KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI

COLLEGE OF SCIENCE

ASSESSMENT OF SOME HEAVY METALS IN SEDIMENT OF LAKE BOSOMTWI IN THE ASHANTI REGION OF GHANA

BY

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QUOTATION

A lake is the landscape's most beautiful and expressive feature. It is

the earth's eye;

Looking into which the beholder measures the depth of his own nature

Henry David Thoreau Walden

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 or material which has been accepted for the award of any other degree of the university, except where acknowledgement has been made in the text.

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Signature Date

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Certified by;

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(Supervisor) Signature Date

Certified by;

Dr. Isaac K.Tetteh …… …….

(Head of Department) Signature Date

DEDICATION

This work is dedicated to my parents, Mr. and Mrs. Nartey, my siblings Nathaniel Nartey, Emilia Nartey, Pearl Nartey, and Olivia Nartey, my cherished wife, Anna Nartey and my two daughters, Ursula Nartey and Lorraine Nartey whose encouragement and prayers made the completion of this work a success.

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ABSTRACT

It is important to monitor the level of heavy metal contaminants in Lake Bosomtwi, thus, assessing its suitability for domestic and agricultural use. In order to determine this, fifty (50) sampling points were selected using the Global Positioning System (GPS) for the collection of fifty 50 sediments samples from April to June 2012. Physicochemical parameters recorded mean values of 111.3±33.4, 2.4 ± 0.5 and 9.1±0.3 for EC, OM and pH respectively. pH recorded a mean value of 9.1 ± 0.3 indicating that the sediment was basic or alkaline in nature. Zn, Cu, Ni, Pb, and Cd sediments were analyzed by Buck Scientific 210 VGP Atomic Absorption Spectrophotometry (AAS). The heavy metals concentration in the sediment was of the order Ni > Pb > Zn > Cd > Cu, the highest mean concentration of 70.19 ± 27.87 µg/g, 63.80 ± 33.41 µg/g, 43.53 ± 19.18 µg/g, 2.01±4.27 µg/g and 0.93 ± 0.89 µg/g for Ni, Pb, Zn, Cd, Cu respectively. Significant spatial variation in concentration was observed for all metals. Correlation analysis showed that Zn content of sediment was partially controlled by organic matter. Pollution status was evaluated using geo-accumulation index and sediment quality guidelines. Based on geoaccumulation index, lake Bosomtwi sediment can be considered as unpolluted with respect to Zn, Ni, Cu and unpolluted to moderately polluted with respect to Pb and Cd . Mean concentrations of Zn and Cu were below the Continental Average Shale (CAS), Threshold effect level (TEL), Severe effect level (SEL) and Permissible limit (PL). However, the mean concentration of 70.19 µg/g, 63.80 µg/g and 2.01 µg/g for Ni, Pb, and Cd respectively were above the Continental Average Shale (CAS) and Threshold Effect Level (TEL) in the sediment at lake Bosomtwi. This implies that the waste assimilation capacity of the lake is high, a phenomenon that could be ascribed to dilution, sedimentation and continuous water exchange. This is an indication that an urban, domestic and industrial waste discharged into the lake has a significant effect on the ecological balance of the lake, ecosystem and human health.

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CHAPTER ONE

1. INTRODUCTION

There are principally three reservoirs of metals in any aquatic environment; namely water, sediment and biota. Metal 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 the sediment is the major repository for metals and in some cases, holding over 99% of the total amount of metals, present in the system. The study of lake sediment is therefore a valuable method of studying environmental pollution with heavy metals (Tang *et al.*, 2010). Lakes play major roles in a community especially in the fishing industry, tourism and a source of water supply for people residing within the vicinity of the lake. Lake containing heavy metals will affect humans directly or indirectly as a final consumer. Although some heavy metals are required as micronutrients, they can be toxic when present higher than the required concentrations.

Heavy metals have been introduced into lakes through geological origin (Kaushik *et al*, 2009) and factory waste outlet point discharge. Anthropogenic metals may consistently be retained within the water bodies or may be taken up by organisms such as plankton, benthos or fish and finally transferred to humans. Thus, it is essential to understand the source of heavy metals pollution for future environment planning strategies.

Sediments are essential and integral part of water systems. They provided the substrate for organisms and through interaction with the overlying waters play an essential role in the aquatic ecosystem (Burden, *et al.*, 2002). They are increasingly recognized as both sink and possible sources of contaminants in aquatic systems. Contamination is not necessarily

fixed permanently by the sediment, but may be recycled via biological and chemical agents both within the sedimentary compartment and the water column. Bioaccumulation and food chain transfer may be strongly affected by sediment associated proportions of pollutants. Benthic organisms, in particular, have direct contact with sediment, and the contaminant level in the sediment may have greater impact on their survival than do aqueous concentrations (Malins, D.C., 1984).

In aquatic environments, many heavy metals transported predominantly in association with particulate matter, and consequently, a high concentration of heavy metals is often detected in sediments in many industrialized harbours and coastal regions around the world (Miller, *et al*., 2000, Chen, and Lin, 2001, Feng, *et al.,* 2004, Wang, *et al*., 2007).

Contaminated sediments are crucial indicators of pollution in aquatic environments and can be defined as soils, sand, organic matter or minerals accumulated at both the surface and bottom of a water body (USEPA, 1998). Contaminants contained in sediments can be released to overlying waters and sediments can be important sources of contaminants in water (Allen 1995, Guven and Akinci 2008). Many of the sediments in seas, lakes and oceans have been contaminated by pollutants. These pollutants are directly discharged by industrial plants and municipal sewage treatment plants, others come from polluted runoff in urban and agricultural areas, and some are as a result of historical contamination (Begum, *et al.,* 2009, Pempkowick, *et al*., 1999).

Contaminated sediments can threaten creatures in the aquatic environment. Some kinds of toxic sediments kill benthic organisms, reducing the food available to larger animals such

as fish. Some contaminants in the sediments are taken up by benthic organisms, in a process called bioaccumulation. When larger animals feed on these contaminated smaller organisms, the toxins are taken into their bodies, moving up the food chain in increasingly concentrations in a process known as bio – magnification. As a result, fish and shellfish, waterfowl, freshwater and marine mammals may accumulate hazardous concentrations of toxic chemicals (Begum, *et al*., 2009).

Contaminated sediments are not always retained at the bottom of a water body. Anything that suits up the water, such as dredging, can re–suspend sediments. Re–suspension may mean that all of the animals in the water and not just at the bottom – dwelling organisms will be directly exposed to toxic contaminants. Different aquatic organisms often respond to external contaminating in different ways, where the quantity and form of the element in the water, sediment or food will determine the degree of accumulation (Begum, *et al*., 2008). Many dangerous chemical elements, if released into the environment, accumulate in the soil and sediments of water bodies. Under certain conditions, chemical elements accumulated in the silt and bottom sediments of water bodies can be migrated back into the water. Silt can become a secondary source of heavy metal pollution (Begum, *et al.*, 2009).

The distribution of heavy metals in sediments can provide researchers with evidence of the anthropogenic impact on aquatic ecosystems and therefore, aid in assessing the risks associated with discharged waste. River and lake bed sediments acting as both carriers and sources of contamination in an aquatic environment; not only play an important role in river and lake water pollution but can also provide a record of lake pollution history (Tsai

et al., 2003). By integrating the chemical, toxicological and ecological data, the impact of heavy metal pollution in Le An river in China was assessed by Wang and Tang (1998) and reported that water and sediment pollution has affected aquatic ecosystem due to effluent discharges into the river. The metals contamination levels in the sediments were wide–ranging significant among river site sampling stations and three main effluent discharging tributaries. The sediments collected from tributaries showed significantly higher tendency towards metallic pollution in sediments than that of river system. In sediments, mean metal levels (Cu, Mn, Zn, Cr, Ni and Pb) were generally higher than the mean levels in water (Ubaidullah, *et al* 2004).

Heavy metals are accumulated in the sediments in different forms which affect their recycling between solution and sediment. The stability of compounds formed during the sedimentation is affected by some water quality parameters such as pH and salinity (Waide, 1986). Changes in these parameters may cause the metals to dissolve back into solution and can impact negatively on human health and the health of aquatic organisms.

Heavy metals cycle between the bottom sediments and the overlying water. This makes the general characteristics of the sediment an important factor in the availability of these heavy metals. Sediment characteristics such as organic matter, pH and electrical conductivity determine the amount of the heavy metals that can be present in the overlying water (Waide, 1986). As a sink and source of metal, sediments contribute most of the lakes bioavailable heavy metals and play an important role in geobiochemical cycle (Hart, 1982). The mobility and bioavailability of metals in sediments strongly depend on the chemical forms in which they occur. (Baeyens *et al.*, 2003).

According to the studies of Rauf *et al.,* (2009), heavy metals pollution in sediments of River Ravi, Pakistan was assessed to contain different ranges for Cd, Cr, Co, Zn and Cu from nineteen sampling stations. The highest concentration of Cu was found in Taj company nulla, while minimum concentration of Cd was observed at Lahore siphon. The result showed that the metal concentrations in the sediments accumulated over the years in the river bed sediment which could act as secondary source of pollution to the overlying water column in the river.

Heavy metal contamination in sediments of Shing Mun River, Hong Kong was reported by Sin *et al.,* (2001). Highest concentrations of Cu, Pb, Zn and Cr were recorded in Fo Tan tributaries, while Al and Cd were found in the Shing Mun River.

Other studies performed by McGregor *et al.*, (2000) were focused on the assessment of the consequences of land use practices within peri-urban watersheds around Kumasi which were being compromised by a variety of activities. Untreated sewage and untreated domestic waste, hospital waste, industrial waste, including assortment of chemicals and heavy metals, oil from informal motor repair businesses, urban and rural run-off including agricultural chemicals and residues and leachate from ground water in to the river system being the main cause of the pollution.

Bosque-Hamilton *et al.*, (2004) compared Weija, Brimsu and Inchaban reservoirs in Ghana and found that the Weija Reservoir was well mixed and aerated but less transparent with high phytoplankton abundance. The water and sediment chemistry showed the cationic

pattern of the reservoir waters as similar to sea waters due to its proximity to sea but anionic pattern was intermediate between freshwater and sea water. The reservoir had more aquatic weeds as evidenced by nutrient dominance with higher nutrients recorded in the wet season. Land use and human activities were identified as principal sources of pollution that greatly influenced the quality of water, biota and sediment.

A study also conducted by Abankwa (2010) on the assessment of sediment and water quality on the Owabi reservoir indicated that all the water quality parameters were above the WHO acceptable limits for drinking water and as such people using water from the reservoir for domestic and agricultural purposes must be warned of the eminent dangers. It was also reported that the sediment samples were acidic and polluted with zinc and lead which are potentially bioavailable and which makes the sediment potential toxic to the aquatic life and the ecosystem as a whole.

Monitoring and assessment of the sediment quality in Lake Bosomtwi would provide the needed scientific information to finding solutions to problems that arise in future as a result of an increased levels of heavy metals in sediment of Lake Bosomtwi which may also affect humans that depend on the Lake.

However, as far as available literature indicates, information on levels of heavy metals in sediments of Lake Bosumtwi is not available.

The present study therefore aims at evaluating the levels of heavy metals (Cd, Cu, Zn, Ni and Pb) in the sediments of Lake Bosomtwi, in the Ashanti Region of Ghana, which will

be used in obtaining the extent of pollution of the lake sediment using the geoaccumulation index.

1.2 Objectives of the study

The general objective of the study is to assess the quality of sediments in Lake Bosomtwi in the Ashanti Region of Ghana.

The specific objectives of this research are to

- Determine the levels of heavy metals namely Ni, Zn, Cd, Cu and Pb in sediments from Lake Bosomtwi.
- Compare the levels with standard guidelines.
- Determine the organic matter content of the sediment.
- Determine the pH and electrical conductivity of the sediment.

CHAPTER TWO

2.0 LITERATURE REVIEW.

2.1 Heavy metals, sources and uses

Metals are natural constituents of rocks, soils, sediments, and water. However, over the 200 years following the beginning of industrialization huge changes in the global budget of critical chemicals at the earth's surface have occurred, challenging those regulatory systems which took millions of years to evolve (Wood and Wang, 1983). The heavy metal content of 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 etc. (Güven and Akıncı, 2008). The metals must be both abundant in nature and readily available as soluble species. Abundance generally restricts the available metals to those of atomic numbers below 40, some of which are virtually unavailable due to the low solubility of their hydroxides. Viewed from the standpoint of environmental pollution, metals may be classified according to three criteria (Wood, 1974);

(i)Noncritical (Na, Mg, Fe, K, Ca, Al, Sr, Li, Rb),

(ii)Toxic but very insoluble or very rare (Ti, Hf, Zr, W, Ta, Ga, La, Os, Ir, Ru,Ba, Rh), and

(iii) Very toxic and relatively accessible (Be, Co, Ni, Cu, Zn, Sn, Cr, As, Se, Te,Ag, Cd, Hg, Tl, Pb, Sb, Bi).

Environmental pollution with toxic metals is becoming a global phenomenon. As a result of the increasing concern with the potential effects of the metallic contaminants on human health and the environment, the research on fundamental, applied and health aspects of trace metals in the environment is increasing (Vernet, 1991).Advances in information of the distributions and concentrations of trace metals in the marine environment have occurred since the mid 1970s (Burton and Statham, 2000). This is mainly due to developments in procedures for contamination free sampling, the adoption of clean methodologies for handling and analysis of samples, and increased application of improved analytical methods such as inductively coupled plasma-mass spectrometry

(ICP-MS) (Burton and Statham, 2000, Plant, *et al*., 2003) and Atomic Absorption Spectrophotometer.

Heavy metals occur naturally as they are components of the lithosphere and are released into the environment through volcanism and weathering of rocks (Fergusson, 1990). However, large scale release of heavy metals to the aquatic environment is often a result of human intervention (Mance, 1987, Denton, *et al*., 1997). Coastal regions are some of the most sensitive environments and yet they are subject to growing human pressures (David, 2003) because of increasing urbanization, industrial development, and recreational activities. Therefore, pollution levels are often elevated in the coast because of nearby land based pollution sources (Fergusson, 1990, Wang, *et al.,* 2007). Industrial processes that release a variety of metals into waterways include mining, smelting and refining. Almost all industrial processes that produce waste discharges are potential three sources of heavy metals to the aquatic environment (Denton, *et al.,* 2001). Domestic wastewater, sewage sludge, urban runoff, and leachate from solid waste disposal sites are also obvious sources of heavy metals into rivers, estuaries and coastal waters (Mance, 1987). A proportion of the total anthropogenic metal input in the sediments in near shore waters, adjacent to urban and industrial growth centers comes from the combustion of fossil fuels. Other potential sources include ports, harbours, marinas and mooring sites, also subjected to heavy metal inputs associated with recreational, commercial, and occasionally, military boating, and shipping activities (Denton, *et al*., 1997).

