minimum value of 3.7 mg/L. The low mean sulphate concentrations from the water samples therefore pose no threat to humans who drink from these streams.

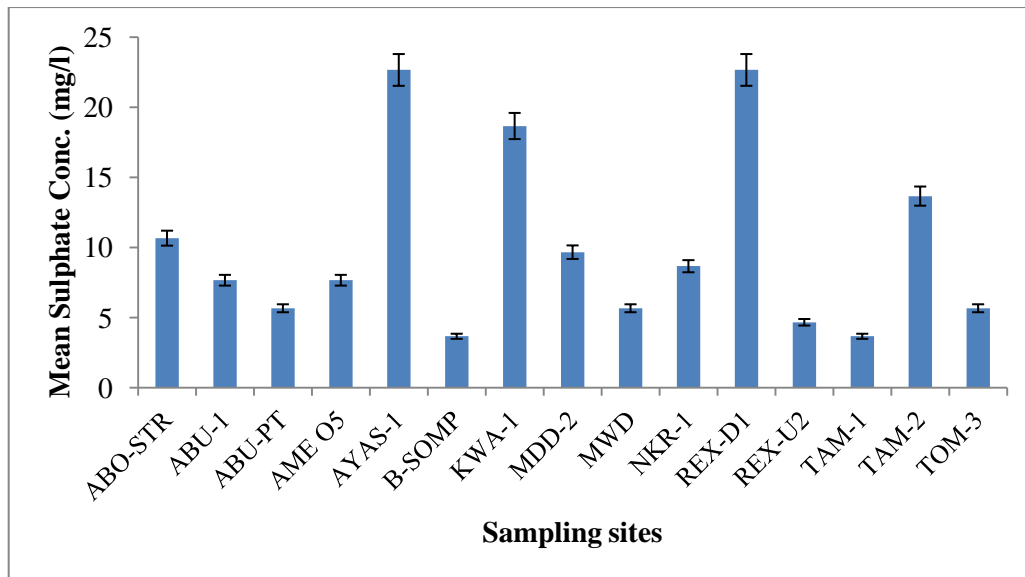


Figure 4.1.7 Mean Sulphate of water samples from the streams

4.1.8 Nitrate-Nitrogen

Significant sources of nitrate are chemical fertilizers from cultivated land, human and animal excreta and mining waters. The results in Figure 4.1.8 shows that out of fifteen (15) samples only one stream thus MDD-2 has value of 52.2 mg/L slightly above WHO level of 50 mg/L for drinking water. B-SUMP and MWD streams recorded 11.7 and 22.1 mg/L respectively, while the rest have values from 0.07 mg/L to 2.3 mg/L. The high nitrate values by B-SUMP, MDD-2 and MWD indicates a probable leachate inflow into the drainage network from waste rock dumpsite and the proximity of MDD-2 and MWD to the plant. Probably the contamination is not due to agriculture chemicals because most of the streams running through farms such as AYAS-1, TAM-1, TAM-2 and TOM-3 are not polluted with nitrate.

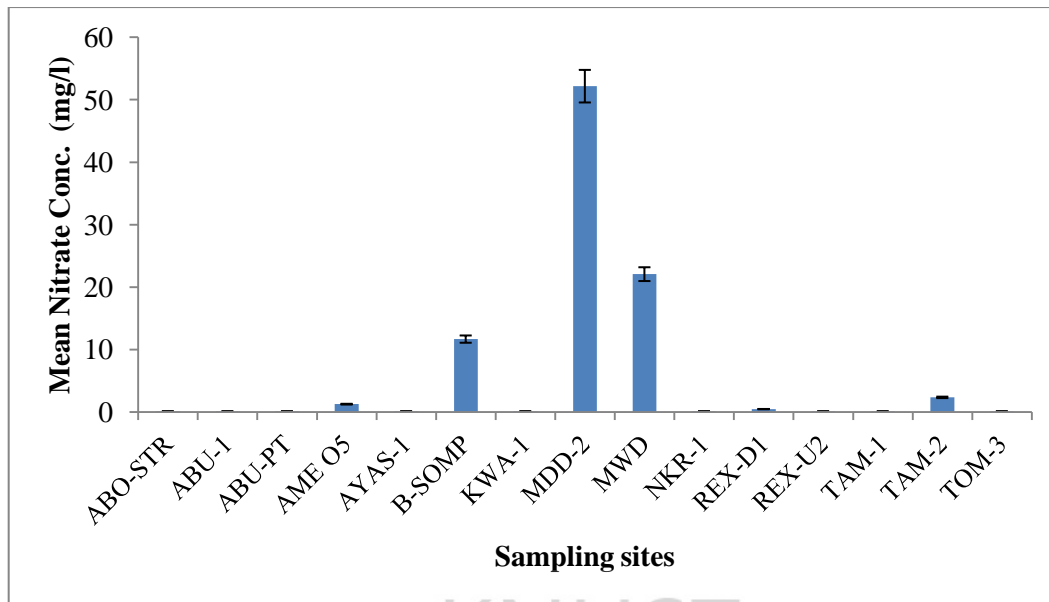


Figure 4.1.8 Mean Nitrate-Nitrogen of water samples from the streams

4.1.9 Nitrite-Nitrogen

All the recorded mean nitrite concentrations were below WHO recommended value of 3.0 mg/L for drinking water as shown in Appendix IV and Figure 4.1.9. A maximum value of 1.05 mg/L was recorded from TAM-1 stream. Nitrite is an unstable, intermediate stage in the nitrogen cycle and is found in water either by the oxidation of ammonia or by reduction of nitrate. Thus, biological processes can cause a rapid change in the nitrite concentration in a water sample (UNEP/WHO, 1996). This might have influence the low concentration of nitrite in water samples from the streams.

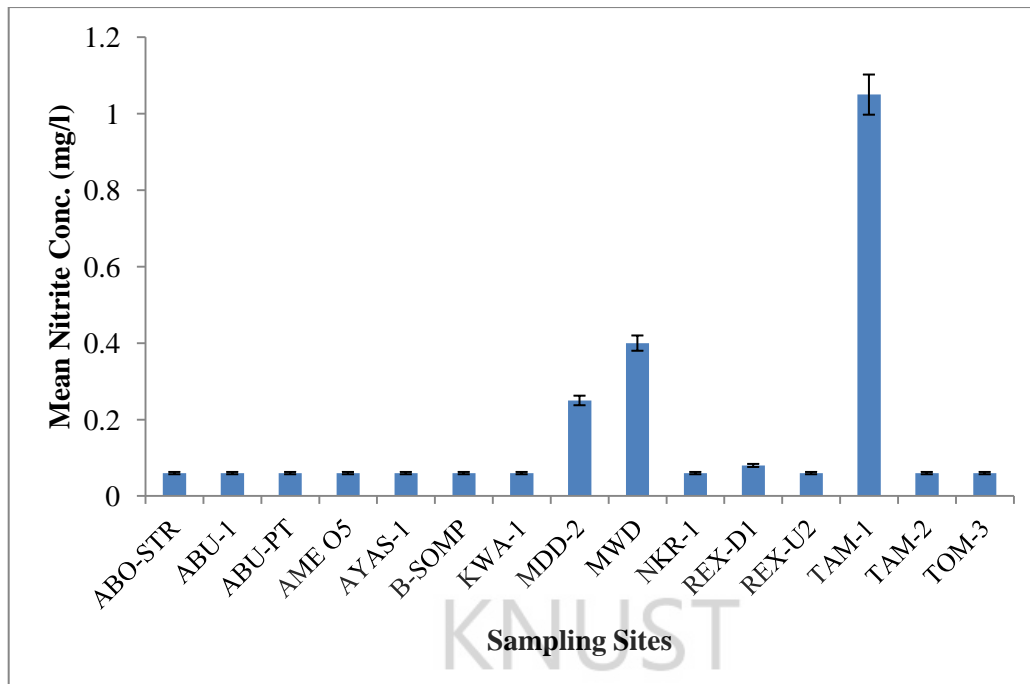


Figure 4.1.9 Mean Nitrite-Nitrogen of water samples from the streams

4.1.10 Fluoride

Fluoride may be present in water as a result of natural decomposition of rocks. It assists in control of dental caries but excessive amounts of fluoride can result in mottling of teeth. As in Figure 4.1.10, the Fluoride concentrations in all the samples were low ranging from 0.06-0.36 mg/L. These levels were below the WHO limit for drinking water of 1.5 mg/L.

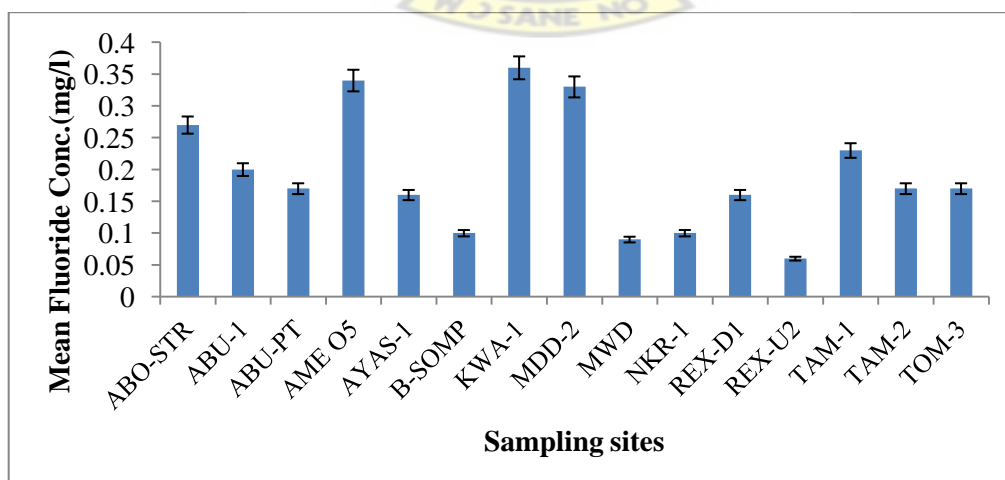


Figure 4.1.10 Mean Fluoride of water samples from the streams

4.1.11 Total Dissolved Solids (TDS)

According to Tay, 2007, total dissolved solids (TDS) can be used as a common indicator for polluted waters. All recorded values as shown in Figure 4.1.11 were higher than WHO recommended level of 20 mg/L for drinking water. Values of TDS ranged from a minimum of 340.87 mg/L from MDD-2 to a maximum of 5158 mg/L from ABO-STR. McCutcheon *et al.*, (1983) established that at TDS level less than 600 mg/L water is generally considered palatable and those above 1200 mg/L are considered not palatable. In view of this only water from the streams KWA-1, MDD-2 and TAM-2 can be considered to be palatable since they recorded a mean TDS less than 600 mg/L. High TDS waters are not clear, have colour and taste when used in the manufacturing. High concentrations of TDS above 500mg/L limit the suitability of water for drinking and for irrigation.

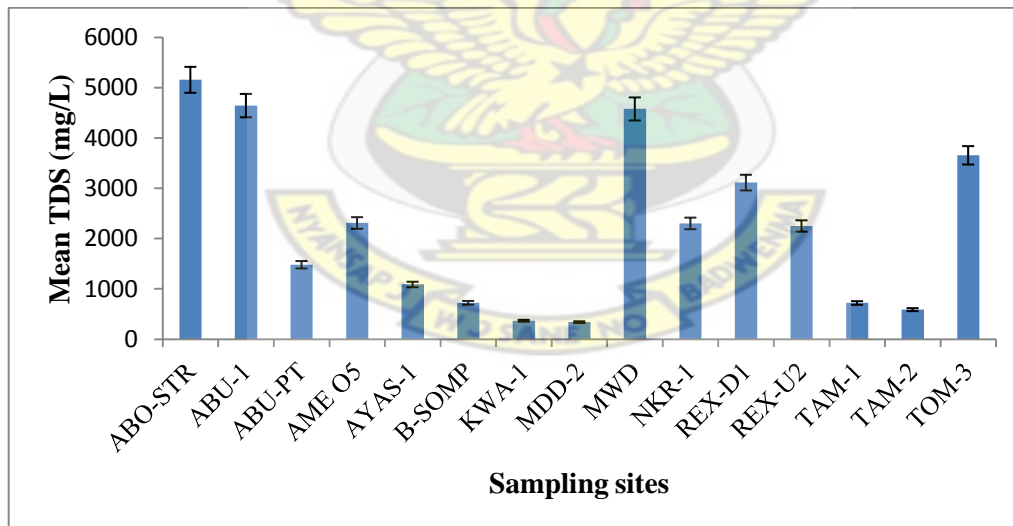


Figure 4.1.11 Mean Total Dissolved Solids of water samples from the streams

4.1.12 Turbidity

The readings for turbidity as seen in Figure 4.1.12 ranged from a maximum of 48.22 NTU from stream AYAS-1 to a minimum of 2.16 NTU from ABU-PT stream. Samples from ABU-1, ABU-PT, MWD, TAM-1, TAM-2 and TOM-3 streams recorded values

less than WHO limit of 5.0 NTU for drinking water, while the rest have turbidity values higher than WHO recommended level. High turbidity values can be attributed to suspension of fine organic and inorganic particulates as a result of high algae growth, erosion from rock dumpsite and tailings materials and improper waste disposal along the streams (Akoto *et al.*, 2008)

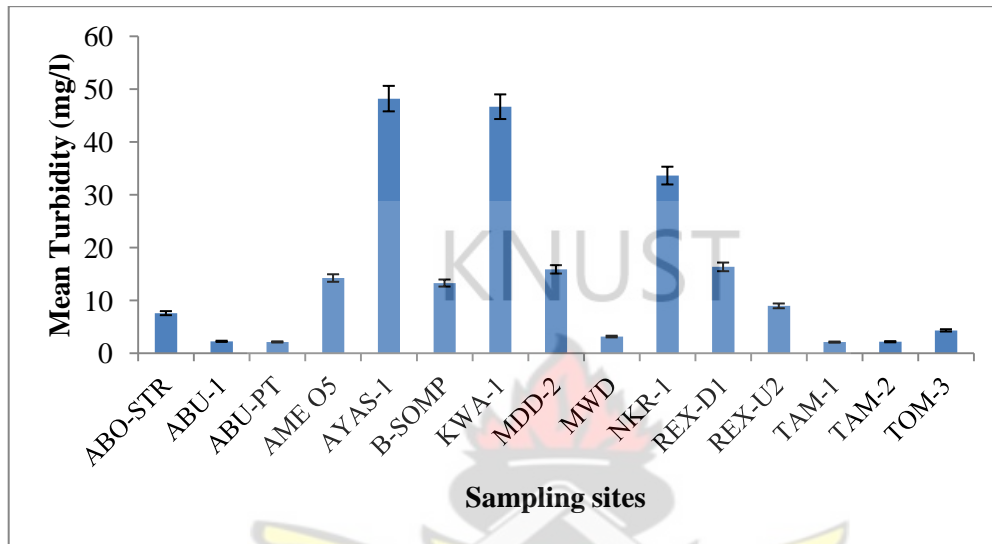


Figure 4.1.12 Mean Turbidity of water samples from the streams

4.2.0 ARSENIC AND HEAVY METAL CONCENTRATION IN THE WATERSAMPLES

Detailed results of arsenic and some heavy metals analysed in the water samples are presented in Appendix II.

