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ASSESSMENT OF SOME HEAVY METAL (Pb, Zn, Mn, Cu, Fe) CONCENTRATIONS IN RAW WATER, SEDIMENTS AND AQUATIC MACROPHYTES AT THE BAREKESE RESERVOIR

By

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DECLARATION

I hereby declare that this submission is my own work towards the MSc and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement is made in the text.

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ABSTRACT

In this study, the concentrations of five heavy metals (Pb, Zn, Mn, Cu and Fe) were determined in raw water, sediments and aquatic macrophytes from selected sites at the Barekese reservoir in Ghana over a 6 month period. The obtained results revealed that the mean concentration ranges for lead (0.04-0.25 mg/L) and iron (0.49-0.89 mg/L) in water samples exceeded the WHO (2008) guidelines for drinking water. The reservoir water is therefore unfit for drinking except after adequate treatment. To assess metal contamination in sediments several indices of contamination (contamination factor, degree of contamination and PLI) and the Numerical Sediment Quality Guidelines (SQGs) were applied. Based on comparison with Numerical SQGs values, the sediment samples at the reservoirs intake were classified as heavily polluted with Pb and Cu. The values of the concentration factor (>1) confirmed the tremendous capacity of sediments to accumulate higher concentration of heavy metals as compared to water samples. Good information was also provided by analysis of whole plants and organs of passive aquatic macrophytes represented by four species: *Typha domingensis*, *Ceratophyllum demersum*, *Pistia stratiotes* and *Lemna paucicostata*. Metals in all the species were higher in their roots than their shoots. The Biological Accumulation Factor (the ratio of heavy metal content of the plant/water) for all plant species decreased in the order: Fe (279) > Cu (268) > Pb (259) > Mn (206) > Zn (143). The obtained values have elaborated the usefulness of aquatic macrophytes in biological monitoring of heavy metal contamination in water bodies. The overall concentration of the heavy metals in in the sediments was higher than those in the aquatic macrophytes. The raw water samples recorded the least concentration of heavy metals. The mean heavy metal concentrations in all the samples were however observed in the sequence; Fe > Cu > Mn > Pb > Zn.

CHAPTER ONE

INTRODUCTION

1.1Background

Heavy metal pollution of aquatic environments has become a serious environmental problem, which threatens aquatic ecosystems, agriculture, and human health (Wang *et al*., 2007). Heavy metals are natural ingredients of fresh water ecosystems where they are found in relatively low concentrations usually in milligram or nanogram level (Nussey, 1998). However, in recent times, the occurrence of heavy metals in excess of natural loads has arisen as a result of anthropogenic sources such as industrial and domestic effluents, urban storm-water run-offs, leaching of metals from garbage and solid waste dump (Biney *et al.*, 1994; Idris *et al*., 2004).

Over the last few decades, in many African countries, considerable population growth has taken place accompanied by a steep increase in urbanization, industrial and agricultural land use (Idodo-Umeh and Oronsaye, 2006). This has entailed a great increase in discharge of pollutants to receiving water bodies, causing undesirable effects on the aquatic environment. Most of these pollutants are heavy metals, which eventually settle in bottom sediments (Oguzie, 2002). The danger of heavy metals has been aggravated due to their relative high toxicity and persistent nature in the environment (Aboud and Nandini, 2009; Wepener *et. al*., 2001).

Heavy metal accumulation in the food web can occur either by bioconcentration from the surrounding medium such as water or sediment, or by bioaccumulation from the food source (Aboud and Nandini, 2009). These may have devastating effects on the ecological balance of the aquatic environment. High discharge of heavy metals into the aquatic environment eventually accumulates in water, sediments and dependent biotic components like fishes and aquatic plants (Ahern & Morris, 1998). Unusually high inputs of heavy metals into the aquatic environment have resulted in great financial losses, affected commercial fisheries and in some cases, have been hazardous to human health (Banerjee, 2003).

Monitoring programmes and research on heavy metals in aquatic environments have become widely important due to concerns over accumulation and toxic effects in aquatic organisms and to humans through the food chain (Otchere *et al*., 2003). Metal concentration in the aquatic environment has been analyzed using water samples (Akoto *et al.*, 2008), sediments (Aboud and Nandini, 2009) and aquatic biota (Ramdan, 2003) taken from study sites. These and other studies have revealed that the concentration of these metals is significantly higher in bottom sediment than in the water columns. Sediments act as a major reservoir of metals and also as a source of contaminants in aquatic environments under favourable conditions (Aboud and Nandini, 2009). The occurrence of elevated concentrations of trace 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 (Idodo-Umeh and Oronsaye, 2006). The analyses of water or sediment samples alone as indicators of heavy metal contamination are however subject to a variety of shortcomings as they do not allow for the estimation of the quantity bioavailable metals (Etim *et al*., 1991). It is against this background that bio-indicators are preferred in monitoring heavy metal pollution.

Aquatic macrophytes are effective biological monitors and have been widely used for heavy metal monitoring purposes worldwide (Salt *et al.*, 1995; Ramdan, 2003). Macrophytes are an important component of aquatic communities and play major roles in oxygen production, nutrient cycling, water quality control, sediment stabilization and provision of habitat and shelter for aquatic life (Ravera *et al.*, 2003).

Heavy metal accumulation in the aquatic macrophytes (*Typha domingensis, Ceratophyllum demersum, Pistia stratiotes* and *Lemna paucicostata*) has been thoroughly investigagted (Rai *et al*., 1995; Stankovic *et al*., 2000; Kadlec *et al*., 2002). Macrophytes accumulate heavy metals from surrounding water and sediments, producing an internal concentration several fold greater than their surroundings (Pip and Stepaniuk, 1992). This phenomenon known as bioaccumulation has led investigators to be interested in the toxicity of heavy metals in plants, in the use of macrophytes as biological filters for polluted waters as well as biological monitors of metals in the environment (Jackson, 1998). Of importance too is the fact that contaminated aquatic vegetation can be a source of food for a variety of herbivores and detritivores, leading to the possibility of bioaccumulation of metals in higher trophic levels of the food chain (Lilit and Baban, 2006). Metal concentration in aquatic macrophytes varies with plant species (Falaky *et al*., 2004), in different parts of a plant (Baldatoni *et al*., 2004), and with its concentration in growth media (Taylor and Crowder, 1983). Taking into account the selective capacity of aquatic macrophytes to absorb various substances, they have been proposed as useful indicators of heavy metals such as lead (Pb), zinc (Zn), copper (Cu) and arsenic (As) in water and bottom sediments (Rainbow, 1995).

Reservoirs, which are man-made lakes, are vital aquatic ecosystems that serve important environmental and economic purposes, including potable water supply, hydroelectric power generation, maintenance of water quality and flow, reproduction area for fishes and other aquatic organisms (Okurut *et al*., 2000). During the last 4 to 5 decades, many reservoirs such as the Volta Lake, Barekese Dam, Kpong Dam and Weija Dam have been constructed in Ghana by damming some rivers (Asante *et al*., 2005). These reservoirs ensure adequate and sustainable source of raw water for treatment into potable water for major cities and towns. In recent years however, the fresh water obtained directly from these reservoirs to satisfy the needs of the rapidly growing urban population has declined in quality (DFID, 1999). The assessment of water quality in reservoirs is essential because reservoirs are often one of the main sources of water for human consumption and irrigation (Rai *et al.*, 1995).

The Barekese Dam situated on the Offin River, is one of the major sources of potable water supply for the people of Kumasi and its environs (Kumasi *et al*., 2007). The reservoir which has a surface area of approximately 6.4 km^2 was constructed in 1969 by damming the Offin River at Barekese. The most representative macrophytic species in the Barekese reservoir are *Arthropteris orientalis*, *Ceratophyllum demersum, Nymphaea mexicana, Pistia stratiotes, Lemna paucicostata* and *Polygonum lanigerum* (Anning and Yeboah-Gyan, 2007). The Barekese catchment area has recently been identified by Boakye *et al*. (200.8) as one of the places which need to be protected by the Government of Ghana. Human activities found within the Barekese catchment include residential, farming, transportation and municipal waste disposal. These anthropogenic activities are likely to impact negatively on the water quality of the Bareksese reservoir (Boakye *et al*., 2008; Kumasi, 2008).

This study is therefore aimed at assessing the levels of heavy metals in this vital man-made aquatic system using samples of water, sediments and aquatic macrophytes from the reservoir.

1.2 Problem Statement

Water pollution in developing countries has reached an alarming situation and Ghana is no exception (Boakye *et al*., 2008). Control and sustainable management of river catchment areas are major issues in Ghana because of a variety of pressures placed upon land and water resources. Ansa - Asare and Asante (1998) have attributed the situation to nutrient enrichment of surface waters from urban sources, agricultural chemicals, sediment loading from deforestation, improper land management and the abstraction of water for human consumption and irrigation.

The Barekese reservoir provides 80 percent of the total public pipe borne water to the Kumasi metropolis and its environs. However over the past two decades the Barekese river basin has seen persistent degradation through anthropogenic activities in its catchment which also raises concern on the deteriorating water quality (Kumasi *et al*., 2007). Recent studies have shown that the rapid population growth accompanied by anthropogenic activities such as farming, deforestation and improper disposal of waste, have caused major reduction of water quality and siltation of the Barekese reservoir (Blokhius *et al*., 2005; Boakye *et al*., 2008). The uses of fertilizers in farming within a reservoirs catchment are potential sources of heavy metals discharge into water bodies (Blokhius *et al*., 2005). Manufactured fertilizers, animal manures, biosolids and recycled industrial wastes may all contain heavy metals such as arsenic (As), chromium (Cr), lead (Pb), mercury (Hg), nickel

(Ni), copper (Cu) and zinc (Zn). These metals may accumulate in the soil with repeated applications of crop nutrients and may eventually be discharged into water bodies through overland flow. High inputs of metal contaminants in aquatic environments could pose serious water quality problems resulting in potential long-term implications on human health and the ecosystem.

1.3 Justification

Despite the increasing global concern about heavy metal contamination in aquatic environments, little work has been done on the levels of these metals in water, sediments and aquatic biota of the Barekese reservoir (Biney *et al*., 1994; Kumasi *et al*., 2007). It is anticipated that the data generated on the levels of heavy metals in water, sediments and aquatic macrophytes would provide useful information on the pollution status of the reservoir for possible remediation measures.

In this study, *Typha domingensis, Ceratophyllum demersum, Pistia stratiotes* and *Lemna paucicosta* were selected due to their sedentary nature, abundance and ease of sampling. Moreover, various studies have indicated that these plants can accumulate contaminants such as heavy metals and are thus useful in water quality studies (Stankovic *et al.,* 2000; Odjegba and Fasidi, 2004).

1.4 Main Objective

The main objective of this study was to assess the concentrations of some heavy metals (lead, zinc, manganese, copper and iron) in raw water, sediments and aquatic macrophytes from the Barekese reservoir.

1.5 Specific Objectives

The specific objectives were;

1. To measure the concentrations of heavy metals in raw water.
2. To measure the concentrations of heavy metals in sediments at the reservoir.
3. To measure the concentrations of heavy metals in whole plants of *C. demersum* and *L. paucicosta.*
4. To measure the concentrations of heavy metals in roots and leaves of *T. domingensis* and *P. stratiotes*.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy Metals

Heavy metal is a general collective term which applies to the group of metals and metalloids with an atomic density greater than 4g /cm³ (Duffus, 2002). Examples of heavy metals are cadmium, mercury, zinc, copper, nickel, chromium, cobalt, vanadium, iron, manganese and lead. According to Alloway (1995), ‘‘all living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc’’. However, excessive concentrations of these metals can become detrimental to organisms with unusual high concentrations becoming toxic to aquatic organisms.

Heavy metals exist in surface waters in colloidal, particulate, and dissolved phases (NCSU, 2006). The colloidal and particulate metals may be found as hydroxides, oxides, silicates, or sulfides and can be adsorbed to clay, silica, or organic matter. Soluble forms of metals are generally ions or unionized organometallic chelates or complexes. NCSU (2006) also states that, ‘‘the solubility of heavy metals in surface waters is predominantly controlled by the water pH, the type and concentration of ligands on which the metal adsorbs the oxidation state of the mineral components and the redox environment of the system’’.

2.2 Heavy Metal Pollution of the Aquatic Environment

Heavy metal pollution typically refers to heavy metals in concentrations greater than would occur under natural conditions (McCartney *et al*., 2001). According to Rashed (2004), uncontrolled anthropogenic activities in recent times have increased the discharge of heavy metals into the aquatic systems. Rashed (2004) further recognizes the most important heavy metals in water pollution to be Zn, Cu, Pb, Cd, Hg and Cr.

According to NCSU (2006), metals have many sources from which they can flow into water bodies. These sources are:

(i) Natural sources: Heavy metals occur in the earth's geological structures, and can therefore enter water resources through natural processes. For example, heavy rains or flowing water can leach heavy metals out of geological formations. Weathering of rocks also discharges heavy metals into water bodies;

(ii) Industrial sources: Industrial processes that discharge wastewater into streams and rivers may pollute both fresh and salt water. Heavy metals may be contained in some industrial waste. These metals, such as mercury, lead, or beryllium, may settle on the bottom of streams and tidal basins. The lead-acid battery manufacturing industry for instance generate metal-rich effluents as well as airborne lead pollution which can subsequently be deposited in surface water resources (and of course on land).

(iii) Domestic wastewater: The prevalence of heavy metals in domestic formulations, such as cosmetic or cleansing agents could find their way into domestic wastewater and eventually pollute water bodies.

(iv)Agricultural sources: Agricultural production often emits pollutants that affect the quality of water resources. Activities that can contribute to water pollution include confined animal facilities, grazing, plowing, pesticide spraying, irrigation, fertilizing, planting, and harvesting. Agricultural discharges contain residuals of pesticides and fertilizers which often contains metals.