2.1.1 Cadmium (Cd)

Cadmium is a common impurity as complex oxides, sulfides, and carbonates in zinc, lead and copper ores, and it is most often isolated during the production of zinc. Some zinc ores concentrates from sulfidic zinc ores contain up to 1.4 % of cadmium (Finkelman, 2005). Cadmium is extremely toxic to most plants and animal species particularly in the form of

free cadmium ions (Denton, *et al*. 1997). The major sources of cadmium include metallurgical industries, municipal effluents, sewage sludge and mine wastes, fossil fuels and some phosphorus containing fertilizers. In sediments, cadmium does not appear to be absorbed to colloidal material, but organic matter, appear to be the main sorption material for the metal. Cadmium levels tend to increase with decrease in size and increase in density in terms of partition of sediment samples by size and density. The sorption of cadmium to sediments, and to the clay content, increases with pH. The release of cadmium from the sediment is influenced by a number of factors including acidity, redox conditions and complexing agents in the water. Cadmium is less mobile under alkaline conditions (Fergusson, 1990). The average concentration of cadmium in the lithosphere is ~0.1µg/g and it is strongly chalcophilic (Callender, 2003).

Concentrations in pristine areas are <0.2 µg/g with levels exceeding 100 µg/g at severely contaminated sites (Naidu and Morrison, 1994). The major effects of cadmium poisoning are experienced in the lungs, kidney sand bones. Acute effects of inhalation are bronchitis and toxemia in the liver. Chronic inhalation of cadmium compounds as fumes or dust produce pulmonary emphysema, where the small air sacs of the lungs become distended and eventually destroyed reducing lung cancer**.**

2.1.2 Zinc (Zn)

Zinc is a very common environmental contaminant and usually outranks all other metals considered in this study in terms of abundance and it is commonly found in association with lead and cadmium (Denton *et al*., 1997, Finkelman, 2005). Major sources of Zinc to the aquatic environment include the discharge of domestic wastewaters; coal-burning power plants; manufacturing processes involving metals; and atmospheric fallout (Denton,

et al., 2001). Approximately one third of all atmospheric zinc emissions are from natural sources, the rest come from nonferrous metals, burning of fossil fuels and municipal wastes, and from fertilizer and cement production (Denton *et al.,* 2001., Callender, 2003). Sediments are known as major sinks for zinc in the aquatic environment, and residues in excess of 3000 µg/g have been reported close to mines and smelters (Denton *et al.,* 2001). The highest sedimentary zinc levels are found to be from enclosed harbours reaching as high as 5700 µg/g. This is mainly due to restricted water circulation and also particularly prone to zinc contamination from a variety of localized sources including brass and galvanized fittings on boats, wharves and piers; zinc-based anti-corrosion and anti-fouling paints (Denton *et al*., 1997). The average zinc content of the lithosphere is approximately 80 µg/g (Callender, 2003), sediments from uncontaminated waters typically contain zinc concentration in the order of 5-50 µg/g. Ingesting high levels of zinc for several months may cause anaemia, damage to pancreas, and decrease levels of high-density lipoprotein (HDL) cholesterol (Finkelman, 2005)

2.1.3 Copper (Cu)

Copper is a moderately abundant heavy metal with mean concentration in the lithosphere of about 39 µg/g. It is an essential trace element for the growth of most aquatic organisms however it becomes toxic to aquatic organisms at levels as low as 10 µg/g

(Callender 2003). Heavily polluted sediments have been reported to exceed 200 µg/g. Inputs of copper into the natural waters come from various source including mining, smelting, domestic and industrial wastewaters, steam electrical production, incinerator emissions, and the dumping of sewage sludge (Denton *et al*. 1997). Algaecides and antifouling paints are identified as major contributors of copper to harbor areas whereas

coastal waters are generally receiving inputs from rivers and atmospheric sources (Denton, *et al.* 1997). Copper has a high affinity for clay mineral fractions, especially those rich in coatings containing organic carbon and manganese oxides (Callender, 2003) and as a result, residues are often elevated in sediments near localized sources of inputs (Denton *et al*. 1997). Copper is essential for good health. However, exposure to higher doses can be fatal. Long term exposure to copper results in nose irritation, mouth, and eyes, and cause headache, and diarrhea (Finkelman, 2005).

2.1.4 Lead(Pd)

Lead occurs naturally in the environment .However ,most lead compounds that are found in the environment are as a result of human activities. Lead is among the most recycled non-ferrous metals. Its physical and chemical properties are applied in the manufacturing, construction and chemical industries. Lead is most common in batteries and was previously used as petrol additives in the EU and some other countries (WHO, 2003f). Exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Lead is toxic to both the central and peripheral nervous system, inducing subencephalopathic neurological and behavioral effects (WHO, 2003f). There is an electrophysiological evidence of effects on the nervous system in children with blood lead levels well below 30 mgL^{-1} (WHO, 2003f). Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in

entire food chains (WHO, 2003f).

2..1.5 Nickel (Ni)

Nickel is a very abundant element. In the environment, it is found primarily combined with oxygen (oxides) or sulphur (sulphides). It is found in all soils and is emitted from volcanoes. Pure nickel is a hard, silvery-white metal that is combined with other metals to form alloys. Some of the metals that nickel can be alloyed with are iron, copper, chromium and zinc. These alloys are used in the making of metal coins and jewellery and in industry for making metal items. Nickel compounds are also used for nickel plating, to colour ceramics, to make some batteries, and as catalysts that increase the rate of chemical reactions. Nickel and its compounds have no characteristics odour or taste.

Nickel is required to maintain health in animals. A small amount of nickel is probably essential for human, although a lack of nickel has not been found to affect the health of humans. Small nickel particles in the air settle to the ground or are taken out of the air in rain. Much of the nickel in the environment is found with soil and sediments because nickel attaches to particles that contain iron or manganese, which are often present in soil and sediments. Nickel does not appear to collect in fish, plants, or animals used for food.

Major sources of exposure are: tobacco smoke, auto exhaust, fertilizers, superphosphate, hydrogenated-fats-oils, industrial waste, stainless steel cookware, testing of nuclear devices, baking powder, combustion of fuel oils, dental work and bridges. By breathing air or smoking tobacco containing nickel. By eating food containing nickel, which is the major source of exposure for most people. By drinking water which contains small amounts of nickel. By handling coins and touching other metals containing nickel. The most common adverse health effect of nickel in humans is an allergic reaction. People can become sensitive to nickel when things containing it are in direct contact with the skin, when they

eat nickel in food, drink it in water, or breathe dust containing it. The most common reaction is a skin rash at the site of contact.

2.2 Sedimentation in lake

Natural sediments are complex mixtures of various phases, namely residues of weathering and erosion of materials such as clays and alumosilicates, iron and aluminium oxyhydroxides , sulphides, substances produced by biological activity, both organic (living microorganisms, biological detritus and humic substances) and inorganic (carbonates, phosphates and silica) (Tessier *et al*. 1979). Sediment from anthropogenic sources includes atmospheric precipitation, settling of suspended solids, decaying organic matter and erosion. Sediment loads delivered to reservoirs dramatically increases in response to waterborne erosion in catchments in which large tracts of native vegetation have been cleared and replaced with intensive agriculture (Hodgkin and Hesp, 1998) and urban areas (Hancock and Hunter, 1999; Mc Laughlin, 2000; Marston *et al*., 2001). Turbidity levels and the amount of sediment-bound nutrients such as total phosphorus, total nitrogen and total organic carbon, trace elements such as Fe, Zn, Pb and other toxicants entering reservoirs from catchments also tend to increase sedimentation (McComb and Lukatelich, 1995; Chenhall, 1995). Greater nutrient loads can lead to eutrophication which can further enhance sedimentation rates because the amount of organic matter being deposited also increases (Nixon, 1995).

2.3 Effects of lake sediments on water quality

Sedimentation affects both the useful life of a reservoir for such important purposes as flood control and water supply as well as its aesthetic quality. Sediment quality is an

important environmental concern because sediment may act as a sink for water-quality constituents and as a source of constituents to the overlying water column and biota (Casey *et al.,*2007). Once in the food chain, sediment-derived constituents may pose an even grater concern due to bioaccumulation because their concentrations increase as they reach the top of the food chain. Increased sedimentation rates allow more organic matter to be degraded by anoxic processes (example sulphate reduction) because the exposure time of organic matter to dissolved oxygen in the water column is shortened (Chenhall, 1995). Denitrification efficiencies are lowered under anoxic conditions, and more dissolved nutrients are recycled to the water column.

2.4 Metals in sediments

Natural background levels of heavy metals exist in the majority of sediments due to mineral weathering and natural soil erosion. It is when man's activities accelerate or antagonize these processes that the background levels are increased to levels that have detrimental effects on the environment. Sediments with low heavy metal concentrations are not necessarily "natural" just because the levels are low. They may represent a mixture of small quantity of pollutants diluted by a large amount of natural sediment with low heavy metal content (Herut *et al*., 1993).

The introduction of metallic pollutants into a reservoir, whether it is natural or artificial (anthropogenic), can occur in dissolved and particulate form. Depending on physicchemical conditions of the water, the pollutants in dissolved form can later precipitate. They can also be adsorbed by the iron or manganese oxides and hydroxides or

coprecipitated with these, or form dissolved organic or inorganic complexes (Salomons and

Forstner, 1984; Drever,1988).

Metals are partitioned amongst soluble phases, suspended and bottom sediments and biota in aquatic systems (Elder, 1988). The major pathways of metal partitioning include adsorption, complexation, precipitation and biological uptake. Adsorption is usually the predominant process because metals have strong affinities for iron and manganese oxyhydroxides, particulate organic matter, and to a lesser extent clay minerals (Elder, 1988). Consequently, Metals tend to accumulate in bottom sediments. The soluble phase represents the principal source of bioavailable metals. The dissolved fraction is favored under conditions of low pH, low particulate loads and high concentrations of dissolved organic matter. More metals may also enter solution as water hardness increases, because cations (especially Ca^{2+} and Mg^{2+}) also compete with metal concentrations because clayorganic particles form flocs with a high settling velocity (Elder, 1988).

2.5 Factors that influence the quality and behavior of sediment

Comparison of total heavy metal content in sediments in different areas may be a convenient way of expressing some measure of pollution, but this method has its limitations. Sediment metal concentrations are influenced by a range of factors. They include physical and hydrological characteristics of the region and its benthos, atmospheric conditions, productivity, pH, soil texture, redox potential and cation exchange capacity among others (Belize *et al*., 2004).

All sediments contain some amount of heavy metals from natural sources. However, these background levels can vary widely depending on a number of factors such as parent material and sedimentation processes in water bodies. It is usually through human activities that levels of heavy metals increase. Due to this, Pollution in sediments can rise to the point where they represent a potential health or ecological risk (Chen and Lin, 2001).

Heavy metals that are soluble in water are highly mobile and are also readily available for plant and animal uptake. Exchangeable metals, however, are those that rather than existing in the water column, are primarily bound to soil surfaces by cation exchange processes. Metals that are found in this form are considered to be bonded very weakly and may be displaced easily to the water-soluble form. Together, the metals in the soluble and exchangeable form are considered readily mobilized. When changes occur in the oxidation status of soils and sediments, transformations of metals between chemical forms, soluble and insoluble, may occur. This affects the mobility and plant availability of metals (Chuan *et al* 1996).

The quantity of heavy metals retained in sediments is also affected by the characteristics of the sediment into which they are adsorbed. Grain size, cation exchange capacity, organic matter content and mineral constituents are some of the factors that influence the uptake of heavy metals in the aquatic environment (CSIRO, 2000). However elevated concentrations of metals do not necessarily pose a threat as they may never be released from the sediments and therefore may not be available for excessive plants and animals' uptake (Elder, 1998).

2.6 Organic matter content

Sediment organic matter is derived from plant and animal detritus, bacteria or plankton formed in-situ, or derived from natural and anthropogenic sources in catchments. Organic matter in sediment consists of carbon and nutrients in the form of carbohydrates, proteins, fats and nucleic acids (CSIRO, 2000). Sewage and effluent from homes and industry such as food processing factories are examples of organic-rich waster of human origin. Organic matter has a high affinity for fine-grained sediment because it adsorbs onto mineral surfaces (CSIRO, 2000). Sewage and effluent from homes and industry such as food processing factories are examples of organic-rich wastes of human origin. Organic matter has a high affinity for fine-grained sediment because it adsorbs onto mineral surfaces (CSIRO, 2000). Sediment organic matter can be a source of water column nutrients when it degrades (Twilley *et al*., 1999). This release of nutrients during degradation can also release metals including heavy metals that are bound to their surfaces. Dissolved oxygen concentrations are usually lowered when organic matter is degraded by aerobic bacteria, and anoxic and hypoxic conditions may develop under stratified conditions and this raises the acidity of the reservoir system (Enriquez *et al*., 1993).

High organic matter content in sediments also implies immobilization of the metals that are bound to the fulvic or humic acids. On the other hand, binding on smaller organic molecules may increase metal mobility and bioavailability (Kabata-Pendias and Pendias, 1992). Angehrn-Bettinazzi *et al*. (1989) reported high ability of Pb to form complexes with

insoluble humic substances, while Cd and Zn form complexes with mobile organic substance of low molecular weight.

