

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY
INSTITUTE OF DISTANCE LEARNING

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**ASSESSMENT OF HEAVY METAL CONTAMINATION IN WATER,
SEDIMENT AND FISH FROM THE JIMI RESERVOIR, OBUASI**



KWAME ASANTE

NOVEMBER 2013

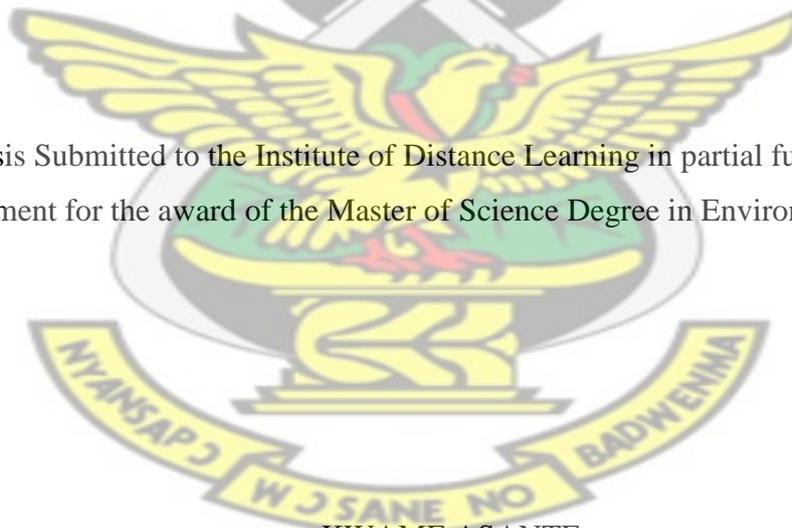
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**ASSESSMENT OF HEAVY METAL CONTAMINATION IN WATER,
SEDIMENT AND FISH FROM THE JIMI RESERVOIR, OBUASI**

A Thesis Submitted to the Institute of Distance Learning in partial fulfillment of the requirement for the award of the Master of Science Degree in Environmental Science



KWAME ASANTE

NOVEMBER, 2013

DECLARATION

I declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the qualification of any other degree or diploma of a university or other institution of higher learning, except where due acknowledgement is made

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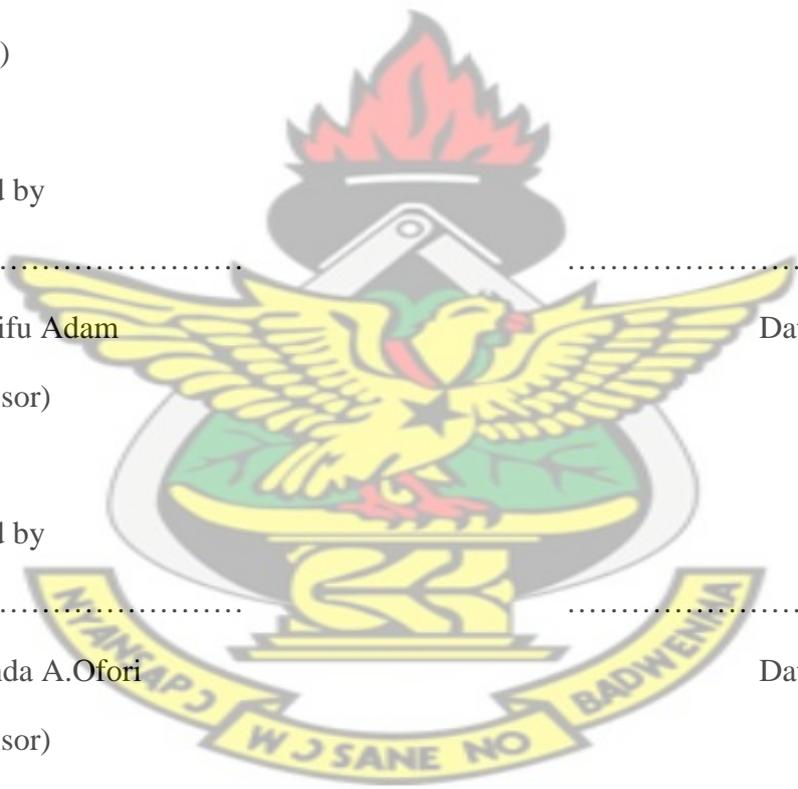
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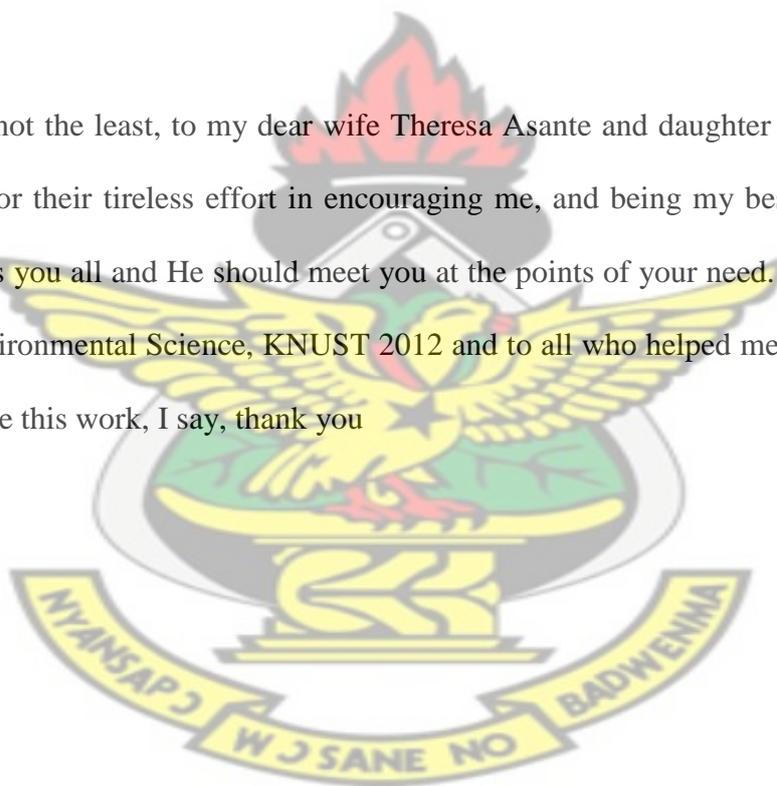


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ABSTRACT

This study was carried out to assess the levels of four heavy metals, Arsenic (As), Copper (Cu), Lead (Pb) and Cadmium (Cd) in the water, sediment and fish of the Jimi Dam in Obuasi over a four-month period from April to July, 2012. Heavy metal concentrations in the water were found to be very low, and in the cases of Arsenic and Cadmium, concentrations were found to be in trace amount and below detection. Mean Lead concentrations were however found to be well above the WHO, Drinking Water Quality Guideline Value of 0.01 mgL^{-1} . The recorded Lead concentrations at some sampling stations were as much as approximately 10 times higher than the regulatory standard. Copper levels at all the sampling stations on the other hand were found to be low throughout the study period. The study also revealed very highly measurable concentrations of the studied heavy metals, especially in the bottom sediments and in the flesh of the two sampled fish species *Tilapia zillii* and *Oreochromis niloticus* harvested from the Dam. With the exception of Lead, all the heavy metal concentrations in the bottom sediments of the Dam were found to be above the USEPA Safety Reference Standards for all or some of the sampling month. Arsenic concentrations in the bottom sediments at all the sampling stations were all well-above the threshold value of 30 mgkg^{-1} . The mean Arsenic concentrations at some of the sampling station were almost 3 times higher than the safety reference standard. Cadmium levels recorded in the bottom sediments were above the Safety Reference Value of 3 mgkg^{-1} at all the sampling points and fell within the levels for moderately polluted sites. The fish samples of the two species were categorized into two size classes, small (<10cm) and large (>10cm) for the metal analysis. The observed metal concentrations in the bottom sediments and fish were similar to those observed in areas under moderate to heavy pollution. The concentrations of As, Cu

and Pb in the flesh of the two fish species were found to be above safety reference standards for human consumption stipulated by the WHO, and hence can pose a serious health threat to people who consume the fish from the Dam. Mean As concentrations in the flesh of the *Tilapia zillii* ranged from 15.83 ± 0.19 to 16.35 ± 0.07 mgkg^{-1} for the small size group and 16.05 ± 0.21 to 26.65 ± 0.35 for the large size class. As concentrations in the flesh of the *Oreochromis* were similar to the concentrations in the *Tilapia zillii* and ranged from 10.65 ± 0.49 to 12.60 ± 0.14 mgkg^{-1} for the small size class and 15.45 ± 0.21 to 27.30 ± 0.57 mgkg^{-1} for the large size class. Mean Copper concentrations in the flesh of the *Tilapia zillii* was found to range from 9.55 ± 0.77 to 11.35 ± 0.07 mgkg^{-1} and 8.30 ± 0.00 to 11.70 ± 0.56 mgkg^{-1} for the small and large size classes respectively. Copper in the flesh of the *Oreochromis* ranged from 10.65 ± 0.49 to 12.60 ± 0.14 mgkg^{-1} and from 13.10 ± 0.14 to 13.30 ± 0.14 mgkg^{-1} for the small and large size classes respectively. For the small size *Tilapia zillii*, mean Lead concentration ranged from 7.55 ± 0.07 to 8.45 ± 0.07 mgkg^{-1} while the large size class recorded mean concentrations ranging from 8.55 ± 0.21 to 11.50 ± 0.21 mgkg^{-1} . Cadmium concentrations in the flesh of the two fish species were below the WHO Safety Reference Standard of 1 mgkg^{-1} . Mean cadmium concentrations in the small and large size *Tilapia zillii* ranged from 0.55 ± 0.07 to 0.65 ± 0.07 mgkg^{-1} and from 0.50 ± 0.00 to 0.80 ± 0.00 mgkg^{-1} respectively. Mean Cadmium concentrations in the flesh of the *Oreochromis niloticus* ranged from 0.60 ± 0.00 to 0.90 ± 0.14 mgkg^{-1} for the small size class and from 0.70 ± 0.00 to 0.85 ± 0.07 mgkg^{-1} for the large size class. It is therefore imperative that fishing from the Jimi Dam is prohibited and consumption of fish from it discouraged because of the high levels of the heavy metals in the flesh of the two fish species. The study revealed no significant spatio-temporal variations in

the concentrations of the four studied heavy metals as far as the water and biota were concerned indicating an even distribution of the metals in the dam.

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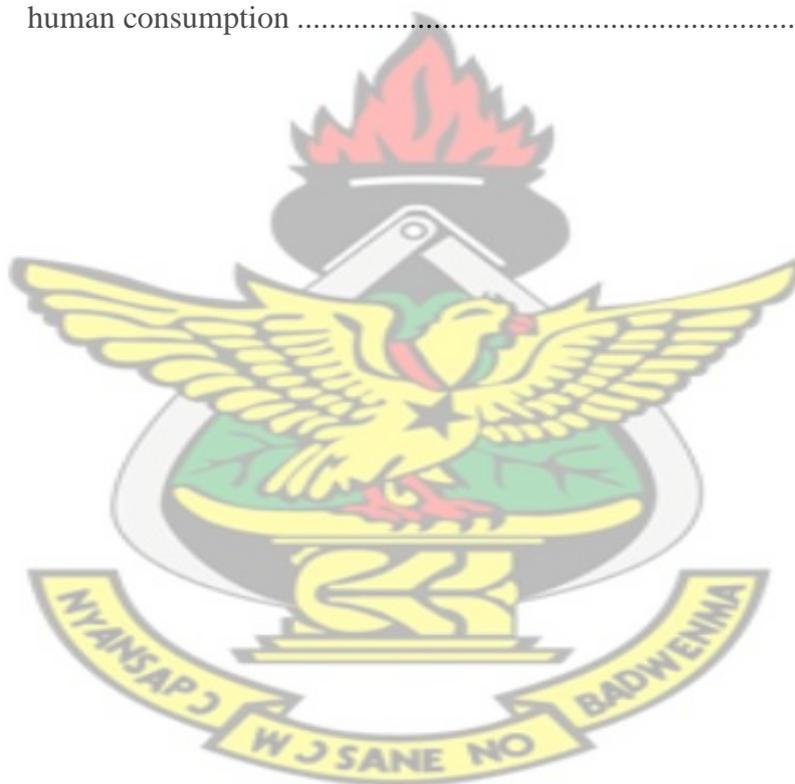
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CHAPTER ONE

INTRODUCTION

1.1 Background

Heavy metals may occur in aquatic environments from natural processes and from discharges or leachates from several anthropogenic activities (Connell *et al.*, 1999; Franca *et al.*, 2005). Contamination of natural waters by heavy metals negatively affects aquatic biota and poses considerable environmental risks and concerns (Cajaraville *et al.*, 2000; Ravera, 2001). Monitoring programmes and research on heavy metals in aquatic environment have become important due to concerns of over accumulation and toxic effects to aquatic organisms and to humans through the food chain (Othman, 2003). Contaminants can persist for many years in sediments where they hold the potential to affect human health and the environment (Mackevičienė *et al.*, 2002).

Sediments are an important sink of a variety of pollutants, particularly heavy metals and may serve as an enriched source of these contaminants for benthic organisms (Wang *et al.*, 2002). Metals may be present as dissolved species, as free ions or forming organic complexes with humic and fulvic acids. Additionally, many metals e.g. Pb associate readily with particulates and become adsorbed or co-precipitated with carbonates, oxyhydroxides, sulphides and clay minerals. Exposure of sediment-dwelling organisms to metals may then occur via uptake of interstitial waters, ingestion of sediment particles and via the food chain (Luoma, 1989). The occurrence of elevated levels of heavy metals in sediments found at the bottom of the water column can be a good indicator of man-induced pollution rather than natural

enrichment of the sediment by geological weathering (Davies *et al.* 1991, Chang *et al.* 1998).

1.2 Problem Statement

Mining operations usually results in the release of waste materials (tailings) into the environment and consequently cause problems for the growth and performance of flora and fauna (Montgomery *et al.*, 2003). Moreover, some mine tailings contain arsenic, lead, mercury, cadmium and that are harmful to human and other living organisms (Enger *et al.*, 2004). In addition the use of toxic chemicals such as cyanide in separating valuable mineral components from the ores and the formation of Acid Mine Drainage (AMD) from the waste also cause pollution in soils and water.

Historically, AngloGold Ghana Limited in Obuasi has concentrated on mining and processing of gold deposits solely accessible by underground methods. In 1989, in line with the Ashanti Mine Expansion Project, the Sansu Project, a mosaic of open pit mines and cyanide heap leach processing facilities was started. These surface mines, unlike underground mines, interfere considerably with the livelihood activities of communities within the project concession area largely because of their aerial coverage. They have the potential to pollute extensive sections of drainage networks which supply water for the surrounding villages (Akazbaa, 2007).

The active mining concession of AngloGold Ghana Limited lies within the Jimi River basin which serves the domestic needs of Obuasi and some surrounding villages. The Obuasi ores have significant sulphide mineralisation, the oxidation of which leads to the generation of acidic waters and the mobilisation of toxic metals into water sources. Waste disposal from the processing of underground sulphide ores rich in arsenic has led to severe water pollution problems in the area. Cases of arsenic

pollution from the plants that roast sulphide ores to facilitate gold removal are well documented. (Amonoo- Neizer and Busari, 1980; Jetuah, 1997; Carbo and Safo-Armah, 1997; Clement *et al.*, 1997).

1.3 Justification for the Research

Heavy metals are non-biodegradable and undergo a biogeochemical cycle in which natural waters are the main pathways (CIFA, 1994; Ukpebor *et al.*, 2005) and fish species can accumulate these heavy metals in their tissues at concentrations greater than the ambient water and pose a health threat to humans who consume them.