(v) Mining activities: Mineral processing operations can also generate significant heavy metal pollution, both from direct extraction processes (which typically entail size reduction - greatly increasing the surface area for mass transfer - and generate effluents) as well as through leaching from ore and tailings stockpiles. The tailings piles from mining activities contain elevated levels of heavy metals, such as lead and arsenic. These metals often migrate into the surrounding residential soil, ambient air, neighboring wetlands, and surface water.

According to Biney *et al.* (1994), heavy metals are portioned between water, sediments, suspended solids and aquatic biota in water bodies. An accelerated release of these toxic metals into the aquatic environment poses a major water quality problem due to their toxicity, persistence and bioaccumulation in food chains (Aboud and Nandini, 2009). Heavy metals are not biodegradable, and undergo a biogeochemical cycle with substantially different residence times in the various spheres and compartments of the environment. Nnaji and Okoye (2006) observed that even at low levels in water, some elements like cadmium (0.01 mg/L), lead (0.10 mg/L) and copper (0.05 mg/L) pose threats to humans. Deadly diseases like edema of eyelids, tumor, congestion of nasal mucous membranes and pharynx, stuffiness of the head and malfunctions in genetic make-up, gastrointestinal cavity, muscular, reproductive and neurological systems caused by some of these heavy metals have been documented (Abassi *et al*., 1998; Johnson, 1998). Excessive concentrations of heavy metals may also affect different aspects of water use, such as oxygen consumption by organisms in the environment, water permeability, and osmoregulation (Ahern and Morris, 1998). High inputs of heavy metals causes contaminated drinking water, damage of wildlife habitat, reduced fish stocks, loss of unique natural features and aesthetic losses.

2.2.1 Assessment of lead pollution in aquatic environments

Lead is the most common of the heavy metals, accounting for 13 mg/kg of the earth's crust. Lead has no known biological function (Wepener *et al*., 2001) and its excessive concentrations in aquatic environments is a major concern (Biney *et al.,* 1994). It is a hazardous heavy metal to most forms of life, very toxic and relatively accessible to aquatic organisms (Abassi *et al*., 1998). Lead has various uses; in the production of lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors, ammunition, glazes and plastic stabilizers (WHO, 2004; Abassi *et al*., 1998).

Lead is a typical example of anthropogenic metal pollution. Beginning with very low levels at about 2,700 years ago, lead concentration in water bodies increased during the industrial age and has risen rapidly since lead was added to gasoline fuel of vehicles (Harrison and Laxen, 1981). Lead in water comes from industrial, mines and smelter discharges before it is deposited in the sediment sinks (Denton *et al*., 1997). It is also discharged by vehicles into air, and then adsorbed from the air by environmental samples such as soil and plants. It then enters the waterways from soil, thus affecting the levels of lead in waters bodies. In the aquatic environment, lead is immobile and tends to accumulate in sediments close to its point of entry (NCSU, 1996).

Within the aquatic environments, lead is bioaccumulated in benthic bacteria, freshwater plants, invertebrates and fish (DWAF, 1996). The assessment of lead concentrations in water bodies is very important as lead has been reported to be toxic and often leads to anaemia (Denton *et al*., 1997). High consumption of lead could also damage the kidney, liver, nervous system, blood vessels and other tissues (Denton *et al*., 1997).

2.2.2 Assessment of zinc pollution in aquatic environments

Zinc is one of the important trace elements that play a vital role in the physiological and metabolic process of many organisms (Aboud and Nandini, 2009). It plays an active role in a variety of enzyme systems which contribute to energy metabolism, transcription and translation (Abassi *et al*., 1998). Zinc can be released by natural processes, but mostly results from anthropogenic activities. Surface water can be impacted by discharges of metal manufacturing and chemical industrial wastes, and also by run-off following precipitation on soils high in zinc, either due to the natural setting or human applications, including use of zinc fertilizer on agricultural soils. Particles released from vehicle tyres and brake linings are a major source of zinc in the environment (WHO, 2001).

According to Rajappa *et al*. (2010), zinc shows fairly low concentrations in water samples due to its restricted mobility from the place of rock weathering or from the natural sources. In lakes and rivers, some zinc remains dissolved in water or as fine suspended particles, while other zinc settles to the bottom in association with heavier particles. Rajkovic *et al*. (2008) asserted that elevated zinc levels as toxic to some species of aquatic life. From an environmental pollution standpoint, zinc is generally considered as a toxic element and has the potential to bioaccumulate in the food chain (Abassi *et al.,* 1998; WHO, 2004).

2.2.3 Assessment of manganese pollution in aquatic environments

Manganese is an essential micronutrient which serves as a functional component of nitrate assimilation and an essential catalyst of numerous enzyme systems in organisms (Adriano, 2001). In plants manganese is necessary in many redox enzymatic processes and in photosynthesis (Carranza-A´lvarez *et al.*, 2008). Manganese is one of the abundant elements in the earth's crust and is widely distributed in soils, sediments, rocks, water, and biological materials (NCSU, 2006).

The major sources of man-made environmental pollution by manganese arise in the manufacturing of alloys, steel, and iron products. NCSU (2006) also states that over 90% of the manganese produced in the world is used in the making of steel, either as ferromanganese or silicomanganese. Manganese is also used in the production of non-ferrous alloys, such as manganese bronze, for machinery requiring high strength and resistance to sea water, and in alloys with copper, nickel, or both in the electrical industry. Other sources include mining operations, the production and use of fertilizers and fungicides, and the production of synthetic manganese oxide and dry-cell batteries (Abbasi *et al.,* 1998). Manganese dioxide is used in dry-cell batteries and as an oxidizing agent in the chemical industry. Many manganese chemicals, e.g., potassium permanganate, manganese (II) sulfate, manganese dichloride, and manganese dioxide are used in fertilizers, animal feeds, pharmaceutical products, dyes, paint dryers, catalysts, wood preservatives and, in small quantities, in glass and ceramics. Some of these uses contribute to environmental pollution. Manganese pollution may also arise from the incineration of refuse containing manganese (WHO, 1981).

In surface water, manganese can oxidize or adsorb to sediment particles and settle to the bottom. Manganese bioaccumulate in lower organisms (e.g., phytoplankton, algae, molluscs and some fish) but not in higher organisms; bio-magnification in food chains is not expected to be very significant (WHO, 2004). Some manganese compounds are readily soluble in water, so significant exposures can also occur by ingestion of contaminated drinking water. Manganese concentrations above 0.1 mg/L impart an undesirable taste to drinking water. Manganese is believed to have a neurotoxic effect; a provisional health-based guideline value of 0.5 mg/L is proposed to protect public health (WHO, 1996). In chronic inhalation exposure to manganese, the main organ systems affected are the lungs, nervous system, and reproductive system, although effects on other organ systems have also been observed (Kondakis *et al*., 1989).

2.2.4 Assessment of copper pollution in aquatic environments

Copper is an essential micronutrient required by all organisms, being rapidly accumulated by plants and animals (Avenant - Oldewage and Marx, 2000). NCSU (2006) identifies copper as one of the worlds's most widely used metals with the electrical industry probably making use of it the most. Copper is used in electrical wiring, roofing, various alloys, pigments, cooking utensils and in the chemical industry. Copper compounds are also used as or in food additives, fungicides, algaecides, insecticides and wood preservatives or can be added to fertilizers and animal feeds as a nutrient to support plant and animal growth (Abbasi *et al.*, 1998). In water supply systems, copper salts are used to control biological growths in reservoirs and distribution pipes (WHO, 2004).

According to Kabata-Pendias and Pendias (2001), ‘‘copper reaches aquatic systems through anthropogenic sources such as industrial, mining, plating operations, influxes of copper containing fertilizers as well as traffic emissions’’. Consequently its existence in high concentration in waters within an area of study is an index of pollution from leachates and effluents of the polluted environments where the water sources are located. Although copper toxicity in humans is rare, it can be potentially serious if high levels are present in drinking water (Adriano, 2001). Long term exposure to copper causes irritation of nose, eyes and nose as well as headache, diarrhoea, chronic anaemia and kidney damage in humans (Abassi *et al.*, 1998).

2.2.5 Assessment of iron pollution in aquatic environments

Iron is one of the most abundant metals on Earth. It is essential to most life forms and to normal human physiology. In plants, iron is involved in many life processes such as chlorophyll biosynthesis, photosynthesis, respiration, nitrogen fixatiom, nitrate and nitrite reduction, metabolism of carbohydrates and in different redox systems (Branković *et al*., 2009).

Iron is a non-conservative trace element found in significant concentration in drinking water because of its abundance in the earth’s crust (Ghulman *et al*., 2008). Natural sources of iron in the aquatic environment include weathering of sulphide ores, igneous, sedimentary and metamorphic rocks. Human activities such as burning of coke and coal, acid mine drainage, mineral processing, sewage and landfill leachates also contributes to excessive iron concentrations in water bodies (NCSU, 2006). In water, iron occurs mainly in ferrous or ferric state (Ghulman *et al*., 2008). The chemical behavior of iron in the aquatic environment is however determined by oxidation - reduction reactions, pH and the presence of coexisting inorganic and organic complexing agents (Anon, 1996).

As a precaution against storage of excessive iron in the body a provisional maximum tolerable daily intake was calculated to be 2 mg/L for drinking water. This level does not present a hazard to health. The taste and appearance of drinking water will usually be affected below this level, although iron concentrations of 1-3 mg/L can be acceptable for people drinking anaerobic well-water. No health-based guideline value for iron is proposed (WHO, 1996). The shortage of iron causes anaemia and prolonged consumption of drinking water with high concentration of iron may lead to liver diseases (Rajappa *et al*., 2010).

2.3 Sediments

Sediments have been recognized as an integral and inseparable part of the aquatic environment as it provides foodstuffs and habitat for many aquatic organisms (Milenkovic *et al*., 2005). They also help to determine the overall assessment of heavy metals in water vis-avis aquatic life and survivability (Aboud and Nandini, 2009). Since sediments play a very important role in physico-chemical and ecological dynamics, any change in toxic concentrations of heavy metal residues in sediments will affect the natural aquatic life support systems.

2.3.1 Aquatic sediment contamination

Contaminated sediments, in both freshwater and marine systems, are a significant issue worldwide (Weng *et al.*, 2008). Contaminants can persist for many years in sediments, where they have the potential to adversely affect human health and the environment. One of the effects of environmental pollution is an increase in heavy metal content in lake sediments, which is commonly regarded as a good indicator of human-induced pollution (Aboud and Nandini, 2009).

Heavy metals in sediments comes from natural sources (rock weathering, soil erosion, dissolution of water-soluble salts) as well as anthropogenic sources such as municipal wastewater-treatment plants, manufacturing industries, and agricultural activities (Wang *et al*., 2007). Depending on their solubility, heavy metals may eventually become associated to suspended particulate matter and/or accumulate in the bottom sediments (Chen *et al*., 2008). Anthropogenic contamination can therefore be traced from the level of excess metal concentrations in sediments whose initial natural composition is known.

Lake sediments are especially susceptible to heavy metal accumulation and typically have metal concentrations several orders of magnitude higher than those in the overlying water (Nnaji and Okoye, 2006; Nirmal *et al.*, 2007). Contaminants are not necessarily fixed permanently by the sediments, and under changing environmental conditions they may be released to the water column by various processes of remobilisation (Allen, 1995). Thus, in aquatic systems, sediments may be both a carrier and possible source of pollutants. Consequently, sediments enriched by heavy metals constitute a threat to the health of aquatic organisms (USEPA, 1998).

2.3.2 Factors influencing the concentration of heavy metals in sediments

In their work, Basaham and El-Sayed (1997) shows that, the concentration of heavy metals in sediments can be influenced by variation in their texture, composition, reduction/oxidation reactions, adsorption/desorption, and physical transport or sorting in addition to anthropogenic input. Potentially, toxic compounds, especially heavy metals, are adsorbed on mineral or organic particles either in their organic or inorganic forms (Kabata-Pendias and Pendias, 2001). Most of these metals are stored in the sediments and some elements are taken up by plants. Metals have different behaviour patterns. For example, copper and zinc can remain in the sediments only temporarily, whilst iron and lead tend to be strongly bound to the sediments.

2.3.3 Importance of sediment analysis

According to Caccia *et al*. (2003), the analysis of sediments is a useful method in studying aquatic pollution with heavy metals. There are basically three reservoirs of metals in the aquatic environment: water, sediment and biota where levels in each of these three reservoirs are dominated by a complex dynamic equilibrium governed by various physical, chemical and biological factors. Among these three reservoirs, sediment is the major repository for metals, in some cases, holding over 99% of the total amount of metal present in the system (Wang *et al*., 2007). Davies *et al*. (1991) points out that, ‘‘the occurrence of elevated concentrations of trace 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’’.

Data from sediment analysis provides time - integrated mean values of considerable time – stability compared to data on pollutants from, for example water sources

(Hakanson, 1980). Monitoring of heavy metals in sediments thus provides vital information regarding their sources, distribution and degree of pollution (Denton *et al*., 1997). The assessment of sediment quality is therefore recognized as a critical step in estimating the risks associated with man-made pollution in riverine systems (Vignati *et al*., 2003).

2.4 Monitoring Bioavailable Metals in Aquatic Environments

Metals occur in the environment as a result of natural processes and as pollutants from anthropogenic activities (Rashed, 2004). These metals 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). 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. 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 (Ansari *et al.*, 2004).

2.4.1 Bioindicators

In the attempt to define and measure the presence and effects of pollutants on aquatic systems, bioindicators have attracted a great deal of interest. Bioindicators are biological indicators of environmental quality that characterize environmental conditions (Gadzała-Kopciuch *et al*., 2004) and reflect changes in the condition of an organism resulting from exposure to a toxicant (Chambers *et al*., 2002). According to Etim *et al*. (1991), ‘‘the analyses of water and sediment samples are subject to a variety of shortcomings, in that the methods do not allow for the estimation of the quantity of the metal which is biologically available''. It is against this background that bio-indicators are preferred in environmental monitoring.