2.7 Acidity

This is the measure of the hydrogen ion concentration in the sediment. This parameter also greatly affects metal availability. A higher acidity (implying a lower pH) increases metal availability since H^+ has a higher affinity for the negative charges on the colloidal surfaces. This affinity for negative charges thus leads to competition between the metals and the H^+ ions thereby releasing the metals (Koning and Kroos, 1999). A lower pH is a common phenomenon since degradation of organic matter and detritus in the sediment produces acids that tend to decrease the pH. Soil oxidation conditions also influence soil pH, a major factor influencing metal chemistry (Gambrell, 1994). The pH value of the solution is the master variable that oversees the desorption of metal ions at surfaces (Schlinder,1991). High pH values promote adsorption whereas low pH actually prevents the retention of metals by sediment (Belize *et al*., 2004). The pH can not only markedly affect the type of surface sites, but also the speciation of the metal ion in solution adsorbed out of solution (Stumm and Morgan, 1981). The results of Gambrell (1994) support this idea and indicate that permanently flooded sediment becomes strongly acidic upon drainage, the process which retains metals tends to be intensified.

2.8 Extent of pollution of sediment by heavy metals

2.8.1. Geoaccumulation Index

The geoaccumulation index (*Igeo*) has been used since the late 1960s, and has been widely employed in European trace metal studies (Yaqin *et al*., 2008). Originally used for bottom

sediments, it has been successfully applied to the measurement of soil pollution (Cabrera *et al*., 1999; Grzebisz *et al.*, 2002; Yagin *et al*., 2008, Okweye *et al*., 2009). The Igeo values enable the assessment of pollution by comparing current and preindustrial concentrations, although it is not always easy to reach pre-industrial sediment layers (Yaqin *et al*., 2008). Geoaccumulation Index is calculated using the formula;

$$\boldsymbol{Igeo} = \mathbf{Log_2}\left(\frac{\mathbf{Cn}}{\mathbf{1.5 \times Bn}}\right)$$

Where **Cn** is the measured concentration of the element in soil or sediment,

Bn is the geochemical background value and 1.5 is a constant. The constant 1.5 allows for analyses of natural fluctuations in the content of a given substance in the environment and to detect very small anthropogenic influences (Teng *et al*., 2004; Lokeshwari and Chandrappa, 2007; Yaqin *et al*., 2008). The equation indicates that the index will be affected by the content of the samples and the geochemical background values. The world average shale, Earths crust, and the world average soil are some of the materials often used to provide background values (Turekian and Wedepohl, 1961; Karbassi *et al*., 2008; Yaqin *et al*., 2008). The world average shale concentrations of elements of interest are either directly measured in texturally equivalent uncontaminated sediments or size fractions or taken from literature (Teng *et al*., 2004). The geoaccumulation index consists of 7 grades or classes (Grzebisz *et al*., 2002; Lokeshwari and Chandrappa, 2007; Yaqin *et al*., 2008) [Table 2.1]. Class 7 is an open class and comprises all values of the index higher than class 6. The elemental concentrations in class 7 may be hundredfold greater than the geochemical background value (Teng *et al*., 2004; Lokeshwari and Chandrappa, 2007; Yaqin *et al*., 2008).

Table 2.1 : Pollution Grades Of Geo-accumulation Index Of Metals

Igeo class	*Igeo* values	pollution intensity
0	I*geo* < 0	Unpolluted
1	0 < *igeo* < 1	unpolluted to moderately polluted
2	1 < *igeo* < 2	moderately polluted
3	2 < *igeo* < 3	moderately polluted to strongly polluted
4	3 < *igeo* < 4	strongly polluted
5	4 < *igeo* < 5	strongly to very strongly polluted
6	5 < *igeo*	very strongly polluted

CHAPTER THREE

3 Materials and methods

3.1 Study area

Lake Bosomtwi is located 35 km southeast of Kumasi, the capital city of the Ashanti region in Ghana. Kumasi is at about 6.5° N, 150 km from the Coast, and has an elevation of 310 m. Other nearby towns include Konongo (elevation 233 m), 30 km to the northeast of the lake, and Bekwai (elevation 230 m), 20 km to the southwest (Turner *et al.,* 1995).

Lake Bosomtwi, (Fig 3.1) located along 6° 30' N and 1° 25' W (Fig. 3.1 and 3.2) is a 1.07 ± 0.05 million years old meteorite impact crater (Koeberl *et al.,* 1997). The crater has a diameter of 11 km, and the circular lake, which currently has no surface outlet, is 8 km across. The maximum depth is 75 m at the centre and has a surface area of about 50 km^2.

Lake Bosomtwi is hydrologically closed, and is maintained by direct precipitation, groundwater, and numerous small streams. Lake Bosomtwi is also affected by two major air masses: the West African monsoon off the Atlantic Ocean, which brings precipitation to the region during much of the year, and dry, northeasterly flow (harmattan winds) that penetrates into West Africa. Annual rainfall in the region averages 1380 m, with a monthly maximum in June and a secondary peak in October. Both rainfall and lake levels are variable from year to year, and appear highly correlated with regional rainfall (Talbot *et al.,* 1984; Nicholson, 1986).

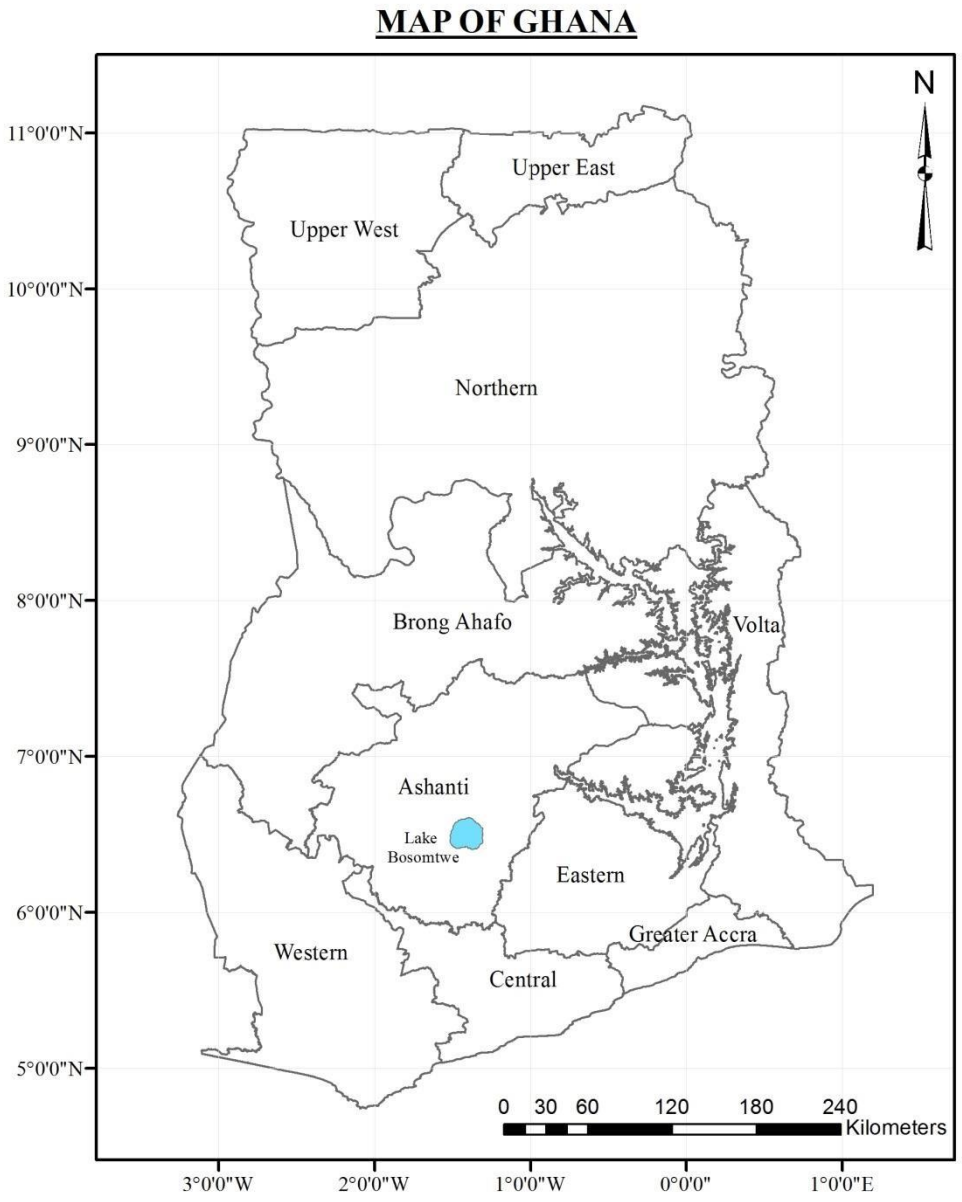

Figure 3.1.The location of the Lake Bosomtwi on the map of Ghana

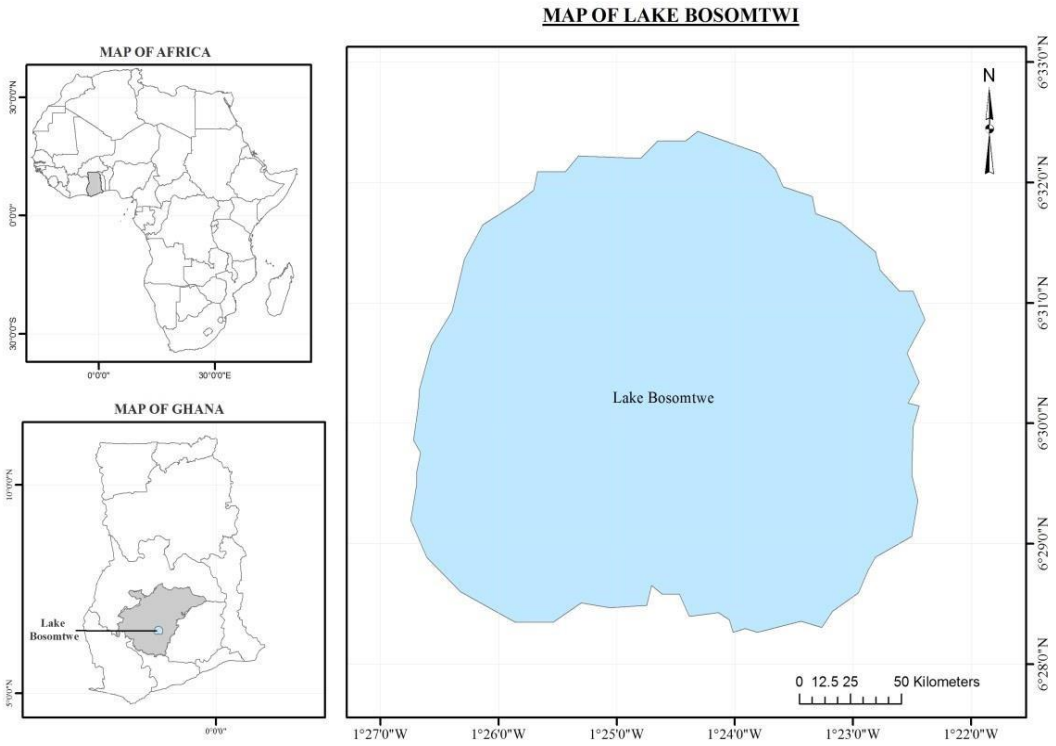

Figure 3.2. Geological map of Lake Bosomtwi area (after Jones *et. al*. 1981).

3.2. Apparatus.

- ❖ Retsch -2mm sieve for mechanical or manual, wet or, dry sieving (D x H 250mm x 50mm was used for sieving.
- ❖ Manual burette.
- ❖ Hanna 209 pH meter.
- ❖ Hot plate.
- ❖ Buck Scientific 210 VGP AAS.
- ❖ Hanna conductivity meter.
- ❖ Ekman grab.

- ❖ Global Positioning System (GPS).

3.3 Sampling.

3.3.1 Sample Collection

Fifty (50) samples were collected from the lake bottom between March 20, 2012 and April 19, 2012 from 50 locations using a boat. The boat was stationed at a specific location which is to be sampled on the lake and the longitude and latitude readings were taken using the global positioning system (GPS).

The Ekman grab was lowered to the bottom of the lake. The messenger of the grab was open and held in the left hand (over the side of the boat) and the rope dropped with the right hand. When the grab reached the bottom, the rope was lifted slightly to get the rope vertical. The messenger was then released to close the grab. The sediment (i.e. 2 cm – 8 cm), was scooped into a plastic bag and then labeled with the name of the location (eg P1).

This procedure was repeated for all the 50 samples collected.

3.4. Sample Preparation / Treatment.

Collected sediment samples were transferred to a polyethylene bag. The samples were air dried for 48 hours and sieved through a polyethylene size to remove large particles. The samples were then ground in mortar to obtain a homogenous sample. The ground samples were sieved through a 225 µm mesh.

3.5. Reagents and solutions

All chemicals used were of analytical reagent grade. De-ionized water was used for all dilutions throughout the study. All plastic containers were cleaned by soaking in 5% (v/v) nitric acid for 24 hours and rinsed with distilled water and de-ionized water prior to use. HCl, HNO_3, H_2SO_4 and $HClO_4$ were used for wet digestion. The working standard solutions of the metal for calibration procedure were prepared by diluting Zn, Pb, Mn, Cu, and Cd standard solutions of 1000 ppm.

3.6. Reagent and Solution for Organic Matter

- $K_2Cr_2O_7$ solution (1.0 M) $K_2Cr_2O_7$ - pure solid was dried at 105°C, for 2 hours, and 24.52 g was dissolved in 250 ml of deionized water. It was diluted to 500 ml with deionized water.

- Conc, H_2SO_4 (Merck -98% (w/w) density = 1.84 g/ml Molar mass = 98.04 g/mol)

- $(NH_4)_2$ Fe ($SO_4)_2$.$6H_2O$ solution (0.2 M) - pure solid was dried and 78.39 g was dissolved in 50 ml conc. H_2SO_4. It was diluted to 1000 ml with deionized water and then stored in a dark bottle. It was standardized with $K_2Cr_2O_7$ Solution.

- Ferroin indicator $(C_{12}H_8N_2)_3$ $FeSO_4$): 1,10 phenanthroline monohydrate-Ferrous Sulphate. Pure solid of 1,10 phenanthroline monohydrate was dried and 1.485 g $C_{12}H_8N_2.H_2O$ was dissolved in 100 ml of 0.025 M ferrous sulphate (0.69 g Ferrous sulphate $FeSO_4.7H_2O$) in 100 ml of deionized water.