In the human body, toxic metals attack the proteins notably the enzymes (Ademoroti, (1996) and their toxic effects are cumulative and cause slow poisoning of the system over a period of time (Nriagu, 1988; Ukpebor *et al.*, 2005). Heavy metals have been implicated in the upsurge of liver and kidney diseases, and is believed to be responsible for a high proportion of mortality caused by kidney and liver morbidity (Friberg, *et al.*, 1986; Herber *et al.*, 1988; Ndiokwere, 2004), pains in bones (Tsuchiya, 1978), mutagenic, carcinogenic and teratogenic effects (Fischer, 1987; Friberg *et al.*, 1986, Kazantzis, 1987, Heinrich, 1988), neurological disorders, especially in the foetus and in children which can lead to behavioral changes and impaired performance in IQ tests (Lansdown, 1986; Needleman, 1987).

1.4. Objective of the Research

In the light of the above problems this study was carried out;

1. To measure the concentrations of Arsenic, Lead, Cadmium and Copper in water, sediment and fish (*Oreochromis niloticus* and *Tilapia zillii*) of the Jimi reservoir in Obuasi
2. To examine the spatial and temporal trends of Arsenic, Lead, Cadmium and Copper in water, sediment and fish (*Oreochromis niloticus* and *Tilapia zillii*) of the Jimi Dam in Obuasi



CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy metals

Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. Heavy metals are often problematic environmental pollutants, with well-known toxic effects on living systems (Evanko *et al.*, 1997). They are introduced into the environment during mining, refining of ores, combustion of fossil fuels and industrial processes. They cannot be degraded or destroyed (Davydova *et al.*, 2005). To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. Copper, Selenium, Zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning.

2.1.1 Toxicity of Metals

The presence of metals in water and soils can pose significant threat to human health and ecological systems. Heavy metal toxicity represents an uncommon, yet clinically significant, medical condition. If unrecognized or inappropriately treated, heavy metal toxicity can result in significant morbidity and mortality. Many metals are essential to biochemical processes in correct concentrations but at higher doses, heavy metals can cause negative health effects such as irreversible brain damage. Some metals such as lead and mercury easily cross the placenta and damage the brain (Levine *et al.*, 2006).

Metals have the potential to be toxic to living organisms if present above a threshold level. This threshold varies between taxa and metal speciation. Most urban and industrial runoff contains a component of trace and heavy metals in the dissolved or

particulate form (Defew et al; 2004). Since heavy metals cannot be degraded biologically, they are transferred and concentrated into plant tissues from soils and pose long-term damaging effects on plants. Nevertheless, different plants react differently to wastewater irrigation; some are more resistant to heavy metals. The ability of mangrove plants to tolerate heavy metals in wastewater is not clear and the impact of wastewater on plant growth must be understood before the system can be employed for removing heavy metal from wastewater. Heavy metals that accumulate in soils not only exert deleterious effects on plant growth, but also affect the soil microbial communities and soil fertility. Yim & Tam (1999) found that microbial biomass and enzyme activities decreased with increasing heavy metal pollution, but decreases vary depending on the types of enzymes. The potential hazard to the marine environment of pollutants depends mostly on their concentration and persistence. Persistent pollutants, such as heavy metals, can remain in the environment unchanged for years and thus may pose a threat to man and other organisms.

Many of the heavy metals are toxic to organisms at low concentrations. However, some heavy metals, such as copper and zinc are also essential elements. Concentrations of essential elements in organisms are normally homeostatically-controlled, with uptake from the environment regulated according to nutritional demand. Effects on the organisms are manifest when this regulation mechanism breaks down as a result of either insufficient (deficiency) or excess (toxicity) metal (Duffus, 2002).

Copper is one of several heavy metals that are essential to life despite being as inherently toxic as non-essential heavy metals exemplified by Lead (Pb) and Mercury (Hg) (Scheinberg, 1991). Plants and animals rapidly accumulate it. It is toxic at very low concentration in water and is known to cause brain damage in mammals (DWAf,

1996). Interest in these essential metals which are required for metabolic activity in organisms lies in the narrow “window” between their essentiality and toxicity (Skidmore, 1964; Spear, 1981). Non-essential metals like Aluminium (Al), Cadmium (Cd) and Lead (Pb) exhibit extreme toxicity even at trace levels (Merian, 1991).

Cadmium (Cd) has been found to be toxic to fish and other aquatic organisms (Rao and Saxena, 1981; Woodworth and Pascoe, 1982). The effect of Cd toxicity in man includes kidney damage (Friberg, *et al.*, 1986; Herber *et al.*, 1988) and pains in bones (Tsuchiya, 1978). Cd also has mutagenic, carcinogenic and teratogenic effects (Fischer, 1987; Friberg *et al.*, 1986, Kazantzis, 1987, Heinrich, 1988).

Lead is defined by the United States Environmental Protection Agency (USEPA) as potentially hazardous to most forms of life, and is considered toxic and relatively accessible to aquatic organisms (USEPA, 1986). Lead is bioaccumulated by benthic bacteria, freshwater plants, invertebrates and fish (DWAF, 1996). The chronic effect of lead on man includes neurological disorders, especially in the foetus and in children. This can lead to behavioral changes and impaired performance in IQ tests (Lansdown, 1986; Needleman, 1987).

2.1.2 Mobility and Speciation of Metals in Water and Soil

Understanding the environmental behaviour of a metal by determining its speciation, mobility and occurrence is of paramount importance. The term speciation is related to the distribution of an element among chemical forms or species. Heavy metals can occur in several forms in water and soil (Maiz *et al.*, 2001). Based on this information the most appropriate method for soil and water remediation can be determined (Garrido *et al.*, 2005).

Soils are significant sinks for metals, while water represents an important pathway for the dispersion of metals over extremely large areas (Gabler, 1997). The mobility of a metal in soil and water depends significantly on the chemical form and speciation of the metal. The mobility of metals in ground-water systems is hindered by reactions that cause metals to adsorb or precipitate, or chemistry that tends to keep metals associated with the solid phase and prevents them from dissolving. These mechanisms can retard the movement of metals and also provide a long-term source of metal contaminants. While various metals undergo similar reactions in a number of aspects, the extent and nature of these reactions varies under particular conditions (Mulligan *et al.*, 2001, Shen *et al.*, 2005). Studies on the mobility of heavy metals in soils have shown that the mobility is strongly influenced by several factors, e.g. pH, redox potential, clay mineral content, organic matter content and water content. Various processes, e.g., adsorption-desorption, complex and ion-pair formation or activities of microorganisms are also involved (Gibler *et al.*, 1997). Simple and complex cations are the most mobile, exchangeable cations in organic and inorganic complexes are of medium mobility and, chelated cations are slightly mobile (Kelly *et al.*, 2003, Gibler *et al.*, 1997). Metals in organic particles are only mobile after decomposition or weathering. Precipitated metals are mobile under dissolution conditions (e.g. change in pH) (Kelly *et al.*, 2003).

2.1.2.1 Influence of Soil Properties on Mobility of Heavy Metals

Chemical and physical properties of the contaminated matrix influence the mobility of metals in soils and groundwater (Gäbler *et al.*, 1997). Contamination exists in three forms in the soil matrix: solubilized contaminants in the soil moisture, adsorbed contaminants on soil surfaces, and contaminants fixed chemically as solid compounds. The chemical and physical properties of the soil influence the form of the

metal contaminant, its mobility, and the technology selected for remediation (Garrido *et al.* 2005)

2.1.2.2 Chemical Properties

The presence of inorganic anions (carbonate, phosphate, sulphide) in the soil water can influence the soil's ability to fix metals chemically (Garrido *et al.*, 2005). These anions can form relatively insoluble complexes with metal ions and cause metals to desorb and precipitate in their presence. Soil pH values generally range between 4.0 and 8.5 with buffering by Al at low pH and by CaCO₃ at high pH. Metal cations are most mobile under acidic conditions while anions tend to sorb to oxide minerals in this pH range. At high pH, cations precipitate or adsorb to mineral surfaces and metal anions are mobilized. The presence of hydrous metal oxides of Fe, Al, Mn can strongly influence metal concentrations because these minerals can remove cations and anions from solution by ion exchange, specific adsorption and surface precipitation (Gäbler *et al.*, 1997).

Sorption of metal cations onto hydrous oxides generally increases sharply with pH and is most significant at pH values above the neutral range, while sorption of metal anions is greatest at low pH and decreases as pH is increased. Cation exchange capacity (CEC) refers to the concentration of readily exchangeable cations on a mineral surface and is often used to indicate the affinity of soils for uptake of cations such as metals. Anion exchange capacity (AEC) indicates the affinity of soils for uptake of anions, and is usually significantly lower than the CEC of the soil. In addition to hydrous oxides, clays are also important ion exchange materials for metals. The presence of natural organic matter (NOM) has been shown to influence the sorption of metal ions to mineral surfaces. NOM has been observed to enhance

sorption of Cu^{2+} at low pH, and suppress Cu^{2+} sorption at high pH (Gäbler *et al.*, 1997).

2.1.2.3 Physical Properties

Particle size distribution can influence the level of metal contamination in a soil. Fine particles ($<100\mu\text{m}$) are more reactive and have a higher surface area than coarser material. As a result, the fine fraction of a soil often contains the majority of contamination. The distribution of particle sizes with which a metal contaminant is associated can determine the effectiveness of a number of metal remediation technologies, for example, soil washing (Martinez *et al.*, 2006).

Moisture influences the chemistry of contaminated soil. The amount of dissolved minerals, pH and redox potential of the soil water depend on the soil moisture content. Soil structure describes the size, shape, arrangement and degree of development of soils into structural units. Soil structure can influence contaminant mobility by limiting the degree of contact between groundwater and contaminants. It has been demonstrated that the speciation of trace metals in natural soils depends on the physical and chemical characteristics of the soil. Soil pH, redox, organic, carbonate, clay and oxide contents all influence metal speciation and mobility. A study by Maturi, *et al.*, (2006) showed that zinc and cadmium in soil are mostly associated with exchangeable, water soluble and organic fractions. Copper is mainly organically bound and exchangeable, whereas, lead is slightly mobile and bound to the residual fraction (Maturi *et al.*, 2006). After discharge to an aquatic environment, metals are partitioned between solid and liquid phases. Within each phase, further partitioning occurs among ligands as determined by ligand concentrations and metal-ligand bond strengths. In solid phases, soil, sediment, and surface water particulates, metals may be partitioned into six fractions: (a) dissolved, (b) exchangeable, (c) carbonate, (d)

iron-manganese oxide, (e) organic, and (f) crystalline (Khan *et al.*, 2004). Partitioning is affected strongly by variations in pH, redox state, organic content, and other environmental factors. The dissolved fraction consists of carbonate complexes, whose abundance increases with pH, and metals in solution, including metal cation and anion complexes and hydrated ions whose solubilities are affected strongly by pH and tend to increase with decreasing pH.

Exchangeable fractions consist of metals bound to colloidal or particulate material (Khan *et al.*, 2004). Metals associated with carbonate minerals in soil constitute the carbonate fraction, which can be newly precipitated in soil (Davydova, 2005). The iron-manganese oxide fraction consists of metals adsorbed to iron-manganese oxide particles or coatings. The organic fraction consists of metals bound to various forms of organic matter. The crystalline fraction consists of metals contained within the crystal structure of minerals and normally not available to biota. Hydrogen ion activity (pH) is probably the most important factor governing metal speciation, solubility from mineral surfaces, transport, and eventual bioavailability of metals in aqueous solutions. pH affects both solubility of metal hydroxide minerals and adsorption-desorption processes. Most metal hydroxide minerals have very low solubilities under pH conditions in natural water (Davydova, 2005). Adsorption, which occurs when dissolved metals are attached to surfaces of particulate matter (notably iron, manganese, and aluminium oxide minerals, clay, and organic matter), is also strongly dependent on pH and, of course, the availability of particulate surfaces and total dissolved metal content. Metals tend to be adsorbed at different pH values, and sorption capacity of oxide surfaces generally varies from near 0 percent to near 100 percent over a range of about 2 pH units (Bourg *et al.*, 1988, Elder *et al.*, 1989). The adsorption edge, the pH range over which the rapid change in sorption capacity

occurs, varies among metals, which results in precipitation of different metals over a large range of pH units. Consequently, mixing metal-rich acidic water with higher pH metal-poor water may result in dispersion and separation of metals as different metals are adsorbed onto various media over a range of pH values. Cadmium and zinc tend to have adsorption edges at higher pH than iron and copper, and consequently they are likely to be more mobile and more widely dispersed. Adsorption edges also vary with concentration of the complexing agent thus, increasing concentrations of complexing agent increases pH of the adsorption edge (Bourg *et al.*, 1988). Major cations such as Mg^{2+} and Ca^{2+} also compete for adsorption sites with metals and can reduce the amount of metal adsorption. Particulate size and resulting total surface area available for adsorption are both important factors in adsorption processes and can affect metal bioavailability (Luoma *et al.*, 1989). Small particles with large surface-area to-mass ratios allow more adsorption than an equivalent mass of large particles with small surface-area-to-mass ratios. Reduced adsorption can increase metal bioavailability by increasing concentrations of dissolved metals in associated water. The size of particles released during mining depends on mining and beneficiation methods. Finely milled ore may release much smaller particles that can both be more widely dispersed by water and wind, and which can also serve as sites of enhanced adsorption. Consequently, mine tailings released into fine-grained sediment such as silty clays found in many places can have much lower environmental impact than those released into sand or coarse-grained sediment with lower surface area and adsorption (Mitchell *et al.*, 1999). Temperature exerts an important effect on metal speciation, because most chemical reaction rates are highly sensitive to temperature changes (Luoma *et al.*, 1983). An increase of 10 °C can double biochemical reaction rates, which are often the driving force in earth surface conditions for reactions that are kinetically

slow, and enhance the tendency of a system to reach equilibrium. Temperature may also affect quantities of metal uptake by an organism, because biological process rates (as noted above) typically double with every 10 °C temperature increment (Mulligan *et al.*, 2001). Because increased temperature may affect both influx and efflux rates of metals, net bioaccumulation may or may not increase (Mulligan *et al.*, 2001). The chemical form and speciation of some of the studied metals are discussed below.

2.2 Review of the Studied Metals

2.2.1 Copper

Copper (Cu) is mined as a primary ore product from copper sulphide and oxide ores. Mining activities are the major source of copper contamination in groundwater and surface waters. Other sources of copper include algicides, chromated copper arsenate (CCA), pressure treated lumber and copper pipes. Solution and soil chemistry strongly influence the speciation of copper in ground-water systems. In aerobic conditions, sufficiently alkaline systems, CuCO_3 is the dominant soluble copper species (Kelly *et al.*, 2003). The cupric ion, Cu^{2+} , and hydroxide complexes, CuOH^+ and $\text{Cu}(\text{OH})_2$, are also commonly present. Copper forms strong solution complexes with humic acids (Khan *et al.*, 2004). The affinity of Cu for humates increases as pH increases and ionic strength decreases. In anaerobic environments, when sulphur is present $\text{CuS}(\text{s})$ will form. Copper mobility is decreased by sorption to mineral surfaces. Cu^{2+} sorbs strongly to mineral surfaces over a wide range of pH values (Mulligan *et al.*, 2001). The cupric ion (Cu^{2+}) is the most toxic species of copper. Copper toxicity has also been demonstrated for CuOH^+ and $\text{Cu}_2(\text{OH})_2^{2+}$ (Mulligan *et al.*, 2001).