4.2.1 Arsenic

The mean concentration of arsenic in the streams varied from 6.30 ± 1.06 to 22.87 ± 1.36 mg/L with the sample collected from ABO-STR recording the highest value of 22.87 ± 1.36 mg/L and the lowest value of 6.30 ± 1.06 mg/L was recorded for MDD-2 stream as shown in Figure 4.2.1. All the recorded values of arsenic concentration in water samples were

virtually higher than Ghana Environmental Protection Agency (GEPA) levels of 0.1 mg/L, World Health Organization (WHO) levels of 0.1mg/L and Ghana Standard Board levels of 0.01 mg/L recommended for drinking water. Significant variations were observed among the water sampling points as $p < 0.05$ (Appendix VI). As a result of high levels of Arsenic in the samples, humans who drink from such water sources have high risk of developing lung and bladder cancers (Smith *et al.*, 2000). Water from these streams should be treated before consumption by both humans and other animals. The high levels of As in the water samples may due to anthropogenic sources from the mining, since As is a by- product of refining of Au (Boyle and Jonasson, 1973)

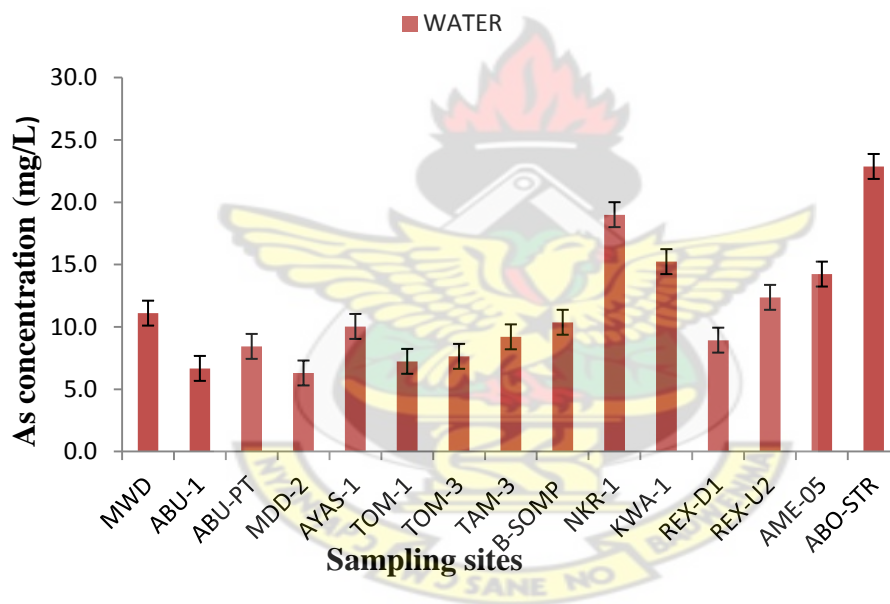


Figure 4.2.1 Mean Arsenic concentrations in water samples from the streams

4.2.2. Calcium

The mean concentration of calcium in stream water samples ranged from 111.87 ± 1.03 to 1735.20 ± 1.74 mg/L with maximum value recorded in sample collected from MWD stream and the lowest value was recorded from samples NKR-1 stream as indicated in Figure 4.2.2 and Appendix II. The concentrations of calcium in water samples were extremely

higher than the recommended levels of World Health Organization (WHO) for drinking water of 0.1 mg/L. High Ca intake plays an important role in building stronger and denser bones early in life and keeping bones strong and healthy later in life (DSFS, 2011). Since $p < 0.05$, there were significant variations among the sampling points for water (Appendix VI).

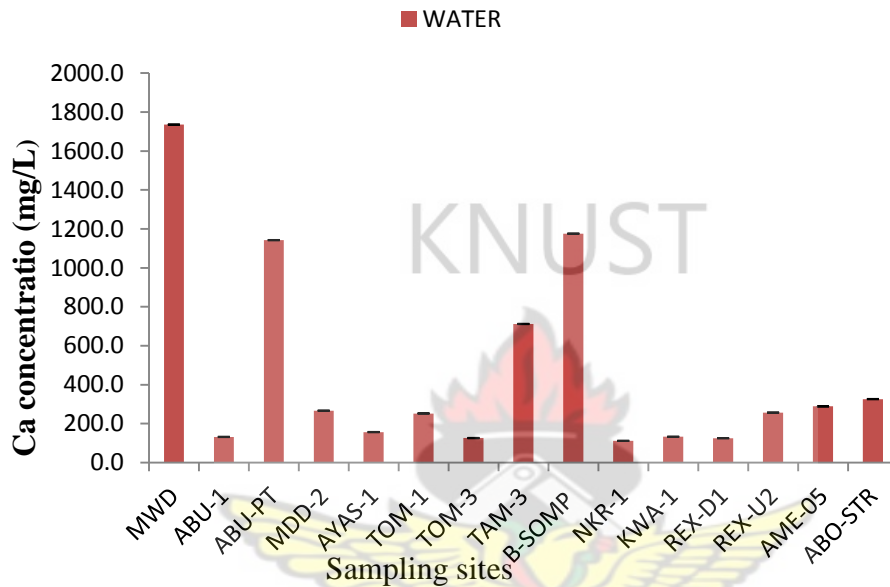


Figure 4.2.2 Mean Calcium concentrations in water samples from the streams

4.2.3 Cadmium

Figure 4.2.3 below indicates that Cadmium was not detected in almost all the samples except that from B-SUMP which recorded high mean cadmium concentration of 0.571 ± 0.06 mg/L in the water. The Cd levels from this site was above the WHO recommended level for drinking water which is 0.003 mg/L, GEPA level of 0.01 mg/L and GSB level of 0.003 mg/L. The sampling site B-SUMP is near the main reservoir for effluents coming from the extraction plant and other anthropogenic activities and this might have contributed for its high level of cadmium in the water samples. Cd is produced mainly as a by-product from mining, Smelting, and refining sulphidic ores of Zn, and, to a

lesser degree, Pd and Cu. These metals are not mined at the study area, hence the absence of Cd in the water samples from most of the streams (Hans, 1995).

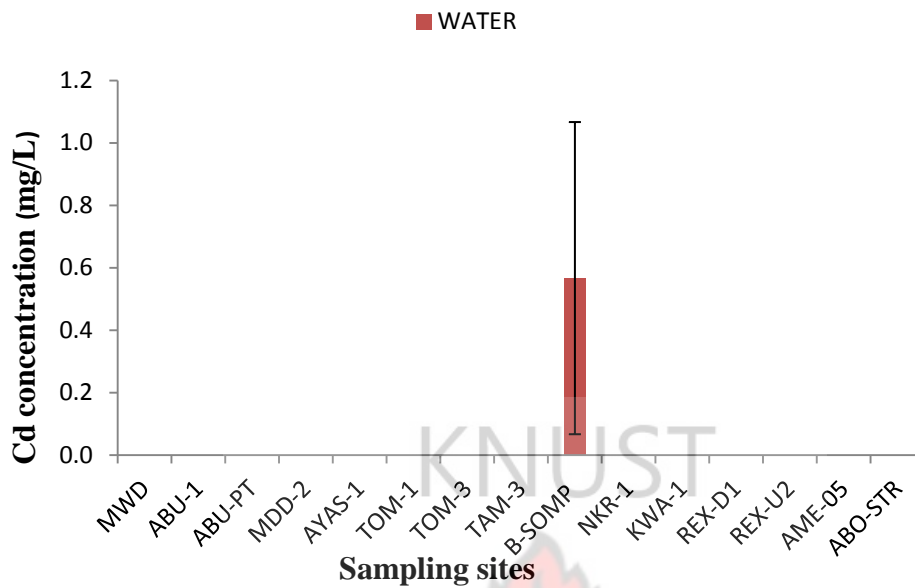


Figure 4.2.3 Mean Cadmium concentrations in water samples from the streams

4.2.4 Copper

From Figure 4.2.4 below, the concentration of copper in water samples from the various streams were all above the WHO acceptable limits of 2.0 mg/L (WHO, 2006) and GSB levels of 1.0 mg/L for drinking water. The maximum recorded value was 52.57 ± 1.00 mg/L from stream TAM-2 while water sample from stream TOM-3 recorded a minimum of 2.20 ± 1.22 . Statistically, there were significant variations in the mean concentration of copper among the sampling points for water samples as $p < 0.05$. In view of the high levels of Cu in the water, the water could be said to be unwholesome for domestic purposes and pose health threat to the aquatic ecosystem. An increased level of Cu in humans could lead to liver and kidney damage (ARD-EHP, 2005). Mining and agricultural activities along banks of the streams may have contributed to the high levels of Cu in the water samples (Gaetke *et al.*, 2003).

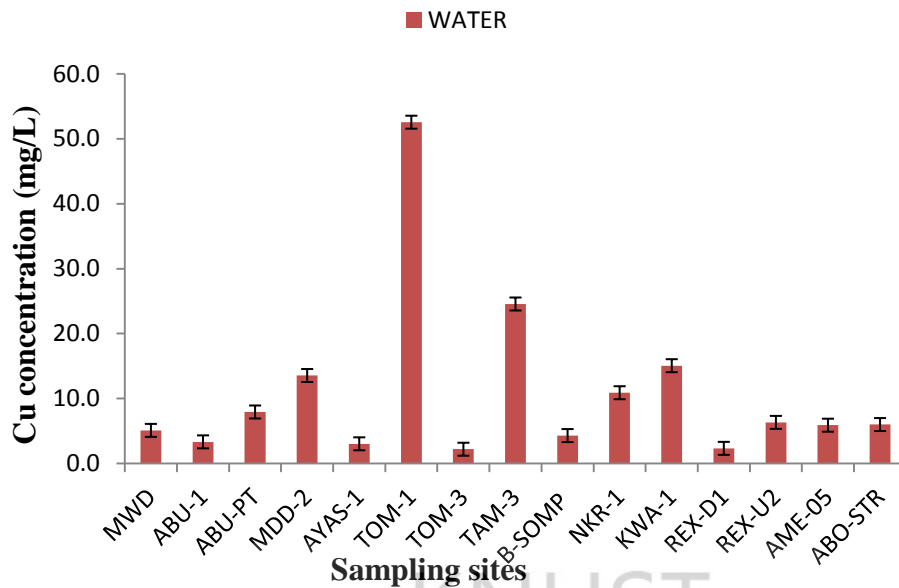


Figure 4.2.4 Mean Copper concentrations in water samples from the streams

4.2.5 Iron

According to Appendix II and Figure 4.2.5 below, a mean minimum iron concentration of 1770 ± 3.38 mg/L and a maximum of 50685 ± 65.86 mg/L were recorded from TAM-1 and TOM-3 streams for water samples respectively. These levels exceed the WHO, GEPA and GSB recommended limits of 0.3 mg/L, 10.00 mg/L, and 0.30 mg/L respectively. There were no significant variations among the water samples as $p > 0.0529$ (Appendix VI). The high level of Fe may be due to the levels in original minerals contained in soils. Increased levels of Fe may cause conjunctivitis, choroiditis and retinitis. The increased concentration of Fe in the streams could be attributed to occurrence of Fe^{2+} compounds which are found in dissolved form (McDonald, 2010).