3.7. Determination of organic matter

In this procedure, 5.0 ml of 1 M $K_2Cr_2O_7$ Solution and 7.5 ml Conc. H_2SO_4 were added to 0.5 g of ground soil in a digestion tube. The solution was swirled and allowed to cool (when the potassium dichromate and sulphuric acid were mixed the exothermic reaction occurs). The solution was placed in a pre-heated block at 155 °C for exactly 30 minutes. It was then removed and allowed to cool. The digest was quantitatively transfer to a 100 ml conical flask and 0.3 ml of the ferroin indicator solution was added to the solution. Using a magnetic stirrer to ensure good mixing, the digest was titrated with 0.2 M ferrous ammonium sulphate solution. The endpoint was reached with a colour change from green to brown.

The titre values were recorded (V) and corrected for the mean of two (2) reagent blanks (T).

The equation of this reaction is as follows:

$$2Cr_2O_7^{2-} + 3C + 16H^+ \longrightarrow 4Cr^{3+} + 3CO_2 + 8H_2O$$

The total Organic Matter was calculated using the following equations

$$\% \text{ Organic Carbon} = \frac{(T-V) \times 0.3 \times 0.2}{\text{Sample weight (g)}}$$

$$\% \text{ Organic Matter} = \% \text{ OC} \times 1.72$$

T-mean of two reagent blanks

V- the titre values

3.8 Reagents and Solutions for the Determination of pH and Electrical Conductivity

- Buffer Solutions –Fisher Scientific (pH = 4.01, 7.01 and 10.01)

- KCl Solution (0.01 M) (KCl- Pure solid was dried at 105 °C, for 2 hours and 0.746 g was dissolved in 250 ml of de-ionized water. It was diluted to 1000ml with de-ionized water).

3.8.1 Determination of pH.

The pH meter was calibrated by dipping the electrode in the buffer solutions of pH= 4.01 and 7.01 before measurement of the pH of the soil suspension prepared with one part soil and five parts water which was continuously stirred to obtain homogenous suspension. The pH electrode was inserted into the soil suspension and the pH values recorded.

3.8.2 Determination of electrical conductivity (EC)

Conductivity meter was used for the measurement of EC of soil samples. The EC of KCl solution was measured at the same temperature as the soil suspensions. It has an electrical conductivity of 1413 µS/cm at 25 °C. EC meter was calibrated with this solution before measurement of the EC of soil suspension prepared with one part soil and five parts water which was continuously stirred to obtain homogeneous suspension. The EC electrode was inserted into the soil suspension and the EC values recorded.

3.9. Digestion of Sediment Samples.

One gram of the Sediment sample was weighed into a 50 ml digestion tubes. Exactly 2 ml of distilled water was added and mixed gently, then 4 ml of $HNO_3 – HClO_4$ (1:1) was added followed by the addition of 10 ml H_2SO_4. It was then heated on a hot plate at 200 ºC for 30 minutes and allowed to cooled to room temperature and distilled water added to 50 ml. The content of the digestion tube were then filtered into the polyethylene containers

through a No 1 125 mm Whatman filter paper. Blanks, consisting of distilled water and reagents were subjected to a similar digestion. Samples 34 and 45 were digested in triplicates to check for precision.

3.10. Recovery of heavy metals

About 1g of each of samples P_1 to P_{50} was weighed into four 50 ml digestion tubes. Exactly 2 µg/ml of the standard solution (Pb, Zn, Cu, Ni and Cd) was added to one of the samples and 4 µg/ml was added to the second, 6 ug/ml to the third sample. No standard was added to the fourth sample. The mixtures were digested using the digestion procedure used for the samples. Each determination was carried out at least three times.

Percentage recovery for the spiked solution was calculated using the relation

$$\text{Recovery} = \frac{\text{Conc of metal in Spiked} - \text{Conc of metal in Non spiked sample}}{\text{Conc of metal added}} \times 100\%$$

3.11. Standard Solutions and Calibration curve

Standard aqueous solution of different elements were used to calibrate the AAS machine. For each of the metals, four standard solutions were set for the calibration of the AAS for Ni, Pb, and Zn while three standards solutions for Cd and Cu. These are as follows 0.2 ppm, 0.4 ppm, 0.6 ppm, 1 ppm for Zn metal, 2 ppm, 4 ppm, 6 ppm, 8 ppm for Pb metal, 1.0ppm, 1.5 ppm, 3 ppm, 5 ppm for Ni metal, 0.2 ppm, 0.4 ppm, 0.6 ppm for Cd metal and 0.2 ppm, 0.4 ppm, 0.8 ppm for Cu metal for the Calibration.The Calibration Curves were drawn as the concentration of the standard solution versus absorbance values. A new Calibration Curve was plotted for each element every time a new batch of sample was arranged for analysis. Each standard solution was measured at least three times and mean was plotted.

3.12. Sample analysis

The determination of Zn, Ni, Pb, Cd, and Cu in the digest were carried using Buck Scientific 210 VGP Atomic Absorption Spectrophotometer at the Agriculture Faculty (Soil Science Department) of KNUST. Hollow cathode lamps for Cd, Cu, Zn, Pb, and Ni were used as radiation source. Air acetylene flame was used for atomization. Table 3.2 presents the operating conditions of the AAS.

Table 3.2: Operating Parameters for AAS.

Element	Wavelength (nm)	burner height (mm)	Slit width (nm)	Fuel flow (L/min)	Optimum Working Range (µg/ml)
Ni	232.0	7.0	0.2	2.2	0.1 - 20
Pb	217.0	7.8	1.0	1.0	0.1 - 30
Cu	324.7	6.2	0.5	0.9	1.0 - 4.0
Zn	213.9	6.2	1.0	0.9	0.1 - 2
Cd	228.8	6.0	0.5	0.9	0.2 - 3

Each solution aspirated was followed by aspiration of deionized water, to rinse the sampling system in order to avoid contamination. The blank samples were also measured, and absorbance of the blank sample was subtracted from that of the sample.

Some of the samples were measured in triplicate for precision. The concentrations of the metals were obtained in µg/ml from the calibration curve. Concentrations in µg/g was calculated using the following relation.

Concentrations (µg/g) = $\frac{\text{concentrations (µg/ml)} \times \text{50ml}}{}$

Sample weight (g)

3.13 Instrument operation

1. The instrument was checked for the proper fitting of all the tubings, required type of burner (air acetylene or nitrous oxide acetylene) and hollow cathode lamps.
2. The liquid trap was filled with deionized water.
3. The hollow cathode lamp of the element to be determined was aligned with the optical path of the instrument by rotating the lamp turret.
4. The instrument was switched on and allowed to warm up for at least 30 minutes.
5. The deuterium lamp for background correction, was switched on.
6. The lamp current recommended by the lamp manufacturer was used.
7. The desirable wavelength and the bandpass width or slit width was also selected.
8. The burner position was optimized by using the vertical, horizontal and rotational adjustment knobs until the burner slot was aligned with the beam and was just below the position from where it starts to block the light path.
9. The compressor was switched on in order to generate air.
10. The acetylene supply was turned on, using the fuel control knob of the instrument and the flame ignited.
11. The fuel control knob (acetylene) and air control knobs were adjusted to produce the required kind of flame.
12. The instrument was set to zero by means of the “zero” control against a deionized water.
13. A standard solution was aspirated and fuel, oxidant and sample flow rates optimized by adjusting the fuel knob, fuel support knob and nebulizer so that a maximum signal (absorbance) was achieved.

14. A calibration curve was prepared by recording the absorbance of a series of working standards solution. The calibration was done for each set of analysis.
15. The samples were analysed after each calibration.

3.14 Switching off.

1. The gas from the cylinder was turned off.
2. The fuel control-knob was turned off after waiting for extinction of the flame.
3. The air compressor and fuel-support knob were turned off.
4. The instrument was then switched off.

3.15 Statistical analysis

Data obtained in this study for the levels of the studied heavy metals were determined by one-way analysis of variance (ANOVA) to determine the variability in levels recorded along the various sampling points. The Tukey‘s Multiple Comparison Test was used to further test for significant differences among all the sampling points.

Mean comparisons and Pearson’s correlation were used to assess the degree of association to establish possible relationships between the studied metals in the sediment samples and the organic matter, electrical conductivity as well as the pH of the samples from the different sampling locations. All descriptive statistics and graphs were executed using the GraphPad Prism 6 Software, 2014.

CHAPTER FOUR

4.0. Results.

4.1.1 Calibration curve

The range of linearity and the regression coefficient of calibration curve is of great importance in determining the elemental concentration of the sediment samples because it ensures the accuracy of the results and also serving as a precautionary measure in the determination of the levels of the heavy metals. The calibration curves for Pb, Cu, Cd, Ni, and Zn are shown in figure 4.1, 4.2, 4.3, 4.4 and 4.5. The calibration curves obtained were fairly linear, with very good coefficients.

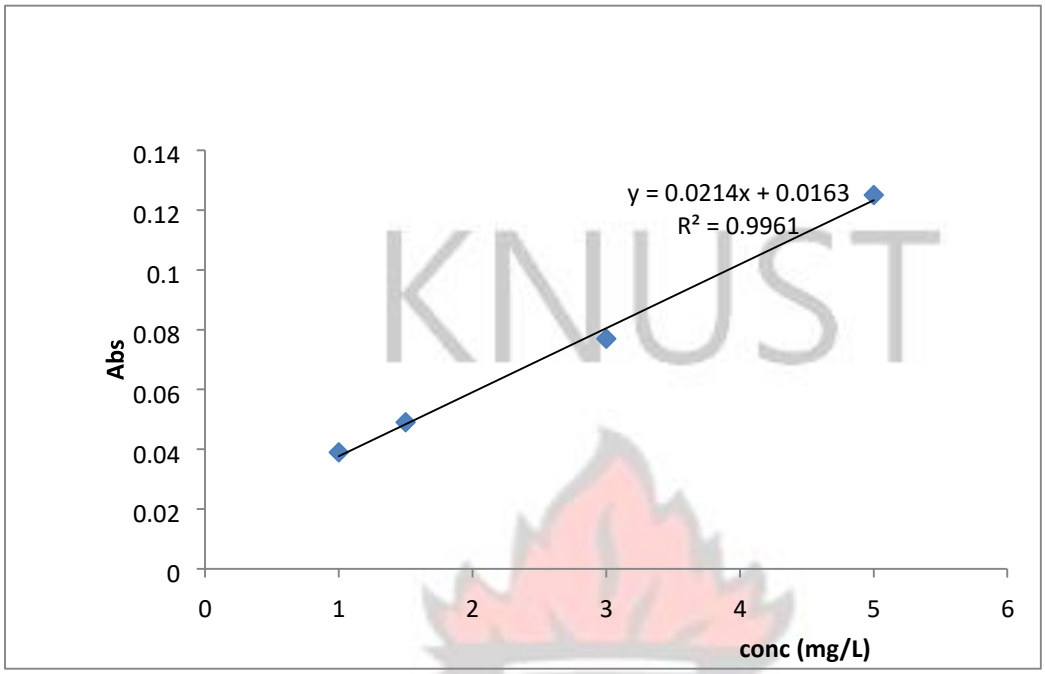

Fig.4.1: Calibration curve for nickel.

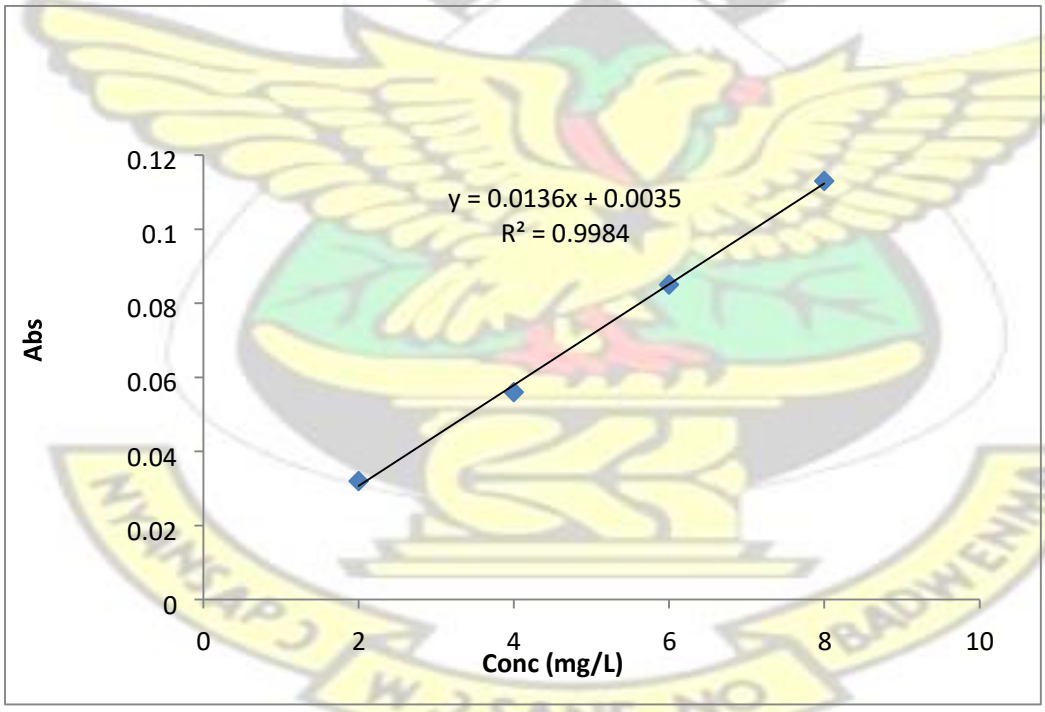

Fig.4.2 : Calibration curve for lead.