2.2.2 Cadmium

Cadmium (Cd) occurs naturally in the form of Cadmium Sulphate or Cadmium Carbonate (CdS or CdCO_3). Cadmium is recovered as a by-product from the mining of sulfide ores of lead, zinc and copper. Sources of cadmium contamination include plating operations and the disposal of cadmium-containing wastes (Garrido *et al.*, 2005). The form of cadmium encountered depends on solution and soil chemistry as well as treatment of the waste prior to disposal. The most common forms of cadmium include Cd^{2+} , cadmium-cyanide complexes, or $\text{Cd}(\text{OH})_2$ solid sludge (Gäbler, 1997). Hydroxide ($\text{Cd}(\text{OH})_2$) and carbonate (CdCO_3) solids dominate at high pH whereas Cd^{2+} and aqueous sulfate species are the dominant forms of cadmium at lower pH (<8). Under reducing conditions when sulfur is present, the stable solid $\text{CdS}(\text{s})$ is formed. Cadmium will also precipitate in the presence of phosphate, arsenate, chromate and other anions, although solubility will vary with pH and other chemical factors (Bourg *et al.*, 1988). Cadmium is relatively mobile in surface water and ground-water systems and exists primarily as hydrated ions or as complexes with humic acids and other organic ligands. Under acidic conditions, cadmium may also form complexes with chloride and sulfate. Cadmium is removed from natural waters by precipitation and sorption to mineral surfaces, especially oxide minerals, at higher pH values (>pH 6). Removal by these mechanisms increases as pH increases. Sorption is also influenced by the cation exchange capacity (CEC) of clays, carbonate minerals, and organic matter present in soils and sediments. Under reducing conditions, precipitation as CdS controls the mobility of cadmium (Gäbler, 1997).

2.2.3 Arsenic

Arsenic (As) is a semi metallic element that occurs in a wide variety of minerals, mainly as As_2O_3 , and can be recovered from processing of ores containing mostly

copper, lead, zinc, silver and gold. It is also present in ashes from coal combustion. Arsenic exhibits fairly complex chemistry and can be present in several oxidation states (-III, 0, III, V) (Luoma *et al.*, 1989, Bourg *et al.*, 1988). In aerobic environments, As(V) is dominant, usually in the form of arsenate (AsO_4^{3-}) in various protonation states: H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , AsO_4^{3-} . Arsenate and other anionic forms of arsenic behave as chelates and can precipitate when metal cations are present. Metal arsenate complexes are stable only under certain conditions. As(V) can also co-precipitate with or adsorb onto iron oxyhydroxides under acidic and moderately reducing conditions (Gäbler, 1997). Coprecipitates are immobile under these conditions but arsenic mobility increases as pH increases. Under reducing conditions As(III) dominates, existing as arsenite (AsO_3^{3-}) and its protonated forms: H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-} . Arsenite can adsorb or co-precipitate with metal sulfides and has a high affinity for other sulfur compounds. Elemental arsenic and arsine, AsH_3 , may be present under extreme reducing conditions. Biotransformation (via methylation) of arsenic creates methylated derivatives of arsine, such as dimethyl arsine $\text{HAs}(\text{CH}_3)_2$ and trimethylarsine $\text{As}(\text{CH}_3)_3$ which are highly volatile. Since arsenic is often present in anionic form, it does not form complexes with simple anions such as Cl^- and SO_4^{2-} . Arsenic speciation also includes organometallic forms such as methylarsinic acid $(\text{CH}_3)\text{AsO}_2\text{H}_2$ and dimethylarsinic acid $(\text{CH}_3)_2\text{AsO}_2\text{H}$. Many arsenic compounds sorb strongly to soils and are therefore transported only over short distances in groundwater and surface water. Sorption and co-precipitation with hydrous iron oxides are the most important removal mechanisms under most environmental conditions. Arsenates can be leached easily if the amount of reactive metal in the soil is low. As(V) can also be mobilized under reducing conditions that

encourage the formation of As(III), under alkaline and saline conditions, in the presence of other ions that compete for sorption (Gäbler, 1997).

2.2.4 Lead

Lead released to groundwater, surface water and land is usually in the form of elemental lead, lead oxides and hydroxides, and lead metal oxyanion complexes. Most lead that is released to the environment is retained in the soil. The primary processes influencing the fate of lead in soil include adsorption, ion exchange, precipitation, and complexation with sorbed organic matter. These processes limit the amount of lead that can be transported into the surface water or groundwater. The relatively volatile organo-lead compound tetramethyl lead may form in anaerobic sediments as a result of alkylation by micro organisms (Mulligan *et al.*, 2001, Garrido *et al.*, 2005). The amount of dissolved lead in surface water and groundwater depends on pH and the concentration of dissolved salts and the types of mineral surfaces present. In surface water and ground-water systems, a significant fraction of lead is undissolved and occurs.

2.3 Pollution of the Aquatic Environment with Heavy Metals

The aquatic environment with its water quality is considered the main factor controlling the state of health and disease in both man and animal (Rashed, 2004). Nowadays, the increasing use of the waste chemical and agricultural drainage systems represents the most dangerous form of chemical pollution particularly heavy metal pollution. The most important heavy metals from the point of view of water pollution are Zinc (Zn), Copper (Cu), Lead (Pb), Cadmium (Cd), Mercury (Hg), Nickel (Ni) and Chromium (Cr) (Rashed, 2004).

When heavy metals enter the aquatic environment, the metal ions can react with constituents of the water or settle to the bottom and react with the sediments. Heavy metals have a greater chance of remaining in solution when complexed to chelating ligands such as specific anions whose concentrations are determined by the pH of the surrounding environment. Metals precipitate as oxides/hydroxides at different pH regions and the amphoteric elements return to solution at higher pH. The hydroxide concentration (or pH) is therefore of great importance for the mobility of metals. Other factors also affect the fate of the metal ions like redox conditions and the presence of adsorbent sediments (Alloway and Ayres 1998).

Water pollution is most commonly associated with the discharge of effluents from sewers or sewage treatment plants, drains and factories to the water body of rivers, seas and marines. The accumulation of metals in an aquatic environment has direct consequences to man and to the ecosystem. Metals have many sources from which they can flow into the water body, these sources are: (i) Natural Sources: Metals are found throughout the earth, in rocks, soil and are introduced into the water body through natural processes, weathering and erosion.

- i. Industrial Sources: Industrial processes, particularly those concerned with the mining and processing of metal ores, the finishing and plating of metals and the manufacture of metal objects. Metallic compounds which are widely used in other industries as pigments in paint and dye manufacture; in the manufacture of leather, rubber, textiles, paint, paper and chromium factories which are built close to water for shipping.
- ii. Domestic Wastewater: Domestic wastewater contains substantial quantities of metals. The prevalence of heavy metals in domestic formulations, such as cosmetic or cleansing agents, is frequently overlooked.

- iii. Agricultural Sources: Agricultural discharge contains residual of pesticides and fertilizers which contains metals.
- iv. Mine runoff and solid waste disposal areas.
- v. Atmospheric pollution: Acid rains containing trace metals as well as suspended particulate matter (SPM) input to the water body will cause the pollution of water with metals. (Source: Rashed, 2004)

2.4. 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 or antagonise these processes that the background levels are increased, by pollution, to levels that have detrimental effects on the environment. Sediments with low heavy metal concentrations are not necessarily "natural" just because the levels are indeed low. They may represent a mixture of small quantity of pollutants diluted by a large amount of natural sediment with low heavy metal content. (Herut *et al.*, 1993). In the past sediments and particulate matter have been considered as purely abiotic material. This is obviously not the case and it is now well known that sediments contain large bacterial populations. 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 trace metals may be taken up by sediments and suspended matter;

- 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 or entrainment

Physicochemical adsorption direct from the water column happens 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 many factors such as pH and oxidation. There is a lack of detailed knowledge about the specific nature of sediment surfaces. This is mainly due to the high concentrations used in most adsorption experiments which are unrealistic and would not occur naturally. A number of studies have shown that metal ions are strongly adsorbed by solid organic matter. The structure and composition of humic matter can vary considerably depending upon its origin and can be expected to influence the results of sorption experiments. Natural organic matter has a very important influence on the distribution of trace metals in aquatic systems. In addition uptake may be actively completed by bacteria and algae. This results in sediment enrichment. Sedimentation of enriched particulate matter is the other potentially important mechanism by which sediments may concentrate trace metals (Hart, 1982). There is no evidence to suggest that trace metal binding to solid natural organic matter should be any different to that by soluble natural organic matter. The difference between these surface types is not well understood particularly with respect to trace metal uptake. Gardner (1974) found that adsorption of cadmium by river mud samples was very rapid (in the order of minutes) and that some additional adsorption occurred over a further 24hour period. Within the soil, trace metals can be either 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 are helped also by the oxidation of surface sediments due to periodic drying between tides. This, incorporated with some biological processes such as bioturbation or O_2 release from mangrove roots, can enhance uptake rates. This

exposure to O_2 results in the oxidation of sulphides in the sediment. A reduction in sediment pore water pH due to production of sulphuric acid, allows the mobilization of metals (Clark *et al.*, 1998). Many authors propose that the interface between water and sediment plays many important roles in the chemistry of trace metals. Firstly, the upper layer of sediment is usually oxidised (as previously stated) and therefore, acts as a diffusion barrier for mobilized solutes travelling upward from reducing zones of sediment. Secondly, the surface sediments on the bed of many estuaries exchange readily with suspended solids in the water column and therefore easily adsorb any passing material. Ultimately, Szefer *et al.*, (1998) suggested that the sediments at the water interface (i.e. the topsoil) are more important to biological fauna than when compared with subsurface meiofauna. They, therefore, offer a higher opportunity for uptake by benthic organisms.

Long (1992) suggested that the oxidation-reduction potential and the concentration of sulphides in the sediments can strongly influence the concentration of trace metals and their availability. Clark *et al.* (1998) explain that the redox potential of the sediment can affect metal trapping directly through change in the oxidation state of the metal itself. Or indirectly through a change in the oxidation state of the ions that can form complexes with the metal. Additional loads of pollution, especially those gained from run-off, in surface waters, of nutrients and trace metals derived from soil erosion processes are largely influenced by the kind of crop grown on the surrounding land. Many heavy metals, especially mercury, have a high capacity for long range atmospheric transport or through marine currents by thousands of kilometres in only a few months (Guzman & Garcia, 2003). Depending upon the environment the sediment particle size distribution may range from very small colloidal particles (of <

0.1µm in diameter) to large sand and gravel particles several millimetres in diameter. There is a small variation between the mobility of particulate in river waters and seawater. This is very surprising due to a wide expected variation in particle types. Therefore, metals and the subsequent pollution will progress equally in both rivers and the ocean. Harbison (1986) has reported that tidal mudflats and particularly mangrove substrates contain a much greater load of trace metals than other shoreline sediments. This is where the sediments are most vulnerable to the environmental parameters that might influence the migration of these metals.

2.5 Mechanism of Heavy Metals uptake by Fish

The uptake of metals into the fish cells is largely dependent on their ability to pass through the cell membrane, irrespective of the metals route of entry (Connell *et al.*, 1999). Uptake can occur through a number of transport pathways, which have been well documented, since first proposed by Simkiss and Taylor (1989). These transport pathways include the passive diffusion of neutral metal species across the membrane, facilitated diffusion of metals, active transport through major ion channels and endocytosis (Wang and Rainbow, 2005). However, the relative uptake and utilization of these routes vary between different sites on body surfaces (i.e. uptake is particularly prominent at the highly permeable gills), organisms (i.e. different species utilize different routes) and environmental conditions (i.e. physicochemical changes control the uptake) (Phillips and Rainbow, 1994). After the bioavailable metals have been taken up into the biological system, an induction of a number of processes that play an important role in controlling the level of toxicity occurs. Some of these detoxifying processes include the transportation, transformation, sequestration and/or excretion of excess metals (Connell *et al.*, 1999). According to Amiard *et al.*, 1987; Durou *et al.*, 2005), toxicity will only occur when the rate of metal uptake and

accumulation exceed the combined rate of excretion and detoxification of the bioavailable metal.

2.6 Monitoring Bioavailable Metals in Aquatic Environments

Metals occur in the environment both as a result of natural processes and as pollutants from anthropogenic activities (Franca *et al.*, 2005). They are distributed between various environmental phases (including atmosphere, water and sediment) depending on the nature of the phase and the nature of the compound (Connell *et al.*, 1999). However, mere observations of the total metal concentrations in either of these phases are rarely a good predictor of impacts on organisms. For example, in an aquatic environment, determination of the metal concentrations in solution or associated with particles may not always indicate the metals that are biologically available (bioavailable) in aquatic environments. Instead, bioavailability is dependent on the chemical and physical (dissolved or particulate) forms of metals in the water column and sediments, which are controlled by several physicochemical parameters such as temperature and salinity (Wang and Fisher, 1999; Ansari, 2004).

In the attempt to define and measure the presence and effects of pollutants on aquatic systems, bioindicators have attracted a great deal of interest. The principle behind the bioindicator approach is the analysis of an organism for their metal contents in order to monitor the metal excesses in their tissues. Various aquatic organisms that occur in rivers, lakes and seas, including fish, oyster, mussels, clams, aquatic animals and aquatic plants and algae are potentially useful as bioindicators of metal pollutants (Rashed, 2004).

2.7 Mining and the Environment

The adverse environmental impact of mining activities on the environment is well documented (Heath et al., 1993; Veiga and Beinhoff, 1997; Warhusrt, 1994; Warhurst 1999). Particular attention has been directed towards the impacts of large scale and small-scale gold mining activities on environmental contamination. While the land degradation caused by the gold mining is pronounced, chemical contamination from the gold extraction process imposes a double burden on the environment, with harmful health implications for mining communities and people residing in close proximity to such activities (Yelpaala, 2004). For instance, due to the informal nature of gold-mining in the South (Africa and Latin America), most studies concentrate on mercury exposure and intoxication incurred in the extraction and processing stage of mining (Camara, Filhote et al. 1997; Malm, 1998; Harada *et al.*, 1999; Tirado *et al.*, 2000; van Straaten 2000a; Rojas, Drake et al. 2001). Results of studies indicate patterns of mercury intoxication during the gold amalgamation process (Camara, Filhote *et al.*, 1997; Tirado, Garcia *et al.*, 2000; van Straaten 2000a; Drasch, Bose-O'Reilly *et al.*, 2001). Most studies involve small numbers and are thus susceptible to predisposition, but some attempt more rigorous design. For example, in one site in the Philippines a study of 102 workers (occupationally Hg burdened ball-millers and amalgam- smelters), 63 other inhabitants (exposed from the environment), 100 persons living downstream of the mine, and 42 inhabitants of another site (serving as controls) was undertaken. Bio-monitors and medical scores for both workers and the surrounding communities were taken. The authors report that “By this method, 0% of the controls, 38% downstream, 27% from Mt. Diwata non-occupational exposed and 71.6% of the workers were classified as Hg intoxicated”(Drasch, Bose-O'Reilly et al. 2001). Another study in Tanzania with a similar design found lower levels of

intoxication and a more complex mix of mining-related and environmental exposures to mercury through household items such as soap (Harada, Nakachi *et al.* 1999). One study in Ecuador reports higher levels of intoxication in children involved in “gold washing” (Harari, Forastiere *et al.*, 1997). One study in Venezuela found no mercury intoxication, despite occupational and community exposures (Rojas, Drake *et al.*, 2001)

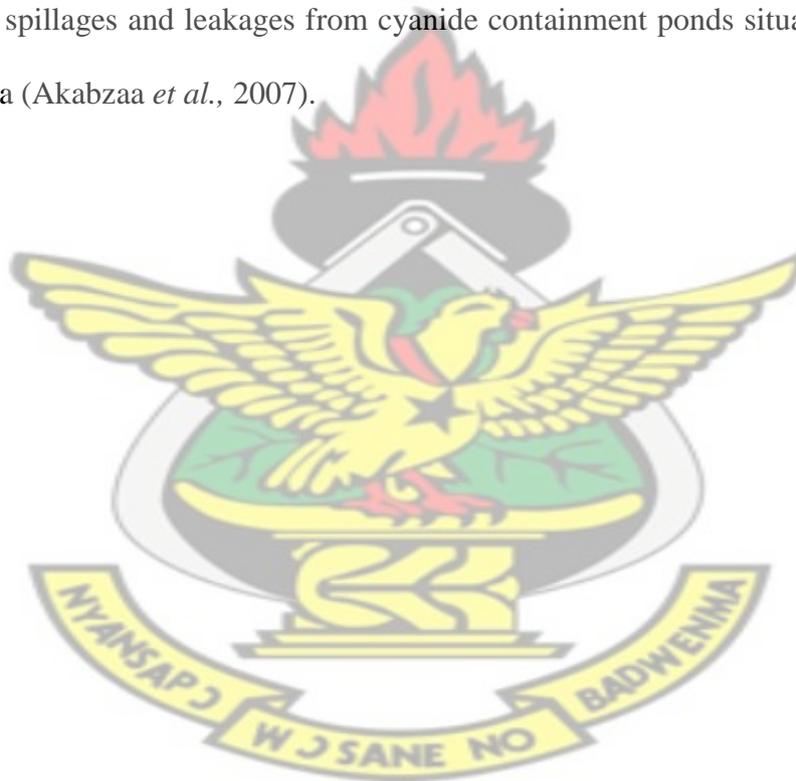
Many mines have an active programme to reduce the water table or divert major watercourses away from the mines. This exercise has disruptive outcomes for the quality and availability of surface and ground water. The concentration of mining operations in Tarkwa has been a chief cause of both surface and groundwater pollution. Four main problems of water pollution have been identified in Tarkwa mining areas. These are chemical pollution of ground water and streams, siltation through increased sediment load, increased faecal matter and dewatering effects (Akabzaa and Darimani, 2001).