The principle behind the bio-indicator approach is the analysis of an organism for their metal contents in order to monitor the metal excesses in their tissues. Bioindicators may be divided into those responding to environmental changes in a visible way (morphological and physiological changes) and those whose reactions are invisible, but which accumulate different substances (pollutants) whose concentrations may be determined (Gadzała-Kopciuch *et al*., 2004).

There are various advantages of bioindicators in pollution monitoring. They are useful as ''early warning'' tools of potentially adverse effects. Also, responses may provide a temporally and spatially integrated measure of bioavailable pollutants. For example biomarkers can detect intermittent pollution events that routine monitoring may miss. Specific responses can be used to attribute exposure to pollutants; bioindicators can provide information on the relative toxicities of specific chemicals; and bioindicators are applicable in both the laboratory and the field (Amiard *et al*., 2000).

Despite these advantages, there are also a number of limitations. Amiard *et al*. (2000), reports that a major handicap in the use of bio-indicators in field conditions is the interference from natural biotic and abiotic factors as it is almost impossible to distinguish between signals of disturbance caused by pollutants and the ''background noise'' due to natural fluctuations. Also chemicals may interact within their environment and therefore the combined action of these chemicals can complicate the interpretation of bioindicators responses (Amiard *et al*., 2000).

2.4.2 Selection of bioindicators

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). According to Phillips and Rainbow (1994) and Connell *et al*. (1999), bioindicators employed in biomonitoring surveys should possess most of the following attributes:

1. Contaminants should be accumulated without lethal impacts.
2. Bioindicators should be sedentary in order to represent the area in which they grow.
3. Bioindicators should be abundant throughout the area.
4. Bioindicators should be relatively long-lived.
5. Bioindicators used should be easy to sample, hardy to survive under laboratory conditions and should provide sufficient tissue for contaminant analysis.
6. Bioindicators should tolerate brackish waters, which are often the most contaminated areas in coastal waters.

2.5 Aquatic Macrophytes

Aquatic macrophytes are non – woody plants that inhabit the littoral zone of lakes and rivers (Jeffries & Mills, 1994). They are grouped as emergent, submerged and floating-leaved aquatic plants according to their leaf's relation with water (Cardwell *et al.*, 2002). Emergent plants have roots attached to sediments and protrude above the water surface. They include reeds (*Phragmites* sp.), club rush (*Typha latifolia*), brooklime (*Veronica beccabunga*) (Greenway, 1993). Submerged macrophytes grow completely below water surface, although some can resist and respond to exposure.

Examples of submerged plants are the capadian pondweed (*Elodea canadensis*), milfoils (*Myriophllum* spp.) and the water hornwort (*Ceratophyllum demersum*) (Greenway, 1993). Floating- leaved macrophytes are either rooted to the bottom, or are completely free- floating. Examples of floating leaved macrophytes include the common water hyacinth (*Eichhornia crassipes*), aquatic fern (*Salvinia* spp.), and water lettuce (*Pistia stratiotes*) (Greenway, 1993).

Macrophytes are excellent indicators of watershed health due to their inherent ability to respond to nutrients, light, toxic contaminants, metals, herbicides, turbidity, water level change, and salt. According to Robach *et al.* (1996), ‘‘the distribution and performance of many aquatic macrophytes is often correlated with water quality’’. Certain aquatic plant species can therefore be used as indicators of low level environmental contamination that might otherwise be difficult to detect.

2.6 Heavy Metal Accumulation in Aquatic Macrophytes

Aquatic macrophytes grow profusely in lakes and waterways all over the world and in recent decades, their negative effects have been magnified by man’s intensive use of water bodies (Falaky *et al.*, 2004). Eradication of these weeds has proved almost impossible and even reasonable control is difficult. Turning these weeds to productive use would be desirable if it would partly offset the costs involved in mechanical removal (Falaky *et al.,* 2004). Among other uses, there has been considerable interest in using aquatic plants in pollution control, as these plants are known to accumulate heavy metal from the water in which they are growing (Salt *et al*., 1995; Melzer, 1999). The emergent, submerged and free-floating aquatic macrophytes are known to accumulate and bioconcentrate heavy metals from the aquatic environment (Melzer, 1999).

Macrophytes absorb heavy metals from surrounding water and sediments, producing an internal concentration several fold greater than their surroundings, a phenomenon known as bioaccumulation (Pip and Stepaniuk, 1992). This property of aquatic macrophytes has found useful applications in the removal of heavy metals from acid mine drainage, agricultural landfill and urban storm-water run-off. As the accumulation of heavy metals in organisms depends upon the concentration of pollutants in water as well as the length of time the organisms have been exposed, the tissue analysis of aquatic macrophytes may provide a cumulative evaluation of exposure (Baldantoni *et al*., 2004).

In his study, Rai *et al*. (1995) demonstrates that the mechanism for the uptake of heavy metals by macrophytes is by direct absorption from the water column to the plant surface followed by passive or active transport across membranes and in a minor scale by root uptake. Sawidis *et al*. (1991) further explains that where root uptake is the principal mode, the metals content of the macrophytes represents remobilization from the sediments. The authors again found that, if foliar uptake is the principal mode, then the metals content of the macrophytes represents a reduction in the water column concentration with the macrophytes serving as at least a temporary sink for these pollutants. In this regard, the uptake of heavy metals by leaves would be expected to become important when metal concentrations in the surrounding waters are high and low when metal concentrations in the sediment interstitial water are low (Guilizzoni, 1991).

Studies on metal accumulation in aquatic macrophytes in laboratory or greenhouse settings using metal-enriched nutrient solutions were usually very impressive with high metal uptake or accumulation (Mishra *et al*., 2008). Metal uptake and bioaccumulation studies done by several workers in aquatic macrophytes in natural populations also yielded very good results (Jackson, 1998). Interested metals accumulated by these aquatic plants were mainly micronutrients or heavy metals, namely, iron, copper, nickel, cobalt, mercury, chromium and lead (Mishra *et al.*, 2008). Metal bioaccumulation depends upon numerous biotic and abiotic factors, such as temperature, pH and dissolved ions in water (Demirezen and Aksoy, 2004). Bioaccumulation of metals varies considerably among species growing in the same area, as well as within species during season (Falaky *et al.*, 2004).

Welsh and Denny (1980), analyzing roots, young and old shoots of the plants, and sediment and water samples, collected in two English lakes, pointed out that in nine taxa of submersed aquatic macrophytes, lead accumulation in the shoots is the result of adsorption from water, while copper accumulation is mainly due to absorption by the roots and translocation within the plant to the shoots. According to Jackson (1998), heavy metals enter the biological cycle through the roots and leaves of plants and are enriched in various plant organs. Baker and Walker (1990) also observed higher copper, zinc, lead and cadmium concentration in the roots than the green leaves of plants taken from contaminated areas.

In his study on the accumulation of heavy metals in aquatic macrophytes in El Bakar drain in Egypt, Falaky *et al.* (2004) observes wide variations of metal concentrations in the various species investigated. The author further proposes *Eichhornia crassipes* (floating plant), *Ceratophyllum demersum* and *Potamogeton crispus* (submerged plants), *Typha domingensis* and *Phragnites australis* (emergent plants) as the most efficient accumulators.

The analysis of heavy metals in plant tissues provides a time integrated information about the quality of lake system as these plants are immobile (Baldantoni *et al*., 2004). In addition, detecting environmental pollution by using aquatic macrophytes as indicators is very cost effective, reliable and a simple alternative to the conventional sampling methods (Zurayk *et al*., 2001). The extent of bioaccumulation of metals in plants is however dependent on the total amount, the biovailability of each metal in the environmental medium, the route of uptake storage and excretion mechanisms. The requirements of different organisms for essential metals vary substantially but optimal concentration ranges are narrow and frequently under careful homeostatic control. Excess metal concentration in an organism must be actively excreted, compartmentalized in cells or tissues, or metabolically immobilized. Some metals escape all these actions causing toxic and other adverse effects (Chapman, 1996).

2.6.1 Heavy metal accumulation in *Typha domingensis* and other emergent macrophytes

Typha domingensis (Cattail) is an emergent, perennial aquatic macrophyte with an extensive rhizome system, flat leaves and a height of about 4m (Kadlec *et al*., 2002). The plants normally grow tall and stick out of the water at the lake edge. Like other emergent plants, *T. domingensis* have roots in deoxygenated mud rather than well aerated soils. The root cells possess aerial reproductive structures for uptake of oxygen (Burgis and Morris, 1987). *T. domingensis* plays an important role in the remediation of pollutants due to their densely spreading rhizomes and roots in the littoral zone of aquatic ecosystems. *Typha* species have important properties such as a high natural productivity and the ability to accumulate large amounts of heavy metals and nutrients (Anon, 2005). They play an important role in metal bioavailability through rhizosphere secretions and exchange processes. This naturally facilitates metal uptake by other floating and emergent forms of macrophytes.

In their study, Dunbabin and Bowmer (1992) observed that *Schoenoplectus* and *Typha* spp. (rushes) can be more tolerant than other species and further explained metal tolerance as a function of plant phenology, vigour and growth as well as metal speciation and aquatic chemistry. According to the authors, the roots of *T. domingensis* accumulate more metals than the rhizome (possibly due to iron plaque), and the leaves accumulate the least amount of metals. Cardwell *et al.* (2002) studies on metal accumulation in aquatic macrophytes form Southeast Queensland Australia found that, for *T. domingensis* samples, the order of accumulation for the non-essential elements cadmium and lead was; roots > rhizomes > leaves. Dunbabin and Bowmer (1992) elucidates that, *T. domingensis* influences metal storage indirectly by modifying the substratum through oxygenation, buffering, pH and adding organic matter.

The possibility of *Typha* species utilization to investigate waste–water treatment was investigated by Singh *et al*. (2012). They found *Typha* species could produce large quantities of biomass, the total annual productivity being approximately 56.6 ton/ha. The study also showed that *Typha* species have a rather high capacity to absorb heavy metals such as copper, manganese and zinc in broad–leaf *T. latifolia* than narrow–leaved *T. angustifolia*. It was further noted that seasonal dynamics affect the concentration of chemical elements and biomass in *Typha* species. On these bases they concluded that *Typha* species can be used for water purification and they should be harvested during summer to remove metals from waste–water (Anon, 2005).

Typha latifolia has been tested for their removal capacities of heavy metals in a number of laboratory-scale experiments. Ye *et al*. (1997) observed that, cadmium, lead and zinc in the leaves of four populations of *T. latifolia* collected from metal - contaminated and uncontaminated sites were maintained at low levels, while the roots accumulated relatively high levels. The uptake of trace metals by the root systems of aquatic plants depend both on the kind of metal and on the species of plant absorbing the metal. Seedlings from metal–contaminated populations also accumulated considerably more metals in their roots than the uncontaminated population, in a pot trial (Ye *et al*., 1997). Dunbabin and Bowmer (1992) demonstrated that under contaminated conditions, the greater proportion of heavy metals taken up by plants was retained in the roots with metal concentrations decreasing in the following order: roots > rhizomes >non-green leaves > green leaves. The high contents of metals in roots and low concentrations in leaves indicate that only a fraction is transferred from roots to the aboveground parts of the plant (Dunbabin and Bowmer, 1992).

2.6.2 Heavy metal accumulation in *Ceratophyllum demersum* and other submerged macrophytes

Ceratophyllum demersum L. (*Ceratophyllaceae*), hornweed or coontail grows in shallow, muddy, quiescent water bodies at lowlight intensities. It is a submerged rootless, perennial macrophyte which grows with the base of its stem buried in sandy or silt substrate (Greenway, 1993). *C. demersum* is prone to dislodgement, and its buoyant stems may become free-floating. The leaves are very thin with no strengthening tissue and are thus supported by water (Armstrong *et al*., 2003). It has a high capacity for vegetative propagation and biomass production even under low nutritional conditions.

Stankovic *et al*. (2000) pointed to the use of *C. demersum* as a measure of lake pollution as it can contain trace metals such as cadmium and lead in its tissue. The plants have very thin cuticle and therefore readily take up metals from water through the entire surface. Hence the integrated amounts of bioavailable metals in water and sediment can be indicated to some extent by using these macrophytes (Armstrong *et al*., 2003).

In his investigation on the role of macrophytes in accumulation of heavy metals, Kara (2005) observed that, submerged species accumulate relatively high heavy metal concentrations compared with emergent species in the same area. Whereas emergent aquatic macrophytes generally accumulate low concentrations of heavy metals in their harvestable biomass and have a small contribution to the overall removal of metals in constructed wetlands the situation is different for submerged macrophytes. Submerged macrophytes have been suggested as useful species in reducing metal concentrations in storm water and secondarily treated wastewaters (Falaky *et al.*, 2004).

2.6.3 Heavy metal accumulation in *Pistia stratiotes* and other floating leaved macrophytes

Pistia stratiotes (Water lettuce) is a floating leaved aquatic macrophyte that consists of a rosette of pale velvety green leaves, a very short stem and long feathery roots suspended in water (Armstrong *et al*., 2003). The hairy cover of its leaves trap air and are water repellent, preventing the plant from being submerged by heavy rains. The flowers of *P. stratiotes* are bisexual and reproduction is by means of stolons and seeds. Seeds are easily carried by water for long distances, since they float during the first two days after they reach maturity (Holm *et al*., 1991). Since the surface of the water is a region subject to severe mechanical stresses from wind and water movements, *Pistia* spp. need strong morphological resistance. Adaptations here include strong, leathery and peltate leaves, circular in shape with an entire margin, hydrophobic surface and with long pliable petioles (Holm *et al*., 1991).

Odjegba and Fasidi (2004) investigated the ability of *P. stratiotes* to tolerate and accumulate several distinct heavy metals for eventual use in phytoremediation of natural water bodies polluted with these heavy metals. They observed that, although the plant exhibited different patterns of response to cadmium, copper, chromium, lead and nickel concentrations as high as 5m/L resulted in distinct levels of growth inhibition and biomass production, all the elements accumulated at high concentrations mainly in the root system than the leaf system. Other floating-leaved plants, water hyacinth (*Eichhornia crassipes*), pennywort (*Hydrocotyle umbellata*), and common salvinia (*Salvinia minima*) has also been described as suitable candidates for phytoremediation of heavy metals (Mishra *et al*., 2008).