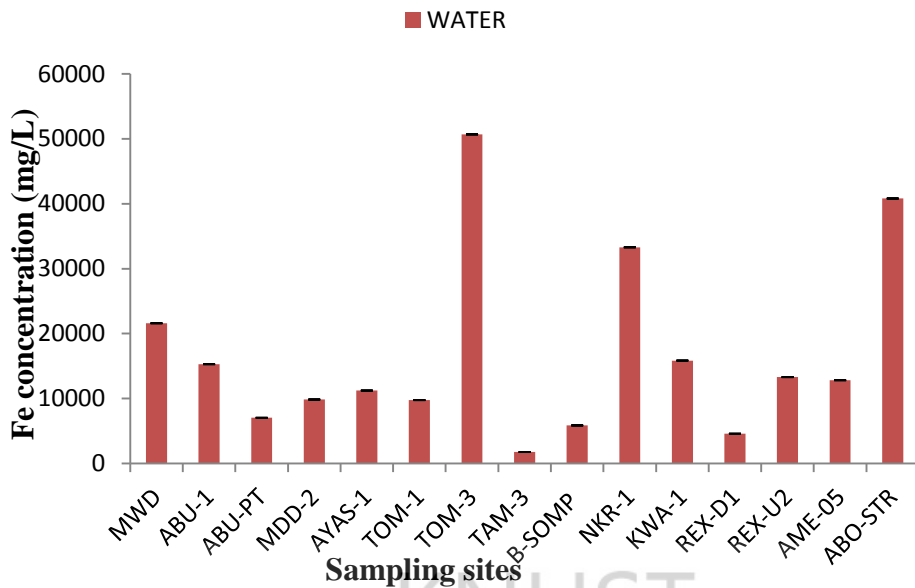


Figure 4.2.5 Mean Iron concentrations in water samples from the streams

4.2.6 Manganese

ABU-PT recorded the highest mean manganese concentration value of 749.13 ± 4.39 mg/L and the lowest 4.07 ± 1.03 mg/L was recorded at REX-D1 as shown in Figure 4.2.6 below. The mean concentrations were higher than WHO and GSB limits for drinking water of 0.5 mg/L. These levels may pose serious health threat to humans who use the water from these streams for domestic purposes since it becomes toxic when too high concentrations are assimilated in the human body (Huber et al., 2004). This can cause Parkinson, lungs embolism and bronchitis. High levels Mn in aerobic waters are usually associated with industrial and human activities (Petrus and Warchol, 2005; IPCS, 2002). The high levels of Mn in stream ABU-PT could be attributed to the closeness of the stream to the processing plant. Statistically, there were significant variations among the sampling points for water. $p < 0.05$, in all the samples

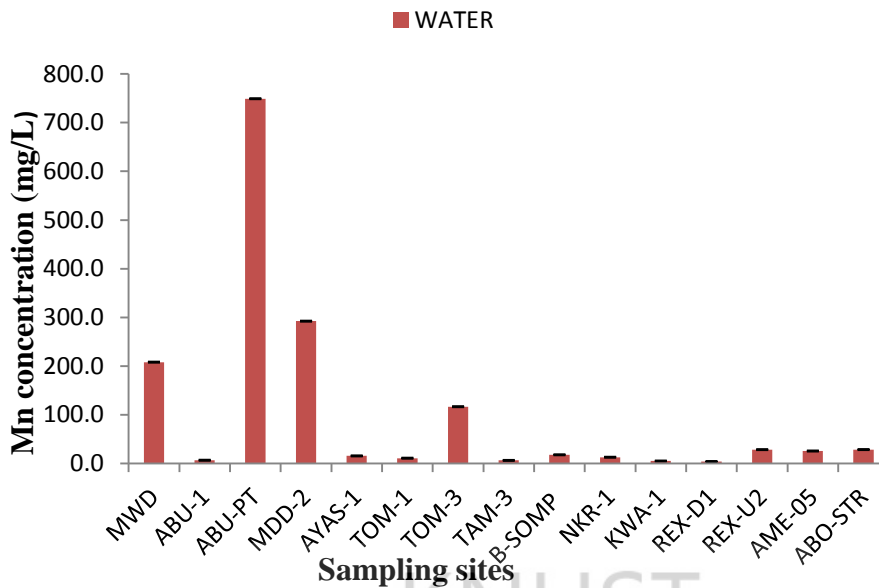


Figure 4.2.6 Mean Manganese concentrations in water samples from the streams

4.2.7 Lead

As shown in Figure 4.2.7 below, levels of lead in the water samples analyzed ranged from 1.43 ± 1.10 mg/L to 23.87 ± 1.00 mg/L. The minimum concentration of Pb was recorded in stream KWA-1 whereas the highest value was obtained from ABU-PT stream. All the recorded values of lead concentration in the water samples were extremely higher than the recommended WHO limits of 0.01 mg/L for drinking water. These levels are high and can cause permanent brain damage and even death (ATSDR, 2007). Children with greater Pb levels may have problems with learning and reading abilities, delayed growth and loss of hearing (ATSDR, 2007). In the blood Pb is associated with erythrocytes (red blood cells). Pb interferes with the sulphhydryl groups responsible for the proper functioning of the enzymes for synthesising haemoglobin, resulting in abnormal production of haemoglobin is produced (De Vries *et al.*, 2007). The high level of lead at ABU-PT may be due to the closeness of the stream from the mechanical workshop. There were significant variations among the sampling points in all the cases, $p < 0.05$.

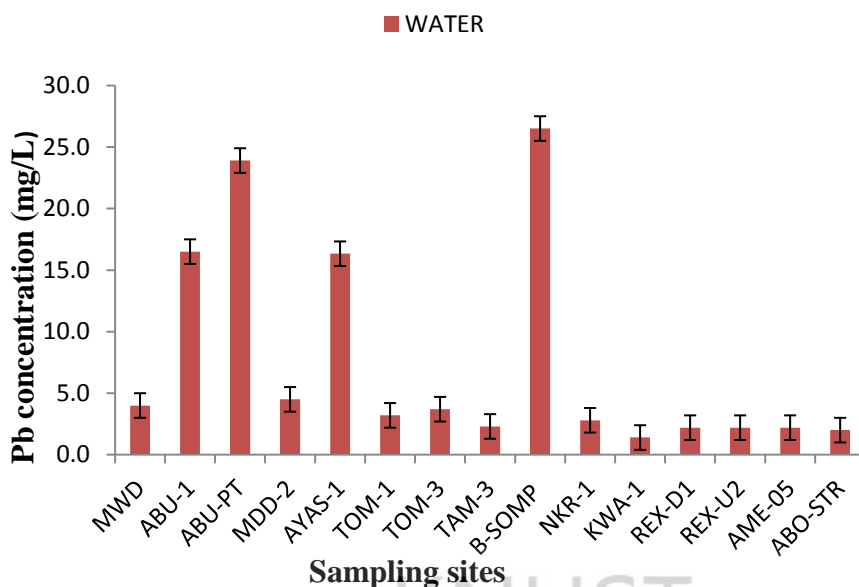


Figure 4.2.7 Mean Lead concentrations in water samples from the streams

4.2.8 Zinc

From Figure 4.2.8 below, the maximum and minimum mean zinc concentrations of 87.37 ± 1.36 mg/L and 2.93 ± 1.18 mg/L were recorded from AYAS-1 stream and REX-D1 stream water samples, respectively. The mean Zn concentrations were above both the WHO and GSB limits of 3.00 mg/L for drinking water, except REX-D1 stream (WHO, 2004). High levels of Zn ions in solution is highly toxic to plants, invertebrates and fish (Milbury and Richer, 2008; Muysen et al., 2006). Cu is essential for normal growth and development of human foetuses, infants, and children (Ralph and McArdle, 2001), but excess absorption of Zn suppresses Cu absorption (Fosmire, 1990). The high levels of zinc concentrations in some of the areas may be due to their nearness to the tailings dam. Significant variations were observed among the water from sampling points as $p < 0.05$.

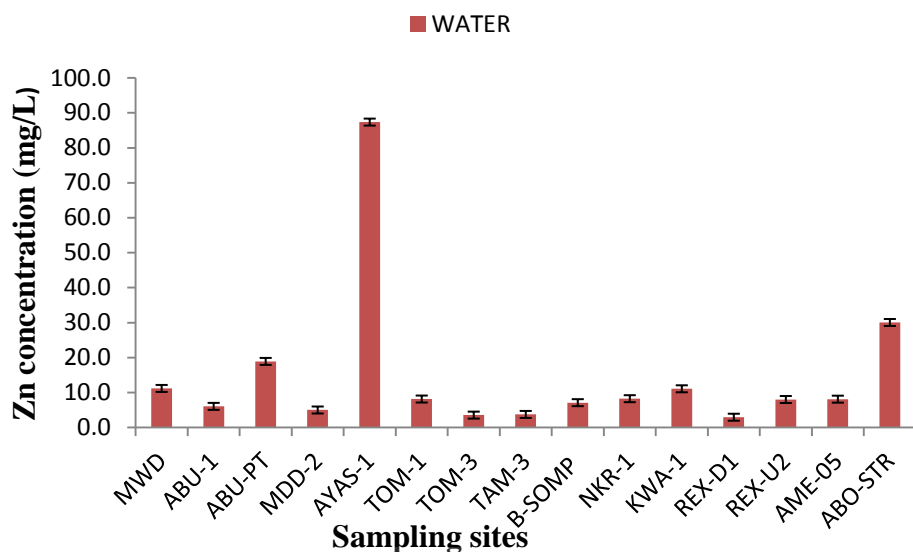


Figure 4.2.8 Mean Zinc concentrations in water samples from the streams

4.3.0 Physicochemical Properties of Sediment Samples

The range, mean and standard deviation of physicochemical properties that were measured in the sediments are presented in Appendix III.

4.3.1. pH

In Figure 4.3.1, sample site NKR-1 recorded the lowest mean pH of 5.36 and the highest value of 8.94 was recorded at ABU-PT. The pH levels of the sediments showed slightly alkaline, except at NKR-1 which was slightly acidic. The dissolution of gold with cyanide is sensitive to the pH of the solution. The optimum dissolution rate of gold with respect to pH is often found near a pH of 10.5. The pH of cyanide solution is adjusted by adding CaCO_3 (Nicol *et al.*, 1979). Discharge of effluents from the extraction plant may have run into these streams thus the slightly high pH levels in the sediment samples.

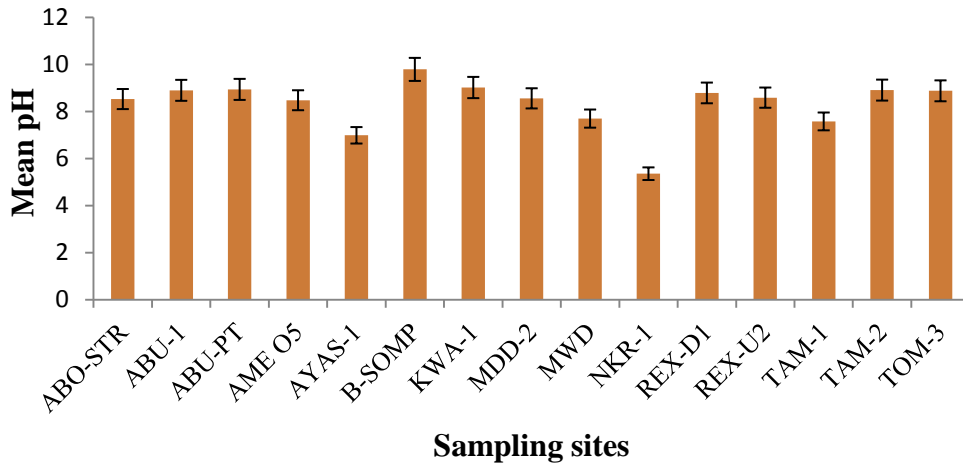


Figure 4.3.1. Mean pH of sediment samples from the streams

4.3.2 Electrical Conductivity

Electrical Conductivity is a measure of the ionic content of the sediment. The Electrical Conductivity of all the sediment samples analysed as indicated in Figure 4.3.2 and Appendix III, were below the EPA Guidelines of 750 $\mu\text{S}/\text{cm}$. The EC values ranged from a minimum of 180 $\mu\text{S}/\text{cm}$ at NKR1 to a maximum of 611 $\mu\text{S}/\text{cm}$ at B-SUMP.

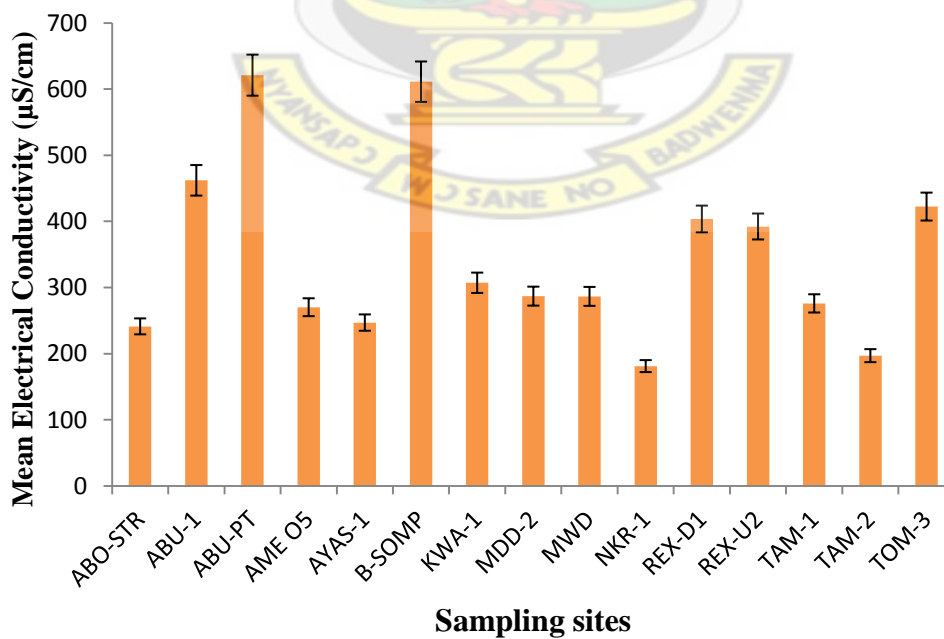


Figure 4.3.2 Mean Electrical conductivity of sediment samples from the streams

4.3.3 Organic Matter

Figure 4.3.3 shows the results of % Organic Matter of the sediment samples. The organic matter content of the sediment samples ranged from a minimum of 0.21% recorded at sites B-SUMP and REX-U2 to a maximum of 1.01% at ABU-PT stream. Organic matter decreases with increasing temperature. The relatively high temperatures of the sediment samples speed up the degradation of organic matter (Franzmeier *et al.*, 1985), hence low organic matter content in the sediment samples. Fine-textured sediment can hold more organic matter than sandy sediments. Clay-particles form chemical bonds that hold organic compounds and decomposition of organic matter occurs faster in well-aerated sandy sediments. High organic matter contents were therefore expected in most of the sediment samples since only two of the samples were sandy. Low organic matter content could not be explained in terms of sediment texture.