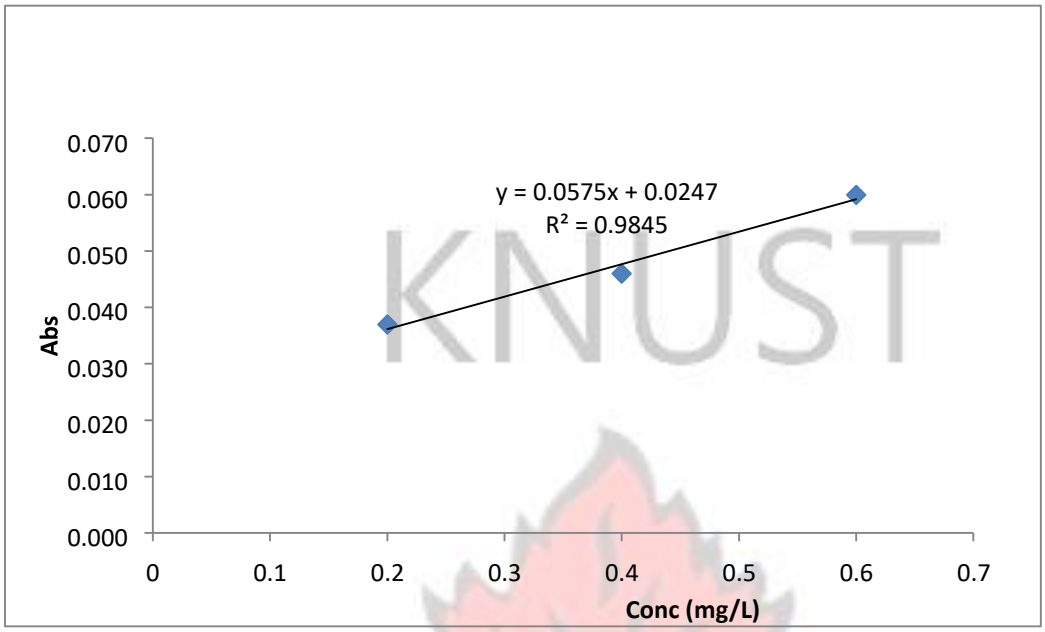

Fig.4.3: Calibration curve for cadmium.

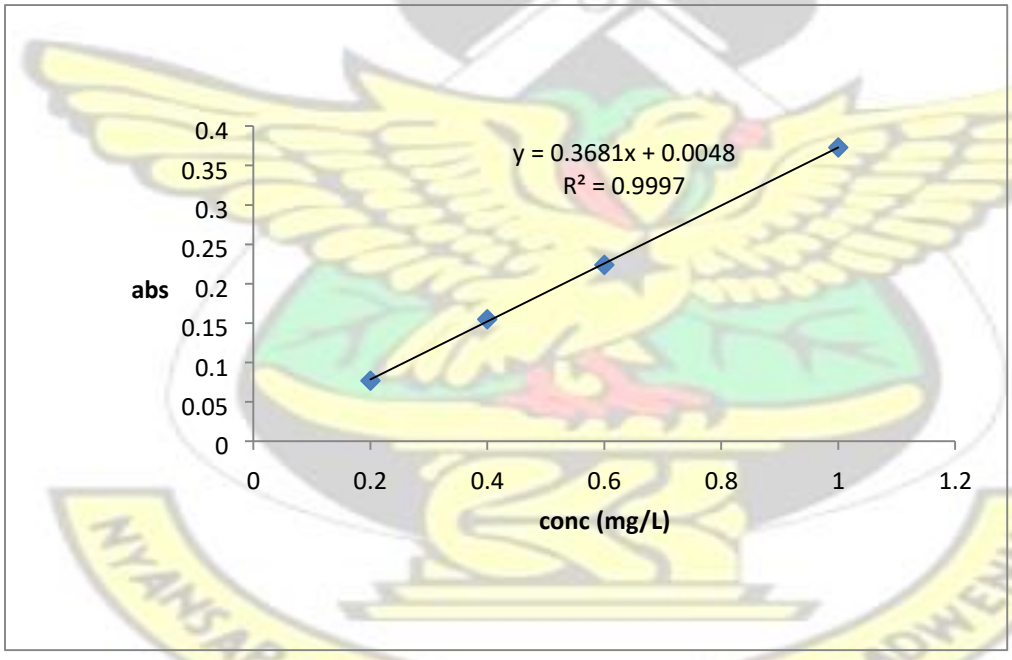

Fig.4.4: Calibration curve for zinc.

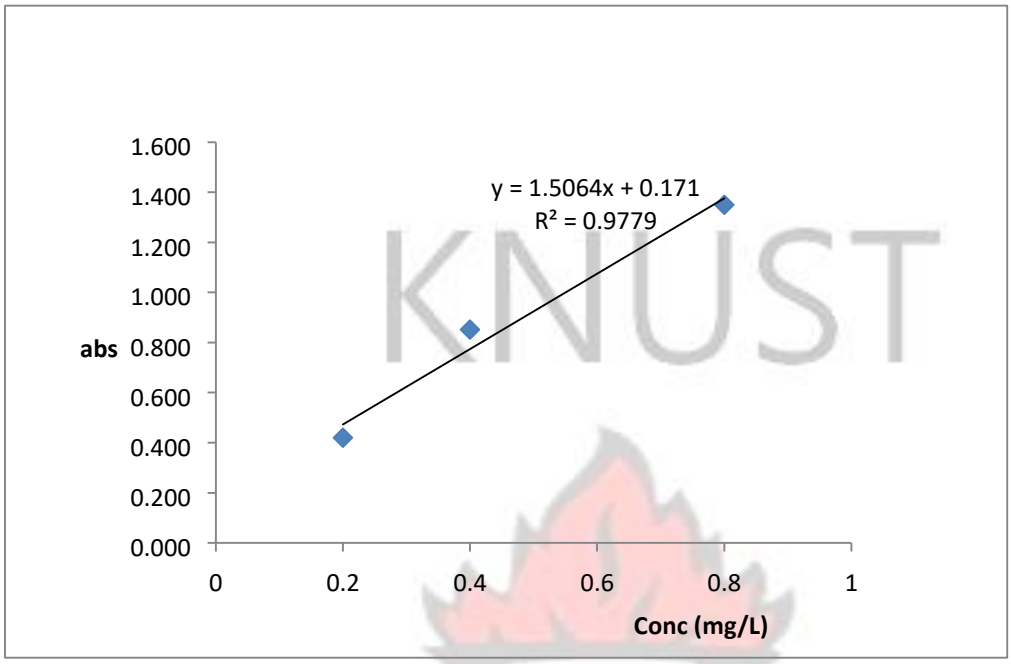

Fig4.5: Calibration curve for copper.

4.1.2 Method validation.

The reliability of the method used was validated by determining the recovery of each metal. This was done by adding known amounts of standard solution to sample. The samples and the added standard solutions were subjected to same digestion procedure as the samples. The digests were then analysed by Atomic Absorption Spectrophotometer (AAS). The recovery for zinc was a mean of 91.3%. The recoveries for the other metals ranged between 79% and 106% and are presented in Table 4.1 – 4.4.

Table 4.1 Determination of recovery for zinc metal (Zn)

Sample g	Vol. added (µg/ml)	Conc. (µg/g)	Metals found (µg/g)	Recovery	% recovery
1.0035	0	0	13.4	0	0
1.0024	2	20	28.8	15.4	77
1.0028	4	40	48.6	35.2	88

1.0023	6	60	79.0	65.6	109
MEAN					**91.3%**

Table 4.2 Determination of recovery for lead metal Pb)

Sample g	Vol. added (µg/ml)	Conc. (µg/g)	Metals found (µg/g)	Recovery	% Recovery
1.0035	0	0	71.4	0	0
1.0040	2	20	92.4	21.0	105
1.0028	4	40	110.5	39.1	98
1.0026	6	60	141.2	69.8	116
MEAN					**106%**

Table 4.3 Determination of recovery for cadmium metal (Cd)

Sample g	Vol. added (µg/ml)	Conc. (µg/g)	Metals found (µg/g)	Recovery	% Recovery
1.0035	0	0	2.90	0	0
1.0020	2	20	18.1	15.2	76
1.0030	4	40	34.4	31.5	79

1.0033	6	60	58.6	55.7	93
MEAN					**83%**

Table 4.4 Determination of recovery for copper metal (Cu)

Sample g	Vol. added (µg/ml)	Conc. (µg/g)	Metals found (µg/g)	Recovery	% Recovery
1.0035	0	0	1.07	0	0
1.0028	2	20	14.4	13.33	66.5
1.0032	4	40	32.8	31.73	79.3
1.0031	6	60	55.6	54.53	90.9
MEAN					**79%**

4.1.3 Results of sediment analysis.

The summary of the results for the physicochemical parameters of sediment from lake Bosomtwi is presented in Table 4.2 below. The raw data on physicochemical parameters is presented in appendix 1F. Correlation between physicochemical parameters and the selected heavy metals was also carried out.

Table 4.5 : The range, mean, standard deviation of physicochemical parameters of sediment from lake Bosomtwi.

PARAMETERS	RANGE	MEAN ± STD.DEV

pH	8.5 - 9.6	9.1 ± 0.3
Organic Matter (%)	1.4 - 3.6	2.4 ± 0.5
EC	48.4 - 193.3	111 ± 33.4

A graphical representation of the OM, pH and EC of the sediment samples is shown in fig. 4.6,4.7,4.8

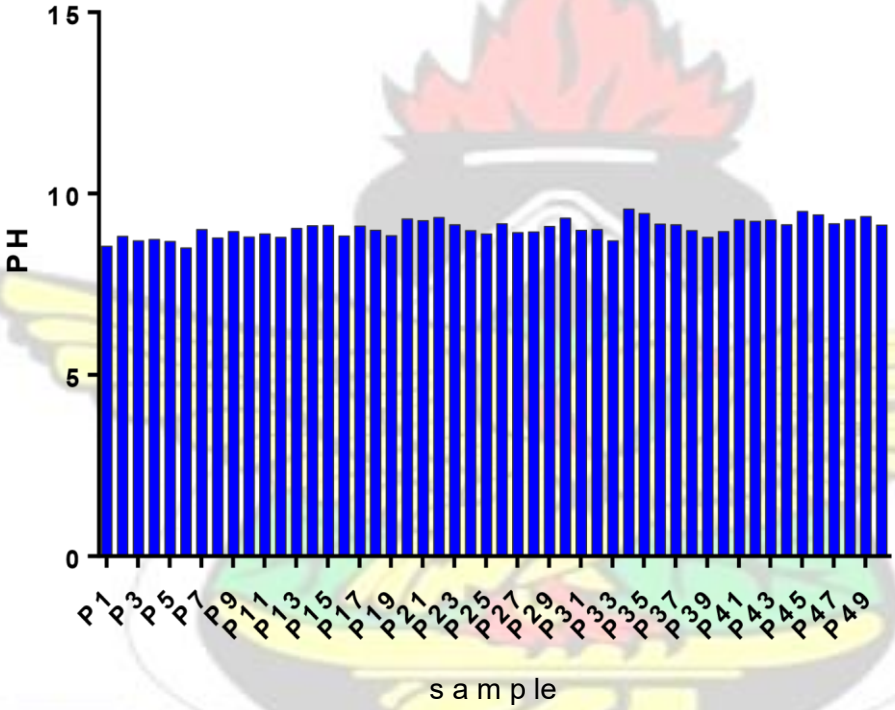

Fig 4.6:A Graph of pH of the sediment sample.

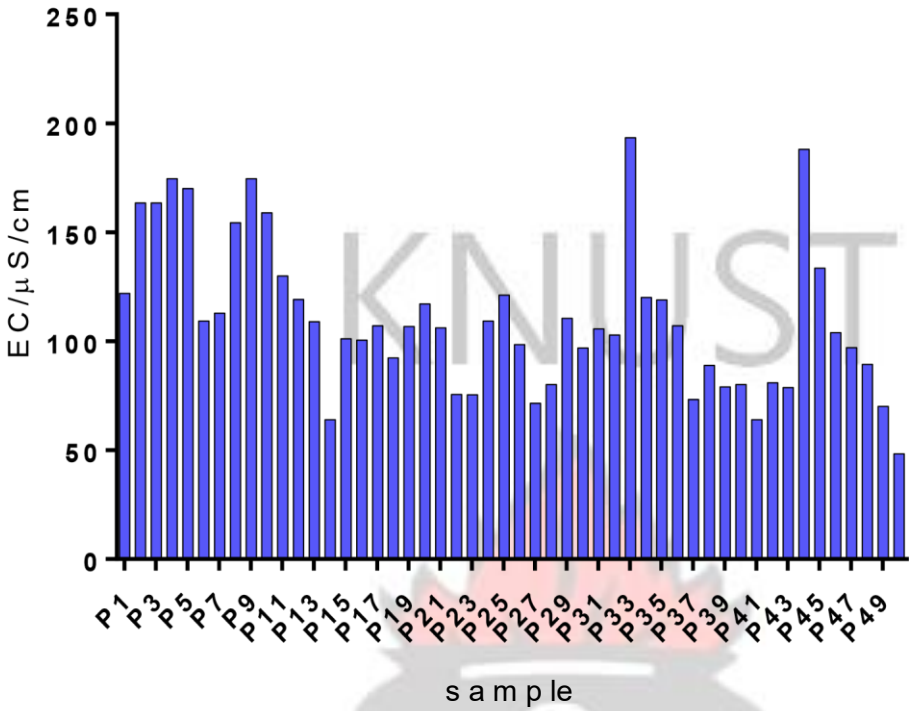

Fig.4.7:A graph of EC of the sediment sample.

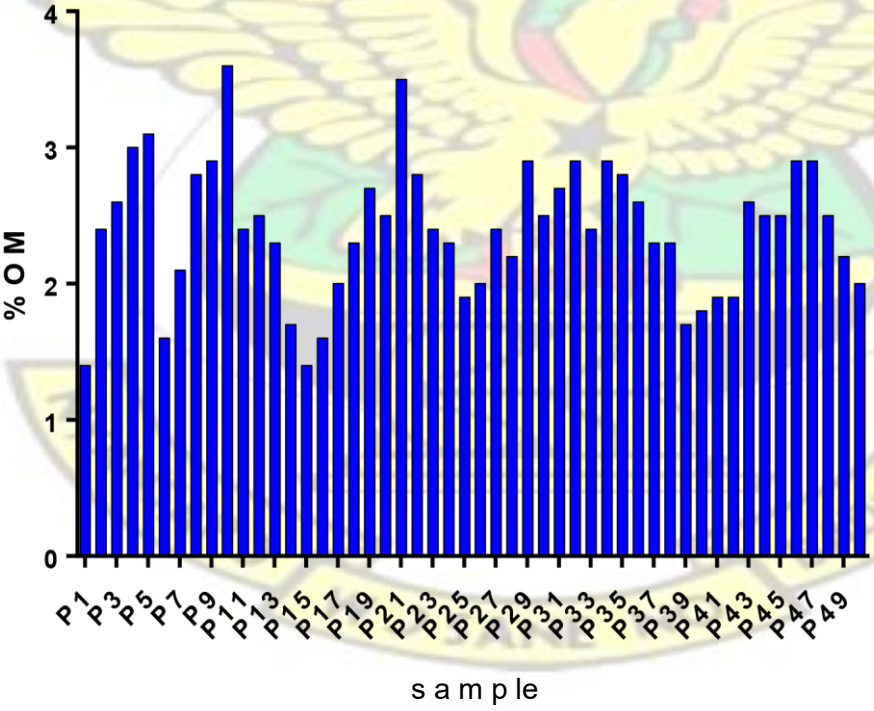

Fig. 4.8 : A graph of OM of the sediment sample.