2.6.4 Heavy metal accumulation in *Lemna paucicostata* and other free – floating aquatic macrophytes

Lemna paucicostata (Duckweed) is a small, fragile, free-floating aquatic plant from the duckweed family. The plant grows as simple free-floating thalli on or just beneath the water surface. It is fast growing, adapts easily to various climatic conditions, and plays an important role in the extraction and accumulation of metals from water (Rai *et al*., 1995). The plants grow mainly by vegetative reproduction: two daughter plants bud off from the adult plant. *L. paucicostata* flourishes in quiescent, shallow water bodies and can survive best between pH of 4.5 to 8.3 (Rai *et al*., 1995).

Many reports are available on the uptake of metal ions by duckweeds and the numerous interactions that occur. Duckweeds will uptake and concentrate Cd, N, Cr, Zn, Sr, Co, Fe, Mn, Cu, Pb, Al and even Au. *Lemna* spp has an exceptional capability and potential for the uptake and accumulation of heavy metals, surpassing that of algae and other aquatic macrophytes (Rai *et al*., 1995). Like other free floating plants *Lemna* spp. are useful in phytoremediation due to their high growth rate, high capacity to accumulate heavy metals and metalloids, survival under adverse conditions and tolerance to high concentrations to heavy metals (Mishra *et al.*, 2008). It is potentially useful as an indicator of pollution because of its ability to integrate and rapidly monitor the pollutants' variations in the water''. Moreover, they tolerate unstable environmental conditions and exhibit high sensitivity to heavy metal toxicity.

Free - floating plants absorb the bulk of mineral salts either from the sediments via the root system, from the water phase by the leaves, or from both sources (Rai *et al*., 1995). Guilizzoni (1991) asserts that some floating rooted plants may absorb metals directly from water when they are not readily available in sediments and/or in high concentrations in the surroundings. For monitoring of water quality, it seems logical that free-floating plants should be used in place of rooted species since such plants derive their nutrients solely from the water column (Rai *et al*., 1995).

2.7 Heavy Metals in the Ghanaian Aquatic Environment

Studies on the occurrence and distribution of metals in Ghana have been conducted on all the major environmental matrices (water, sediment, fauna and flora). In his study, Akoto *et al*. (2008) determined the levels of heavy metals in streams serving the Owabi Reservoir. His study reveals the levels of lead and arsenic to be higher than the WHO (2004) limits for drinking water. The concentrations of iron, manganese, zinc and copper in all the streams were however within the acceptable WHO (2004) limits. The results showed that all the streams were polluted and must be treated before consumption Akoto *et al*. (2008) also recommends that, human activities within the Owabi catchment should be monitored closely to minimize their polluting impacts on the water quality.

Heavy metal concentrations in sediments from different sampling sites of the Volta Estuary in Ghana have also been determined by Adu (2010) who concludes that the concentrations of the elements are well below the Sediment Standard values. He further indicated that, the local metal fabrication industries and the surrounding agricultural lands have not severely impacted negatively on the Estuary.

Laar *et al*. (2011) conducted a survey of trace elements in the Sakumono wetland sediments and measured high concentrations of Cd, Co, Cr, Cu, Ni and Mn in the sediment materials. They also reported significant concentrations of Fe varying from 63.9 to 172 mg/kg. The excessive Fe concentrations in the sediment were attributed to human activities such as the discharge of untreated sewage, use of the metals in industrial processes as well as the ability of the sediment to also act as a sink for the metal.

Studies on the distribution of Hg, Cd, Pb, Cu, Zn and Fe in water, finfish and shellfish, macrophytes and sediments from Kpong headpond and lower Volta River showed the highest concentration of iron and lead in sediments and of manganese and cadmium in macrophytes (Biney, 1991).

Hagan *et al.*, (2011) assessed the level of heavy metal contamination of the Densu River Basin in Ghana and found that the mean values for the heavy metals, Fe and Mn exceeded the WHO maximum guideline values for drinking water. The levels of Fe which were above the WHO guideline maximum value of 0.3 mg/L for drinking water was attributed to the weathering of the rocks underlying the basin. Enrichment factor computation for the soil sediments revealed that there could be moderate anthropogenic contributions to the levels of Mn and Zn in the sediments.

Bentum *et al*. (2011) also investigated the concentrations of heavy metals in sediments at the Fosu Lagoon and observed the concentration of heavy metals in the sequence; Fe > Pb > Cu > Zn. The average geoaccumulation values and pollution load index calculated for the five studied sites however indicated the lagoon as practically unpolluted with Fe, Cu and Zn, but moderately polluted with Pb.

In a review by Biney *et al.* (1994), it was concluded that generally lower concentration of heavy metals occur in African aquatic ecosystems compared to other areas of the world. However, due to increases in urbanization and socioeconomic activities, the threat of pollution was bound to increase within our aquatic systems. For effective water pollution control and management there is a need for a clear understanding of the inputs (loads), distribution and fate of contaminants, including trace metals from land-based sources into aquatic ecosystems. In particular, the quantities and qualities need to be considered together with the distribution pathways and fate and the effects on biota (Biney *et al*., 1994).

The need to make an assessment of the level of heavy metal contamination in the African environment has led to the initiation of several pollution monitoring programmes and research work in various universities and scientific institutions in the region. The most relevant programmes are the Mediterranean Pollution Monitoring Programme (MEDPOL) covering North Africa, the West and Central Africa Marine Pollution and Research programme (WACAF 2) and the Eastern Africa Marine Pollution and Research Programme (EAF/6) (Biney *et al*., 1994).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

The Barekese reservoir which is a major source of drinking water for the Kumasi metropolis and its environs was constructed in 1969 by a dam transversely across the Offin River at Barekese. The Barekese reservoir is located approximately 26 km North of Kumasi, a region in Ghana. It lies on latitude 6°44'N and longitude 1°42'W (Figure 3.1). The reservoir has a surface area of approximately 6.4 km^2 with a maximum length of 13km and width of 1.25km.The overall crest length is 6.096 m above sea level (Kumasi *et al*., 2007). The reservoir has an ultimate design capacity of 218 400 m^3/day but the reservoir is considered to be heavily silted (Blokhuis *et al.*, 2005). The Barekese reservoir has a catchment area of 351sq miles (10800acres). It lies within the wet semi-equatorial zone marked by double maximum rainfall ranging between 170cm and 185cm per annum (Blokhuis *et al*., 2005). The major rainfall season is from Mid-March to July and minor season is between September and mid-November (Kumasi *et al*., 2007).

The Barekese catchment forms part of the Offin River catchment. The river flows through the catchment before it eventually feeds into the Barekese reservoir. The Barekese catchment is located in the Atwima Nwabiagya District in the Ashanti region of Ghana and is enclosed by the following towns and villages: Barekese, Nkwantakese, Nkwanta Penteng, Ahenkro, Offinso and Ayensua Kokoo (Fig. 3.1). Most of the communities depend on the Offin River and its tributaries for their and domestic water needs, recreation, irrigation, fish farming washing of vehicles over the past decades. The Ayensua Fufuo, Nkwantakese and Denasi communities, however, have no access to pipeborne water and depend solely on the Barekese Reservoir and its feeder streams for potable water (Kumasi *et al*., 2007).

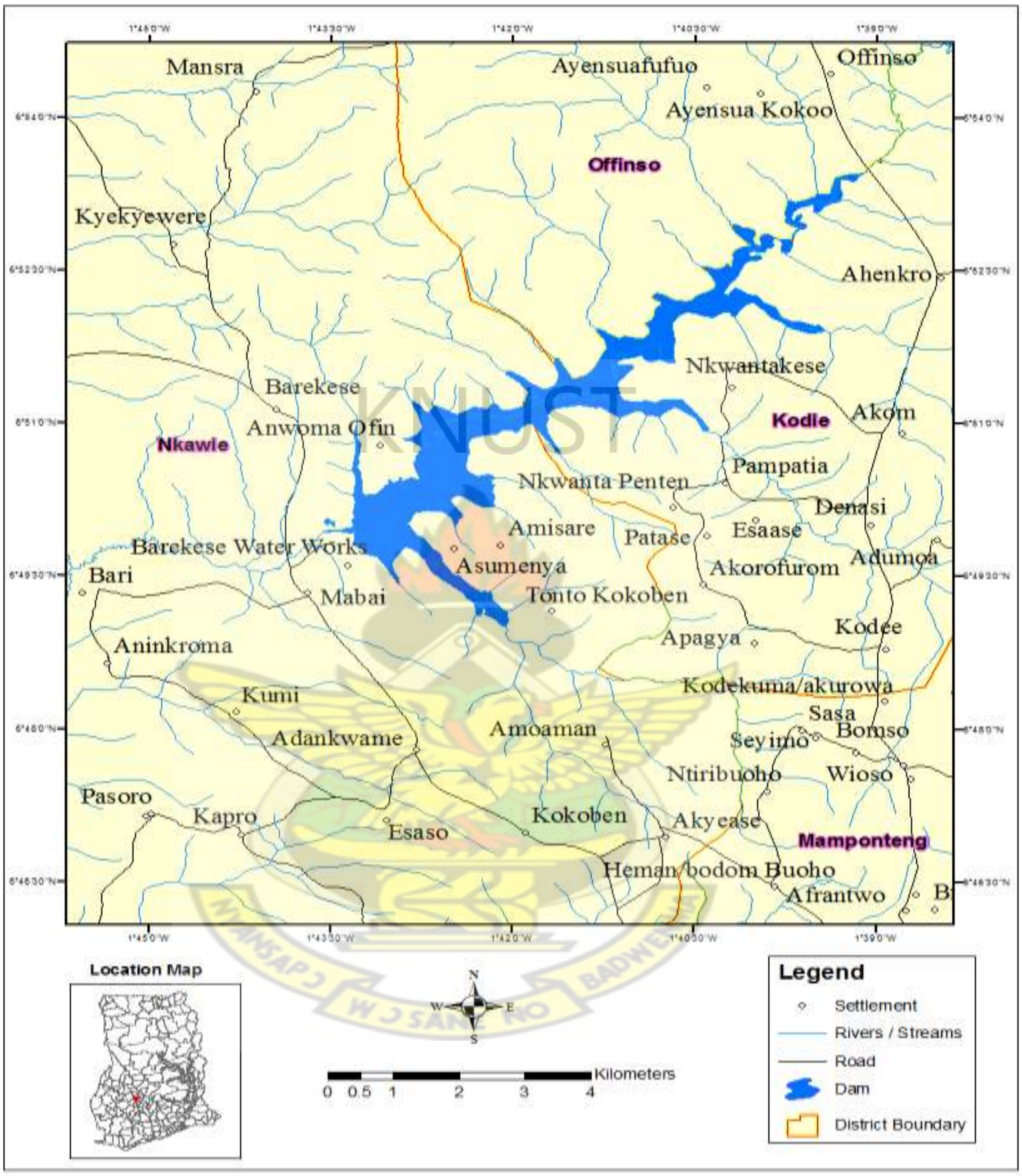

Figure 3.1 Map showing the Barekese reservoir within its catchment area

3.2 Field sampling

Samples of water, sediments and aquatic macrophytes were collected monthly from October, 2010 to March 2011 at six different sites namely; Site 1 and 2 (immediately before the dam), sites 3 and 4 (central section of the reservoir) and sites 5 and 6 (close to the reservoir intake). The sampling sites were chosen to cover extensively the whole dam. All samples were collected at the various sites with the aid of a rowing board.

To minimize contamination, sample containers and devices were carefully cleaned before use following the method of USEPA (2001). The glassware for the digestion process were first cleaned under running tap water and soaked in 10% (v/v) Nitric acid (HNO_3) for 24 hours. They were then rinsed with distilled water followed by 0.5% (w/v) potassium permanganate ($KMnO_4$). Distilled water was used to finally rinse the glassware which was subsequently dried. Precautions (cold storage on ice, use of plastic materials for storage, avoidance of undue agitation) were taken during transportation of samples to minimize any kind of disturbances following the method of Simpson *et al*. (2004).

3.2.1 Water sampling and preparation

The water samples were collected wearing polyethylene gloves, and facing the direction of flow of the reservoir. Water samples were collected at 10 cm below water surface in polyethylene bottles (washed with detergent then with double-distilled water followed by 2 M nitric acid, then double-distilled water again and finally with sampled water). The water samples were acidified with 10% nitric acid, stored in an ice-chest and was later conveyed to the laboratory for analysis. The addition of acid to the water sample is to keep the metal ions in the dissolved state, as well as to prevent microbial activities (Serfor – Armah *et al*., 2006).

Preliminary digestion of water sample was necessary to release the metals associated with suspended as well as colloidal organic matters. For this, water samples were first acidified with concentrated HCl to ensure pH ≤ 2. 5 ml concentrated HNO_3 was added to each 50 ml acidified water sample and allowed to evaporate slowly in a hot plate, reducing the volume to about 15-20 ml. The digested samples were allowed to cool to room temperature. They were then filtered through Whatman 0.45 μm filter paper and the final volume was adjusted to 50 ml with double distilled water and stored for analysis.