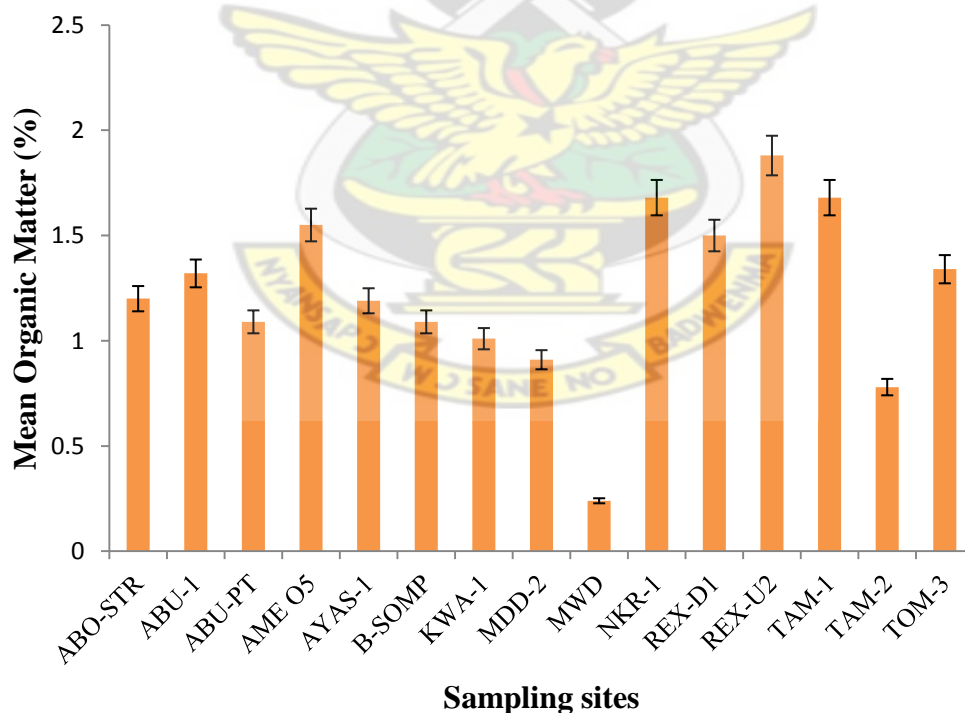


Figure 4.3.3 Mean Organic Matter of Sediment Samples from the streams

4.3.4 Sediment Texture

Results in Appendix IIB shows that eight of the sediment samples were established as silt, five as clay and two of the samples contained sand using the soil profile triangle. Silt levels being high can be attributed to the erosion and runoff from the waste rock dumpsite, tailings and agriculture fields. These particles become suspended and later settling at the beds of the streams. Heavy metal concentrations in sediments are affected by particle size and composition of sediments (Krumlkgalz, 1989). The clay content in sediment influences the binding of heavy metals in sediment solution (Gustafsson *et al.*, 2003). The results show that eight of the samples (ABO-STR, ABU-PT, B-SUMP, KWA-1, MDD, MWD, NKR-1 and TAM-1) were silty, ABU-1, AYAS-1 TAM-2, TOM-3 and REX-U1 were clayey, while AME-02 and REX-U2 were sandy.

4.4.0 Arsenic and some Heavy Metal Distribution in Sediments

Detailed results of arsenic and some heavy metals analysed in the sediment samples are presented in Appendix I. The Geoaccumulation Index (Igeo) introduced by Muller (1979) was also used to assess metal pollution in sediments to quantify the degree of anthropogenic contamination in the stream sediments. The result of the Geoaccumulation Index of the various metals is presented in Appendix X.

4.4.1 Arsenic

Mean As concentrations as in Figure 4.4.1 below, shows that a maximum value of 83.7 ± 1.15 mg/Kg was recorded at ABO-STR, while a minimum of 23.3 ± 1.15 mg/Kg was recorded at ABU-1. The pollution levels of arsenic in the sediment samples expressed in terms of geoaccumulation indices indicate that the study area is unpolluted to moderately

polluted with As. This gives an indication that there is no form of pollution with respect to arsenic.

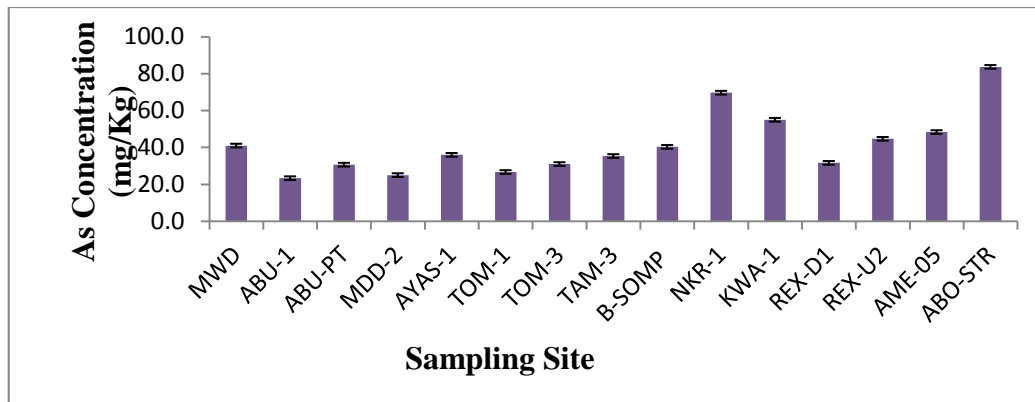


Figure 4.4.1 Mean arsenic concentrations in sediment samples from the stream

4.4.2 Calcium

Levels of calcium in the sediments as shown in Figure 4.4.2, ranged from 478 ± 1.44 mg/Kg to 6597 ± 6.43 mg/Kg with maximum value recorded at site MWD and lowest observed at site ABU-1. There were significant variations in the mean concentration of calcium among the sample points for the sediment ($P < 0.05$) (Appendix VI). Calcium in sediment is necessary for plant and animal life since Ca enhances effective physiological processes. According to Geoaccumulation Index calculated, the sediments at all the sampling points are highly polluted with calcium.

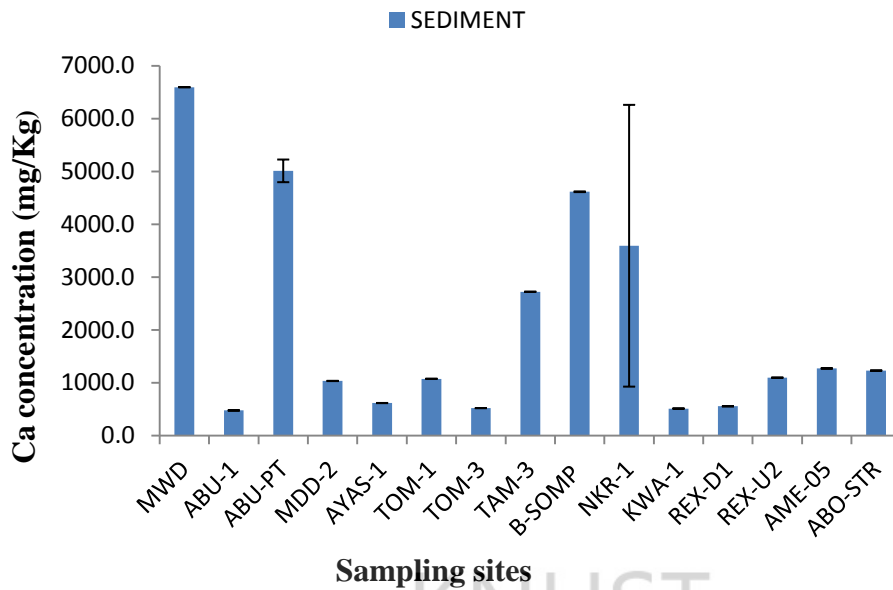


Figure 4.3.2 Mean calcium concentrations in sediment samples from the streams

4.3.3 Cadmium

Figure 4.4.3 below shows that, with the exception of B-SUMP which recorded a mean cadmium concentration of 0.53 ± 0.05 mg/Kg and TAM-1 obtaining a low value of 0.013 ± 0.0057 mg/Kg in the sediment, cadmium was below the detection limit in the remaining sediment samples. The undetectable level of cadmium in sediment samples beside B-SUMP and TAM-1 suggests that, apart from these streams, the effect of cadmium poisoning in the stream samples of the area is likely to be very minimal. The sampling point B-SUMP is the main reservoir for effluent coming from the extraction plant and other anthropogenic activities and this might have contributed for the high level Cd. The Geoaccumulation Index indicates that the sediments at the sampling points are not polluted with regard to cadmium.

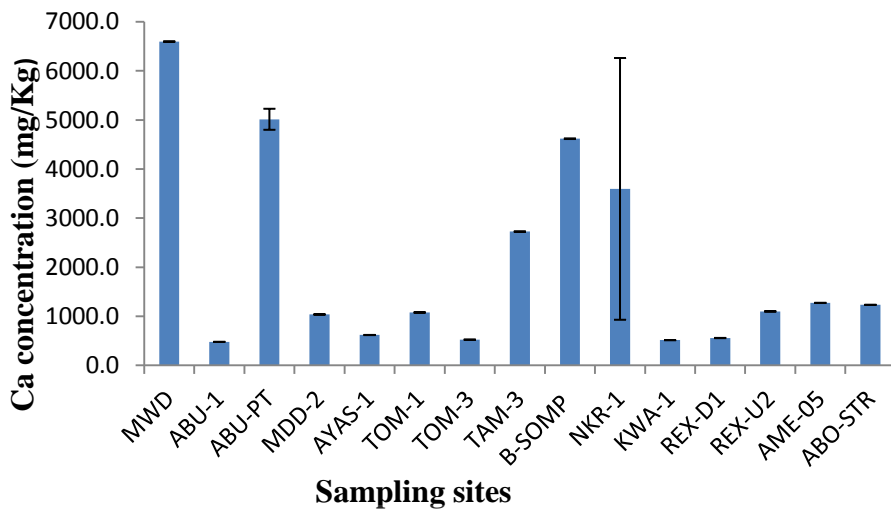


Figure 4.3.3 Mean cadmium concentrations in sediment samples from the streams

4.3.4 Copper

As shown in Figure 4.4.4 below, the mean Cu concentration in the sediments ranged between 5.50 ± 1.22 mg/Kg and 91.80 ± 1.01 mg/Kg. The maximum value was recorded from stream TAM-1 and the lowest value from TOM-3 stream. Significant differences were observed among the sediment samples ($P < 0.05$) (Appendix VI). The high concentration of copper could have resulted from human activities mainly gold mining and agriculture. The soils are eventually washed into streams where copper compounds settle and are bound to sediment particles. According to the Geoaccumulation Index calculated, the sediments are unpolluted with Cu.

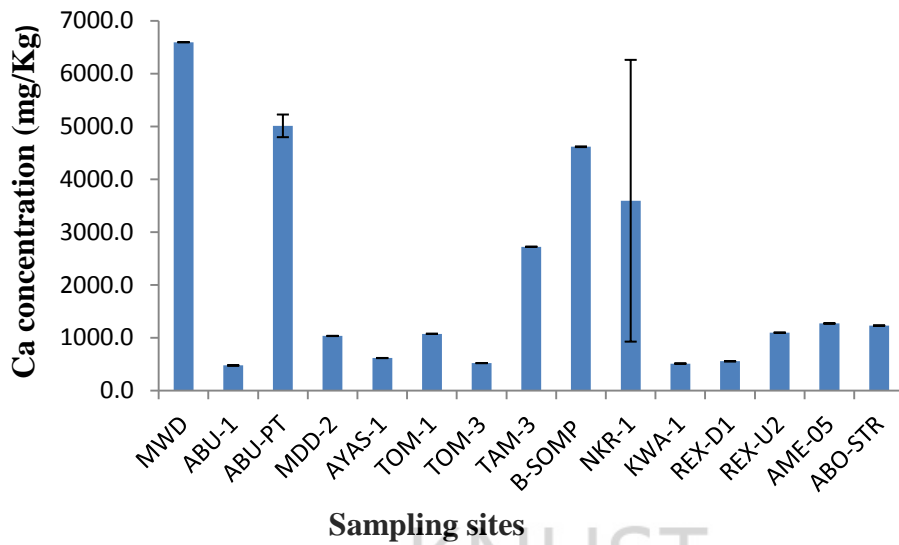


Figure 4.3.4 Mean copper concentrations in sediment samples from the streams

4.3.5 Iron

Mean iron concentration as in Figure 4.4.5 below ranged from 8268 ± 5.29 mg/Kg to 163191 ± 7.57 mg/Kg (Appendix I). Stream NKR-1 recorded the highest Fe concentration and lowest was recorded from TOM-3 stream. Statistically, there were no significant variations at the sampling points for Fe because $p < 0.05$. The mean high levels of iron in the sediments may be probably due to adsorption of the oxide forms of Fe to clay and organic particles in the sediments. With respect to the Geoaccumulation Index presented in Appendix IX, the sediments are highly polluted with Fe.