4.1.4 Physicochemical Parameters of Sediments from Lake Bosomtwi.

The pH values recorded ranged from a minimum of 8.5 recorded at point P_6 to a maximum of 9.6 at point P_{34}. The average pH of 9.1 ± 0.3 makes the sediment basic. The pH values recorded at points 34 and 45 which were in triplicates also indicated good precision of the determination.

Electrical Conductivity (EC) of the sediment samples ranges from a minimum of 48.4 µS/cm recorded at point P_{50} to a maximum of 193.3 µS/cm recorded at point P_{33}. The average EC is 111±33.4 which is attributed to the high content of soluble salts in sediment (Mohammad and Mazahreh, 2003).

The organic matter content of the sediment samples ranged from a minimum of 1.4% recorded at point P_1 to a maximum of 3.6% recorded at point P_{10} . The average OM of 2.4 ± 0.5 of the sediment makes the OM to be within the medium range of between 2.0 - 3.0 which is favourable for aquatic organisms.

Table 4.6 : The ranges, mean and standard deviation of selected heavy metals in sediments from lake Bosomtwi compared with threshold effect level (TEL), continental average shale (CAS), severe effect level (SEL) and permissible limit.

HEAVY METAL CONCENTRATION (µg/g)

Parameter	Range	Mean± Std. Dev	TEL	SEL	CAS	P.L
Pb	nd - 133.63	63.80±33.41	35.0	250	20	31 - 250
Cd	nd - 16.72	2.01±4.27	0.6	10	0.3	0.6 - 10
Ni	nd - 132.15	70.19±27.87	16	75	68	16 - 75
Cu	nd - 3.75	0.93±0.89	35.7	110	45	16 - 110
Zn	7.80 - 70.61	43.52±19.18	123	820	95	120 - 820

nd-non detectable.

4.2.0 Heavy Metal Distribution

4.2.1 Zinc (Zn)

The concentrations of zinc in the sediments fluctuated between a minimum of 7.80 µg/g at point P_2 and maximum of 70.61 µg/g at point P_{44} with an average of 43.52 ± 19.18 µg/g. All the recorded values were below the threshold effect level (TEL) of 123 µg/g (Buchman, 2008), the continental average shale of 95 µg/g (Turekian and Wedepohl ,1961) severe effect level (SEL) of 820 µg/g (Buchman, 2008) and permissible level (P.L) of between 120-820 µg/g (Persuad *et al,* 1990).

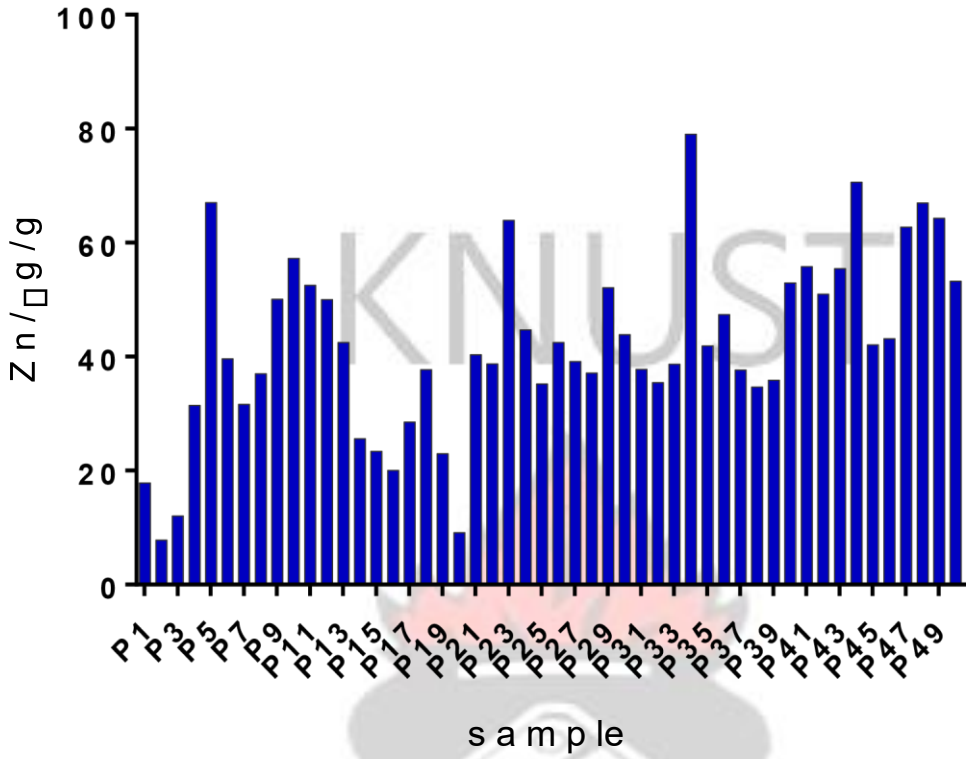

Fig 4.9: Graph of zinc concentration at the various sampling point in the lake.

4.2.2 Copper (Cu)

Copper was below detection at points P_{12}, P_{22}, P_{25}, P_{26}, P_{36}, P_{37}, P_{43}, and P_{45} and a maximum of 3.75 µg/g. at point P_5. The average concentration was 0.93 ± 0.89 µg/g. All the points fromP_1 to P_{50} recorded values below the threshold effect level (TEL) of 35.7 µg/g (Buchman, 2008), severe effect level of 110 µg/g (Buchman, 2008), and continental average shale of 45 µg/g (Turekian and Wedepohl, 1961).

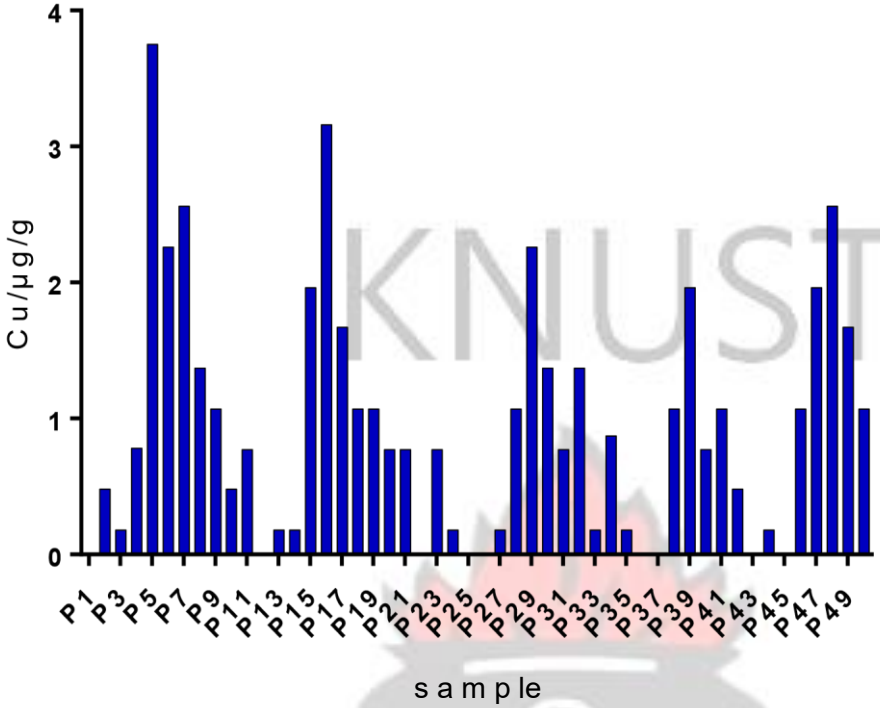

Fig.4.10: Graph of copper concentration at the various sampling point in the lake.

4.2.3 Cadmium(Cd)

Cadmium was below detection at points $P_{1\text{-}5}$, $P_{9\text{-}14}$, $P_{19\text{-}23}$,$P_{25\text{-}30}$, $P_{32\text{-}37}$, $P_{39\text{-}45}$ and a maximum of 16.72 µg/g recorded at point P_{47}. The average concentration was 2.01±4.27 µg/g. Most of the recorded values were above the threshold effect level (TEL) of 0.6 µg/g (Buchman, 2008), and continental average shale (CAS) of 0.3 µg/g (Turekian and Wedepohl, 1961), except the points below the detection level.

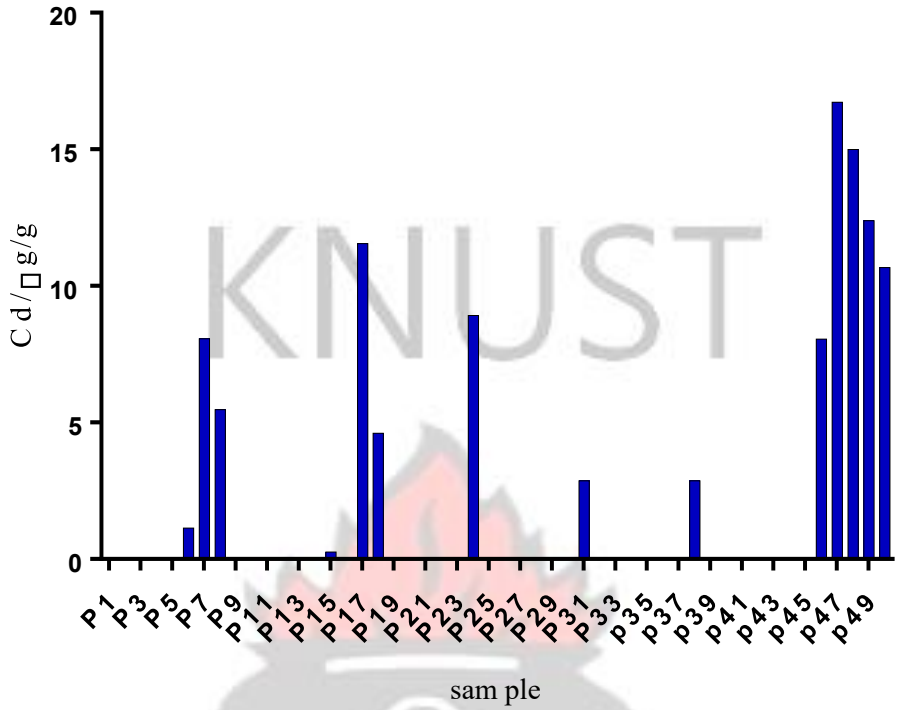

Fig.4.11: Graph of cadmium concentration at the various sampling point.

4.2.4 Lead (Pb)

Lead was below detection at point P_{31} and a maximum of 133.63 µg/g recorded at point P_{46}. The average concentration was 63.80±33.41 µg/g. All the recorded values were above the threshold effect level (TEL) of 35.0 µg/g (Buchman, 2008) , continental average shale (CAS) of 20 µg/g (Turekian and Wedepohl, 1961) except at P_1, P_2, P_4, P_6, P_7, P_8, P_9, P_{10},P_{15}, P_{16}, P_{17}, and P_{31} (Buchman, 2008), but below the severe effect level (SEL) of 250 µg/g (Buchman, 2008).

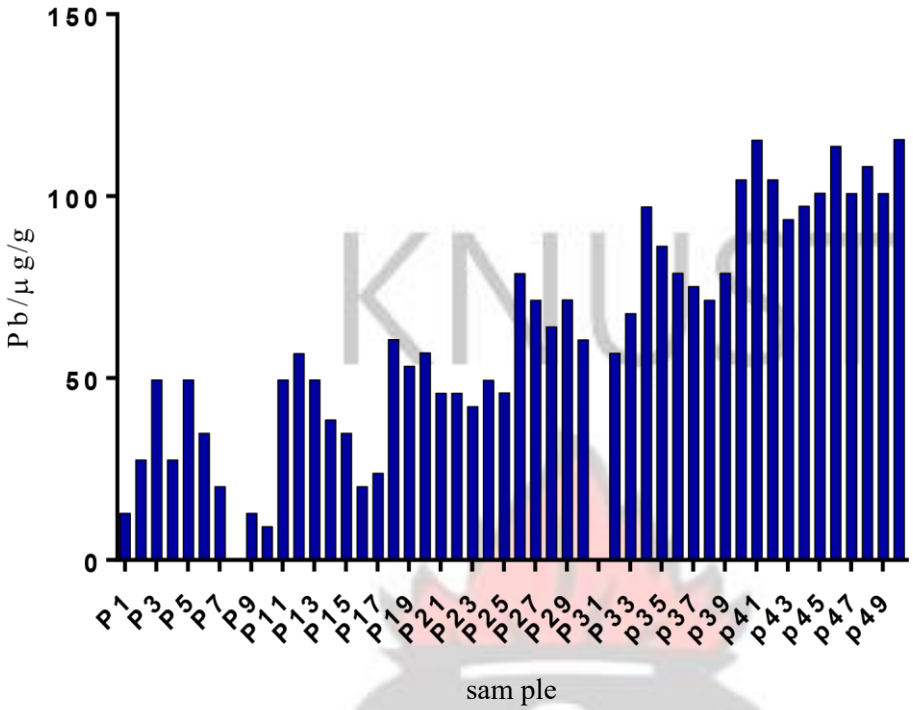

Fig.4.12: Graph of lead concentration at the various sampling point in the lake.

4.2.5 Nickel (Ni)

Nickel was below detection at points P_{13}, $P_{23}$and P_{44} and a maximum of 132.15 µg/g at point P_{50}. The average concentration was 70.19 ± 27.87 µg/g. All the recorded values were above the threshold effect level (TEL) of 16 µg/g (Buchman, 2008) with the exception of points P_{13}, P_{23}, and P_{44}. All the recorded values were above the severe effect level (SEL) of 75 µg/g

(Buchman, 2008) except at points P_6, P_{11}, $P_{13\text{-}17}$, $P_{20\text{-}35}$, $P_{39\text{-}43}$. Points P_6, P_{11}, $P_{13\text{-}16}$, $P_{20\text{-}28}$, $P_{30\text{-}32}$, P_{35}, P_{41}, P_{42}, and P_{44} values recorded were found to be below the continental average shale (CAS) of 68 µg/g (Turekian and Wedepohl, 1961).