3.2.2 Sediment sampling and preparation

Sediment samples were collected using Eckman grabber and put into wide mouthed plastic containers. The samples were kept in ice boxes containing wet ice during the sampling trip and later stored at -80 ºC until analysis. Sediment samples were prepared for analysis by air drying for three days to remove moisture. Organic debris and other unwanted large particles were handpicked from each sample. The air dried samples were then ground into a homogenous mixture using a porcelain mortar and pestle and sieved through 2 mm mesh screen to remove coarse materials. The sediments were digested following the method of Mekonnen *et al*. (2012). Samples were prepared in triplicate according to the following procedure: About 0.5 g of dried and ground sediment samples was accurately weighed and placed in 100 ml beaker. Freshly prepared aqua regia (5 ml) was added. After the completion of the reaction, it was refluxed on a hot plate for 2 h at a temperature not exceeding 160 ºC. The digest was filtered with Whatman No. 42 filter paper after cooling, diluted with deionised water to 50 ml and placed in the refrigerator prior to analysis using the flame Atomic Absorption Spectrometer. Blanks were determined in similar fashion and all measurements were done in triplicate. For the calibration curve, a series of working standard solutions of metals were prepared by appropriate dilution with deionised water of the metal stock solutions of 1000 mg/l. The concentrations of Pb, Cu, Zn, Mn and Fe in the acid digested sediment samples were determined by F-AAS analysis (Buck Scientific Model VGP).

3.2.3 Macrophytes sampling and preparation

Samples of *Typha domingensis*, *Lemna paucicostata*, *Pistia stratiote*s and *Ceratophylum demersum* (Plate 3.1 - 3.4) were collected by hand wearing polyethylene gloves and washed with water to remove periphyton, sand and suspended sediments. At each site, areas with the highest infestation of the investigated macrophytes were considered for sample collection in order to assess their indicator value. The samples were stored in well labeled dried polythene bags before being transported to the laboratory.

In the laboratory, the plant samples were prepared following the method of Pavlović *et al*. (2005).The plant samples were washed in distilled water until removal of all impurity, and after that it was dried at a temperature of 105 °C for 24 hours. Drying of plant samples protects the plant material from microbial decomposition and also ensures a constant reference value (Demirezen and Aksoy, 2004). 2 g of the dried plant samples was measured on analytic scale by method of differentiation in mass.

Measured sample was transferred in balloon according to Kjeldal and perfused with concentrated HNO_3. Reaction mixture was heated carefully by flame, until the solution became dry. Treatment was repeated until clearing up of the solution, and stopping of releasing of nitric vapors. After that, sample was cooled, and content in the Kjeldal′s dish was perfused with 6 ml of concentrated $HClO_4$ and then heated.

Heating was stopped at solution volume of approximately 3 ml in Kjedal′s dish unclear and achromatic. After cooling of solution, distillated water was added. After that, content from Kjeldal′s dish was filtrated through quantitative sieve in normal dish of 50 ml volume. On this way prepared solutions were used for determination of heavy metals in plant material by atomic absorption spectrometer.

Plate 3.1 **Macrophyte infestation at the Barekese reservoir**

Plate 3.2 Sampling of *Typha domingensis* from the Barekese reservoir

Plate 3.3 Samples of *Lemna paucicostata* from the Barekese reservoir

Plate 3.4 *Ceratophyllum demersum*

3.3 Determination of Heavy Metals

Concentrations of lead, zinc, manganese, copper and iron were determined at the Soil Science laboratory of the KNUST using a Flame Atomic Absorption Spectrophotometer (Buck Scientific Model VGP) (Plate 3.5).

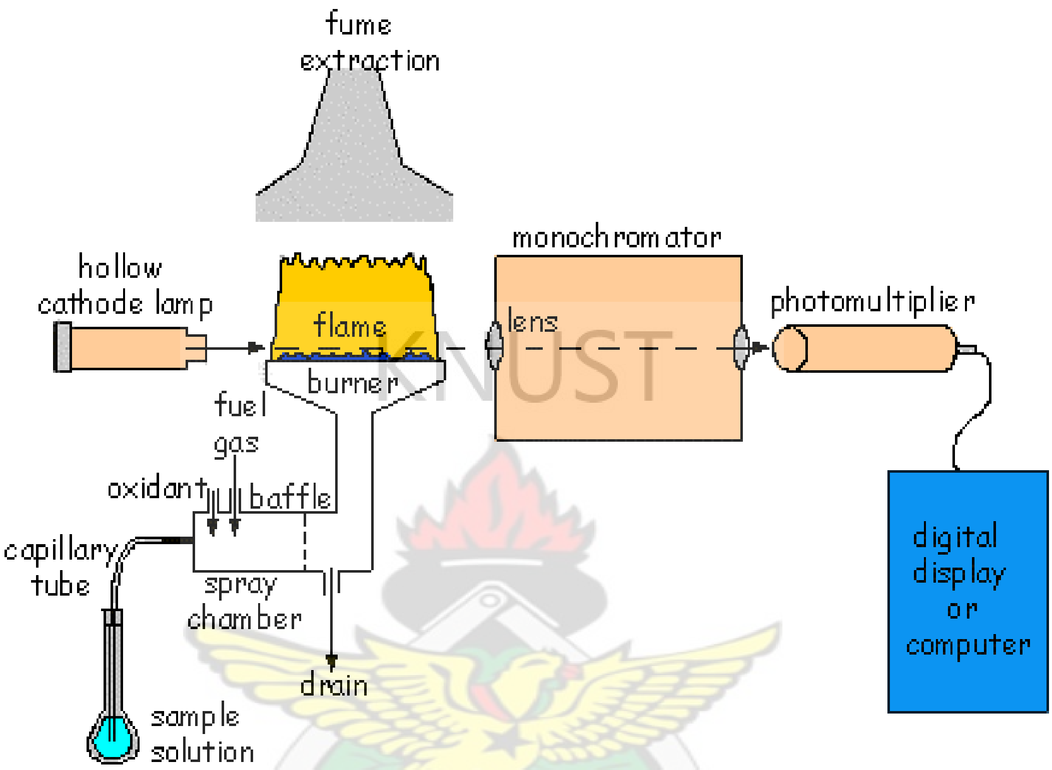

Plate 3.5 Schematic diagram of Flame Atomic Spectrometer

The Flame Atomic Absorption Spectrophotometer operates in flame mode using air as oxidant and acetylene as fuel. An aqueous sample containing the metal analyte is aspirated into an air-acetylene flame, causing the evaporation of the solvent and vaporization of the free metal atoms (atomization). This causes the atoms to absorb ultraviolet or visible light from hollow cathode lamp and make transitions to higher electronic energy levels. The analyte concentration is then determined from the amount of absorption after which the absorbance is measured with a conventional UV-visible dispersive spectrometer with photomultiplier detector. The absorbance of the blank is taken before the analysis of the samples.

The total concentrations of Pb, Zn, Mn, Cu and Fe in filtrate were determined with specific wavelengths (Table 3.1). Calibration curves were drawn for each metal by running suitable concentrations of their standard solutions, from which the concentrations of the elements are obtained by extrapolation. The standard solutions for calibration and all other required solutions were prepared with distilled water. Quality assurance was guaranteed through double determinations and use of blanks and background correction if necessary.

Table 3.1 Wavelengths and detection limits for the studied heavy metals

Element	Slit width (mm)	Wavelength (nm)	Detection limit (mg/L)
Lead	0.7	217.0	0.01
Zinc	0.7	213.9	0.0005
Copper	0.7	324.8	0.001
Manganese	0.7	385.2	0.002
Iron	0.7	248.3	0.005

3.4 Water Pollution Analysis

The metal index (MI) was calculated to assess the water contamination with heavy metals. The MI was preliminary defined by Tamasi and Chini (2004) and is expressed as the following equation;

$$\mathrm{MI} = \sum_{i=1}^{n} \frac{C_i}{MAC_i}$$

where MI is the metal index, C is the concentration of each element in the solution, MAC is the maximum allowed concentration for each element, and subscript i is the i^{th} sample. The higher the concentration of a metal compared to its respective MAC value, the more harmful the water. If the concentration of a certain element is higher than the respective MAC value (i.e. MI > 1), the water cannot be used, according to this index. Therefore, the value of one for MI is a threshold of warning, even in the case where C_i is less than MAC_i for all the elements. For the sake of calculation of the MI, the heavy metals of Pb, Zn, Mn, Cu and Fe were considered. The WHO guideline values were used for MAC in the index.

3.5 Sediment Pollution Analysis

The concentrations of the five metals in the sediment samples were subjected to various calculations and comparisons with guideline values in order to ascertain the extent of metal pollution at the reservoir as far as sediments are concerned.

3.5.1 Sediment Quality Guidelines (SQG)

Sediment Quality Guidelines (SQG's) are very useful to screen sediment contamination by comparing sediment concentrations with the corresponding quality guideline. These guidelines evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and are designed to assist sediment assessors and managers responsible for the interpretation of sediment quality (Wenning and Ingersoll, 2002).

The classification of the studied heavy metals based on SQG values are shown in Table 3.2.

Table 3.2 Sediment Quality Guidelines according to Perin *et al.* (1997)

Heavy metal	**Not Polluted (mg/kg)**	**Slightly Polluted (mg/kg)**	**Severely Polluted (mg/kg)**	**Average conc. in earth crust (mg/kg)**
Lead	<40	40-60	>60	16
Zinc	<90	90-200	>200	80
Manganese	<300	300-500	>500	1000
Copper	<25	25-50	>50	70
Iron	<17000	17000-25000	>25000	50000

3.5.2 Contamination factor (C_F)

Contamination factor was calculated to get a fair idea of the extent of anthropogenic pollution and accumulation of heavy metals in the sediments at the various sampling locations. Calculation was done following the equation:

C_F = Cn /mean Bn +one S.D.

Cn in the above formula is the concentration of the examined element 'n' in the surface sediments, and Bn is the geochemical background concentration of metal 'n'. In this study, Hakanson (1980) background values of 8, 67, 597, 14 and 5000 mg/kg for Pb, Zn, Mn, Cu and Fe respectively, in uncontaminated sediments were used for calculation of C_F.

Contamination was classified into four groups: $C_F < 1$ refers to a low contamination factor; $1 \leq C_F < 3$ refers to a moderate contamination factor; $3 \leq C_F < 6$ refers to the considerable contamination factors; $C_F \geq 6$ refers to a very high contamination factor Hakanson (1980).

3.5.3 Degree of Contamination (Dc)

The degree of contamination (Dc), defined as the sum of all contamination factors for a given basin was also used in the study. For the description of the degree of contamination the following terminologies were adopted following (Hakanson, 1980): $Dc < 7$ low degree of contamination; $7 < Dc < 14$ moderate degree of contamination; $14 \leq Dc < 28$ considerable degree of contamination; $Dc > 28$ very high degree of contamination.

3.5.4 Pollution Load Index (PLI)

Pollution load index (PLI) for the sediments at each site was evaluated following the method of Tomilson *et al*. (1980). This empirical index provides a simple, comparative means for assessing the level of heavy metal pollution and can be expressed as:

$$PLI = (CF_1 \text{x } CF_2 \text{ x } CF_3 \text{ x} \ldots\ldots\ldots \text{x } CF_n)^{1/n}$$

Where n is the number of metals (five in the present study) and CF_1x CF_2 x CF_3 etc. is the contamination factor. The PLI value > 1 is polluted whereas PLI value < 1 indicates no pollution (Seshan *et al*., 2010).

3.6 Element Concentration Ratio between Sediments and Water (Concentration Factor)

The values of the ratio between the concentrations of heavy metals in the sediments to those of water (Concentration factor) (C.F) were calculated. C.F values greater than 1 (C.F >1) indicates that the sediments concentration of heavy metals were far higher than those for the same elements in water.

3.7 Biological Accumulation Factor (BAF) in Aquatic Macrophytes

The ratio between plant metal and water metal concentration indicates the Biological Accumulation Factor (BAF). These BAF reflects the affinity of the studied aquatic macrophytes to specific element or pollutant. In calculation of the BAF, the concentration of the heavy metal in the biomass of the plant was divided by the concentration of the metal in the water. High BAF values express the high affinity of macrophytes to bioaccumulate specific element.

3.8 Statistical Analysis

Statistical analyses of data were performed using SPSS Version 16 statistical package (SPSS Inc. Chicago, USA). The means of the replicates and the evaluation of significant differences between different samples were determined using descriptive statistics and analysis of variance (ANOVA). Pearson correlation coefficients were used to examine the relationship between the levels of elements in plants, sediments and water. The products of the correlation coefficient (r) were evaluated according to (Norusis, 1993) as follows:

0–0.3: No correlation;

0.3–0.5: Low correlation;

0.5–0.7: Medium correlation;

0.7–0.9: High correlation;

0.9–1.0: Very high correlation

A lack of significant correlation among the heavy metals indicates different anthropogenic and natural sources.

Where it was necessary to determine the differences between two sets of samples, paired sample student's t-tests were conducted. Results of testing (2- tailed, unequal variances) were considered significant if calculated P-values were ≤ 0.05

All descriptive statistics and graphs were executed using Microsoft Excel 2007.

CHAPTER FOUR

RESULTS

4.1 Heavy Metals in Water

The results of heavy metal concentrations (Pb, Zn, Mn, Cu and Fe) in the water samples from the various sampling sites are presented in Table 4.1.

Table 4.1 Mean concentrations of heavy metals in water

Location (Site No.)	Heavy Metals (mg/L)				
	Pb	Zn	Mn	Cu	Fe
Dam site (S1)	0.04±0.01	0.01±0.01	0.25±0.03	0.42±0.01	0.57±0.02
Dam site (S2)	0.06±0.01	0.01±0.01	0.22±0.02	0.41±0.02	0.49±0.01
Centre (S3)	0.14±0.01	0.04±0.01	0.28±0.02	0.44±0.01	0.67±0.02
Centre (S4)	0.12±0.02	0.03±0.02	0.23±0.01	0.41±0.01	0.62±0.03
Reservoir intake (S5)	0.24±0.03	0.08±0.01	0.31±0.02	0.39±0.03	0.74±0.01
Reservoir intake (S6)	0.25±0.01	0.07±0.05	0.38±0.02	0.42±0.03	0.89±0.02

The mean concentration ranges for the various heavy metals in mg/L were as follows: Pb: 0.04 ± 0.01 to 0.25 ± 0.01; Zn: 0.01 ± 0.01 to 0.08 ± 0.01; Mn: 0.22 ± 0.02 to 0.38 ± 0.02; Cu: 0.39 ± 0.03 to 0.42 ± 0.03 and Fe: 0.49 ± 0.01 to 0.89±0.02. The variations of heavy metals among the sampling sites were statistically significant (5% level) for all the heavy metals except for Zn (Appendix 1).