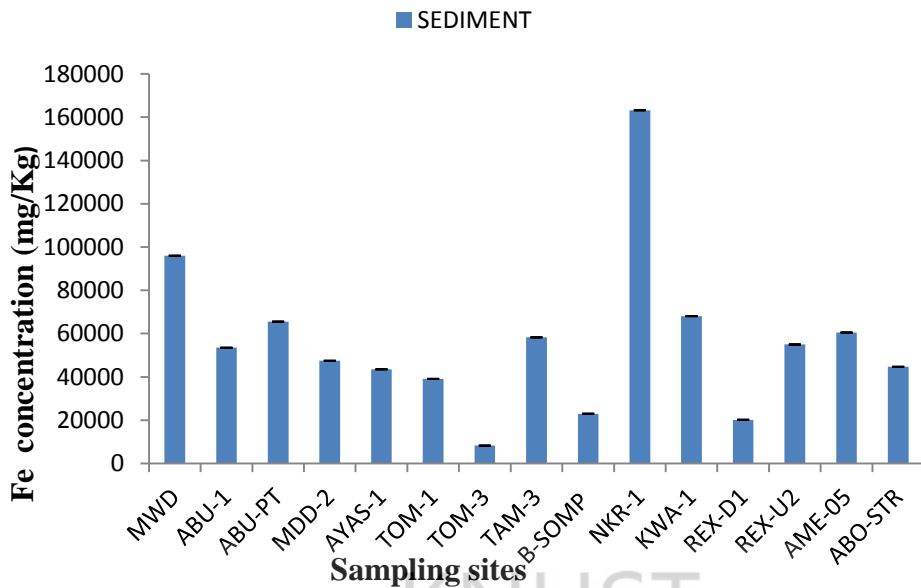


Figure 4.3.5 Mean iron concentrations in sediment samples from the streams

4.3.6 Manganese

Sediment sample from MDD-2 recorded the maximum Mn concentration of 1177.00 ± 2.00 mg/Kg and REX-D1 recorded the minimum value of 13.03 ± 1.10 mg/Kg. Significant variations were observed among the sediment samples ($P < 0.05$) (Appendix V). By the Geoaccumulation Index, the sediment samples from all the streams were unpolluted with Mn.

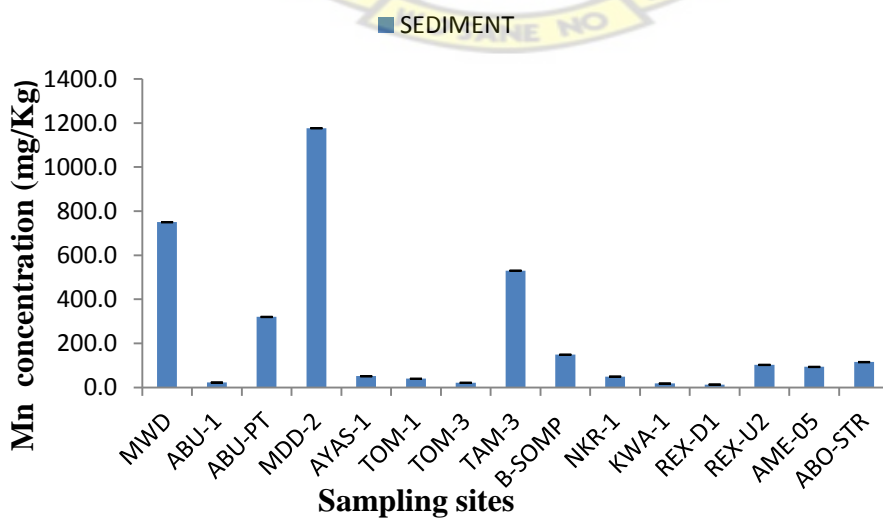


Figure 4.3.6 Mean manganese concentration in sediment samples from the streams

4.3.7 Lead

A maximum mean lead concentration of 114.00 ± 1.06 mg/Kg in sediments was obtained at B-SUMP and a minimum value of 4.20 ± 1.06 mg/Kg was recorded from stream REX-D1 as seen in Figure 4.4.7. Variations of Pd in the samples among the stream sediments were statistically significant ($p < 0.05$). The results of Geoaccumulation Index of lead as presented in Appendix X indicate that the sediment is unpolluted to moderately polluted by lead.

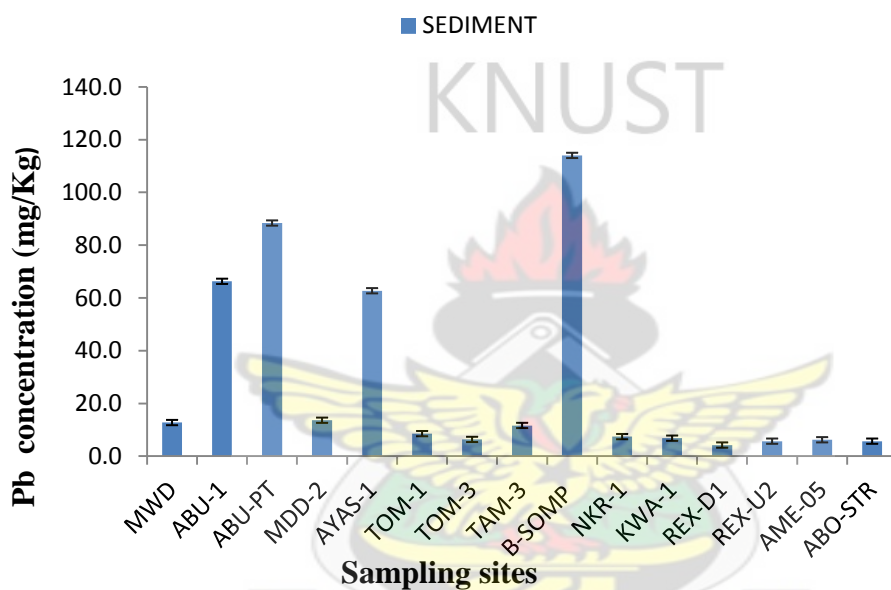


Figure 4.3.7 Mean lead concentrations in sediment samples from the streams

4.3.8 Zinc

Figure 4.4.8 below shows that, the highest mean Zn concentration was measured in AYAS-1 stream with a value of 386.50 ± 4.44 mg/Kg and REX-D1 recorded a minimum mean concentration of 8.20 ± 1.183 mg/Kg. The variations of zinc in the sediment among the samples from the streams were statistically significant ($p < 0.05$). (Appendices VI). The relatively high concentration of zinc in the sediments may be due to the presence of high organic matter and clay minerals which have colloidal particles that easily form compounds with zinc. Although zinc is considered essential for physiological processes in

humans, excessive intake can be hazardous since it has detrimental consequences on human health at high concentrations (Moore and Ramomoorthy, 1984). The Geoaccumulation index shows that the sediments were unpolluted with respect to zinc.

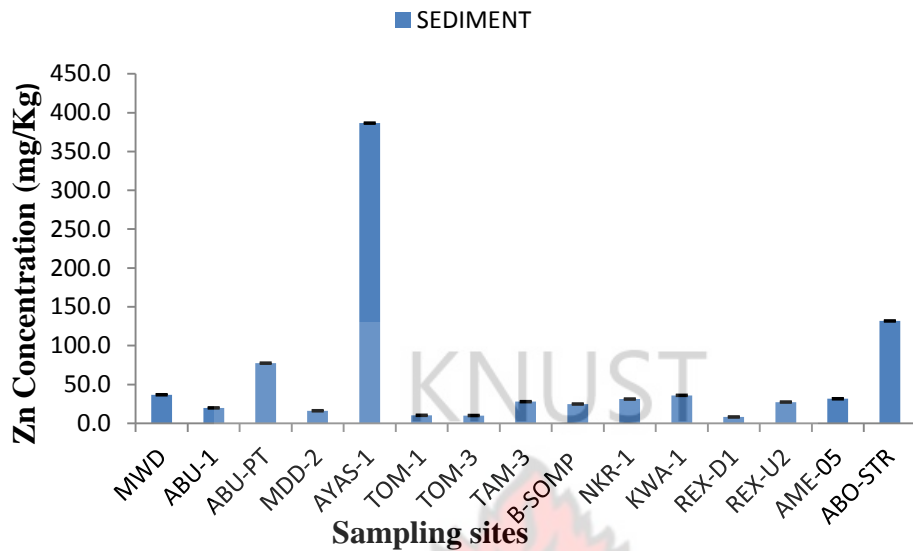


Figure 4.3.8 Mean zinc concentrations in sediment samples from the streams

The results from the study area revealed higher concentrations of the heavy metals both in the stream water and the sediment samples. The sediment samples generally showed high concentrations of heavy metals than the streams water samples. Depinto and Martins (1980), reported that, bottom sediments contain higher concentrations of heavy metals than that of stream water. The results were also consistent with that reported, by Adomako *et al.*, (2008), that, the concentrations of the heavy metals in the underlying sediments are higher than that of the stream water samples. They suggested that, this might be due to the fact that metals transported with water or suspended metals are stored within the sediments. The sediments are reservoirs for the metals. Also, it is believed that suspended metallic solids after they aggregate to form larger and denser particles, settle to the bottom of the water and are embedded in sediments. Forstner, (1990); Salomons, (1995); Burton, (2002); Salomons and Brills, (2004), have reported

that sediments function as a final storage of heavy metals and other contaminants. They content that, as long as the sediments remain undisturbed, most of the metals are strongly bound to them. Consequently, metal concentrations in sediments may generally be higher than the overlying water. Other factors such as changes in temperature, pH, redox potential and organic matter might have contributed to the high concentrations of heavy metals in the sediment.

The levels of heavy metals recorded in both the stream waters and sediments with the exception of Cd were found to be alarmingly high in comparison with the recommended WHO Guidelines. This raises public health concern since human beings are the final destination of this metal accumulation. The high concentration of these metals could be attributed to mining and agricultural activities in the Tarkwa municipality resulting in the release of waste in the waters which usually contain traces of these heavy metals. This is potentially hazardous to human in the following ways: (i) direct drinking of water from these sources can cause accumulation of heavy metals in the human organs which eventually leads to health hazards (WHO 1992). (ii) use of the water for irrigation of farms is likely to contaminate soil leading to absorption by plants. Continuous absorption of these metals by crop plants causes increase in accumulation in plants tissues which and eventually ends up in humans when such crops are consumed. High concentration of these metals may become toxic to fishes and other aquatic plants thus can create imbalance in the entire aquatic ecosystem.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The present study evaluated the content of arsenic, calcium and six heavy metals and their toxicity in sediments and water collected from 15 streams within the Damang mine area. Heavy metals determined were cadmium, copper, iron, manganese, lead and zinc. Metal concentrations in both sediments and stream waters from all the sampling points were generally higher than the WHO recommended values for drinking water. Metal contamination is a potential danger for the health of human and animal populations in the vicinity of mining activities. All the stream water samples exhibited an elevated TDS. However, the remaining physiochemical properties studied were generally all lower than the Standard for the WHO Drinking Water Guidelines. The source of pollution is mainly due to erosion and runoff from the waste rock dumpsite and not from the discharge of effluent of the treatment plant.

5.2 RECOMMENDATION

Based on the result of the study conducted and the conclusions, the following are recommended.

- The gradient of the current waste rock dump should be reassessed and if possible it should be reduced to minimize the rate of erosion and runoff from the waste dumpsite.
- Boreholes should be provided for the communities whose stream waters have been contaminated.
- Metal speciation should be performed on the sediments to assess risk of bioavailability and the behaviour of the metals in the environment.

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APPENDICES

Appendix 1: METAL CONCENTRATION IN SEDIMENT SAMPLES (mg/Kg)

Parameter	Statistics	ABO-STR	ABU-1	ABU-PT	AME O5	AYAS-1	B-SUMP	KWA-1	MDD-2
As	range	83-85	22-24	30-32	47-49	34-38	39-41	53-57	24-26
	mean	83.67	23.33	30.67	48.33	36.00	40.33	55.00	25.00
	std.	1.15	1.15	1.15	1.15	2.00	1.15	2.00	1.00
Ca	range	1229-1235	476-479	4889-5261	1270-1275	616-619	4615-4622	512-514	1034-1038
	mean	1232	478	5014	1272	618	4618	513	1036
	std.	3.06	1.44	214.20	2.52	1.80	3.61	1.06	2.00
Cd	range	0	0	0	0	0	0.15-0.52	0	0
	mean	0	0	0	0	0.00	0.5133	0.00	0.00
	std.	0	0	0	0	0.00	5.77E-03	0.00	0.00
Cu	range	22.7-24.7	9.3-11.5	26.7-29.3	19-21	8-10	15.6-17.9	62-66	54-57
	mean	23.73	10.10	27.77	19.80	8.93	16.47	63.73	55.47
	std.	1.00	1.22	1.36	1.13	1.10	1.25	1.80	1.48
Fe	range	44000-45032	53490-53500	65550-65552	60495-60500	42900-43802	23000-23002	68000-68102	44800-48805
	mean	44687	53494	65551	60497	43501	23001	68067	47469
	std.	595.25	5.29	1.15	2.52	520.19	1.15	58.32	2311.70
Mn	range	114-116	21.5-23.6	319-322	92-95	50-52	148-149	16.6-19.1	1175-1179
	mean	115.13	22.23	320.33	93.40	51.03	148.80	17.60	1177.00
	std.	1.04	1.18	1.53	1.57	1.18	1.13	1.32	2.00
Pb	range	4.8-7.1	65-67	86.9-90.1	5-7.8	62-64	113-115	6-8	12.6-15.1
	mean	5.67	66.27	88.37	6.20	62.70	114.00	6.80	13.60
	std.	1.25	1.00	1.62	1.44	1.01	1.06	1.13	1.32
Zn	range	130-133	19-21	76-79	31-33	382-390	24-26	32-41	15-17
	mean	131.83	19.90	77.47	31.63	386.50	24.87	36.03	16.20
	std.	1.48	1.13	1.36	1.03	4.44	1.08	5.18	1.00