2.8 Heavy Metal Pollution in Obuasi

The long period of mining and the more recent extensive surface mining operations have together generated considerable waste and affected the quality of water, especially surface water in the study area. During the over hundred years of its operations, the Obuasi goldmine was estimated to have crushed 150 million tonnes of ore rock and generated an estimated 600 million tonnes of waste with considerable effects on water resources in the area and the environment in general. (Akabzaa *et al.*, 2007). The major activities and facilities impacting on the host communities and their water sources in the study area are surface mining operations, gold processing activities, waste rock and tailings dumps as well as sites of spent cyanide solution containment ponds. Most of the communities immediately downstream or within the

operational area of AGC bear the full brunt of the mining operations. Even communities relatively distant from mining and processing facilities are adversely affected due to offsite migration of these pollutants. Communities such as Sansu, Bidiem, Anyinam, Akatakyieso, Odumase, and Tutuka are directly impacted by surface mining and processing activities. Anyinam and Kwabrafoso are within the periphery of ore processing facilities and clusters of tailings dumps while Dokyiwa, Binsere, Adaase and Ntonsua are near to the spent cyanide containment ponds (200).

A major source of heavy metal pollution in the area is the frequent but unreported cyanide spillages and leakages from cyanide containment ponds situated upstream of Dokyiwa (Akabzaa *et al.*, 2007).



CHAPTER THREE

METHODOLOGY

3.1 Study Area

Obuasi is situated at latitude 6° 12' 00 North and longitude 1° 40' 00 West. It is geologically situated within the principal greenstone belt of Proterozoic (Birimian) age which consist of volcano-sedimentary and igneous formations. This belt extends over a distance of approximately 300 km in a north-east/south-west trend in south-western Ghana (Anglogold Ashanti, 2005). The vegetation in the area is mainly secondary forest, forbs re-growth and swamp. There are two rainy seasons, with the major reaching its maximum in May and June and the minor in October. The month of July, August and early September are generally much drier than the remaining months. The annual rainfall ranges from 130 cm to 230 cm/yr with temperature between 22°C and 32°C. The area has a population of over 100 000 scattered over many small to large villages throughout the area and is mainly drained by the Nyam and Jimi Rivers. Besides mining, the majority of the people are farmers (Griffis *et al.*, 2002). The dam on the Jimi River is three miles from Obuasi town and is reached by a track 500 metres past Jimiso village (Figure 3.2). It is a fertile area where maize, cocoyam, cassava, plantain, tomatoes and aubergines are grown.

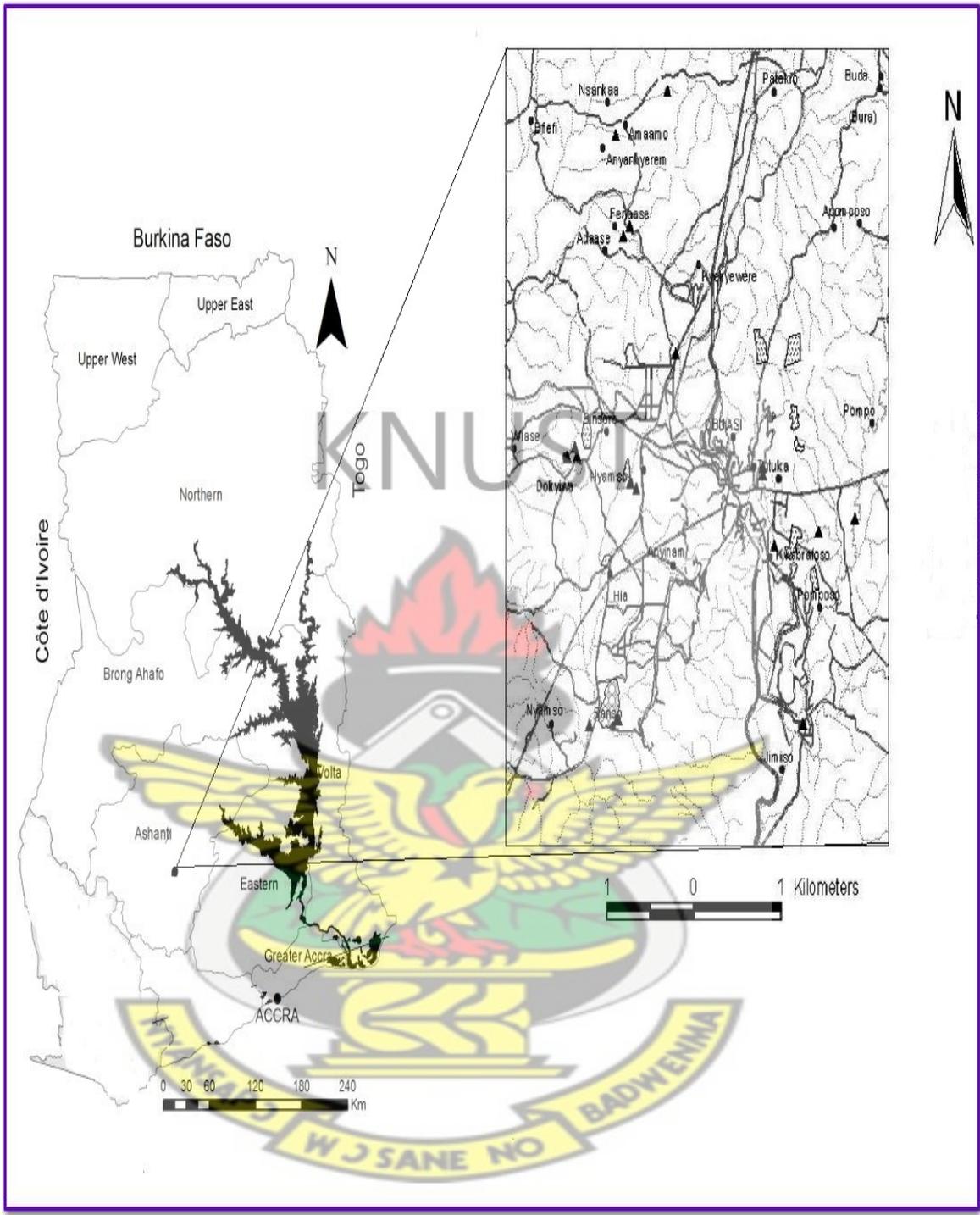


Figure 3.1 Location map of the study area and its environs



Figure 3.2 The Jimi Reservoir

3.2 Sampling and Sample Preparation

Sampling stations were selected in the Jimi Dam to give adequate spatial coverage and to represent the variety of conditions in the Dam. Sediment, water and fish samples were collected from the stations on a monthly basis. A systematic aligned sampling method was devised in order to obtain a comprehensive and representative assessment of the heavy metal levels in the dam. The sampling stations were divided along a transect running perpendicular to the shore-water interface (Figure 3.3). The three sampling stations were named as near-shore (NS), mid-point (MP) and

far-point (FP) and at each sampling station two water and sediment samples were taken each month.

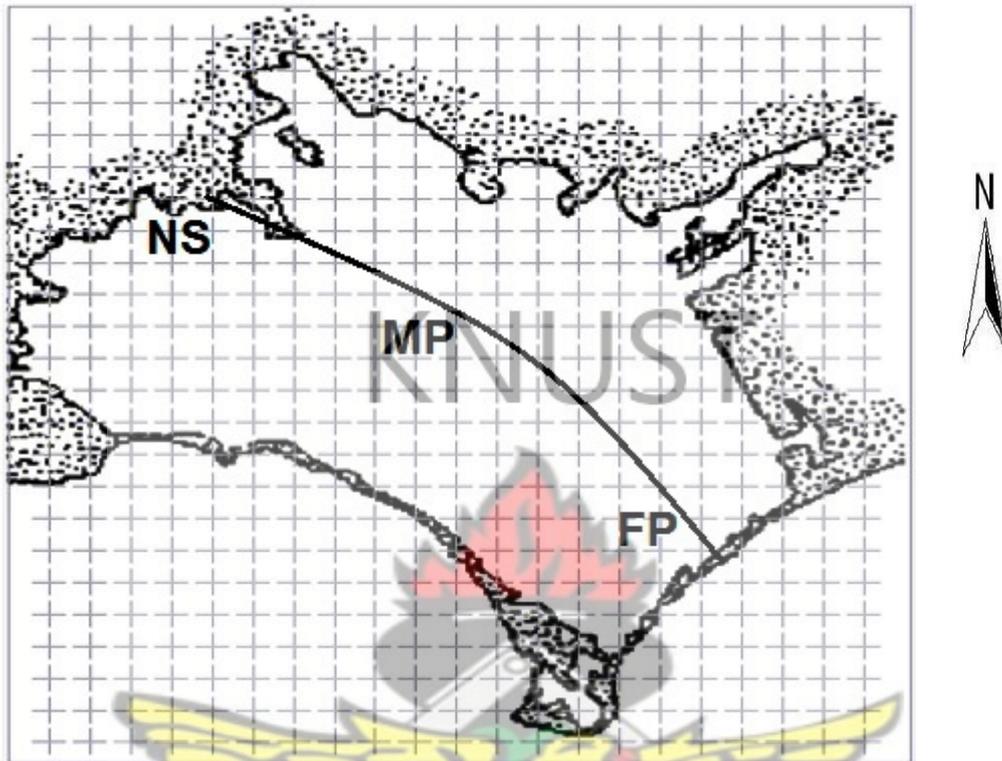


Figure 3.3 Sketch map of the Jimiso Reservoir showing the three sampling stations (not drawn to scale)

3.4 Sample Collection and Preparation

Fish samples were obtained from local fishermen on a monthly basis for four months from April to July, 2012. The bottom sediments were collected using a non-contaminating, stainless steel Ekman Grab. The sediments were placed in clean and well-labeled plastic bags. Water samples were collected at each sampling point into pre-washed 1500 ml plastic bottles and acidified with 5 ml concentrated HNO_3 . This was done to preserve the water samples and as an initial step to bring particulate metals into solution form (DAAF, 1996).

The water and fish samples were stored on ice in an ice chest and transported to the laboratory. The fish species were then sorted out, identified using a fish identification

manual at the Department of Fisheries and Watershed Management, Kwame Nkrumah University of Science and Technology (KNUST). Two species, *Oreochromis niloticus* (Figure 3.5) and *Tilapia zillii* (Figure 3.4) were identified as the main species harvested from the Jimi Dam and these species were used for the heavy metal analysis.



Figure 3.4 *Tilapia zillii*



Figure 3.5 The Nile Tilapia, *Oreochromis niloticus*

The fish samples were kept in a freezer at -20°C prior to preparation for chemical analysis. Thereafter, the fish samples were thawed, washed with distilled water, dried

on tissue paper, the length and body weight of each was then taken. Fish lengths and weights were taken using a measuring board fitted with a centimeter rule and an Ohaus (CL Series) portable balance. The fish samples were then categorized into two size classes as follows: Small (<10 cm) and Large (>10 cm). Four individual fish selected per each size class of the two species, implying that 16 individual fish were used on each month.

Muscle tissues was removed from the dorsal part of each fish using a stainless steel kitchen knife, homogenized on size classification basis and stored for analysis. Exactly 1g of the homogenized muscle tissues of sample was digested for heavy metal analysis. The sediment samples were air-dried in a room, ground and sieved into a powdery form with a porcelain mortar and pestle prior to digestion and analysis.

3.5 Digestion of Sediment and Fish Samples for Heavy Metal Analysis

Approximately 1g of each completely homogenized fish and the finely-ground sediment samples were placed separately into 300 ml conical flask and 20 ml of HNO₃ and HClO₄ with ratio 9:4 was added and the contents well mixed by swirling thoroughly. The flask with contents was then placed on a hotplate in the fume chamber and heated at an initial temperature of 85 °C and then raised to 150 °C. The mixture was heated until the production of red NO₂ fumes ceased. The contents were further heated until volume was reduced to 3-4 ml and became colorless or yellowish. This was done to reduce interference by organic matter and to convert metal associated particulate to a form that can be determined by the Atomic Absorption Spectrophotometer (AAS). The completely digested samples were allowed to cool at room temperature, and the undigested portions of the sediments filtered off through a Whatmann Glass Microfibre filter paper (GF/C) to obtain a clear solution. The

resulting solution was then diluted to 100 ml in volumetric flasks with double distilled water and stored for metal analysis.

3.6 Digestion of Water Samples for Heavy Metal Analysis

The water sample was thoroughly mixed by shaking prior to transferring 100 ml into a conical flask. Five (5) ml of concentrated HNO₃ and a few boiling chips were added (APHO, 1992). The mixture was then heated until the volume was reduced to about 15 ml and complete digestion was indicated by either a light colored or clear solution. Contents were washed down with double distilled water and then filtered. The filtrate was transferred into 100 ml prior washed volumetric flask and volume finally adjusted to 100 ml with double distilled water and stored at 4° C, ready for heavy metal analysis (APHO, 1992). The digested samples were transported to the Environmental Laboratory of AngloGold Ashanti at Obuasi for the determination of heavy metals.

3.7 Determination of Physicochemical Parameters

Monthly measurement of temperature, salinity, pH, total dissolved solids (TDS), and conductivity of the overlying water were taken at all the sampling locations for the study period using a Hanna (HI 9828) multi-parameter probe

3.8 Statistical Analysis

Data were presented in tables as means \pm SD. Data obtained in this study for the levels of heavy metals in the reservoir's fish, water and sediments were analysed by the Kruskal-Wallis non-parametric test to determine the variability in levels recorded at the various sampling stations over the sampling period. The Dunn's Multiple Comparison Test was used to further test for significant differences among the three sampling stations. In all cases, standard error difference (s.e.d) at 5% was used to

compare treatment means. All descriptive statistics and graphs were executed using the Graph-Pad Prism 5 Software.

KNUST



CHAPTER FOUR

RESULTS

4.1 Physicochemical Parameters of Water in the Jimi Reservoir

The physicochemical parameters of the Jimi Dam over the three month period were fairly similar and did not vary significantly ($p>0.05$). The pH of the water varied narrowly from 7.39 – 7.69 during the study period with no particular trend as far as the sampling stations were concerned. The levels of total dissolved solids (TDS) did not follow any particular trend. The TDS levels of the different sampling points of the Jimi reservoir were all below 300 mgL^{-1} , with the exception of the Near shore sampling station which recorded a mean conductivity level of 301.60 mgL^{-1} . Mean TDS levels recorded over the sampling period ranged from a minimum of 259.50 mgL^{-1} to a maximum of 301.60 mgL^{-1} .