The mean concentrations for the heavy metals in the water compared to the WHO standards for drinking water are illustrated below (Fig. 4.1).

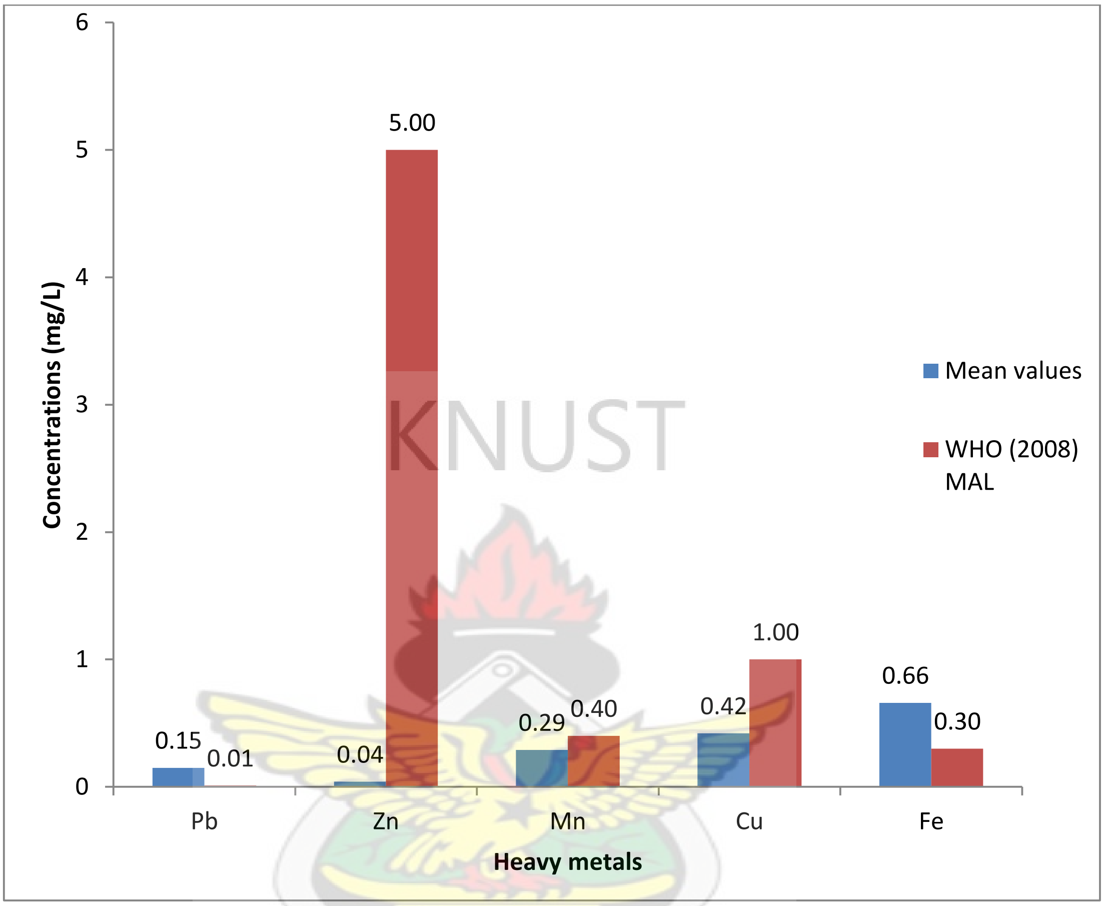

Figure 4.1 Mean concentrations of heavy metals in reservoir water

The graph (Fig. 4.1) showed that, the mean concentrations of Pb (0.15 mg/kg) and Fe (0.66mg/kg) exceeded the WHO (2004) Maximum Allowed Limits (MAL) of 0.01mg/kg and 0.30mg/kg respectively for drinking water.

4.1.1 Metal Index (MI)

The metal index (MI) values for heavy metals at the various sites of the reservoir were calculated for and presented in a histogram (Figure 4.2). The WHO (2008) guideline values were used as the MAC values. Thus, the Maximum Allowed Concentrations (MAC) values used for the calculation were; Pb (0.01mg/L), Zn (5 mg/L), Mn (0.4 mg/L), Cu (1.0 mg/L) and Fe (0.3 mg/L)

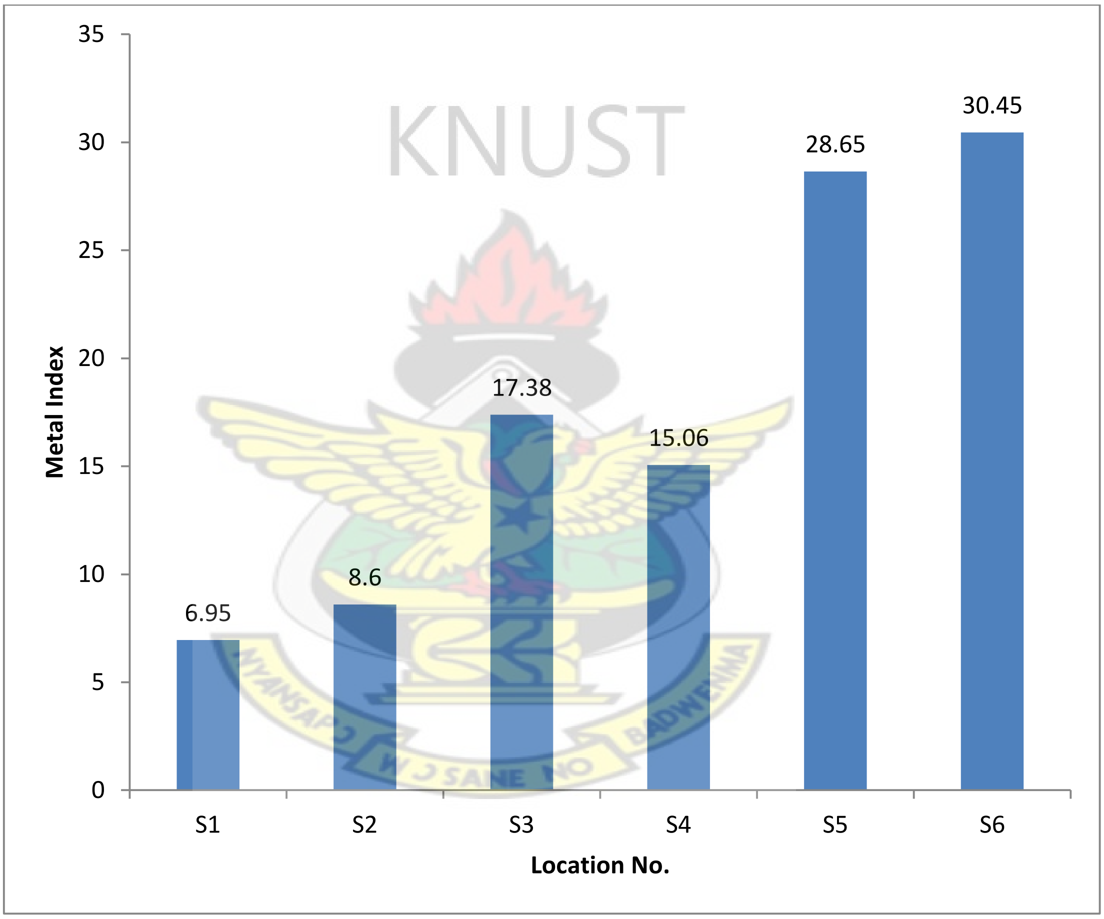

Figure 4.2 Metal Index (MI) for water samples in the study area

The MI values exceeded the threshold value (M I >1) at all the sampling locations. The lowest and highest MI values were recorded at the dam sites (S1) and reservoir intake (S6) respectively.

4.1.2 Correlation coefficient

The correlation coefficient values for the various metal pairs in the raw water samples at the reservoir are shown in Table 4.2. The results reveal positive correlations for all the metal pairs except for Cu-Pb, Cu-Zn, and Fe-Pb. Significant positive correlations were also observed for Mn-Pb and Fe-Zn pairs.

Table 4.2 Correlation matrix for elements in the surface water at study area

	Pb	Zn	Mn	Cu
Zn	0.987			
Mn	0.837*	0.784		
Cu	-0.282	-0.328		
Fe	-0.918	0.882*	0.955	0.000

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

4.2 Heavy Metals in Sediments

The concentrations of heavy metals in the sediments collected from six sites of the Barekese reservoir are presented in Table 4.3. The background values of` the heavy metals and the Sediment Quality Guidelines (SQGs) for the investigated elements are also shown in the table.

Table 4.3 Mean concentrations of heavy metals in sediments

Location (Site No.)	Heavy Metals (mg/kg)				
	Pb	Zn	Mn	Cu	Fe
Dam site (S1)	24.29±3.2	1.50±0.2	52.60±4.2	46.20±2.2	50.20±2.6
Dam site (S2)	28.33±2.8	1.60±0.2	56.90±5.7	47.00±3.5	49.50±3.1
Centre (S3)	26.58±1.5	3.20±0.6	54.30±6.3	59.50±7.2	62.50±6.3
Centre (S4)	25.43±1.6	4.60±0.8	54.30±4.2	61.50±3.3	50.80±5.8
Reservoir Intake (S5)	112.40±2.4	6.80±0.5	68.57±4.7	261.40±6.5	283.50±4.4
Reservoir Intake (S6)	125.80±3.7	6.34±0.7	74.29±6.8	246.50±5.9	253.70±6.1
Background value	**8**	**67**	**597**	**14**	**5000**
SQG non-polluted	**<40**	**<90**	**<300**	**<25**	**<17000**
SQG moderately polluted	**40-60**	**90-200**	**300 -500**	**25-50**	**17000-25000**
SQG heavily polluted	**>60**	**>200**	**>500**	**>50**	**>25000**

Source: Background value data from Hakanson (1980); SQG values from Perin *et al*. (1997).

The mean concentration ranges for Pb (24.29±3.2 to 125.80± 3.7) and Cu (46.20±2.2 to 261.40±5.9) were higher than the background values of 8 and 14 mg/kg respectively. The mean concentration ranges for Zn (1.50±0.2 to 6.80±0.5), Mn (52.60±4.2 to 74.29±6.8) and Fe (50.20±2.6 to 283.50±4.4) mg/kg were however lower than background values of 67, 597 and 5000 mg/kg respectively. The variations of heavy metals among the sampling sites were statistically significant (5% level) for all the heavy metals except for Pb (Appendix 1).

4.2.1 Indices of sediment contamination

The Contamination factor (C_F), degree of contamination (Dc) and Pollution Load Index (PLI) at the various sites of the reservoir are shown in Table 4.4.

Table 4.4 Contamination factor (C_F), Degree of contamination (Dc) and Pollution Load Index (PLI) of sediments

Location (Site No.)	C_F					Dc	PLI
	Pb	Zn	Mn	Cu	Fe		
Dam site (S1)	1.21	0.02	0.08	1.03	1.07	3.4	0
Dam site (S2)	1.42	0.02	0.08	1.04	1.05	3.61	0
Centre (S3)	1.33	0.03	0.08	1.32	1.34	4.1	0
Centre (S3)	1.27	0.05	0.08	1.37	1.07	3.83	0
Reservoir Intake (S5)	5.62	0.07	0.1	5.81	6.08	17.68	0.28
Reservoir Intake (S6)	6.25	0.07	0.11	5.47	5.43	17.33	0.26
Mean±SD	**2.85±2.4**	**0.04±0.02**	**0.09±0.01**	**2.67±2.31**	**2.67±2.4**		

Based on Hackanson (1980's) descriptions for the C_F values, all the sampling points have contamination factors less than unity $C_F < 1$ for Zn and Mn (Table 4.4). Pb had a contamination ranging from low value of 1.21 at Site 1 with the highest value of 6.25 at Site 6. Cu also obtained low contamination value of 1.03 (S1) and highest value of 5.81 at Site 5. C_F values for Fe also ranged from 1.05 to 6.08 at sites 2 and 5 respectively (Table 4.4). For the degree of contamination (Dc), the dam site and centre of the reservoir had a moderate degree of contamination ($6 \leq Dc < 12$) whiles the intake of the reservoir had a considerable degree of contamination ($12 \leq Dc < 24$). Pollution Load Index (PLI) values at all the sites were less than unity (PLI<1) (Table 4.4).

4.2.2 Correlation coefficient

In order to ascertain sources that affect heavy metals distribution in the reservoir sediments, inter-elemental association were evaluated using the Pearson correlation coefficient and the results are presented in Table 4.5.

Table 4.5 Correlation matrix for elements in sediment samples of the study area

	Pb	Zn	Mn	Cu
Zn	0.860*			
Mn	0.985	0.822*		
Cu	0.989	0.899*	0.955	
Fe	0.984	0.876*	0.945	0.998

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

From the results, all the investigated metal pair had a strong positive correlation with each other. These correlations were significant for Zn-Pb, Mn-Zn, Cu-Zn and Fe-Zn pairs.

4.3 Ratio of Heavy Metal Concentration in Sediments to those of Water (Concentration Factor)

The calculated Concentration Factor (C.F) values for individual heavy metals are presented in Table 4.6.

Table 4.6 Concentration Factor for sediments and water

Heavy metals	Sediment (mg/kg)	Water (mg/L)	Conc. Factor (Sediment/Water)
Pb	57.02	0.15	380.13
Zn	3.97	0.04	99.25
Mn	60.16	0.29	207.45
Cu	120.32	0.42	286.48
Fe	124.87	0.66	189.20

The highest mean C.F value was 380.13 for Pb whilst Zn recorded the lowest C.F of 99.25.