APPENDIX 1: CONTINUED

Parameter	Statistics	MWD	NKR-1	REX-D1	REX-U2	TAM-1	TAM-2	TOM-3
As	range	40-42	69-71	31-33	43-46	34-36	24-29	30-32
	mean	41.00	69.67	31.67	44.67	35.33	26.67	31.00
	std.	1.00	1.15	1.15	1.53	1.15	2.52	1.00
Ca	range	6590-6602	515.7-5136.4	554.5-558.1	1095-1100	2722-2728	1074-1079	521-523
	mean	6597	3596	556	1098	2725	1077	522
	std.	6.43	2667.20	1.80	2.65	3.06	2.52	1.10
Cd	range	0	0	0	0	0.01-0.02	0	0
	mean	0.00	0	0	0	0.0133	0.00	0
	std.	0.00	0	0	0	5.77E-03	0.00	0
Cu	range	16.9-19.1	40-42	5.9-8.3	18.6-21.1	91-93	9-11	4.7-6.9
	mean	17.70	40.53	6.83	19.60	91.80	9.83	5.50
	std.	1.22	1.04	1.29	1.32	1.01	1.01	1.22
Fe	range	95000-98000	163186-163200	20200-20212	54601-55700	58200-58302	39100-39105	8200-8304
	mean	96001	163191	20207	54968	58267	39103	8268
	std.	1731.50	7.57	6.43	633.93	58.32	2.52	59.20
Mn	range	747-753	47.6-51	12.3-14.3	102-104	528-532	39-41	21-23
	mean	750.33	49.20	13.03	102.63	530.07	39.63	21.37
	std.	3.06	1.71	1.10	1.10	2.05	1.01	1.15
Pb	range	12-14	6.4-8.9	3.4-5.4	5-7	11-13	7.8-9.9	5.4-7.8
	mean	12.73	7.40	4.20	5.67	11.63	8.53	6.33
	std.	1.10	1.32	1.06	1.08	1.10	1.18	1.29
Zn	range	36-38	30.4-32.7	7.5-9.5	26.6-28.8	27-29	9.6-11.7	9-11
	mean	36.80	31.27	8.00	27.40	27.90	10.33	10.07
	std.	1.13	1.25	1.13	1.22	1.00	1.18	1.15

APPENDIX II

METAL CONCENTRATION IN WATER SAMPLES (mg/L)

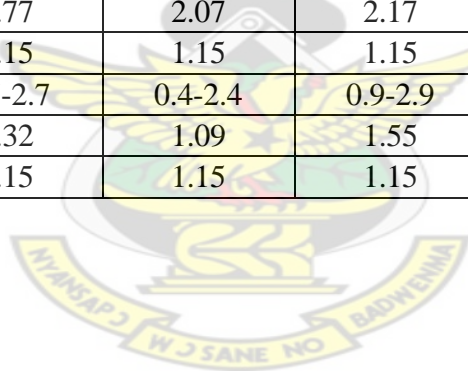
Parameter	Statistics	ABO-STR	ABU-1	ABU-PT	AME O5	AYAS-1	B-SUMP	KWA-1	MDD-2
As	range	21.8-24.4	5.8-8.1	7.7-9.7	13.1-15.8	9.5-10.8	9.5-11.8	14.1-16.8	5.5-7.5
	mean	22.87	6.67	8.43	14.23	10.03	10.37	15.23	6.30
	std.	1.36	1.25	1.10	1.40	0.68	1.25	1.40	1.06
Ca	range	324.5-327.8	130.8-132.8	1139.3-1144.4	287.8-289.8	154.9-157.9	1170.6-1183.3	131.6-134.4	265.1-268.3
	mean	326.03	132.03	1142.00	288.73	156.57	1175.50	132.80	266.57
	std.	1.66	1.08	2.57	1.01	1.53	6.83	1.44	1.62
Cd	range	ND	ND	ND	ND	ND	0.5-0.6	ND	0
	mean	ND	ND	ND	ND	ND	0.57	ND	0.00
	std.	ND	ND	ND	ND	ND	0.06	ND	0.00
Cu	range	5.0-7.0	2.6-4.7	7.0-9.4	5.2-7.2	2.3-4.4	3.5-5.5	14.2-16.2	12.8-14.8
	mean	6.00	3.33	7.93	5.90	3.03	4.30	15.07	13.55
	std.	1.00	1.18	1.29	1.13	1.18	1.06	1.03	1.07
Fe	range	40800-40836	15283-15303	1700.5-17716	12800-12871	11231-11237	5842.2-5897.4	15837-15862	9801-9956
	mean	40813	15295	7040	12825	11234	5861	15853	9853
	std.	20.23	10.84	9246.10	40.43	2.95	31.31	13.89	89.26
Mn	range	27.6-29.6	5.8-7.8	744.2-752.6	24.5-27.2	14.4-17.2	5.4-40.8	4.3-6.3	290.3-294.3
	mean	28.60	6.67	749.13	25.63	15.60	17.87	5.07	292.30
	std.	1.00	1.03	4.39	1.40	1.44	19.89	1.08	2.00
Pb	range	1.3-3.3	15.2-18.2	22.9-24.9	1.4-3.6	16.28-16.36	25.6-27.6	0.7-2.7	3.7-5.9
	mean	2.03	16.53	23.87	2.20	16.33	26.47	1.43	4.50
	std.	1.10	1.53	1.00	1.22	4.44	1.03	1.10	1.22
Zn	range	28.9-31.6	5.3-7.4	17.9-20.4	7.1-9.6	86.3-88.9	6.3-8.5	10-12.6	4.3-6.3
	mean	30.03	6.03	18.90	8.10	87.37	7.10	11.07	5.00
	std.	1.40	1.18	1.32	1.32	1.36	1.22	1.36	1.13

APPENDIX II: CONTINUED

Parameter	Statistics	MWD	NKR-1	REX-D1	REX-U2	TAM-1	TAM-2	TOM-3
As	range	10.3-12.5	18.2-20.4	8.1-10.1	11.3-13.9	8.3-10.3	6.4-8.4	6.8-8.8
	mean	11.10	19.00	8.93	12.37	9.20	7.23	7.63
	std.	1.22	1.22	1.04	1.36	1.01	1.04	1.04
Ca	range	1733.3-1736.8	111-113	123.6-127.2	255.6-258.2	708.6-716.3	250.5-254.4	124-128
	mean	1735.20	111.87	125.33	256.67	711.83	252.43	126.00
	std.	1.74	1.03	1.80	1.36	4.00	1.95	2.00
Cd	range	ND	ND	ND	ND	ND	ND	0
	mean	ND	ND	ND	ND	ND	ND	0.00
	std.	ND	ND	ND	ND	ND	ND	0.00
Cu	range	4.4-6.4	10.1-12.1	1.6-3.6	5.0-8.0	23.3-26.2	51.6-53.6	1.4-3.6
	mean	5.10	10.90	2.33	6.33	24.57	52.57	2.20
	std.	1.13	1.06	1.10	1.53	1.48	1.00	1.22
Fe	range	21590-21602	33286-33303	4586.3-4593.2	13300-13317	1766.2-1772.8	9760-9775.8	12660-126731
	mean	21597	33293	4589	13306	1770	9766	50685
	std.	6.43	9.29	3.55	9.46	3.38	8.60	65858.00
Mn	range	206.9-208.9	11.8-13.8	3.2-5.2	27.6-29.6	5.0-8.0	9.9-12.4	115.2-118.4
	mean	208.13	12.83	4.07	28.50	6.33	10.90	116.67
	std.	1.08	1.00	1.03	1.01	1.53	1.32	1.62
Pb	range	3.3-5.4	1.9-4.2	1.4-3.6	1.5-3.5	1.6-3.6	2.4-4.6	2.9-5.1
	mean	4.03	2.77	2.20	2.20	2.30	3.20	3.70
	std.	1.18	1.25	1.22	1.13	1.13	1.22	1.22
Zn	range	10.3-12.6	7.5-9.6	2.2-4.3	72-9.4	2.8-5.2	2.8-4.8	7.4-9.4
	mean	11.17	8.23	2.93	8.00	3.73	3.53	8.13
	std.	1.25	1.18	1.18	1.22	1.29	1.10	1.10

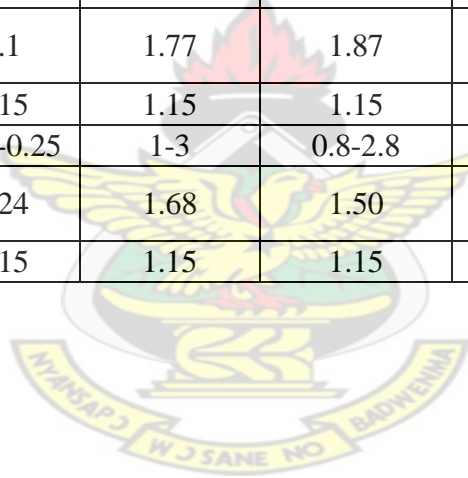
APPENDIX III A: PHYSICOCHEMICAL PROPERTIES OF SEDIMENT SAMPLES

Parameter	Statistics	ABO-STR	ABU-1	ABU-PT	AME O5	AYAS-1	B-SUMP	KWA-1
pH	range	7.9-9.8	8.2-10.2	8.3-10.3	7.8-9.8	6.3-8.3	9.1-11.1	8.4-10.4
	mean	8.53	8.90	8.94	8.48	6.99	10.1	9.02
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Conductivity ($\mu\text{S}/\text{cm}$)	range	241-243	461-463	620-622	270-271	246-248	610-612	306-308
	mean	241.17	461.97	620.97	270.13	246.87	611.07	307.07
	std.	1.15	1.15	1.15	0.58	1.15	1.15	1.15
Bulk density (g/cm^3)	range	1.4-3.4	1.1-3.1	1.4-3.4	1.5-3.5	1.3-3.3	1.3-3.3	1.6-3.6
	mean	2.07	1.77	2.07	2.17	1.97	1.97	2.27
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Organic Matter (%)	range	0.5-2.5	0.7-2.7	0.4-2.4	0.9-2.9	0.5-2.5	0.4-2.42	0.3-2.3
	mean	1.20	1.32	1.09	1.55	1.19	1.09	1.01
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15



APPENDIX III A: CONTINUED

Parameter	Statistics	MDD-2	MWD	NKR-1	REX-D1	REX-U2	TAM-1	TAM-2	TOM-3
pH	range	7.9-9.9	7.4-7.9	4.7-6.7	8.1-10.1	7.9-9.9	6.9-8.9	8.2-10.2	8.2-10.2
	mean	8.56	7.7	5.36	9.3	8.59	7.58	8.91	8.88
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Conductivity ($\mu\text{S}/\text{cm}$)	range	286-288	285-288	180-182	403-405	392-394	275-277	196-198	422-424
	mean	286.87	286.5	181.07	403.57	392.17	275.87	196.87	422.27
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Bulk density (g/cm^3)	range	1.1-3.1	1.0-1.2	1-3	1.2-3.2	1.4-3.4	1.3-3.3	1.5-3.5	1.4-3.4
	mean	1.77	1.1	1.77	1.87	2.07	1.97	2.17	2.07
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Organic matter (%)	range	0.2-2.2	0.21-0.25	1-3	0.8-2.8	1.2-3.2	1.0-3.0	0.1-2.1	0.67-2.67
	mean	0.91	0.24	1.68	1.50	1.88	1.68	0.78	1.34
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15



APPENDIX III B: SEDIMENT TEXTURE

Sample	Silt	Clay	Sand	Soil Texture
ABO-STR	48	40	12	silt
ABU-1	10	50	40	clay
ABU-PT	95	2	3	silt
AME-02	5	38	57	sandy
AYAS-1	20	75	5	clay
B-SOMP	90	4	6	silt
KWA-1	85	7	8	silt
MDD	85	8	7	silt
MWD	82	5	13	silt
NKR-1	92	7	1	silt
TAM-1	88	6	6	silt
TAM-2	15	45	40	clay
TOM-3	25	52	23	clay
REX-UI	10	40	50	sandy
REX-U2	18	55	27	clay