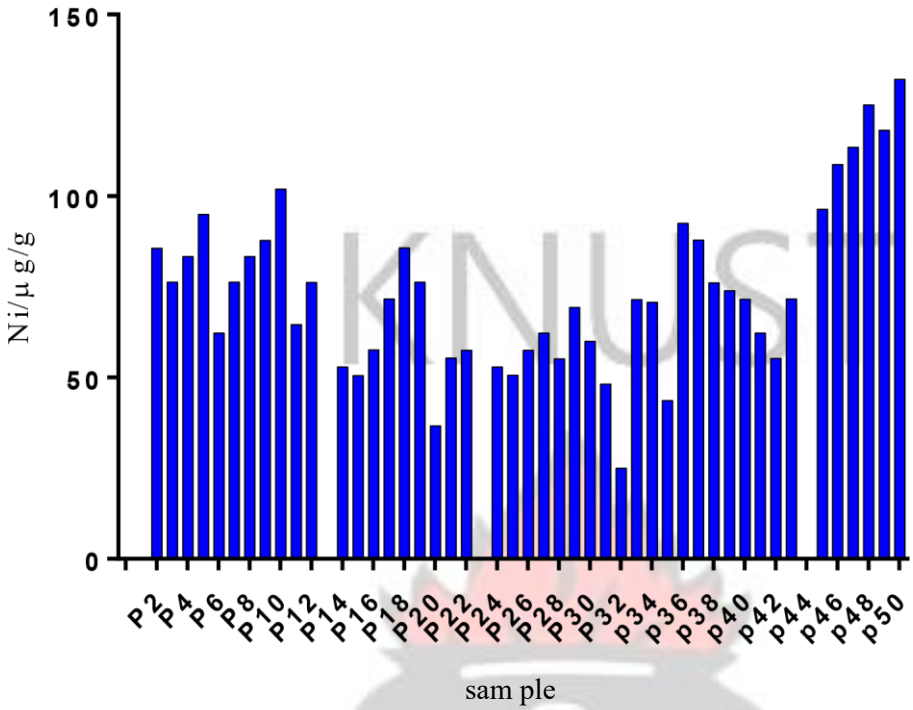

Fig.4.13: Graph of nickel concentration at the various sampling point in the lake

4.2.6 Metal type.

The graph below shows the mean values for the various metals.

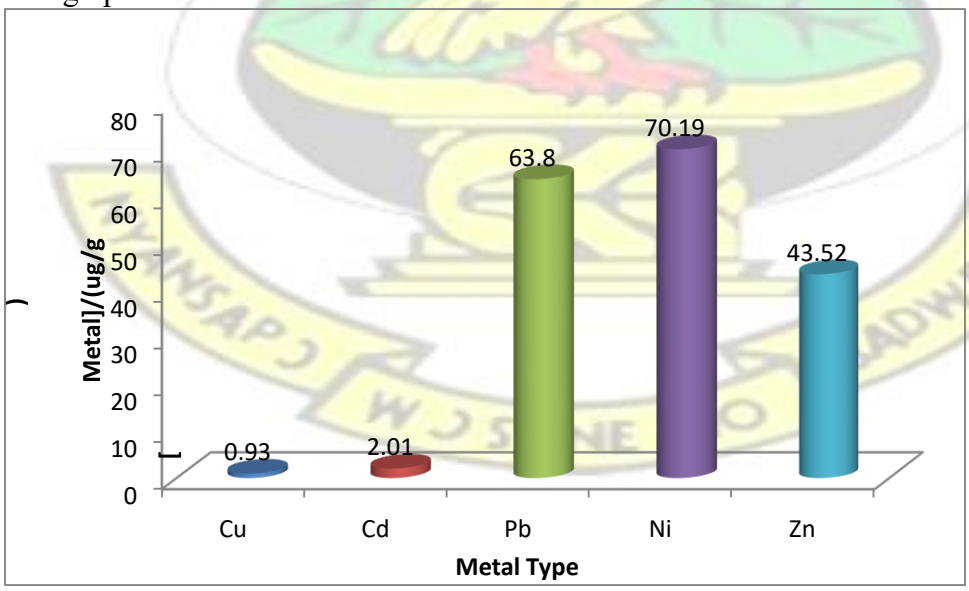

Fig.4.14:Graph of mean concentration of the various metals.

4.3 Correlation analysis.

The results of correlation analysis between the physicochemical parameters and the heavy metals in the sediment is presented in **Table 4.7**. Correlation analysis indicating the correlation coefficients r-values between the measured parameters (significant relationship are bolded).

	OM	pH	EC	Zn	Cu	Cd	Ni	Pb
OM	1							
pH	0.2427	1						
EC	**0.4087****	**-0.2859***	1					
Zn	**0.3124***	**0.3898****	0.3040	1				
Cu	-0.1136	-0.2513	-0.06261	0.02592	1			
Cd	-0.02077	0.1113	-0.2421	0.1516	**0.3685***	1		

Ni	0.2274	0.05488	0.008952	0.1161	0.2041	**0.4723 *****	1	
Pb	0.01715	**0.6357******	**-0.3248**	**0.422****	-0.1639	0.1723	0.2703	1

4.4 Extent of pollution of sediment by heavy metals

The extent of pollution of the sediment by the heavy metals was calculated as the geo-accumulation index and results presented in table 4.4 below. Cadmium recorded the maximum value of 0.92 with copper recording the minimum value of -5.17. Lead, nickel and zinc recorded 0.81, -0.51 and -1.88 respectively.

Table 4.8 : Geo-accumulation index of the various heavy metals.

Heavy metal	Geoaccumulation Index (*Igeo*)	pollution intensity
Copper	-5.17	Unpolluted
Lead	0.87	Unpolluted to moderately polluted
Cadmium	0.92	Unpolluted to moderately polluted
Zinc	-1.88	Unpolluted
Nickel	-0.51	Unpolluted

CHAPTER FIVE

5.0 Discussion

5.1.1 Physicochemical Analysis of sediment from Lake Bosomtwi

5.1.2 pH.

The average pH of 9.1 ± 0.3 makes the sediment basic with point P_6 recording a minimum pH of 8.5. Most lakes are basic (alkaline) when they are first formed and become more acidic with time due to the build up of organic materials. As organic substances decay, carbon dioxide (CO_2) forms and combines with water to produce carbonic acid, a weak acid, which lowers water pH as well as lowering sediment pH. Although these small changes in pH are not likely to have a direct impact on aquatic life, they greatly influence the availability and solubility of all chemical forms in the lake and may aggravate nutrient problems. The pH values for point P_1 to P_{50} were within the stipulated values of 6.0-10.0 for sediment which in effect is transferred to the water which is used for full contact recreation. pH correlated significantly with lead (r = 0.6357). pH correlated significantly with lead implying that an increase in pH will increase the bioavailability of lead. This is

contrary to the observation that a media favour the dissolution of metals. However, they depends on the form in which the metal exist.

5.1.3 Electrical Conductivity

The average EC is 111±33.4 which is attributed to the high content of soluble salts in sediment (Mohammad and Mazahreh, 2003). Electrical conductivity indicates the amount of soluble (salt) ions in the sediment. Although electrical conductivity did not show any significant correlation with all the heavy metals, it cannot be concluded that this parameter does not effect the heavy metal concentration but could do so in combination with other heavy metals.

5.1.4 Organic Matter Content (OM)

The average OM of 2.4 ± 0.5 of the sediment makes the OM to be within the medium range of between 2.0 - 3.0 which is favourable for aquatic organisms. The organic matter (OM) content in the sediment varied due to its origin and geological history in the aquatic environment. Phytoplankton and zooplankton are the most abundant source of the organic matter content of sediment which is a result of distribution of teregenous materials and the decomposition of plants and animals by the action of bacteria.. The high content of organic matter at point (P_{10}) could be attributed to the discharging of sewage and domestic waste from the nearby houses and other activities going on within the vicinity of the lake.

The positive correlation (r = 0.3124) though not significant recorded between organic matter content and zinc concentration in the sediment, may probably due to the organic matter associated with sediment particles. This implies that an increase in organic matter

content increases the zinc concentration of the sediment which is due to the ability of sediment to adsorb the metal. On the other hand, binding on smaller organic molecules may increase metal mobility and bioavailability (Kabata -Pendias and Pendias, 1992).

5.2.0 Heavy metal concentration in the sediment from Lake Bosomtwi.

5.2.1 Zinc (Zn)

Zinc recorded an average concentration an average of 43.52 ± 19.18 µg/g. All the recorded values were below the threshold effect level (TEL) of 123 µg/g (Buchman, 2008), the continental average shale of 95 µg/g (Turekian and Wedepohl ,1961) severe effect level (SEL) of 820 µg/g (Buchman, 2008) and permissible level (P.L) of between 120-820 µg/g (Persuad *et al,* 1990).

The relative increase at point P_5 (67.03 µg/g), P_{23} (63.92 µg/g) and P_{44} (70.61µg/g) could be related to high rate of erosion along the lake. This gives an indication that there is no form of pollution with respect to zinc. The variations of zinc in the sediment among the sampling points were statistically not significant (r = 0.3124) with organic matter and (r = 0.3898) with pH. This positive correlation though not significant indicates that an increase in organic matter increases the level of zinc in the sediment sample in the lake. Also, an increase in pH increases the level of zinc in the sediment sample in the lake.

5.2.2 Copper (Cu)

The average concentration was 0.93 ± 0.89 µg/g. All the points from P_1 to P_{50} recorded values below the threshold effect level (TEL) of 35.7 µg/g (Buchman, 2008), severe effect level of 110 µg/g (Buchman, 2008), and continental average shale of 45 µg/g (Turekian and Wedepohl, 1961). This gives an indication that there is no form of pollution of the sediment sample. In general, the increase in copper content in the sediment from the different points may be attributed to the removal of copper from the water column mediated by the decay of the plankton or due to adsorption on the suspended matter or complexation with organic matter leaving the water body to the sediments. Also, copper did not show significant correlation with any of the physicochemical parameters but did so with cadmium (r = 0.3685) meaning an increase in cadmium concentration can result in an increase in copper concentration in the sediment sample in the lake.

5.2.3 Cadmium (Cd)

The average concentration was 2.01 ± 4.27 µg/g. Most of the recorded values were above the threshold effect level (TEL) of 0.6 µg/g (Buchman, 2008), and continental average shale (CAS) of 0.3 µg/g (Turekian and Wedepohl, 1961), except the points below the detection level. Also, most of the values recorded were below the severe effect level (SEL) of 10.0 µg/g (Buchman, 2008) except at points P_{17},P_{47}, P_{48}, P_{49}, P_{50} with concentrations of 11.55 µg/g, 16.72 µg/g, 14.99 µg/g, 12.39 µg/g and 10.67µg/g respectively. This is an indication of the extent of pollution in the sediment samples. The high level of cadmium in sediment could be attributed to industrial and agricultural discharges (Mason, 2002) through drains which directly discharges into the lake. There is a high level of cadmium in the sediment at point P_{47} (16.72 µg/g), probably due to the high erosion rate. Cadmium

correlated but not significantly with all the physicochemical parameters and correlated moderately with nickel (r = 0.4723). This indicates that an increase in nickel concentration in a sampling point increases the cadmium concentration.

5.2.4 Lead (Pb)

The average concentration was 63.80±33.41 µg/g. All the recorded values were above the threshold effect level (TEL) of 35.0 µg/g (Buchman, 2008) , continental average shale (CAS) of 20 µg/g (Turekian and Wedepohl, 1961) except at P_1, P_2, P_4, P_6, P_7, P_8, P_9, P_{10},P_{15}, P_{16}, P_{17}, and P_{31} (Buchman, 2008), but below the severe effect level (SEL) of 250 µg/g (Buchman, 2008).

The USEPA has classified Pb as a probable human carcinogen (Adriano, 2001). Lead is a good indicator of traffic related sources or battery recycling plants, and combustion of leaded fuel which is considered as an indicator of pollution by runoff water (Mukai *et al*, 1994). The results depict that lake Bosomtwi sediment is polluted by lead and highest lead pollution is observed at sampling point P_{46} containing 133.63 µg/g. Lead correlated significantly with pH, electrical conductivity (EC) as well as zinc metal. The strong correlation with pH (r = 0.6357) indicates that an increase in pH increases the concentration of lead in the sediment in the lake. Also, lead correlated though not significantly with electrical conductivity (r =-0.3248) which indicates an increase in EC increases the concentration of lead in the sediment in the lake.

5.2.5 Nickel (Ni)

The average concentration was 70.19 ± 27.87 µg/g. All the recorded values were above the

threshold effect level (TEL) of 16 µg/g (Buchman, 2008) with the exception of points P_{13}, P_{23}, and P_{44}. All the recorded values were above the severe effect level (SEL) of 75 µg/g (Buchman, 2008) except at points P_6, P_{11}, $P_{13\text{-}17}$, $P_{20\text{-}35}$, $P_{39\text{-}43}$. Points P_6, P_{11}, $P_{13\text{-}16}$, $P_{20\text{-}28}$, $P_{30\text{-}32}$, P_{35}, P_{41}, P_{42}, and P_{44} values recorded were found to be below the continental average shale (CAS) of 68 µg/g (Turekian and Wedepohl, 1961). The results indicate that lake Bosomtwi sediments is polluted by nickel metal and the highest nickel pollution is shown at sampling point P_{50} containing 132.15 µg/g. This form of pollution could be attributed to discharge of fuel oil, auto-exhaust, fertilizers, industrial waste into the water body which settles in the sediment. Nickel correlated though not significantly with physicochemical parameters and correlated significantly with cadmium (r = 0.4723) which indicates an increase in cadmium increases the concentration of nickel in the sediment in the lake.