4.4 Heavy Metals in Aquatic Macrophytes

The concentrations of heavy metals in the roots and leaves of *T. domingensis* and. *P. stratiotes* are shown in Table 4.7. *C. demersum* and *L. paucicostata* were analysed whole because of their incoherent phenophases (Table 4.7)

Table 4.7 Concentrations of heavy metals in organs and whole plant parts

Macrophyte	Plant part	Heavy metal				
		Pb	Zn	Mn	Cu	Fe
T. domingensis	R	37.06±5.4	7.34±1.3	45.43±7.1	120.32±12.6	203.94±7.9
	L	21.01±4.7	2.31±0.8	39.50±5.9	83.23±7.9	109.64±13.7
C. demersum	W.P	39.75±4.5	6.25±1.5	72.12±5.2	121.37±10.2	139.23±13.2
P. stratiotes	R	30.40±5.5	6.16±2.1	56.79±3.8	110.94±12.8	259.81±10.2
	L	19.50±3.2	3.28±1.3	41.58±6.4	74.91±3.7	159.39±12.3
L. pauciostata	W.P	47.98±6.3	3.25±1.4	65.48±8.4	98.47±5.9	134.41±15.9

R= roots, L= leaves, W.P= Whole plant

The results reveal that aquatic plants growing in the reservoir exhibit different heavy metal concentrations, depending on the plant species and organ. The differences in metal concentrations for leaves and roots of *T. domingensis* and *P. stratiotes* were statistically significant ($p \leq 0.05$) for all the metals except for Pb in roots and leaves of *P. stratiotes* (Appendices 3 and 4).

1

4.4.1 Comparison of metal concentrations in macrophytes with standard normal and critical ranges in plants

The mean concentration ranges of the heavy metals in the aquatic macrophytes compared to Kabata-Pendias & Pendias (2001) standard normal and critical ranges in plants are presented in Table 4.8.

Table 4.8 Ranges of heavy metal concentrations in the tested plant species, compared with normal and critical ranges in plants

Metal	Mean range in Plant (mg/kg)	Normal range in Plants (mg/kg)	Critical range in Plants (mg/kg)	Toxicity status
Pb	19.5 - 47.9	0.20-20	30-300	Toxic
Zn	2.31 - 7.34	1.00-100	100-400	Normal
Mn	39.5 - 72.12	-	-	-
Cu	74.91 - 121.37	7.53-8.44	25-90	Toxic
Fe	109.64-259.81	-	-	-

Data after Kabata-Pendias (2001)

As shown in the table, the mean range of only Zn (3.25-6.25 mg/kg) falls within the normal range (1-100mg/kg) in plants whilst the mean ranges of Pb (19.5-47.98 mg/kg) and Cu (74.91-121.37 mg/kg) falls outside the normal range of 0.20-20 mg/kg and 7.53-8.44 mg/kg for Pb and Cu respectively. However, the values Pb (19.5 – 47.98 mg/kg) and Cu (74.91-121.37 mg/kg) fall within the critical ranges of 30-300 mg/kg and 25-90 mg/kg respectively. Pb and Cu are therefore considered to be toxic in the plants.

4.4.2 Heavy metal concentration in macrophyte species

The levels of heavy metals in the leaves of the aquatic macrophytes are illustrated in Fig. 4.3. The concentration of Fe was highest in all the various species of macrophytes followed by Cu and Zn had the least concentration.

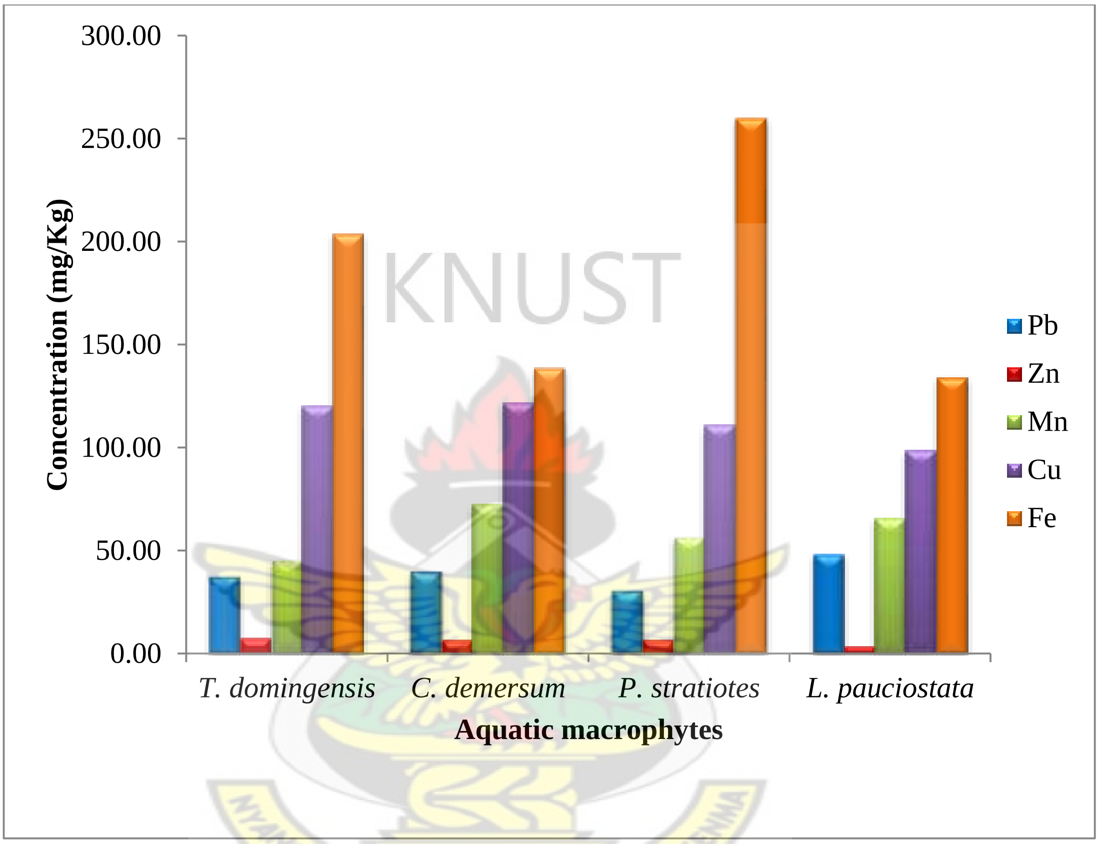

Figure 3.3 Concentrations of heavy metals in aquatic macrophytes

The ratios of heavy metal concentrations in roots to the leaves of *T. domingensis* and *P. stratiotes* are presented in Table 4.9.

Table 4.9 Roots / leaves ratio of heavy metals concentrations in *T. domingensis* and *P. stratiotes*

Heavy metal	*T. domingensis* roots/leaves	*P. stratiotes* roots/leaves
Pb	1.76	1.56
Zn	3.16	1.88
Mn	1.15	1.37
Cu	1.45	1.48
Fe	1.86	1.63

From the table, the ratios of heavy metal concentrations in roots/shoots of the macrophytes (*T. domingensis* and *P. stratiotes*) were greater than 1, implying greater concentration of metals in roots than leaves of the investigated plants.

4.4.3 Biological Accumulation Factor (BAF)

The values for the Biological Accumulation Factor (BAF) for the various elements in the plants roots are presented in Table 4.10

Table 4.10 Biological Accumulation Factor (Ratio of metal concentrations in plants to those of the same elements in water)

Element/Taxon	Pb	Zn	Mn	Cu	Fe
T. domingensis	247.07	182.50	156.66	286.48	309.00
C. demersum	265.00	156.25	248.69	288.98	210.61
P. stratiotes	202.67	154.00	195.83	264.14	393.65
L. paucicostata	319.87	81.25	225.79	234.45	203.65
Mean	**258.65**	**143.50**	**206.74**	**268.51**	**279.23**
Standard deviation	**48.50**	**43.47**	**39.79**	**25.30**	**90.18**

As shown in table 4.10, Zn recorded the lowest mean BAF of 143.50 ± 43.47 whilst Fe recorded the highest mean BAF of 279.23 ± 90.18.

CHAPTER FIVE

DISCUSSION

5.1 Heavy Metal Concentration in Water

In the present study, the mean concentrations of lead in the raw water samples of the Barekese Reservoir ranged from 0.04±0.01to 0.25±0.01mg/L. (Table 4.1). In relation to the WHO (2008) guideline value of 0.01 mg/L for Pb in drinking water, the levels measured in this study were higher. Similar studies by Akoto *et al*. (2008) on the levels of heavy metals in streams serving the Owabi Reservoir reveals higher levels of lead than the WHO (2008) Maximum Allowed Limits for drinking water. A study by Kumasi *et al.* (2007) indicated that, most of the inhabitants living within the Barekese catchment area were mainly farmers (80%) and these farmers used fertilizer and chemicals for the cultivation of their vegetables and cocoa. Kumasi *et al.* (2007) also mentioned that, most of the communities in the Barekese catchment used the River Offin for their domestic, recreational, farming, fish farming and the washing of vehicles. Chemicals used in farming activities mostly contain heavy metals such as lead which accumulate not only in the soil but in the water sources surrounding the area as well. Moreover, grease and soap from car washing activities could contain some heavy metals and these degrade water quality. The use of various iron salts as coagulants in water treatment could also lead to high lead concentrations in the reservoir water.

The levels of zinc in the water samples ranged from 0.01±0.01 to 0.08±0.01mg/L (Table 4.1). These were below the WHO (2008) guideline value of 5.0 mg/L for Zn in drinking water.

The concentration of manganese also ranged between 0.22±0.02 to 0.38±0.02mg/L (Table 4.1). In relation to the WHO (2008) guideline value of 0.40 mg/L for Mn in drinking water, the levels measured in this study were slightly lower. Asante *et al*. (2005) also recorded low concentrations of Mn (0.16 to 0.19 mg/L) in water samples from the Weija Reservoir. Manganese concentrations above 0.1 mg/L impart an undesirable taste to drinking water. Even at about 0.02 mg/l, manganese will form coatings on piping that may later tear off as a black precipitate (Abassi *et al*., 1998).

Copper concentrations (0.41±0.01- 0.44±0.01 mg/L) (Table 4.1) in the water samples at the Barekese dam were below the WHO (2008) guideline range of 1.0 mg/L. This could be attributed to the low copper related industrial and mining activities in the Barekese catchment.

The mean concentrations of iron in the water samples from the Barekese reservoir ranged from 0.49±0.01 to 0.89±0.02 mg/L (Table 4.1), exceeding the WHO (2008) permissible limit of 0.30 mg/L. Asante *et al*. (2005) also recorded higher levels of Fe (0.59 to 0.74 mg/L) at the Weija Reservoir. The mean levels of Fe in water samples from the Densu River Basin in Ghana also exceeded the WHO (2008) guideline values for drinking water (Hagan *et al.*, 2011). The high concentrations of iron in the reservoir could be attributed to the use of chemicals in farming activities within the Barekese catchment area (Kumasi *et al*., 2007). Also, the weathering of the rocks underlying the reservoir basin as well as the reservoir could have accounted for the high concentration of iron in the water samples. The high concentration of iron in the reservoirs require standard water treatment before human consumption because prolonged consumption of drinking water with high iron concentration may lead to liver diseases (Rajappa *et al*., 2010).

The results of correlation coefficient (r) presented in Table 4.2 reveals significant correlation for Mn-Pb, ($r = 0.837$, $p < 0.05$) and Fe-Zn, ($r = 0.882$, $p < 0.05$) pairs. This elemental association may signify that the paired elements have identical source in the stream sediments. The metal pairs which showed no significant correlations imply different anthropogenic and natural sources in the reservoir sediments (Denton *et al*., 2007)

5.1.1 Metal Index (MI)

The calculated Metal Index (MI) in the water samples were all above the threshold of warning (MI >1) (Fig. 4.2). This implies that all the water samples were contaminated according to this index. The Metal Index at the reservoir intake (Site 5 and Site 6) were however comparatively higher than that those for the dam site and centre of the reservoir (Site 1-4). The Offin River passes through the Barekese catchment before it eventually feeds into the Barekese reservoir (Blokhius *et al*., 2005). Considering the nature of human activities such as farming, improper disposal of both solid and liquid waste and washing of vehicles close to the River Offin, the high metal index at the reservoirs intake could be due to influx of pollutants from the upper catchment area. Dilution and dispersion of metal content with increasing distance from source areas could have accounted for the low MI values at the dam sites.

5.2 Heavy Metal Concentration in Sediments

Heavy metals concentration in bottom sediments is an unbiased and reliable index of water contamination and total anthropogenic load (Perin *et al*., 1997) The metal concentrations in the sediments exhibited a similar pattern of concentration with those in water as follows; Fe > Cu > Mn > Pb > Zn. To evaluate the contamination of metals in sediments, comparison with the background value and sediment quality guidelines, calculation of indices of contamination such as the contamination factors (C_F), degree of contamination (Dc) and the Pollution Load Index (PLI) were employed.

In order to effectively assess the metal content in the reservoir sediments, the concentration of heavy metals were compared to the background values and Sediment Quality Guidelines (Table 4.3). The background values refer to the average concentration of heavy metals in uncontaminated sediments (Hakanson 1980). From the results, the mean range of concentrations of Zn (1.5±0.2 to 6.8±0.5 mg/kg), Mn (52.6±4.2 to 74.29±6.8 mg/kg) and Fe (49.50±3.1 to 283.50±4.4 mg/kg) were below the background values of 67, 597 and 5000 mg/kg respectively in sediments (Table 4.3). Comparing these values to the Sediment Quality Guidelines, the concentrations of Zn, Mn and Fe can be classified as unpolluted since they recorded values below 40, 300 and 1700 mg/kg respectively.

The mean range of concentrations for Pb (24.29±3.2 to 125.8±3.7 mg/kg) was however higher than the background values of 8mg/kg at all sites. Based on the Sediment Quality Guideline values, the concentration of Pb at the reservoirs intake is heavily polluted (SQG >60). The high concentrations of Pb in sediments could be attributed to effluent discharges from sewages and use of chemicals in agricultural activities in the Barekese catchment area.