APPENDIX IV

PHYSICOCHEMICAL PROPERTIES OF WATER SAMPLES

Parameter	Statistics	ABO-STR	ABU-1	ABU-PT	AME O5	AYAS-1	B-SOMP	KWA-1	MDD-2
Temperature (°C)	range	25.4-27.4	25.5-27.5	29.1-31.1	23.8-25.8	24.5-26.5	29-31	23.9-25.9	27.6-29.6
	mean	26.07	26.17	29.77	24.47	25.17	30.47	24.57	28.27
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15
pH	range	7.3-9.3	7.7-9.7	8.5-10.5	6.6-8.6	7.7-9.7	6.9-8.9	6.9-8.9	7.2-9.2
	mean	7.92	8.37	9.17	7.28	8.37	7.57	7.57	7.87
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15
D/O (mg/L)	range	2.6-4.6	3.1-5.1	4.5-6.5	1.1-3.1	1.6-3.6	6.6-8.6	1.1-3.1	3.6-5.6
	mean	3.27	3.77	5.17	1.77	2.27	7.27	1.77	4.27
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Conductivity (µs/cm)	range	132-134	229-231	405-407	167-169	71-73	970-972	160-162	980-982
	mean	132.67	229.67	405.67	167.67	71.67	970.67	160.67	980.67
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Alkalinity (mg/L)	range	0-2	0-2	0-2	0-2	0-2	90-92	0-2	700-702
	mean	0.67	0.67	0.67	0.67	0.67	90.67	0.67	700.67
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15
THD(mg/l)	range	29.8-31.8	98-100	211.213	0-2	0-2	355-357	36-38	171-173
	mean	30.47	98.67	211.77	0.67	0.67	356.57	36.87	171.67
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Sulphate (mg/L)	range	10-12	7-9	5-7	7-9	22-24	3-5	18-20	9-11
	mean	10.67	7.67	5.67	7.67	22.67	3.67	18.67	9.67
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Nitrate (mg/L)	range	0.06-0.08	0.06-0.08	0.06-0.08	1.24-1.26	0.06-0.08	11.6-11.8	0.06-0.08	51-53
	mean	0.07	0.07	0.07	1.25	0.07	11.67	0.07	52.17
	std.	0.01	0.01	0.01	0.01	0.01	0.12	0.01	1.15
Nitrite(mg/L)	range	0.05-0.07	0.05-0.07	0.05-0.07	0.05-0.07	0.05-0.07	0.05-0.07	0.05-0.07	0.24-0.26
	mean	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.25
	std.	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fluoride (mg/L)	range	0.2-0.4	0.1-0.2	0.16-0.18	0.33-0.35	0.15-0.17	0.09-0.11	0.35-0.37	0.32-0.34
	mean	0.27	0.20	0.17	0.34	0.16	0.10	0.36	0.33
	std.	0.12	0.01	0.01	0.01	0.01	0.01	0.01	0.01
TDS (mg/L)	range	5156-5158	4643-4645	1481-1483	2311-2313	1088-1090	725-727	367-369	340-342
	mean	5156.70	4644.00	1481.30	2311.20	1089.10	725.77	367.67	340.87
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Turbidity(NTU)	range	6.9-8.9	1.6-3.6	1.5-3.5	13.6-15.6	47.6-49.6	12.6-14.6	46-48	15-17
	mean	7.61	2.28	2.16	14.26	48.22	13.31	46.69	15.90
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15

APPENDIX IV: CONTINUED

Parameter	Statistics	MWD	NKR-1	REX-D1	REX-U2	TAM-1	TAM-2	TOM-3
Temperature (°C)	range	30-32	23-25	28.6-30.6	23.8-25.8	27-29	24.7-26.7	21.9-23.9
	mean	30.67	24.07	29.27	24.47	27.77	25.37	22.57
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15
pH	range	8.2-10.2	6.8-8.8	6.7-8.7	6.6-8.6	7.1-9.1	6.6-8.6	6.9-8.9
	mean	8.87	7.47	7.37	7.29	7.77	7.27	7.57
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15
DO (mg/L)	range	5.2-7.2	1.8-3.8	2.4-4.4	3.2-5.2	4.5-6.5	4.4-6.4	2.2-4.2
	mean	5.87	2.47	3.07	3.87	5.17	5.07	2.87
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Conductivity (µs/cm)	range	899-900	170-172	44-46	120-122	133-135	550-552	88-90
	mean	899.33	170.67	44.67	120.67	133.67	550.67	88.67
	std.	0.58	1.15	1.15	1.15	1.15	1.15	1.15
Alkalinity (mg/L)	range	0-2	0-2	0-2	0-2	0-2	0-2	0-2
	mean	0.67	0.67	0.67	0.67	0.67	0.67	0.67
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15
THD(mg/l)	range	294-296	124-126	32-34	0-2	79.4-81.4	240-242	0-2
	mean	294.77	124.87	32.87	0.67	80.07	240.97	0.67
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Sulphate (mg/L)	range	5-7	8-10	22-24	4-6	3-5	13-15	5-7
	mean	5.67	8.67	22.67	4.67	3.67	13.67	5.67
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15
Nitrate (mg/L)	range	21-23	0.06-0.08	0.45-0.47	0.06-0.08	0.06-0.08	2.3-2.4	0.06-0.08
	mean	22.07	0.07	0.46	0.07	0.07	2.34	0.07
	std.	1.15	0.01	0.01	0.01	0.01	0.01	0.01
Nitrite(mg/L)	range	0.39-0.41	0.05-0.07	0.07-0.9	0.05-0.07	1.0-1.1	0.05-0.07	0.05-0.07
	mean	0.40	0.06	0.08	0.06	1.05	0.06	0.06
	std.	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fluoride (mg/L)	range	0.08-0.10	0.09-0.11	0.15-0.17	0.05-0.07	0.22-0.24	0.1-0.3	0.16-0.18
	mean	0.09	0.10	0.16	0.06	0.23	0.17	0.17
	std.	0.01	0.01	0.01	0.01	0.01	0.12	0.01
TDS (mg/L)	range	4577-4581	2302-2304	3113-3115	2251-2253	721-723	588-590	3655-3657
	mean	4577.80	2302.80	3113.60	2251.80	721.27	589.07	3655.90
	std.	2.31	1.15	1.15	1.15	1.15	1.15	1.15
Turbidity(NTU)	range	2.5-4.5	33-35	15.7-17.7	8.3-10.3	1.5-3.5	1.5-3.5	3.68-5.68
	mean	3.18	33.65	16.37	8.99	2.13	2.20	4.35
	std.	1.15	1.15	1.15	1.15	1.15	1.15	1.15

APPENDIX V

The Physicochemical Parameters of Water and WHO ACCEPTABLE STANDARDS

PARAMETERS	RANGE	WHO LIMITS(2006)
pH	6.6-10.5	6.5 - 8.5
Temperature (°C)	21.9-31.1	-
EC ($\mu\text{s}/\text{cm}$)	44-982	700
TDS (mg/L)	721-5158	20
TSS (mg/L)	0-15	1000
Ca-Hard (mg/L)		500
DO (mg/L)	1.1-8.6	-
F (mg/L)	0.05-0.4	1.5
T-Alk (mg/L)	0-702	400
SO_4^{2-} (mg/L)	3-24	250
$\text{NO}^2\text{-N}$ (mg/L)	0.05-1	3
$\text{NO}^3\text{-N}$ (mg/L)	0.06-53	50
Turbidity (NTU)	1.5-49.6	5

APPENDIX VI

ANOVA TABLE FOR HEAVY METALS IN SEDIMENTS

DESCRIPTIVE STATISTICS

Variable	Mean	SD	Minimum	Median	Maximum
As	41.489	16.611	22.000	36.000	85.000
Ca	2063.4	2010.4	476.30	1095.0	6602.0
Cd	0.0347	0.1285	0.0000	0.0000	0.5100
Cu	27.853	24.268	4.7000	19.100	92.900
Fe	56418	35663	8200.0	53492	163200
Mn	230.12	330.32	12.300	93.100	1179.0
Pb	28.007	35.220	3.4000	8.9000	114.80
Zn	58.427	93.898	7.5000	28.800	390.00

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Completely Randomized ANOVA for As

Source	DF	SS	MS	F	P
Sample	14	12080.6	862.898	426.71	0.0000
Error	30	60.7	2.022		
Total	44	12141.2			

Grand Mean 41.489 CV 3.43

Sample	Mean	Sample	Mean
ABO-STR	83.667	MWD	41.000
ABU-1	23.333	NKR-1	69.667
ABU-PT	30.667	REX-D1	31.667
AME-05	48.333	REX-U2	44.667
AYAS-1	36.000	TAM-3	35.333
B-SUMP	40.333	TOM-1	26.667
KWA-1	55.000	TOM-3	31.000
MDD-2	25.000		

Standard Error of a Mean 0.8210

Std Error (Diff of 2 Means) 1.1611

Completely Randomized ANOVA for Ca

Source	DF	SS	MS	F	P
Sample	14	1635.08	116.78	2.46	0.0000
Error	30	1432.07	47.73		
Total	44	3067.16			
Grand Mean	2063.4	CV 33.48			

Sample	Mean	Sample	Mean
ABO-STR	1232.3	MWD	6597.3
ABU-1	477.5	NKR-1	3595.5
ABU-PT	5013.7	REX-D1	556.2
AME-05	1272.3	REX-U2	1098.0
AYAS-1	617.6	TAM-3	2724.7
B-SUMP	4618.0	TOM-1	1076.7
KWA-1	513.2	TOM-3	522.0
MDD-2	1036.0		
Standard Error of a Mean	398.88		
Std Error (Diff of 2 Means)	564.11		

Completely Randomized ANOVA for Cd

Source	DF	SS	MS	F	P
Sample	14	0.73559	0.05254	11822.0	0.0000
Error	30	0.00013	4.444E-06		
Total	44	0.73572			
Grand Mean	0.0351	CV 6.00			

Sample	Mean	Sample	Mean
ABO-STR	0.0000	MWD	0.0000
ABU-1	0.0000	NKR-1	0.0000
ABU-PT	0.0000	REX-D1	0.0000
AME-05	0.0000	REX-U2	0.0000
AYAS-1	0.0000	TAM-3	0.0133
B-SUMP	0.5133	TOM-1	0.0000
KWA-1	0.0000	TOM-3	0.0000
MDD-2	0.0000		

Standard Error of a Mean 1.217E-03
 Std Error (Diff of 2 Means) 1.721E-03

Completely Randomized ANOVA for Cu

Source	DF	SS	MS	F	P
Sample	14	25865.7	1847.55	1187.88	0.0000
Error	30	46.7	1.56		
Total	44	25912.4			

Grand Mean 27.853 CV 4.48

Sample	Mean	Sample	Mean
ABO-STR	23.733	MWD	17.700
ABU-1	10.100	NKR-1	40.533
ABU-PT	27.767	REX-D1	6.833
AME-05	19.800	REX-U2	19.600
AYAS-1	8.933	TAM-3	91.800
B-SUMP	16.467	TOM-1	9.833
KWA-1	63.733	TOM-3	5.500
MDD-2	55.467		

Standard Error of a Mean 0.7200
Std Error (Diff of 2 Means) 1.0183

Completely Randomized ANOVA for Fe

Source	DF	SS	MS	F	P
Sample	14	5.594E+10	3.996E+09	6390.65	0.0000
Error	30	1.876E+07	625283		
Total	44	5.596E+10			

Grand Mean 56418 CV 1.40

Sample	Mean	Sample	Mean
ABO-STR	44687	MWD	96001
ABU-1	53494	NKR-1	163191
ABU-PT	65551	REX-D1	20207
AME-05	60497	REX-U2	54968
AYAS-1	43501	TAM-3	58267
B-SUMP	23001	TOM-1	39103
KWA-1	68067	TOM-3	8268
MDD-2	47469		

Standard Error of a Mean 456.54
Std Error (Diff of 2 Means) 645.64

Completely Randomized ANOVA for Mn

Source	DF	SS	MS	F	P
Sample	14	4800797	342914	139232	0.0000
Error	30	74	2		
Total	44	4800871			

Grand Mean 230.12 CV 0.68

Sample	Mean	Sample	Mean
ABO-STR	115.1	MWD	750.3
ABU-1	22.2	NKR-1	49.2
ABU-PT	320.3	REX-D1	13.0
AME-05	93.4	REX-U2	102.6
AYAS-1	51.0	TAM-3	530.1
B-SUMP	148.8	TOM-1	39.6
KWA-1	17.6	TOM-3	21.4
MDD-2	1177.0		

Standard Error of a Mean 0.9061
Std Error (Diff of 2 Means) 1.2814

Completely Randomized AOV for Pb

Source	DF	SS	MS	F	P
Sample	14	54534.9	3895.35	2662.37	0.0000
Error	30	43.9	1.46		
Total	44	54578.8			

Grand Mean 28.007 CV 4.32

Sample	Mean	Sample	Mean
ABO-STR	5.67	MWD	12.73
ABU-1	66.27	NKR-1	7.40
ABU-PT	88.37	REX-D1	4.20
AME-05	6.20	REX-U2	5.67
AYAS-1	62.70	TAM-3	11.63
B-SUMP	114.00	TOM-1	8.53
KWA-1	6.80	TOM-3	6.33
MDD-2	13.60		

Standard Error of a Mean 0.6984
Std Error (Diff of 2 Means) 0.9876

Completely Randomized ANOVA for Zn

Source	DF	SS	MS	F	P
Sample	14	387811	27700.8	6449.38	0.0000
Error	30	129	4.3		
Total	44	387940			

Grand Mean 58.427 CV 3.55

Sample	Mean	Sample	Mean
ABO-STR	131.83	MWD	36.80
ABU-1	19.90	NKR-1	31.27
ABU-PT	77.47	REX-D1	8.20
AME-05	31.63	REX-U2	27.40
AYAS-1	386.50	TAM-3	27.90
B-SUMP	24.87	TOM-1	10.33
KWA-1	36.03	TOM-3	10.07
MDD-2	16.20		

Standard Error of a Mean 1.1965
Std Error (Diff of 2 Means) 1.6922



APPENDIX VII

ANOVA TABLE FOR HEAVY METALS IN WATER SAMPLES

Descriptive Statistics

Variable	Mean	SD	Minimum	Median	Maximum
As	11.307	4.7387	5.5000	9.8000	24.400
Ca	462.64	487.60	111.00	256.20	1736.8
Cd	0.0378	0.1435	0.0000	0.0000	0.6000
Cu	10.875	12.752	1.4000	6.0000	53.600
Fe	16919	19745	1700.5	12800	126731
Mn	101.89	193.90	3.2000	17.200	752.60
Pb	115.36	410.27	0.7000	3.5000	1636.5
Zn	14.622	20.821	2.2000	7.6000	88.900

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Completely Randomized ANOVA for As

Source	DF	SS	MS	F	P
Sample	14	946.455	67.6039	48.76	0.0000
Error	30	41.593	1.3864		
Total	44	988.048			