Similar to the TDS levels in the water of the reservoir, conductivity readings were found to be fairly similar over the three-month period and ranged between 499 mgL^{-1} and 570 mgL^{-1} . The dissolved oxygen levels of the water found to be low, although they were just above the minimum DO level for the protection of aquatic life of 5.0 mgL^{-1} at most of the sampling stations during the studyWHO. Mean temperature of the water of the Jimi reservoir were very similar among the three sampling stations. The far point sampling station recorded the lowest mean temperature of $29.50 \text{ }^{\circ}\text{C}$ during the May sampling period. Overall, the mean temperature varied from a lowest reading of $29.50 \text{ }^{\circ}\text{C}$ to a highest of $31.53 \text{ }^{\circ}\text{C}$. Table 4.1 shows Physicochemical parameters (Mean \pm SD) recorded at the different sampling stations over the study period.

Table 4.1 Physicochemical parameters (Mean \pm SD) recorded at the different sampling stations over the study period

Parameter (mgL ⁻¹) Temp (°C) Period		pH	TDS (mgL ⁻¹)	Cond. (μS/cm)	DO
April					
NS	7.48±0.001	289.50±5.36	531.00±4.13	5.12±0.04	31.00±0.07
MP	7.66±0.002	273.50±4.56	547.00±3.62	5.64±0.11	30.00±0.00
FP	7.63±0.001	285.00±1.21	566.00±1.11	5.40±0.13	29.80±0.03
May					
NS	7.69±0.001	259.50±6.36	521.00±14.14	5.02±0.07	30.50±0.70
MP	7.62±0.002	270.50±3.56	550.00±5.66	5.64±0.18	31.00±0.00
FP	7.59±0.001	289.00±1.41	570.00±1.41	5.40±0.10	29.50±0.70
June					
NS	7.58±0.001	279.60±7.08	499.10±3.14	5.32±0.01	31.11±0.60
MP	7.64±0.002	288.54±3.56	513.04±5.63	5.44±0.08	31.10±0.00
FP	7.61±0.001	270.10±2.42	554.00±7.45	5.28±0.02	31.53±0.10
July					
NS	7.39±0.002	301.60±7.26	503.20±12.04	4.99±0.05	30.53±0.70
MP	7.54±0.002	265.40±9.52	567.00±6.13	5.46±0.09	30.03±0.10
FP	7.62±0.001	274.30±6.71	553.06±6.65	5.62±0.11	30.40±0.60

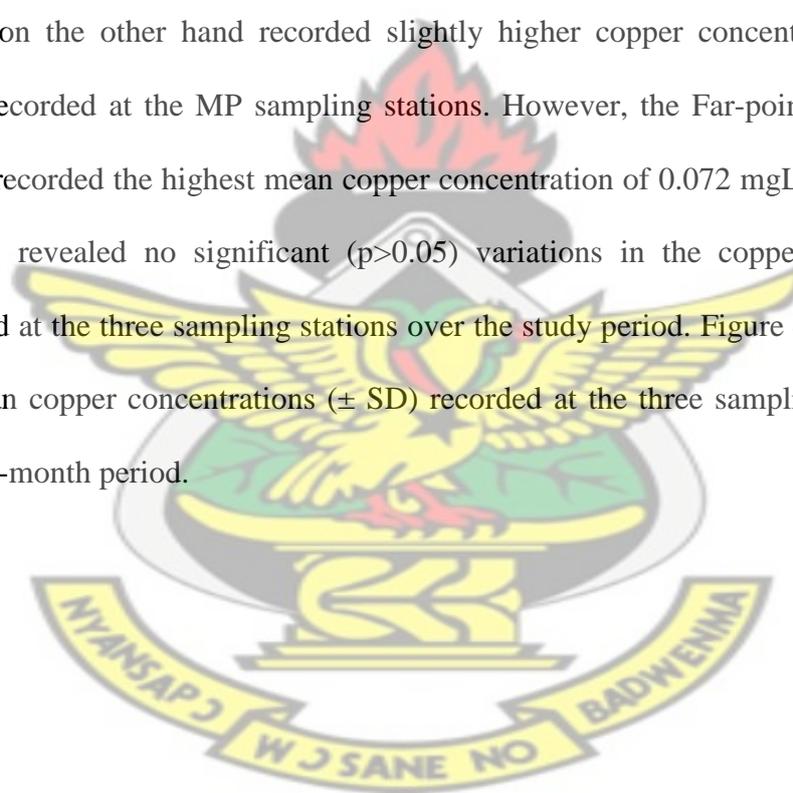
4.2 Heavy Metal Concentrations in the Water, Fish and Sediments

With the exception of Arsenic and Cadmium in the water, there were measurable concentrations of all the four studied heavy metals in the water and fish of the Jimi Dam. The concentrations of the metals in the water and bottom sediments at the sampling stations did not follow any particular trend with irregular distributions. The heavy metal concentrations in the different media are presented in the subchapters below.

4.2.1 Heavy Metals in the Water

The distribution of heavy metals in the water of the Jimi Dam revealed significant concentrations of copper and lead. Arsenic and cadmium however occurred in trace amounts and consistently below detection limits.

The concentrations of copper in the water from the three sampling stations selected on the Dam over the four-month period were not significantly variable. Again spatial distributions were as well not significant. Midpoint (MP) sampling stations recorded the lowest mean copper concentration of 0.052mgL^{-1} . The Near-shore sampling station on the other hand recorded slightly higher copper concentrations than the levels recorded at the MP sampling stations. However, the Far-point (FP) sampling station recorded the highest mean copper concentration of 0.072mgL^{-1} . The ANOVA analysis revealed no significant ($p>0.05$) variations in the copper concentrations recorded at the three sampling stations over the study period. Figure 4.1 below shows the mean copper concentrations (\pm SD) recorded at the three sampling stations over the four-month period.



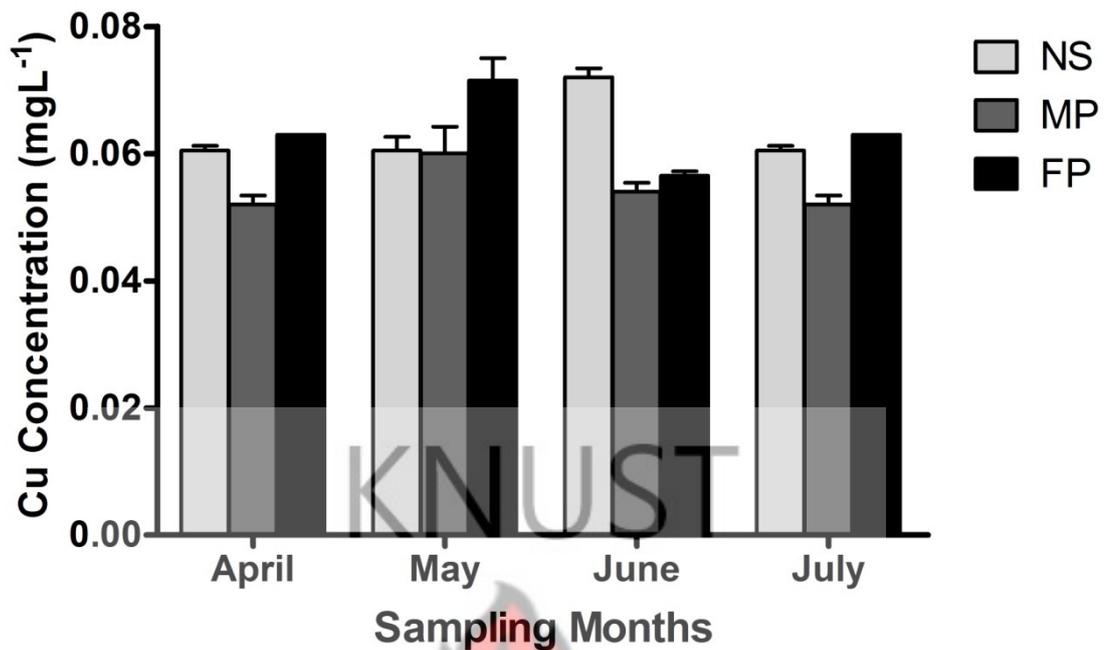


Figure 4.1 Mean \pm SD of copper concentrations recorded at the three sampling stations over the four-month period.

Lead concentrations in the water of the Dam were highly variable among the different sampling stations. The Near-shore sampling station consistently recorded the lowest mean lead concentrations over the four-month period. Mean Lead concentrations at the NS sampling station varied from a lowest mean concentration 0.053 mgL⁻¹ recorded in June to a highest mean concentration of 0.078 mgL⁻¹ recorded in July. The Midpoint sampling station recorded relatively higher mean lead concentrations compared to the Near-shore sampling station with June and May recording the lowest and highest mean concentrations of 0.078 and 0.096 mgL⁻¹ respectively. The FP sampling stations to recorded the highest mean lead concentrations with levels ranging from 0.084 to 0.094 mgL⁻¹ in July and the rest of the months respectively. The ANOVA test revealed highly significant variations ($p < 0.05$) in lead concentrations between the sampling stations. Figure 4.2 below shows the mean lead

concentrations (\pm SD) recorded at the three sampling stations over the four-month period.

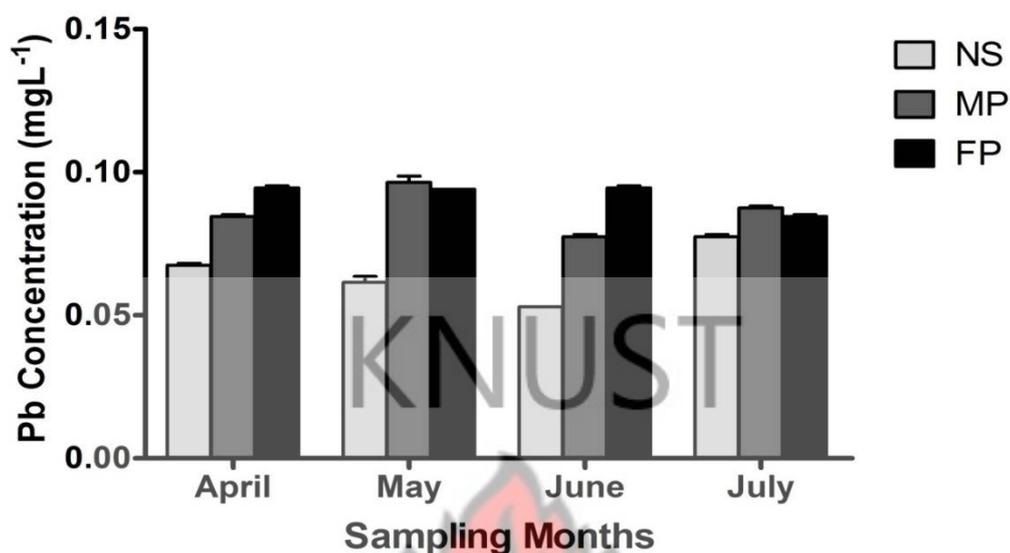


Figure 4.2 Mean \pm SD of lead concentrations recorded at the three sampling stations over the four-month period.

4.2.2 Heavy Metals Concentration in the Sediments of the Jimi Reservoir

Arsenic concentrations in the sediments over the sampling period did not show significant differences ($p > 0.05$). Mean arsenic levels at Near-Shore sampling station varied from a lowest concentration of 69.70 mgkg^{-1} in July to a highest of 87.55 mgkg^{-1} in May. The Mid-point sampling station recorded a mean As concentrations ranging from 66.40 to 76.85 mgkg^{-1} in July and April (as well as June) respectively. The Far-point sampling station recorded the lowest mean concentration of 68.95 mgkg^{-1} recorded in April and a highest concentration of 76.95 mgkg^{-1} recorded in June. Figure 4.3 below shows the mean As concentrations (\pm SD) recorded at the three sampling stations over the four-month period

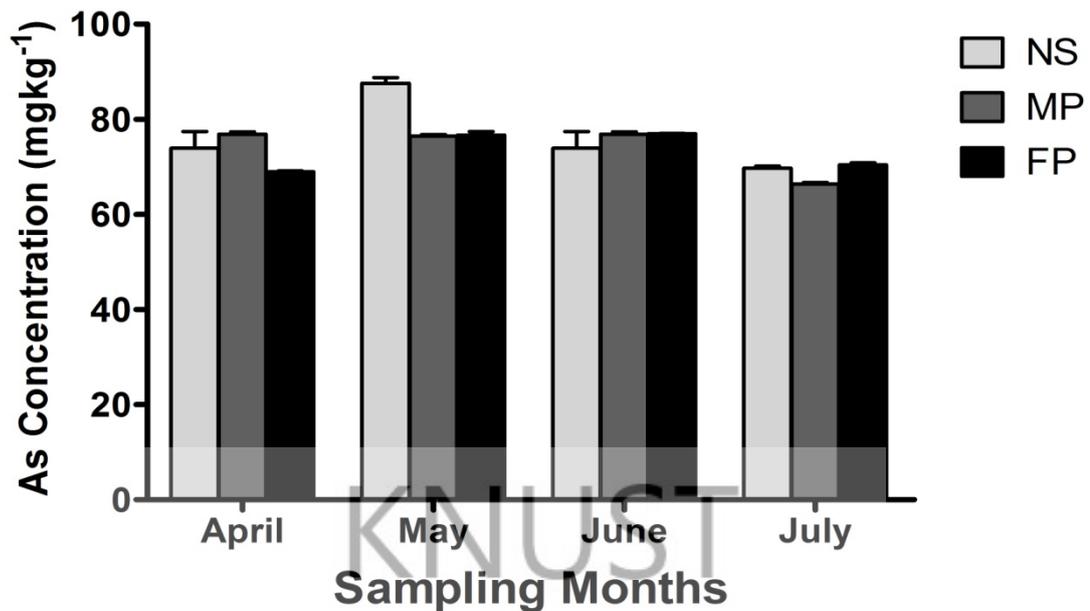


Figure 4.3 Mean \pm SD of As concentrations recorded at the three sampling stations over the four-month period.

Cadmium distribution in sediments among the sampling points over the study period was not significant. Highest Cd concentration was recorded in the month of June. Mean cadmium concentrations for the NS sampling station varied between 4.05 mgkg⁻¹ recorded in April and 4.75 mgkg⁻¹ recorded in July. The Midpoint sampling station had Cadmium concentrations ranging from 4.20 to 5.80 mgkg⁻¹. The FP sampling station recorded Cd concentrations over a narrow range of 4.10 to 4.55 mgkg⁻¹. There were no significant variations ($p > 0.05$) in the Cadmium concentrations measured at the three sampling stations over the study period. Figure 4.4 shows Mean \pm SD of cadmium concentrations recorded at the three sampling stations over the four-month period.