Copper concentrations ranged from 46.20±2.2 to 261.40±6.5 mg/kg at the dam site (S1) and reservoir intake (S5) respectively. These exceeded the background value of 14 mg/kg (Table 4.3). The high levels of Cu in sediments could be attributed to run-off from the use of chemicals containing copper in agricultural activities. Copper can be classified as moderately polluted in the sediments at the dam sites and heavily polluted at the reservoirs intake point using the Sediment Quality Guidelines (Table 4.3).

The analysis of metal-metal relationships in sediment samples reveal strong, significant, positive correlation for Zn-Pb ($r = 0.86$, $p<0.05$), Mn- Zn ($r = 0.82$, $p<0.05$), Cu-Zn ($r = 0.89$, $p<0.05$) and Fe-Zn ($r = 0.88$, $p<0.05$) pairs (Table 4.5). As mentioned by Singh *et al*. (2002), significant correlations between these elements signify their identical sources in the stream sediments.

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5.2.1 Contamination Factor (C_F), Degree of contamination (Dc) and the Pollution Load Index (PLI).

Contamination factor and Degree of contamination value give a standardized description of sediment contamination (Hakanson, 1980). The contamination factor and degree of contamination obtained in this study have shown that the reservoirs intake (Site 5 and 6) are more contaminated compared to the dam site (Site 1 and 2) and centre of the reservoir (Site 3 and Site 4) (Table 4.4). All the PLI values recorded for the various metals were less than one (PLI < 1) (Table 4.4). This suggests unappreciable input of heavy metals from anthropogenic sources (Tomlinson *et al.*, 1980). The study however revealed higher levels of the investigated metals in the sediment deposits at the reservoirs intake. If this trend in metal contamination is allowed to continue, it is most likely that the local food web complexes at the reservoirs intake might be at highest risk of induced heavy metals contamination.

5.3 Concentration Factor (C.F)

The Concentration factor (C.F) values for all the metals in the sediments were greater than one, implying significant accumulation of heavy metals in the sediments compared to the water (Table 4.6). As mentioned by Nirmal *et al.* (2007), heavy metals accumulate more in sediments than in water due to their strong binding affinity for heavy metals. This could have accounted for their higher levels in the sediments than in water in the present study. Heavy metals are not fixed permanently by the sediments, and under changing environmental conditions they may be released to the water column by various processes of remobilization (Allen, 1995).This phenomenon poses a risk of secondary water pollution by heavy metals under sediment disturbance and/or changes in sediment chemistry.

5.4 Heavy Metals in Aquatic Macrophytes

The results from Table 4.7 reveal considerable differences in metal concentrations in various species and organs of the same species. The order of accumulation of metals in plants; Fe > Cu >Mn >Pb > Zn were similar to those of water and sediments. Comparing the concentration of heavy metals in aquatic macrophytes to that of Kabata – Pendias and Pendias (2001) data for normal and critical range in plants, the concentrations of Zn was observed to be within normal ranges, while those of Pb and Cu were observed to be within the critical ranges (Table 4.8).

The concentrations of lead in aquatic macrophytes in the present study, ranged between 19.5 – 47.98 mg/kg (Table 4.7). Kabata-Pendias and Pendias (2001) reported that lead concentrations of plants grown in uncontaminated areas varied between 0.05 and 3.0 mg/kg. It can therefore be inferred that lead concentration found in the plants was in the toxic ranges.

From the study, the mean concentrations of zinc in the plants ranged from 2.31 to 7.34 mg/kg (Table 4.7). Allen (1989) reveals that zinc concentrations above 0.5 mg/kg could be poisonous in plants. Comparing the levels of zinc in the investigated plants to Kabata-Pendias and Pendias (2001) normal and critical ranges in plants, the concentration of Zn in the plant were in the normal range.

The mean concentrations of manganese in the present study ranged from 39.5 to 72.12 mg/kg (Table 4.7). Manganese has a range between 20 and 300 mg/kg in most plants, while its level may be as high as 1500 mg/kg without causing any harm to some plant (Pais and Jones, 2000). It can therefore be concluded that manganese concentrations in the aquatic macrophytes sampled in this study were in the normal ranges for plant growth.

Copper is vital for plant nutrition and needed for various enzymatic activities of oxidation–reduction. In the present study, Cu concentrations (74.91 – 121.37 mg/kg) were within the critical ranges of 25 to 90 mg/ kg (Kabata-Pendias and Pendias, 2001).

The concentration of Fe in the plants ranged from 109.64 to 259.81 mg/kg (Table 4.7). Allen (1995), reports that Fe concentrations above 40-500 mg/kg are toxic to plants. Higher concentration of Fe suggests a high bioaccumulation affinity of Fe for aquatic macrophytes.

5.4.1 Heavy metal concentrations in different species of the macrophytes

The investigated plants showed different bioaccumulation rates for the heavy metals (Table 4.7). The orders of metal concentrations in the various species were as follows;

Pb: *L. paucicostata* > *C. demersum*>*T. domingensis*> *P. stratiotes*

Zn: *T. domingensis*> *C. demersum* > *P. stratiotes* > *L. paucicostata*

Mn: *C. demersum* > *L. paucicostata* > *P. stratiotes* > *T. domingensis*

Cu: *C. demersum* >*T. domingensis*> *P. stratiotes* > *L. paucicostata*

Fe: *P. stratiotes* >*T. domingensis*> *C. demersum* > *L. paucicostata*

Similar studies by Falaky *et al*. (2004) reveal variations in the bioaccumulation of metals among macrophyte species growing in the same area. From the above, it can be deduced that *L. paucicostata* is the most suitable plant for monitoring Pb, *T. domingensis* for Zn, *C. demersum* for Mn and Cu and *P. stratiotes* for Fe. The extent of bioaccumulation of metals in the plants however depends on the total concentration in water, the biovailability of each metal in the environmental medium, the route of uptake, storage and excretion mechanisms.

5.4.1 Heavy metal concentrations in organs

Typha domingensis at all the sites contained relatively low metal concentrations in the leaves than their corresponding roots (Figs. 4.5 - 4.9). Most studies indicate that for *Typha domingensis,* the roots accumulate more metals than the rhizome (possibly due to iron plaque), and the leaves accumulate the least amount of metals (Dunbabin and Bowmer, 1992). Also, for emergent species, the primary source of metals is likely to be the roots; however to a lesser degree leaves can take metals from the ambient water (Taylor and Crowder, 1983). Baldantoni *et al*. (2004), also records different storage capacity of metals between organs of the same species with the roots accumulating more than the leaves. The authors, Baldantoni *et al*. (2004) further explained that, the roots of aquatic plants absorb heavy metals from the interstitial water (or pore water) and accumulate high concentrations than corresponding stems and leaves.

The different trace metal concentrations in the roots and leaves of *T. domingensis* and *P. stratiotes* analysed may reflect different pathways for the elements uptake. Most of the metals investigated had higher metal concentration in the roots than the leaves with a root/leaves (R/S) ratio in metal concentration greater than one (Table 4.9). Baker and Walker (1990) asserted that, macrophytes take up heavy metals mainly through the root although uptake through the leaves may also be significant. Much higher concentrations of heavy metals were also observed in the roots than in the leaves of *T. domingensis* and *P. stratiotes* by the researchers, Dunbabin and Bowmer (1992) and Odjegba and Fasidi (2004) respectively. Jackson (1998) has confirmed that in *T. domingensis*, elements are mostly taken by roots with subsequent translocation to above-ground tissues.

5.4.3 Interpretation of Biological Accumulation Factor (BAF)

The BAF values reveal the unique ability of aquatic macrophytes in the accumulation of heavy metals from water. As presented in Table 4.10, there exist wide variations in Biological Accumulation Factor BAF values. This agrees with the findings of Jackson *et al*. (1998) who states that, ‘‘Macrophytes are excellent bioaccumulators of metals in an aquatic ecosystem as it eliminates metals from water, accumulates and stores them over a long period, even when the concentrations of metals in the water is low’’.

This study shows *L. paucicostata* had the greatest capacity towards bioaccumulation of Pb. This is probably due to the unique ability of *L. paucicostata* in bioaccumulating lead. This has been demonstrated by Srivalstava *et al.* (2008), who records the removal efficiency of lead in *L. paucicostata* to be 90%. Since *L. paucicostata* have the capabilities of extracting even potentially toxic metals like Pb, they have proved to be an innovative and eco-friendly technique for purifying grossly polluted water bodies. However, the lifecycle of *L. paucicostata* is generally very short; after their death and decomposition, chemical elements return in part to the water or are accumulated in bottom sediments. *C. demersum* also recorded the highest accumulation for Mn and Cu. Typically, submerged species have been found to accumulate relatively high concentrations of heavy metals when compared with emergent species in the same area (Kara, 2005). The high concentrations of heavy metals in *C. demersum* may be a function of the growth form of this species, which is truly submerged with no floating or emergent components. Moreover, this plant has very thin cuticle and therefore readily take up metals from water through the entire surface. *C. demersum* has therefore been proposed by Pip and Stepaniuk (2002) as very useful plant in the bioremediation of polluted water bodies.

5.5 Distribution of Heavy Metals in Water, Sediments and Aquatic Macrophytes

The distribution of heavy metals in the investigated samples decreased according to the following sequence: Sediment > Aquatic Macrophytes > Water. Sediments acts as major reservoirs of heavy metals in the aquatic macrophytes and this could have accounted for its higher concentration than the aquatic macrophtes and water samples. Similar studies by Ramdan (2003) also revealed higher concentration of heavy metals in sediments than in aquatic macrophytes. The author (Ramdan, 2003) attributed this to the ability of sediments to act as important sinks for pollutants. In the study, water recorded the least concentration of metals probably due to the dilution and dispersion of heavy metals in water.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

Sediments accumulated the highest concentration of heavy metals followed by aquatic macrophytes and water accumulated the least concentration of heavy metals.

The concentration of heavy metals in the sediments exceeded the standard and background levels. This endangers the water quality at the Barekese reservoir owing to the risk of secondary pollution (export of microelements from the bottom sediments to the water column). The aquatic macrophytes demonstrated high bioaccumulation of heavy metals from the water and sediments and will be very useful in remediation of polluted water bodies. The water samples had concentrations of lead and iron higher than WHO (2008) guidelines for drinking water. The reservoir water is unfit for drinking purposes unless after adequate treatment.

6.2 Recommendations

The study provide a preliminary result; the discussed topic requires involving a wider spectrum of localities, macrophytes, and the data on heavy metals occurrence in the water and the sediments, along with focusing on the relationships between the heavy metals contents in the water, sediments, and macrophytes. There is therefore a great need to gather long term data in order to evaluate heavy metal pollution in the Barekese reservoir and in other water bodies.

The results suggest that special attention must be given to the issue of metal re-mobilization, because a large portion of metals in sediments are likely to be release back into the water column.

Also, since this study was a kind of passive monitoring, which collected plants naturally growing in situ, and also the data from this study itself are not enough, it is premature to conclude that these plants can be used for monitoring water pollution at the Barekese reservoir. Further research work is therefore necessary to study the aquatic macrophytes and their impact on the water quality of the reservoir.

To tackle heavy metals pollution in the reservoir control measures should be adopted to reduce the amount of pollutants discharged into the reservoir by anthropogenic activities. Continued prohibition of farming activities on the reservoirs immediate borderline and construction of sewage treatment plants are suggested to avoid further deterioration of the reservoir water quality.

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LIST OF APPENDICES

APPENDIX 1: One-Sample T-Test for heavy metal concentrations in water samples at different sites of the Barekese reservoir

One-Sample Test

	Test Value = 0.05					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
Pb	2.546	5	.052	.09167	-.0009	.1842
Zn	-.826	5	.447	-.01000	-.0411	.0211
Mn	7.783	5	.001	.23500	.1574	.3126
Cu	54.411	5	.000	.36500	.3478	.3822
Fe	10.735	5	.000	.61333	.4665	.7602

APPENDIX 2: One-Sample T-Test for heavy metal concentrations in sediment samples at different sites of the Barekese reservoir

One-Sample Test

	Test Value = .05					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
Pb	2.135	5	.086	38.39667	-7.8324	84.6257
Zn	4.232	5	.008	3.95000	1.5505	6.3495
Mn	16.338	5	.000	60.10000	50.6440	69.5560
Cu	2.841	5	.036	120.35000	11.4475	229.2525
Fe	2.742	5	.041	124.86667	7.8055	241.9278

APPENDIX 3: Paired Sample T-Test for Heavy Metals in Roots versus Leaves in *T. domingensis*

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference Lower	95% Confidence Interval of the Difference Upper			
Zn roots – Zn leaves	4.99667	2.95493	1.20634	1.89566	8.09767	4.142	5	.009

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference Lower	95% Confidence Interval of the Difference Upper			
Mn roots – Mn leaves	5.92833	5.36044	2.18839	.30289	11.55377	2.709	5	.042

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference Lower	95% Confidence Interval of the Difference Upper			
Cu roots – Cu leaves	3.70883E1	23.27815	9.50326	12.65941	61.51725	3.903	5	.011

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Fe roots – Fe leaves	9.42967E1	29.12903	11.89188	63.72762	124.86571	7.930	5	.001

APPENDIX 4: Paired Samples T-Test for Heavy Metals in Roots versus Leaves in *P. stratiotes*

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pb roots – Pb leaves	1.09017E1	19.04117	7.77352	-9.08081	30.88415	1.402	5	.220

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Zn roots – Zn leaves	2.880	1.78083	.72702	1.01113	4.74887	3.961	5	.011

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Mn roots – Mn leaves	1.52083E1	5.32399	2.17351	9.62115	20.79552	6.997	5	.001

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Cu roots – Cu leaves	3.60233E1	5.00669	2.04397	30.76913	41.27753	17.624	5	.000

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Fe roots – Fe leaves	1.00423E2	16.11269	6.57798	83.51410	117.33257	15.267	5	.000