Grand Mean 11.307 CV 10.41

Sample	Mean	Sample	Mean
ABO-STR	22.867	MWD	11.100
ABU-1	6.667	NKR-1	19.000
ABU-PT	8.433	REX-D1	8.933
AME-05	14.233	REX-U2	12.367
AYAS-1	10.033	TAM-3	9.200
B-SUMP	10.367	TOM-1	7.233
KWA-1	15.233	TOM-3	7.633
MDD-2	6.300		

Standard Error of a Mean 0.6798

Std Error (Diff of 2 Means) 0.9614

Completely Randomized ANOVA for Ca

Source	DF	SS	MS	F	P
Sample	14	1.046E+07	747221	114203	0.0000
Error	30	196.288	7		
Total	44	1.046E+07			

Grand Mean 462.64 CV 0.55

Sample	Mean	Sample	Mean
ABO-STR	326.0	MWD	1735.2
ABU-1	132.0	NKR-1	111.9
ABU-PT	1142.0	REX-D1	125.3
AME-05	288.7	REX-U2	256.7
AYAS-1	156.6	TAM-3	711.8
B-SUMP	1175.5	TOM-1	252.4
KWA-1	132.8	TOM-3	126.0
MDD-2	266.6		

Standard Error of a Mean 1.4768
Std Error (Diff of 2 Means) 2.0885

Completely Randomized ANOVA for Cd

Source	DF	SS	MS	F	P
Sample	14	0.89911	0.06422	289.00	0.0000
Error	30	0.00667	0.00022		
Total	44	0.90578			

Grand Mean 0.0378 CV 39.46

Sample	Mean	Sample	Mean
ABO-STR	0.0000	MWD	0.0000
ABU-1	0.0000	NKR-1	0.0000
ABU-PT	0.0000	REX-D1	0.0000
AME-05	0.0000	REX-U2	0.0000
AYAS-1	0.0000	TAM-3	0.0000
B-SUMP	0.5667	TOM-1	0.0000
KWA-1	0.0000	TOM-3	0.0000
MDD-2	0.0000		

Standard Error of a Mean 8.607E-03
Std Error (Diff of 2 Means) 0.0122

Completely Randomized ANOVA for Cu

Source	DF	SS	MS	F	P
Sample	14	7114.09	508.149	368.57	0.0000
Error	30	41.36	1.379		
Total	44	7155.45			

Grand Mean 10.875 CV 10.80

Sample	Mean	Sample	Mean
ABO-STR	6.000	MWD	5.100
ABU-1	3.333	NKR-1	10.900
ABU-PT	7.933	REX-D1	2.333
AME-05	5.900	REX-U2	6.333
AYAS-1	3.033	TAM-3	24.567
B-SUMP	4.300	TOM-1	52.567
KWA-1	15.067	TOM-3	2.200
MDD-2	13.553		

Standard Error of a Mean 0.6779
Std Error (Diff of 2 Means) 0.9587

Completely Randomized ANOVA for Fe

Source	DF	SS	MS	F	P
Sample	14	8.308E+09	5.934E+08	2.01	0.0529
Error	30	8.846E+09	2.949E+08		
Total	44	1.715E+10			

Grand Mean 16919 CV 101.49

Sample	Mean	Sample	Mean
ABO-STR	40813	MWD	21597
ABU-1	15295	NKR-1	33293
ABU-PT	7040	REX-D1	4589
AME-05	12825	REX-U2	13306
AYAS-1	11234	TAM-3	1770
B-SUMP	5861	TOM-1	9766
KWA-1	15853	TOM-3	50685
MDD-2	9853		

Standard Error of a Mean 9913.9
Std Error (Diff of 2 Means) 14020

Completely Randomized ANOVA for Mn

Source	DF	SS	MS	F	P
Sample	14	1653352	118097	4054.46	0.0000
Error	30	874	29		
Total	44	1654226			

Grand Mean 101.89 CV 5.30

Sample	Mean	Sample	Mean
ABO-STR	28.60	MWD	208.13
ABU-1	6.67	NKR-1	12.83
ABU-PT	749.13	REX-D1	4.07
AME-05	25.63	REX-U2	28.50
AYAS-1	15.60	TAM-3	6.33
B-SUMP	17.87	TOM-1	10.90
KWA-1	5.07	TOM-3	116.67
MDD-2	292.30		

Standard Error of a Mean 3.1160
Std Error (Diff of 2 Means) 4.4066

Completely Randomized ANOVA for Pb

Source	DF	SS	MS	F	P
Sample	14	7406100	529007	201024	0.0000
Error	30	79	3		
Total	44	7406179			

Grand Mean 115.36 CV 1.41

Sample	Mean	Sample	Mean
ABO-STR	2.0	MWD	4.0
ABU-1	16.5	NKR-1	2.8
ABU-PT	23.9	REX-D1	2.2
AME-05	2.2	REX-U2	2.2
AYAS-1	1633.0	TAM-3	2.3
B-SUMP	26.5	TOM-1	3.2
KWA-1	1.4	TOM-3	3.7
MDD-2	4.5		

Standard Error of a Mean 0.9366
Std Error (Diff of 2 Means) 1.3245

Completely Randomized ANOVA for Zn

Source	DF	SS	MS	F	P
Sample	14	19027.7	1359.12	876.73	0.0000
Error	30	46.5	1.55		
Total	44	19074.2			

Grand Mean 14.622 CV 8.51

Sample	Mean	Sample	Mean
ABO-STR	30.033	MWD	11.167
ABU-1	6.033	NKR-1	8.233
ABU-PT	18.900	REX-D1	2.933
AME-05	8.100	REX-U2	8.000
AYAS-1	87.367	TAM-3	3.733
B-SUMP	7.100	TOM-1	3.533
KWA-1	11.067	TOM-3	8.133
MDD-2	5.000		

Standard Error of a Mean 0.7188
Std Error (Diff of 2 Means) 1.0166



APPENDIX VIII

EPA/WHO/GWC FOR WATER SAMPLES

METALS	EPA (mg/kg)	WHO (mg/kg)	GSB (mg/kg)
AS	0.1	0.01	0.01
Ca		0.1	
Cd	0.1	0.003	0.003
Cu	5	2	1
Fe	10	0.3	0.3
Mn		0.5	0.5
Pb	0.1	0.01	0.01
Zn	10	3	3



APPENDIX IX

GEO-ACCUMULATION INDEX (I_{geo}) OF ARSENIC AND HEAVY METALS

ARSENIC(As)			
SAMPLE LOCATIONS	MEAN VALUES	(I_{geo})	POLLUTION INTENSITY
ABO-STR	83.67	2.10	Moderately polluted
ABU-1	23.33	0.26	Unpolluted
ABU-PT	30.67	0.65	Unpolluted
AME-05	48.33	1.31	Moderately polluted
AYAS-1	36.00	0.89	Unpolluted
B-SUMP	40.33	1.05	Moderately polluted
KWA-1	55.00	1.5	Moderately polluted
MDD-2	25.00	0.36	Unpolluted
MWD	41.00	1.07	Moderately polluted
NKR-1	69.67	0.7	Unpolluted
REX-D1	31.67	1.2	Moderately polluted
REX-U2	44.67	0.87	Unpolluted
TAM-1	35.33	0.45	Unpolluted
TAM-2	26.67	0.7	Unpolluted
TOM-3	31.00	1.84	Moderately polluted

CAICIUM(Ca)			
SAMPLE LOCATIONS	MEAN VALUES	(I_{geo})	POLLUTION INTENSITY
ABO-STR	1232	9	Very highly polluted
ABU-1	478	7.64	Very highly polluted
ABU-PT	5014	11.03	Very highly polluted
AME-05	1272	9.05	Very highly polluted
AYAS-1	618	8.01	Very highly polluted
B-SUMP	4618	10.91	Very highly polluted
KWA-1	513	7.74	Very highly polluted
MDD-2	1036	8.75	Very highly polluted
MWD	6597	11.43	Very highly polluted
NKR-1	3596	10.55	Very highly polluted
REX-D1	556	7.86	Very highly polluted
REX-U2	1098	8.84	Very highly polluted
TAM-1	2725	10.15	Very highly polluted
TAM-2	1077	8.81	Very highly polluted
TOM-3	522	7.77	Very highly polluted

CADMIUM(Cd)			
SAMPLE LOCATIONS	MEAN VALUES	(I_{geo})	POLLUTION INTENSITY
ABO-STR	0	-	Unpolluted
ABU-1	0	-	Unpolluted
ABU-PT	0	-	Unpolluted
AME-05	0	-	Unpolluted
AYAS-1	0	-	Unpolluted
B-SUMP	0.57	0.34	Unpolluted
KWA-1	0	-	Unpolluted
MDD-2	0	-	Unpolluted
MWD	0	-	Unpolluted
NKR-1	0	-	Unpolluted
REX-D1	0	-	Unpolluted
REX-U2	0	-	Unpolluted
TAM-1	0.33	0.45	Unpolluted
TAM-2	0	-	Unpolluted
TOM-3	0	-	Unpolluted

COPPER(Cu)			
SAMPLE LOCATIONS	MEAN VALUES	(I_{geo})	POLLUTION INTENSITY
ABO-STR	23.73	-1.50	Unpolluted
ABU-1	10.10	-2.74	Unpolluted
ABU-PT	27.77	-1.28	Unpolluted
AME-05	19.80	-1.77	Unpolluted
AYAS-1	8.93	-2.92	Unpolluted
B-SUMP	16.47	-2.04	Unpolluted
KWA-1	63.73	-0.08	Unpolluted
MDD-2	55.47	-0.28	Unpolluted
MWD	17.70	-1.93	Unpolluted
NKR-1	40.53	-0.73	Unpolluted
REX-D1	6.83	-3.31	Unpolluted
REX-U2	19.60	-1.78	Unpolluted
TAM-1	91.80	0.44	Unpolluted
TAM-2	9.83	-2.78	Unpolluted
TOM-3	5.53	-3.62	Unpolluted

IRON(Fe)			
SAMPLE LOCATIONS	MEAN VALUES	(I_{geo})	POLLUTION INTENSITY
ABO-STR	44687	12.62	Very highly polluted
ABU-1	53494	12.88	Very highly polluted
ABU-PT	65551	13.18	Very highly polluted
AME-05	60497	13.06	Very highly polluted
AYAS-1	43501	12.59	Very highly polluted
B-SUMP	23001	11.67	Very highly polluted
KWA-1	68067	13.23	Very highly polluted
MDD-2	47469	12.71	Very highly polluted
MWD	96001	13.73	Very highly polluted
NKR-1	163191	14.49	Very highly polluted
REX-D1	20207	11.43	Very highly polluted
REX-U2	54968	12.93	Very highly polluted
TAM-1	58267	13.01	Very highly polluted
TAM-2	39103	12.43	Very highly polluted
TOM-3	8268	10.19	Very highly polluted

MANGANESE(Mn)			
SAMPLE LOCATIONS	MEAN VALUES	(I_{geo})	POLLUTION INTENSITY
ABO-STR	115.13	-3.47	Unpolluted
ABU-1	22.23	-5.83	Unpolluted
ABU-PT	320.33	-1.99	Unpolluted
AME-05	93.40	-3.77	Unpolluted
AYAS-1	51.05	-4.65	Unpolluted
B-SUMP	148.80	-3.1	Unpolluted
KWA-1	17.60	-6.18	Unpolluted
MDD-2	1177.00	-0.12	Unpolluted
MWD	750.37	-0.77	Unpolluted
NKR-1	49.20	-4.7	Unpolluted
REX-D1	13.03	-6.61	Unpolluted
REX-U2	102.63	-3.64	Unpolluted
TAM-1	530.63	-1.27	Unpolluted
TAM-2	39.63	-5.01	Unpolluted
TOM-3	21.37	-5.9	Unpolluted

LEAD(Pb)			
SAMPLE LOCATIONS	MEAN VALUES	(I_{geo})	POLLUTION INTENSITY
ABO-STR	5.67	-2.40	Unpolluted
ABU-1	66.27	1.14	Moderately polluted
ABU-PT	88.37	1.56	Moderately polluted
AME-05	6.20	-2.27	Unpolluted
AYAS-1	62.70	1.06	Moderately polluted
B-SUMP	114.00	1.93	Moderately polluted
KWA-1	6.80	-2.14	Unpolluted
MDD-2	13.60	-1.14	Unpolluted
MWD	12.73	-1.24	Unpolluted
NKR-1	7.40	-2.02	Unpolluted
REX-D1	4.20	-2.84	Unpolluted
REX-U2	5.67	-2.40	Unpolluted
TAM-1	11.63	-1.36	Unpolluted
TAM-2	8.53	-1.81	Unpolluted
TOM-3	6.33	-2.24	Unpolluted

ZINC(Zn)			
SAMPLE LOCATIONS	MEAN VALUES	(I_{geo})	POLLUTION INTENSITY
ABO-STR	131.83	-0.1	Unpolluted
ABU-1	19.90	-2.84	Unpolluted
ABU-PT	77.47	-0.87	Unpolluted
AME-05	31.63	-2.17	Unpolluted
AYAS-1	386.50	1.44	Unpolluted
B-SUMP	24.87	-2.52	Unpolluted
KWA-1	36.03	-1.98	Unpolluted
MDD-2	16.20	-3.13	Unpolluted
MWD	36.80	-1.95	Unpolluted
NKR-1	31.27	-2.18	Unpolluted
REX-D1	8.20	-4.12	Unpolluted
REX-U2	27.40	-2.37	Unpolluted
TAM-1	27.90	-2.35	Unpolluted
TAM-2	10.33	-3.78	Unpolluted
TOM-3	10.07	-3.82	Unpolluted