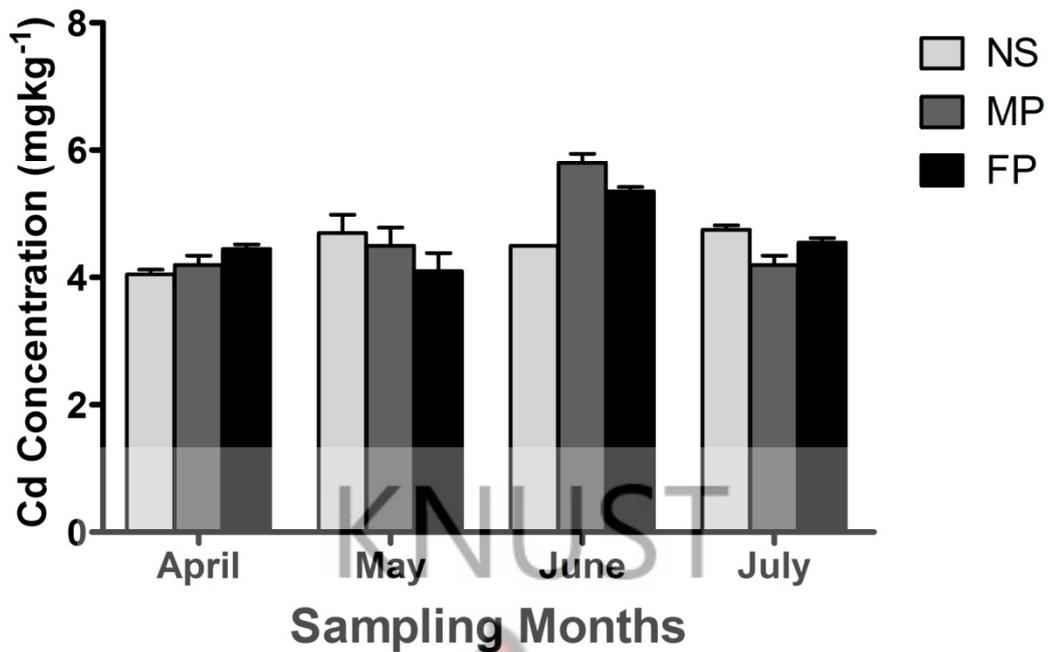


Figure 4.4 Mean \pm SD of Cadmium concentrations recorded at the three sampling stations over the four-month period.

Copper concentrations in the sediments of the Dam showed variable spatio-temporal trends. At the NS sampling station, Mean Copper levels varied from 22.10 mgkg⁻¹ in the month of April to a highest concentration of 42.35 mgkg⁻¹ during the May sampling period. The trends in Copper concentrations recorded at the MP sampling station was similar to the one observed at the NS sampling station with the lowest and highest concentrations of 18.35 mgkg⁻¹ and 49.45 mgkg⁻¹ recorded in April and May respectively. The FP sampling station consistently recorded the highest mean Copper concentrations in the bottom sediments from May to July, with the July sampling month recording the overall highest mean concentration of 79.05 mgkg⁻¹. The lowest mean Copper concentration in the bottom sediments at the FP sampling station of 19.05 mgkg⁻¹ was recorded in April, similar to the NS and MP sampling stations. Generally, there were no significant spatial differences ($p > 0.05$) in the observed Concentrations of Copper in the bottom sediments of the Jimi Dam. Figure 4.5 shows

Mean \pm SD of Copper concentrations recorded at the three sampling stations over the four-month period.

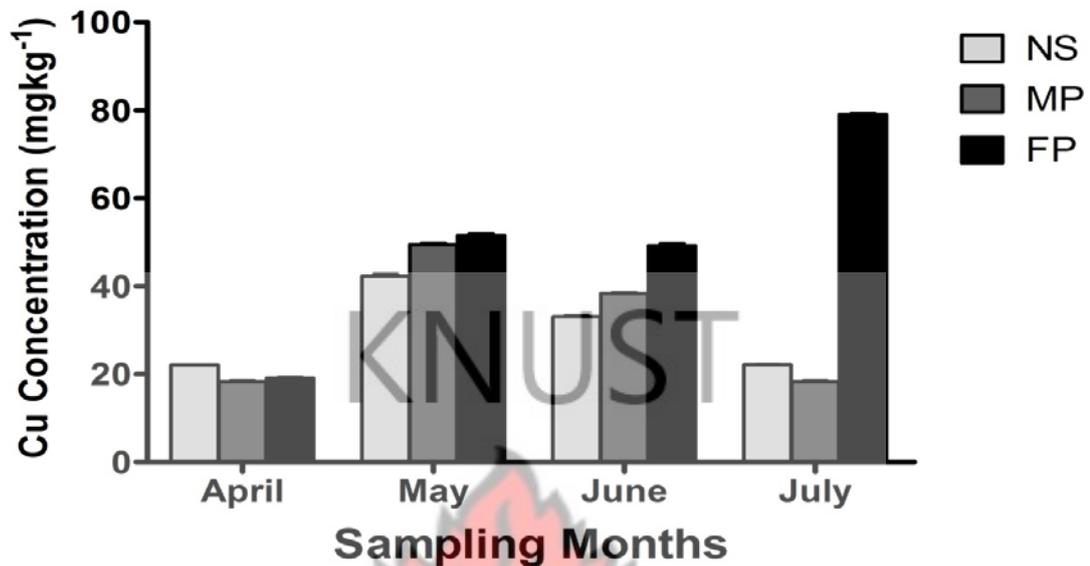


Figure 4.5 Mean \pm SD of Copper concentrations recorded at the three sampling stations over the four-month period.

Mean lead concentrations in the sediments were not significantly different ($p > 0.05$) at the three sampling stations. The FP sampling station recorded the overall highest mean lead concentration. Pb concentration at the NS sampling station varied over a narrow range of 11.90 to 12.85 mgkg⁻¹. The MP sampling station recorded lead concentrations in the sediments which were similar to that of the NS sampling station with a range from 11.85 to 13.85 mgkg⁻¹. That at FP sampling station did not differ significantly, it ranged from 12.95 to 13.65 mgkg⁻¹. Figure 4.6 shows Mean \pm SD of Pb concentrations recorded at the three sampling stations over the four-month period.

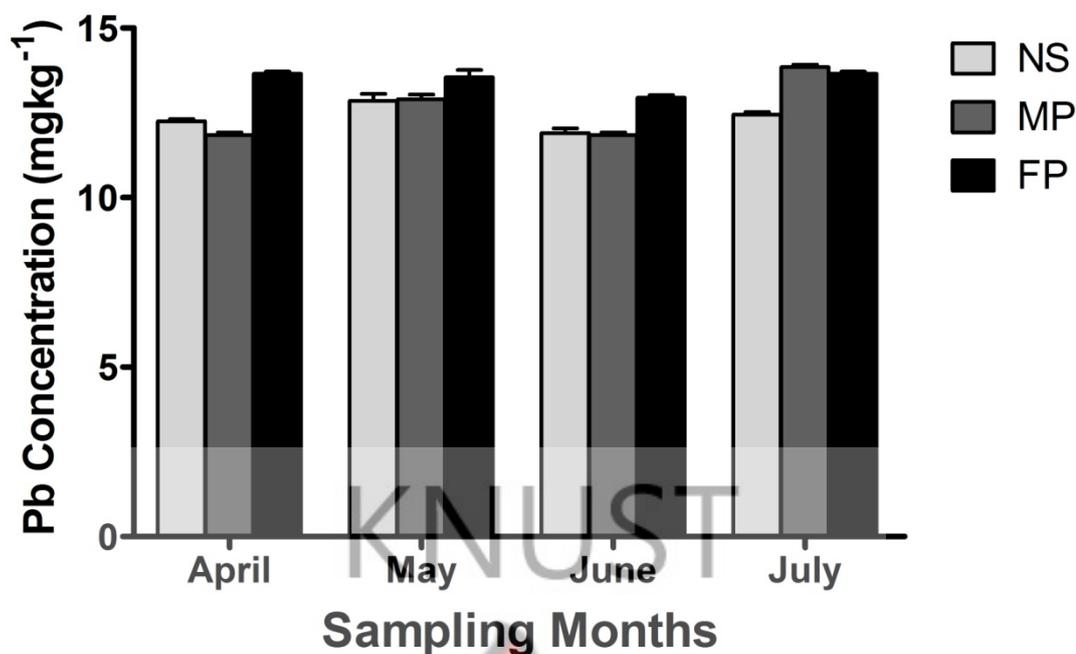


Figure 4.6 Mean \pm SD of Lead concentrations recorded at the three sampling stations over the four-month period.

4.2.3 Levels of Heavy Metals in Fish Muscle

Mean Arsenic concentrations in the different size based classes of the *Tilapia zillii* indicated a positive significant correlation between fish size and As concentration. Arsenic concentrations in the small size class of *Tilapia zillii* ranged narrowly from 15.85 mgkg⁻¹ to 16.35 mgkg⁻¹. Large size class of *Tilapia zillii* recorded higher Arsenic concentrations in their muscle tissues with mean concentrations varying between 16.05 and 26.65 mgkg⁻¹. There were no significant variations in Arsenic concentrations recorded in the two size classes of *Tilapia zillii*. The two size classes of the *Oreochromis niloticus* also exhibited positive correlation between fish sizes and As concentration but recorded significant variations ($p < 0.05$) of As in the two size classes. Mean Arsenic concentrations in the tissues of the small size class of *Oreochromis niloticus* ranged narrowly from 15.15 to 15.90 mgkg⁻¹. The mean As concentrations in the tissues on the large size class also ranged from 25.45 mgkg⁻¹ to

27.30 mgkg⁻¹. Figure 4.7 shows Mean ± SD of arsenic concentrations recorded in the tissues of the different size classes of the two fish species over the four-month period.

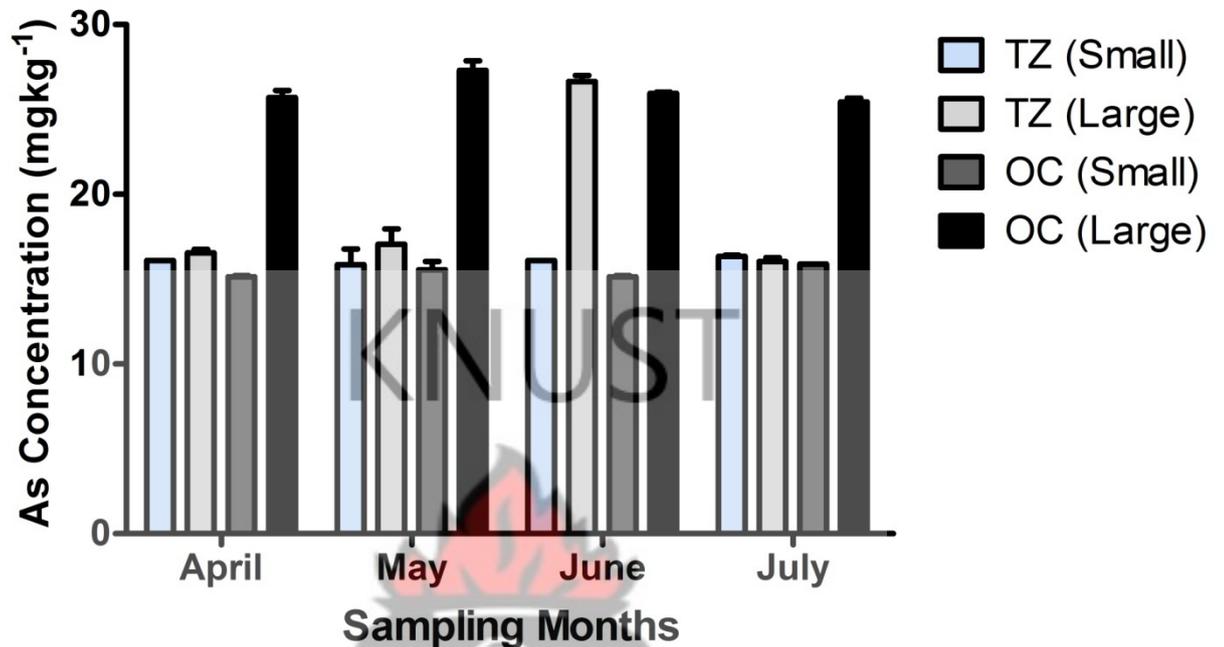


Figure 4.7 Mean ± SD of arsenic concentrations recorded in the tissues of the different size classes of the two fish species over the four-month period.

Copper concentrations also increased with increasing fish size. The small size class recorded mean copper concentrations ranging between 9.55 mgkg⁻¹ and 11.35 mgkg⁻¹. The Large size class of *Tilapia zillii* recorded slightly higher Cu concentrations relative to the small size class with mean values concentrations ranging between 8.30 and 11.70 mgkg⁻¹. Despite the relatively higher Cu concentrations in the large size class, there were no significant differences ($p > 0.05$) in the Cu concentrations between the two classes. The recorded Cu concentrations in the tissues of the *Oreochromis niloticus* were consistently higher than the concentrations recorded in the *Tilapia zillii* throughout the study period. The small size class of *Oreochromis niloticus* recorded mean copper concentrations ranging between 10.65 and 12.60 mgkg⁻¹ while the large size class recorded mean copper concentrations ranging between 13.10 and 13.15

mgkg⁻¹. The two classes did not exhibit any significant differences ($p>0.05$) in copper concentrations in their tissues.

There were, however, significant inter-species differences in copper concentrations among the fishes. Figure 4.8 shows Mean \pm SD copper concentrations recorded in the tissues of the different size classes of the two fish species over the four-month period.

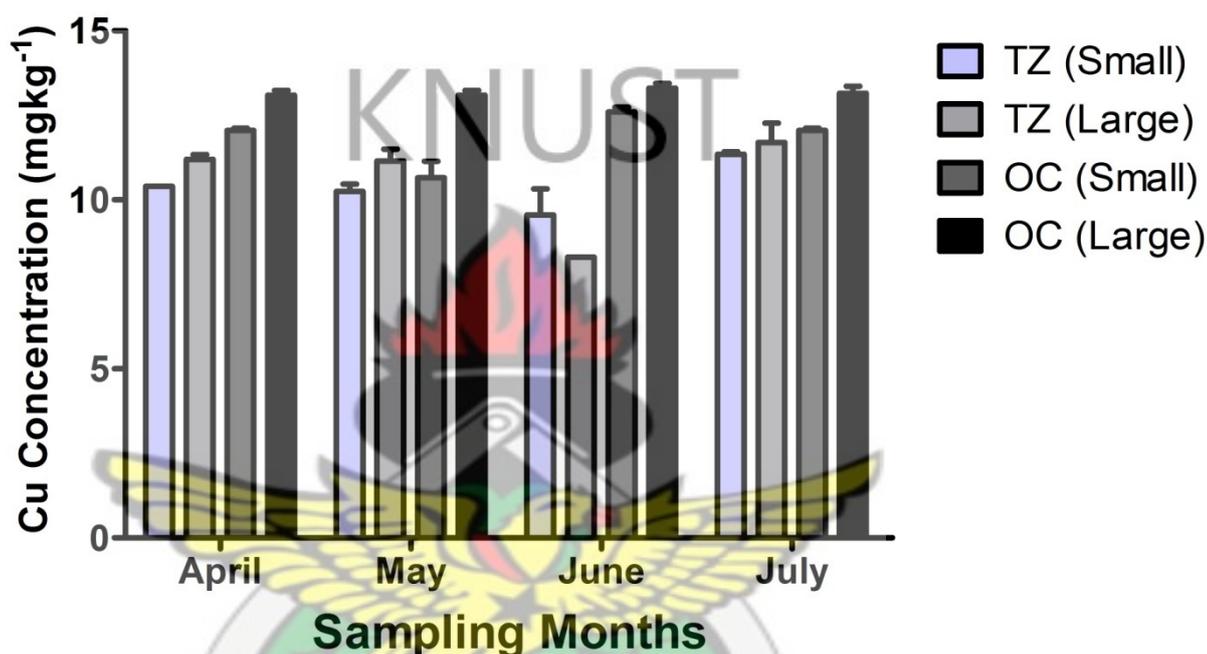


Figure 4.8 Mean \pm SD of Copper concentrations recorded in the tissues of the different size classes of the two fish species over the four-month period.

The mean lead concentrations in the muscle of the small size *Tilapia zillii* ranged from 7.50 and 8.45 mgkg⁻¹. The larger size class of *Tilapia zillii* recorded relatively higher mean. Mean Pb levels in the muscle of the large size classes ranged from 8.55 mgkg⁻¹ to 11.55 mgkg⁻¹. There were no significant differences ($p>0.05$) in the measured concentrations of the two size classes of *Tilapia zillii*. Lead concentrations in the muscle of the *Oreochromis niloticus* were higher than the concentrations measured in the *Tilapia zillii*. Figure 4.9 shows Mean \pm SD of Lead concentrations

recorded in the tissues of the different size classes of the two fish species over the four-month period.

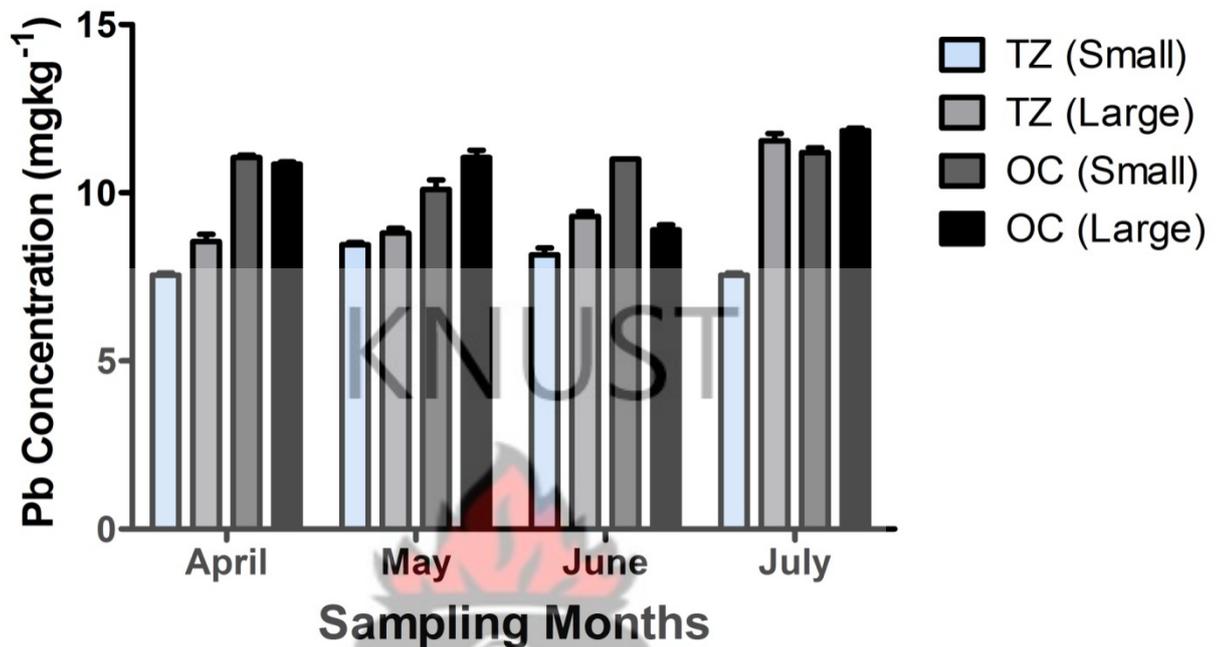


Figure 4.9 Mean \pm SD of Lead concentrations recorded in the tissues of the different size classes of the two fish species over the four-month period.

Cadmium concentrations in the different Class size classes of *Tilapia zillii* did not correlate with size. The large size class had the higher cadmium body burden with mean tissue concentrations ranging from 0.50 to 0.75 mgkg⁻¹. The small size class recorded a mean concentration that ranged from 0.55 to 0.65 mgkg⁻¹. The different sizes class of *Oreochromis niloticus* exhibited a positive correlation in heavy metal levels with size. Cadmium levels in the small size class varied between 0.60 and 0.90 mgkg⁻¹ while the large size class had mean cadmium levels ranging from 0.70 and 0.85 mgkg⁻¹. There was no significant differences ($p > 0.05$) in the Cadmium levels between the different size classes of *Oreochromis niloticus*. Figure 4.10 shows Mean \pm SD of Cadmium concentrations recorded in the tissues of the different size classes of the two fish species over the four-month period.

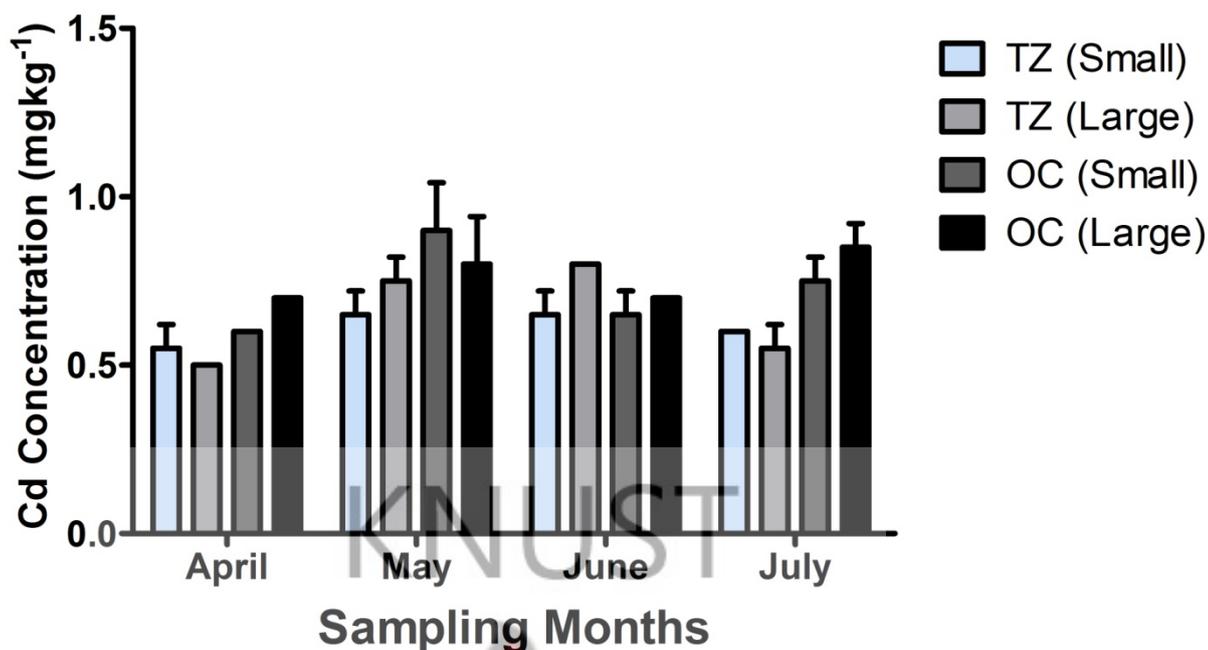


Figure 4.10 Mean ± SD of Cadmium concentrations recorded in the tissues of the different size classes of the two fish species over the four-month period.

4.3 Comparative Analyses of Heavy Metal Concentrations (in water, sediment and fish tissues) and their respective Reference Standards

Heavy metal concentrations in the water of the Jimi Reservoir were found to be low with arsenic and cadmium being below detection limit. Mean lead concentrations were however found to be well above the WHO (2011) drinking water quality guideline value of 0.01 mgL⁻¹. The recorded lead concentrations at some sampling stations were as much as approximately 10 times higher than the regulatory standard. Copper levels at all the sampling stations on the other hand were found to be well below the WHO standard for drinking water of 2 mgL⁻¹. Table 4.2 below details the comparison of the heavy metal concentrations recorded at the different sampling stations to the WHO (2011) drinking water quality guidelines.

Table 4.2 Comparison of heavy metal concentrations (mgL⁻¹) in the water of the Jimi Reservoir to WHO Drinking Water Quality Guidelines

Station	Month	METALS			
		As	Cu	Pb	Cd
Nearshore					
	April	BDL	0.060±0.001	0.068±0.001	BDL
	May	BDL	0.060±0.002	0.061±0.002	BDL
	June	BDL	0.072±0.001	0.053±0.000	BDL
	July	BDL	0.060±0.001	0.078±0.001	BDL
Midpoint					
	April	BDL	0.052±0.001	0.084±0.001	BDL
	May	BDL	0.060±0.002	0.096±0.002	BDL
	June	BDL	0.054±0.001	0.078±0.001	BDL
	July	BDL	0.052±0.001	0.087±0.001	BDL
Farpoint					
	April	BDL	0.063±0.001	0.094±0.001	BDL
	May	BDL	0.072±0.000	0.094±0.000	BDL
	June	BDL	0.057±0.001	0.094±0.001	BDL
	July	BDL	0.063±0.001	0.084±0.001	BDL
WHO (2011)			0.01	2	0.01
0.003					

*BDL: below detection limit

With the exception of Lead, all the heavy metal concentrations in the sediments of the reservoir were found to be above the USEPA Safety Reference Standards. Arsenic concentrations in the sediments at all the sampling stations were all well-above the threshold value of 30 mgkg⁻¹. Copper in the sediments were found to be above the USEPA safety reference standard value of 30 mgkg⁻¹. Lead concentrations in the sediments at all the sampling stations on the other hand, were all found to be below the Safety Reference Value of 40 mgkg⁻¹. Cadmium levels recorded in the sediments were above the Safety Reference Value of 3 mgkg⁻¹ at all the sampling points and fell within the levels for moderately polluted sites. Table 4.3 compares heavy metal concentrations (mgkg⁻¹) in the sediments of the Jimi Reservoir to USEPA Safety Reference Standards (Table 4.4)

Table 4.3 Comparison of heavy metal concentrations (mgkg⁻¹) in the bottom sediments of the Jimi Reservoir to USEPA Safety Reference Standards

Station	Month	As	Cu	Pb	METALS Cd
Nearshore					
	April	73.90±3.53	22.10±0.00	12.25±0.07	4.05±0.07
	May	87.55±1.20	42.35±0.35	12.85±0.21	4.70±0.28
	June	73.90±3.53	33.05±0.21	11.90±0.14	4.50±0.00
	July	69.70±0.42	22.15±0.07	12.45±0.07	4.75±0.07
Midpoint					
	April	76.85±0.50	18.35±0.21	11.85±0.07	4.20±0.14
	May	76.45±0.35	49.45±0.35	12.90±0.14	4.50±0.28
	June	76.85±0.49	38.35±0.21	11.85±0.07	5.80±0.14
	July	66.40±0.28	18.35±0.21	13.85±0.07	4.20±0.14
Farpoint					
	April	68.95±0.21	19.05±0.21	13.65±0.07	4.45±0.07
	May	76.65±0.78	51.55±0.49	13.55±0.21	4.10±0.28
	June	76.95±0.07	49.25±0.50	12.95±0.07	5.35±0.07
	July	70.40±0.42	79.05±0.21	13.65±0.07	4.55±0.07
USEPA		30	30	40	3

Table 4.4 USEPA Guidelines for Sediments Quality (mg/kg Dry Weights)

Metal	Not Polluted	Moderately Polluted	Heavily Polluted
Pb	<40	40-60	>60
Cd	<3	3-6	>6
Cu	<25	25-50	>50
As	<30	30-50	>50

With the exception of Cadmium, all the other heavy metals in the tissues of the two fish species exceeded their regulatory limits for human safety. Arsenic concentrations were several folds higher than the WHO regulatory limit of 1 mgkg⁻¹ and could pose serious health threat to human consumers. *Oreochromis niloticus* were as much as almost 30-times higher than the WHO regulatory standard. Mean copper concentrations in the tissues of the *Tilapia zillii* and *Oreochromis niloticus* were

found to be higher than the regulatory standard of 10 mgkg⁻¹. Lead concentrations in the fish tissues were also found to be approximately 10-times higher than its regulatory standard of 1 mgkg⁻¹. Cadmium concentrations in the two fish species were all found to be below the safety reference standard for human consumption of 1 mgkg⁻¹. With reference to the studied heavy metals, the consumption of fish by humans, from the Jimi Reservoir can pose a serious health risk. Table 4.5 compares the heavy metal concentrations (mgkg⁻¹) in the tissues of *T. zillii* and *O. niloticus* of the Jimi Dam to WHO Safety Reference Standards for human consumption

Table 4.5 Comparison of heavy metal concentrations (mgkg⁻¹) in the tissues of *T. zillii* and *O. niloticus* of the Jimi Dam to WHO Safety Reference Standards for human consumption

Species/Size Cd	Month	METALS			
		As	Cu	Pb	
<i>Tilapia zillii</i> (Small)					
	April	16.10±0.00	10.40±0.00	7.55±0.07	0.55±0.07
	May	15.83±0.19	10.25±0.21	8.45±0.07	0.65±0.07
	June	16.10±0.00	9.55±0.77	8.15±0.21	0.65±0.07
	July	16.35±0.07	11.35±0.07	7.55±0.07	0.60±0.00
<i>Tilapia zillii</i> (Large)					
	April	16.55±0.21	11.20±0.14	8.55±0.21	0.50±0.00
	May	17.05±0.91	11.15±0.35	8.80±0.14	0.75±0.07
	June	26.65±0.35	8.30±0.00	9.30±0.14	0.80±0.00
	July	16.05±0.21	11.70±0.56	11.50±0.21	0.55±0.07
<i>O. niloticus</i> (Small)					
	April	15.15±0.07	12.05±0.07	11.05±0.07	0.60±0.00
	May	15.55±0.49	10.65±0.49	10.10±0.28	0.90±0.14
	June	15.15±0.07	12.60±0.14	11.00±0.00	0.65±0.71
	July	15.90±0.00	12.05±0.07	11.20±0.14	0.75±0.71
<i>O. niloticus</i> (Large)					
	April	25.70±0.42	13.10±0.14	10.85±0.07	0.70±0.00
	May	27.30±0.57	13.10±0.14	10.05±0.21	0.80±0.14
	June	25.95±0.07	13.30±0.14	8.90±0.14	0.70±0.00
	July	15.45±0.21	13.15±0.21	11.85±0.07	0.85±0.07
WHO (2000)		1	10	1	1

CHAPTER 5

5.0 DISCUSSION

5.1 Sources of Heavy Metals into the Jimi Dam

Gold mining in recent times has become unpopular as it is regarded as a significant source of toxic metals contamination in the environment (Essuman *et al.*, 2007; Hanson *et al.*, 2007; Obiri 2007; Singh, 2007). Heavy metal pollution within mining communities of Ghana has been extensively studied (Adimado and Amegbey 2003; Akabzaa *et al.*, 2005; Carbo and Serfor - Armah 1997; Essumang *et al.*, 2007; Hilson 2002; Manu *et al.*, 2004; Obiri 2007; Yidana *et al.*, 2008).

Mining activities in Obuasi can be implicated in the release of high metal concentrations into the environment. The anthropogenic inputs may also play a role in the metal contamination although mining appears to be the main pollution source.

The Jimi Reservoir is situated in an area of intense illegal mining activities and the discharge of mine waste may be a contributing factor to the elevated levels of heavy metals, especially in the biota. The high levels of heavy metal in the water and biota of the Jimi Dam could also be due to the inherent mineralogy of the ores of the study area. Arsenic for example, is a metal naturally associated with gold and may be released through weathering and enter water bodies (Kumi-Boateng, 2007).

Although this study recorded relatively lower concentrations of heavy metals (FP sampling stations recording the highest) in the water samples of the Jimi Reservoir, some earlier studies have reported high metal concentrations in surface water samples and the highest values were recorded in communities living within or using streams draining mining, processing, and mine waste storage facilities. The highest values

were from samples taken from Kwabrafo, Dokyiwa and Ntonsua. At Kwabrafo, arsenic values were as much as 38 times higher than EPA general guidelines, 19 times higher than the EPA's mining and mineral processing guidelines and over 1,800 times higher than the WHO maximum values.

5.2 Accumulation of Heavy Metals in the Fish and Human Health Implications

Similar findings of positive relationships between metal concentrations in muscle tissues and body size have been reported by other researchers (Boyden 1974, 1977, Cossa 1989, Odzak *et al.*, 1994, Obirikorang *et al.*, 2010). It is likely that when tissues grow at a rate faster than metals can be absorbed; there will be a reduction in metal concentrations in the tissues. In nearly all species, smaller (younger) individuals grow at faster rate than the older ones; hence dilution of metal concentrations by tissue growth should have a greater effect in smaller individuals than in larger ones, causing a positive slope in the metal concentration-body size relationship (Strong and Luoma, 1981). The observations by Strong and Luoma, (1981) could explain why metal concentrations in the two fish species from the Jimi Reservoir exhibited a positive trend (an increasing trend with increasing size) in the metal concentration – body size correlation. On the other hand, positive relationships observed in some fish species have been explained in terms of extremely slow rates of elimination of a metal from the body of an organism with non-regulatory uptake (Langston & Zhou 1987a, 1987b). This suggests that the net accumulation of the metals may occur throughout the life of the organisms and higher concentrations in the larger (older) species may reflect longer-term exposures (Boyden 1977 in Obirikorang *et al.*, 2010).

The metal tissue level and level of bioaccumulation in the *Tilapia zillii* and *Oreochromis niloticus* could well be synergistically influenced by a number of abiotic and biotic factors. Among biotic factors, a major role is played by the fish age, sex,

size, genetic type and physiological condition, whereas major abiotic factors include the habitat, water circulation, chemical form of the metal present in water, between-metal competition, temperature, pH, dissolved oxygen, light, salinity, season, and degree of particular biotope contamination (Phillips, 1976; Martincic *et al.*, 1980; Marcus and Thompson, 1986; Giordano *et al.*, 1991; Gold- Bouchot *et al.*, 1995). Non-essential metals do not present any function for the fish's metabolism and are by consequent not regulated by the metabolism. The amount of As, Cd, and Pb in fish organisms can thus serve as an indication of environmental levels of these metals. These results are in agreement with Jobling (1995) who attributed the high accumulation of heavy metals in fish tissues to the metallothionein proteins which are synthesized in liver tissues when fishes are exposed to heavy metals and detoxify them. These proteins are thought to play an important role in protecting them from damage by heavy metal toxicants. Similar observations were reported by many studies carried out with various fish species (Guerrin *et al.*, 1990 and Saeed and Sakr, 2008). Essential heavy metals, on the other hand have intracellular regulatory mechanisms to keep their concentrations in equilibrium in the organisms (Luoma and Rainbow, 2008). The unusually high Pb concentrations in the flesh of the fish harvested from the Dam could lead to neurological disorders, especially in foetuses and children. Lansdown (1986) and Needleman (1987) reported behavioural changes and impaired performance in IQ tests in people exposed to high Pb levels. It is worth knowing that consumption of fish harvested from the Jimi Dam can pose a serious health risk to humans based on the heavy metal analysis.

CHAPTER 6

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

Apart from Arsenic and Cadmium in the water, there were significant concentrations of all the four heavy metals studied in the water and fish of the Jimi Reservoir. The concentrations of the metals in the water and sediments at the sampling stations did not follow any particular trend with irregular distributions.

The distribution of heavy metals in the water of the Jimi Reservoir revealed only measurable Copper and Lead concentrations with Arsenic and Cadmium concentrations being recorded in trace amounts and consistently below detection limits. Mean Lead concentrations were however found to be well above the WHO (2011) Drinking Water Quality Guideline Value of 0.01 mgL^{-1} . The recorded Lead concentrations at some sampling stations were as much as approximately 10 times higher than the regulatory standard. Copper levels at all the sampling stations on the other hand were found to be well below throughout the study period.

The concentrations of heavy metals in the sediments of the Jimi Reservoir were similar to those found in areas impacted by anthropogenic effects. The concentrations of the four metals in the sediments were highly measurable over the sampling period. With the exception of Lead, all the heavy metal concentrations in the sediments of the reservoir were found to be above the USEPA Safety Reference Standards for all or some of the sampling month.

Measurable concentrations of all the four studied metals were detected in the muscles of the two fish species, the Red-belly Tilapia (*Tilapia zillii*) and the Nile Tilapia

Oreochromis niloticus) obtained from the Jimi Reservoir. Heavy metals were identified in the muscles of two different size categories of the two species, Small (<10cm) and Large (>10cm) and results indicated a positive correlation between metal concentrations and fish sizes. With the exception of Cadmium, all the other heavy metals in the muscles of the two fish species exceeded their regulatory limits for human safety.

The study revealed no significant spatio-temporal variations in the concentrations of the four studied heavy metals as far as the water and biota were concerned, indicating homogeneity in the distribution and concentrations of the metals in the reservoir.

6.2 Recommendations

It is therefore recommended that;

- Fishing from the Jimi Reservoir be prohibited and consumption of fish from it discouraged because of the high levels of the heavy metals in the muscles of the two fish species.
- The results of this study can serve as baseline data for further research on freshwater bodies in Ghana.
- Further studies be carried out at the same study area to include other heavy metals and nutrients that were not covered in this research and cover a much longer period.
- Measures be put in place to control the discharge of effluents especially harmful chemical from the artisanal mining activities into the reservoir.

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KNUST



APPENDICES

Appendix A: Heavy Metal Concentrations in the Water, Fish and Sediment of the Jimi Dam

April



KNUST

Test Results

No	Sample Code	As 1	As 2	Cu 1	Cu 2	Pb 1	Pb 2	Cd 1	Cd 2
1	AF 1	0.161	0.161	0.104	0.104	0.076	0.075	0.005	0.006
2	AF 2	0.167	0.164	0.113	0.111	0.084	0.087	0.005	0.005
3	AF 3	0.152	0.151	0.120	0.121	0.111	0.110	0.006	0.006
	AF 4	0.259	0.260	0.130	0.132	0.109	0.108	0.007	0.007
4	AS 1	0.764	0.714	0.221	0.222	0.122	0.123	0.041	0.040
5	AS 2	0.772	0.765	0.182	0.185	0.118	0.119	0.043	0.041
6	AS 3	0.691	0.688	0.192	0.189	0.136	0.137	0.045	0.044
7	AW 1	<0.01	<0.01	0.060	0.061	0.067	0.068	<0.01	<0.01
8	AW 2	<0.01	<0.01	0.053	0.051	0.084	0.085	<0.01	<0.01
5	AW 3	<0.01	<0.01	0.063	0.063	0.095	0.094	<0.01	<0.01
9	Blank 1	0.035	0.034	0.026	0.024	<0.01	<0.01	0.005	0.005
10	Blank 2	<0.01	<0.01	0.013	0.015	<0.01	<0.01	<0.01	<0.01

All results in mg/L

May



KNUST

Test Results

No	Sample Code	As 1	As 2	Cu 1	Cu 2	Pb 1	Pb 2	Cd 1	Cd 2
1	AF 1	0.152	0.154	0.101	0.104	0.084	0.085	0.007	0.006
2	AF 2	0.177	0.176	0.114	0.109	0.089	0.087	0.008	0.007
3	AF 3	0.152	0.159	0.103	0.110	0.099	0.103	0.010	0.008
	AF 4	0.269	0.277	0.130	0.132	0.109	0.112	0.009	0.007
4	AS 1	0.884	0.867	0.421	0.426	0.130	0.127	0.045	0.049
5	AS 2	0.762	0.767	0.492	0.497	0.128	0.130	0.043	0.047
6	AS 3	0.772	0.761	0.512	0.519	0.134	0.137	0.039	0.043
7	AW 1	<0.01	<0.01	0.062	0.059	0.063	0.060	<0.01	<0.01
8	AW 2	<0.01	<0.01	0.063	0.057	0.098	0.095	<0.01	<0.01
5	AW 3	<0.01	<0.01	0.074	0.069	0.094	0.094	<0.01	<0.01
9	Blank 1	0.035	0.034	0.026	0.024	<0.01	<0.01	0.005	0.005
10	Blank 2	<0.01	<0.01	0.013	0.015	<0.01	<0.01	<0.01	<0.01

All results in mg/L

June



KNUST

Test Results

No	Sample Code	As 1	As 2	Cu 1	Cu 2	Pb 1	Pb 2	Cd 1	Cd 2
1	AF 1	0.161	0.161	0.090	0.101	0.080	0.083	0.007	0.006
2	AF 2	0.264	0.269	0.083	0.083	0.094	0.092	0.008	0.008
3	AF 3	0.152	0.151	0.125	0.127	0.110	0.110	0.007	0.006
	AF 4	0.259	0.260	0.134	0.132	0.090	0.088	0.007	0.007
4	AS 1	0.764	0.714	0.332	0.329	0.120	0.118	0.045	0.045
5	AS 2	0.772	0.765	0.382	0.385	0.118	0.119	0.059	0.057
6	AS 3	0.769	0.770	0.496	0.489	0.129	0.130	0.053	0.054
7	AW 1	<0.01	<0.01	0.071	0.073	0.053	0.053	<0.01	<0.01
8	AW 2	<0.01	<0.01	0.053	0.055	0.078	0.077	<0.01	<0.01
5	AW 3	<0.01	<0.01	0.057	0.056	0.095	0.094	<0.01	<0.01
9	Blank 1	0.030	0.030	0.010	0.010	<0.01	<0.01	0.005	0.005
10	Blank 2	<0.01	<0.01	0.011	0.010	<0.01	<0.01	<0.01	<0.01

All results in mg/L

July



KNUST

Test Results

No	Sample Code	As 1	As 2	Cu 1	Cu 2	Pb 1	Pb 2	Cd 1	Cd 2
1	AF 1	0.163	0.164	0.113	0.114	0.076	0.075	0.006	0.006
2	AF 2	0.159	0.162	0.113	0.121	0.114	0.117	0.006	0.005
3	AF 3	0.159	0.159	0.120	0.121	0.111	0.113	0.008	0.007
	AF 4	0.153	0.156	0.130	0.132	0.119	0.118	0.009	0.008
4	AS 1	0.694	0.700	0.221	0.222	0.124	0.125	0.048	0.047
5	AS 2	0.662	0.666	0.182	0.185	0.138	0.139	0.043	0.041
6	AS 3	0.701	0.707	0.792	0.789	0.136	0.137	0.045	0.046
7	AW 1	<0.01	<0.01	0.060	0.061	0.077	0.078	<0.01	<0.01
8	AW 2	<0.01	<0.01	0.053	0.051	0.087	0.088	<0.01	<0.01
5	AW 3	<0.01	<0.01	0.063	0.063	0.085	0.084	<0.01	<0.01
9	Blank 1	0.035	0.034	0.014	0.014	<0.01	<0.01	0.003	0.003
10	Blank 2	<0.01	<0.01	0.013	0.015	<0.01	<0.01	<0.01	<0.01

All results in mg/L

Appendix B: Results of the Analysis of Variance (ANOVA) and the Tukey's Multiple Comparison post-test for the various metals in the different media

Table B1: Results of the Analysis of Variance (ANOVA) and the Tukey's Multiple Comparison post-test for Copper in the Water.



Table B2: Results of the Analysis of Variance (ANOVA) and the Tukey's Multiple Comparison post-test for Lead in the Water.

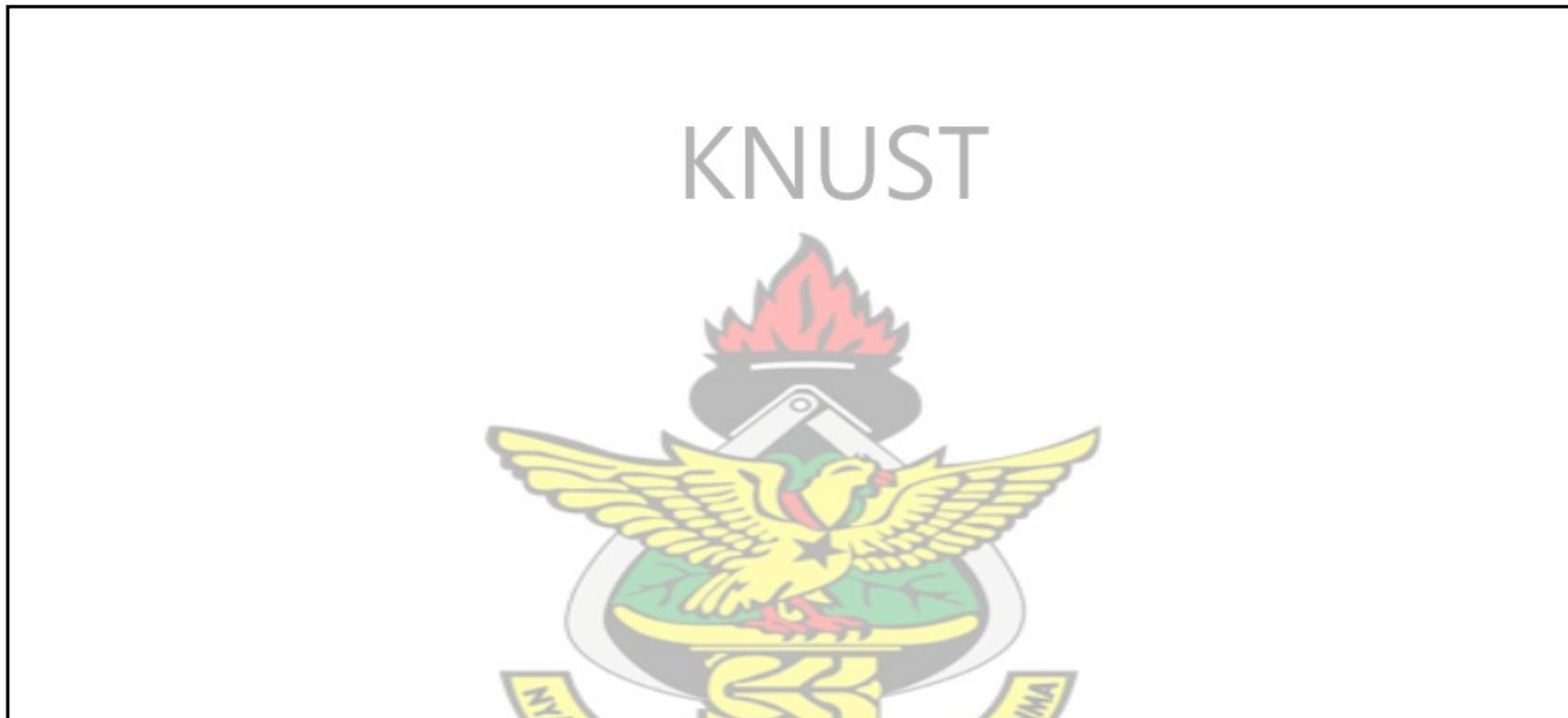


Table B3: Results of the Analysis of Variance (ANOVA) and the Tukey's Multiple Comparison post-test for Arsenic in the Bottom Sediments.



Table B4: Results of the Analysis of Variance (ANOVA) and the Tukey's Multiple Comparison post-test for Cadmium in the Bottom Sediments.



Table B5: Results of the Analysis of Variance (ANOVA) and the Tukey's Multiple Comparison post-test for Cadmium in the Bottom Sediments.



Table B6: Results of the Analysis of Variance (ANOVA) and the Tukey's Multiple Comparison post-test for Cadmium in the Bottom Sediments.



Table B7: Results of the Analysis of Variance (ANOVA) and the Tukey's Multiple Comparison post-test for Arsenic in the Fish Tissues.



Table B8: Results of the Analysis of Variance (ANOVA) and the Tukey's Multiple Comparison post-test for Lead in the Fish Tissues.



Table B9: Results of the Analysis of Variance (ANOVA) and the Tukey's Multiple Comparison post-test for Copper in the Fish Tissues.



Table B10: Results of the Analysis of Variance (ANOVA) and the Tukey's Multiple Comparison post-test for Cadmium in the Fish Tissues.