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5.3 Extent of pollution of sediment by heavy metals

The geoaccumulation index (***Igeo***) which was introduced by Muller (1979) was used to assess metal pollution in sediments to quantify the degree of anthropogenic contamination in the sediment samples at Lake Bosumtwi. The results of the geoaccumulation index of the various heavy metals as presented in table 4.4 indicates that the sediment is unpolluted with respect to nickel, zinc and copper. However, the geoaccumulation index showed that the sediment is moderately polluted with respect to lead and cadmium.

CHAPTER SIX

6.0 Conclusion and Recommendations

6.1 Conclusion

Analysis on sediment samples revealed that the lake sediment was highly basic during the sampling period. It also contains varying levels of the heavy metals. The sediment samples contained very high concentrations of lead and nickel. The trend of the mean concentration of heavy metals measured is as follows**:**

Cu<Cd< Zn <Pb< Ni.

The geoaccumulation index calculated on the levels of the metal present confirms that the lake sediment is unpolluted to moderately polluted with respect to lead and cadmium.

6.2 Recommendation

1.Based on the calculation of the geoaccummulation index of the metals, it was comfirmed that the lake sediment is moderately polluted with respect to lead and

cadmium, therefore requires constant monitoring of these metals to avoid contamination of the water body.

2. Though the concentrations of copper, zinc and cadmium are very low, with time they may accumulate and affect the aquatic life and so requires constant monitoring

3.Moreover, the various activities that goes on around the lake such as agricultural and rural activities should be controlled to prevent the increase of the concentration of the metals studied in future.

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APPENDIX 1A

Raw data of the analysis for zinc metal

		Zn			
Points	**Mass**	**Abs**	**Conc (ppm)**	**µg/g**	***igeo***
P1	1.0029	0.081	0.36	**17.81**	**-3.01**

P2	1.0019	0.036	0.16	**7.80**	**-4.34**
P3	1.0023	0.055	0.24	**12.03**	**-3.66**
P4	1.0014	0.142	0.63	**31.43**	**-2.19**
P5	1.0024	0.302	1.34	**67.03**	**-1.09**
P6	1.0032	0.179	0.79	**39.61**	**-1.84**
P7	1.0019	0.143	0.63	**31.64**	**-2.19**
P8	1.0019	0.167	0.74	**36.98**	**-1.95**
P9	1.0039	0.226	1.00	**50.03**	**-1.52**
P10	1.0023	0.258	1.15	**57.23**	**-1.33**
P11	1.0032	0.237	1.05	**52.51**	**-1.44**
P12	1.004	0.226	1.00	**50.02**	**-1.52**
P13	1.0035	0.192	0.85	**42.49**	**-1.79**
P14	1.0033	0.116	0.51	**25.59**	**-2.48**
P15	1.0039	0.106	0.47	**23.35**	**-2.65**
P16	1.0019	0.091	0.40	**20.05**	**-2.85**
P17	1.0016	0.129	0.57	**28.53**	**-2.33**
P18	1.0011	0.170	0.75	**37.68**	**-1.95**
P19	1.0019	0.104	0.46	**22.95**	**-2.65**
P20	1.0019	0.042	0.18	**9.13**	**-4.08**
P21	1.0021	0.182	0.81	**40.32**	**-1.84**
P22	1.0038	0.175	0.78	**38.69**	**-1.89**
P23	1.0023	0.288	1.28	**63.92**	**-1.95**
P24	1.0042	0.202	0.90	**44.68**	**-1.69**
P25	1.0016	0.159	0.71	**35.21**	**-2.01**
P26	1.0041	0.192	0.85	**42.46**	**-1.79**
P27	1.0038	0.177	0.79	**39.14**	**-1.89**
P28	1.0047	0.168	0.75	**37.10**	**-1.95**
P29	1.0027	0.235	1.04	**52.09**	**-1.48**
P30	1.0026	0.198	0.88	**43.86**	**-1.69**
P31	1.0041	0.171	0.76	**37.79**	**-1.95**
P32	1.0023	0.160	0.71	**35.41**	**-2.01**
P33	1.0042	0.175	0.78	**38.68**	**-1.89**
P34	1.0037	0.242	1.08	**53.60**	**-1.40**
P34	1.0035	0.610	2.72	**135.46**	**-0.07**
P34	1.0035	0.217	0.96	**48.05**	**-1.56**
P35	1.0021	0.189	0.84	**41.88**	**-1.79**
P36	1.0030	0.214	0.95	**47.40**	**-1.61**
P37	1.0028	0.170	0.75	**37.62**	**-1.95**
P38	1.0043	0.157	0.70	**34.67**	**-2.07**

P39	1.0027	0.162	0.72	**35.84**	**-2.01**
P40	1.0034	0.239	1.06	**52.94**	**-1.44**
P41	1.0039	0.252	1.12	**55.81**	**-1.36**
P42	1.0028	0.230	1.02	**50.97**	**-1.48**
P43	1.0022	0.250	1.11	**55.46**	**-1.36**
P44	1.0021	0.318	1.42	**70.61**	**-1.03**
P45	1.0033	0.194	0.86	**42.94**	**-1.74**
P45	1.0033	0.192	0.85	**42.49**	**-1.74**
P45	1.0031	0.184	0.82	**40.72**	**-1.84**
P46	1.0042	0.195	0.87	**43.12**	**-1.74**
P47	1.0035	0.283	1.26	**62.73**	**-1.19**
P48	1.0033	0.302	1.34	**66.97**	**-1.10**
P49	1.0035	0.290	1.29	**64.28**	**-1.16**
P50	1.0025	0.240	1.07	**53.22**	**-1.44**
Mean					-1.79

APPENDIX 1B

Raw data of the analysis for nickel metal

		Ni			
Points	**Mass**	**Abs**	**Conc (ppm)**	**µg/g**	***igeo***
P1	1.0029	-		**0**	0
P2	1.0019	0.053	1.715	**85.585**	-0.25
P3	1.0023	0.049	1.528	**76.227**	-0.42
P4	1.0014	0.052	1.668	**83.295**	-0.29
P5	1.0024	0.057	1.902	**94.866**	-0.1
P6	1.0032	0.043	1.248	**62.184**	-0.72
P7	1.0019	0.049	1.528	**76.257**	-0.42
P8	1.0019	0.052	1.668	**83.253**	-0.29
P9	1.0039	0.054	1.762	**87.742**	-0.22
P10	1.0023	0.06	2.042	**101.869**	-0.01
P11	1.0032	0.044	1.294	**64.513**	-0.67
P12	1.004	0.049	1.528	**76.097**	-0.42
P13	1.0035	-		**0.000**	0
P14	1.0033	0.039	1.061	**52.863**	-0.95
P15	1.0039	0.038	1.014	**50.504**	-1.03
P16	1.0019	0.041	1.154	**57.601**	-0.84
P17	1.0016	0.047	1.435	**71.614**	-0.52
P18	1.0011	0.053	1.715	**85.653**	-0.25
P19	1.0019	0.049	1.528	**76.257**	-0.42
P20	1.0019	0.032	0.734	**36.613**	-1.48
P21	1.0021	0.04	1.107	**55.258**	-0.89
P22	1.0038	0.041	1.154	**57.492**	-0.84
P23	1.0023		-0.762	**-37.997**	-1.44
P24	1.0042	0.039	1.061	**52.816**	-0.95
P25	1.0016	0.038	1.014	**50.620**	-1
P26	1.0041	0.041	1.154	**57.475**	-0.84
P27	1.0038	0.043	1.248	**62.147**	-0.72
P28	1.0047	0.04	1.107	**55.115**	-0.89
P29	1.0027	0.046	1.388	**69.206**	-0.56
P30	1.0026	0.042	1.201	**59.891**	-0.76
P31	1.0041	0.037	0.967	**48.167**	-1.1
P32	1.0023	0.027	0.500	**24.943**	-2.07
P33	1.0042	0.047	1.435	**71.429**	-0.52
P34	1.0037	0.046	1.388	**69.137**	-0.58

P34	1.0035	0.045	1.341	**66.822**	-0.62
P34	1.0035	0.049	1.528	**76.135**	-0.42
P35	1.0021	0.035	0.874	**43.600**	-1.22
P36	1.003	0.056	1.855	**92.480**	-0.14
P37	1.0028	0.054	1.762	**87.838**	-0.22
P38	1.0043	0.049	1.528	**76.075**	-0.44
P39	1.0027	0.048	1.481	**73.866**	-0.48
P40	1.0034	0.047	1.435	**71.486**	-0.52
P41	1.0039	0.043	1.248	**62.141**	-0.72
P42	1.0028	0.04	1.107	**55.219**	-0.89
P43	1.0022	0.047	1.435	**71.572**	-0.52
P44	1.0021	-		**0.000**	0
P45	1.0033	0.056	1.855	**92.452**	-0.14
P45	1.0033	0.057	1.902	**94.781**	-0.1
P45	1.0031	0.06	2.042	**101.787**	-0.01
P46	1.0042	0.063	2.182	**108.656**	0.08
P47	1.0035	0.065	2.276	**113.388**	0.15
P48	1.0033	0.07	2.509	**125.055**	0.3
P49	1.0035	0.067	2.369	**118.045**	0.21
P50	1.0025	0.073	2.650	**132.146**	0.37
Mean					**-0.51**

APPENDIX 1C

Raw data of the analysis for lead metal

		Pb			
Points	**Mass**	**Abs**	**Conc (ppm)**	**µg/g**	***igeo***
P1	1.0029	0.007	0.26	**12.830**	-1.22
P2	1.0019	0.011	0.55	**27.521**	-0.12
P3	1.0023	0.017	0.99	**49.518**	0.72
P4	1.0014	0.011	0.55	**27.535**	-0.12
P5	1.0024	0.017	0.99	**49.514**	0.72
P6	1.0032	0.013	0.70	**34.815**	0.21
P7	1.0019	0.009	0.40	**20.182**	-0.58
P8	1.0019	0.001	-0.18	**-9.174**	0
P9	1.0039	0.007	0.26	**12.818**	-1.22
P10	1.0023	0.006	0.18	**9.170**	-1.74
P11	1.0032	0.017	0.99	**49.474**	0.72
P12	1.004	0.019	1.14	**56.758**	0.92
P13	1.0035	0.017	0.99	**49.459**	0.72
P14	1.0033	0.014	0.77	**38.476**	0.36
P15	1.0039	0.013	0.70	**34.791**	0.21
P16	1.0019	0.009	0.40	**20.182**	-0.58
P17	1.0016	0.01	0.48	**23.859**	-0.34
P18	1.0011	0.02	1.21	**60.595**	1.02
P19	1.0019	0.018	1.07	**53.208**	0.83
P20	1.0019	0.019	1.14	**56.877**	0.92
P21	1.0021	0.016	0.92	**45.860**	0.62
P22	1.0038	0.016	0.92	**45.782**	0.62
P23	1.0023	0.015	0.85	**42.182**	0.5
P24	1.0042	0.017	0.99	**49.425**	0.72
P25	1.0016	0.016	0.92	**45.882**	0.62
P26	1.0041	0.025	1.58	**78.721**	1.4
P27	1.0038	0.023	1.43	**71.420**	1.26
P28	1.0047	0.021	1.29	**64.037**	1.1
P29	1.0027	0.023	1.43	**71.498**	1.26
P30	1.0026	0.02	1.21	**60.504**	1.02
P31	1.0041	-		**0.000**	0
P32	1.0023	0.019	1.14	**56.855**	0.92

P33	1.0042	0.022	1.36	**67.730**	1.18
P34	1.0037	0.032	2.10	**104.393**	1.81
P34	1.0035	0.028	1.80	**89.759**	1.59
P34	1.0035	0.03	1.95	**97.087**	1.7
P35	1.0021	0,027	1.73	**86.216**	1.53
P36	1.003	0.025	1.58	**78.808**	1.4
P37	1.0028	0.024	1.51	**75.157**	1.33
P38	1.0043	0.023	1.43	**71.384**	1.26
P39	1.0027	0.025	1.58	**78.831**	1.4
P40	1.0034	0.032	2.10	**104.424**	0.81
P41	1.0039	0.035	2.32	**115.359**	1.95
P42	1.0028	0.032	2.10	**104.487**	1.81
P43	1.0022	0.029	1.88	**93.544**	1.65
P44	1.0021	0.03	1.95	**97.222**	1.7
P45	1.0033	0.029	1.88	**93.442**	1.64
P45	1.0033	0.028	1.80	**89.777**	1.59
P45	1.0031	0.036	2.39	**119.116**	1.99
P46	1.0042	0.04	2.68	**133.630**	2.16
P47	1.0035	0.031	2.02	**100.750**	1.76
P48	1.0033	0.033	2.17	**108.099**	1.86
P49	1.0035	0.031	2.02	**100.750**	1.76
P50	1.0025	0.035	2.32	**115.520**	1.95
Mean					**0.87**

APPENDIX 1D

Raw data of the analysis for cadmium metal

Points	**Mass**	**Abs**	**Conc (ppm)**	**µg/g**	***igeo***
P1	1.0029	0.023	0.000	**0.00**	**0**
P2	1.0019	0.012	0.000	**0.00**	**0**
P3	1.0023	0.024	0.000	**0.00**	**0**
P4	1.0014	0.0009	0.000	**0.00**	**0**
P5	1.0024	0.014	0.000	**0.00**	**0**
P6	1.0032	0.026	0.023	**1.13**	**1.33**
P7	1.0019	0.034	0.162	**8.07**	**4.18**
P8	1.0019	0.031	0.110	**5.47**	**3.62**
P9	1.0039	0.024	0.000	**0.00**	**0**
P10	1.0023	0.021	0.000	**0.00**	**0**
P11	1.0032	0.018	0.000	**0.00**	**0**
P12	1.004	0.014	0.000	**0.00**	**0**
P13	1.0035	-	0.000	**0.00**	**0**
P14	1.0033	0.01	0.000	**0.00**	**0**
P15	1.0039	0.025	0.005	**0.26**	**-0.78**
P16	1.0019	0.024	0.000	**0.00**	**0**
P17	1.0016	0.038	0.231	**11.55**	**4.7**
P18	1.0011	0.03	0.092	**4.60**	**3.36**
P19	1.0019	0.013	0.000	**0.00**	**0**
P20	1.0019	0.006	0.000	**0.00**	**0**
P21	1.0021	0.016	0.000	**0.00**	**0**
P22	1.0038	0.008	0.000	**0.00**	**0**
P23	1.0023	0.014	0.000	**0.00**	**0**
P24	1.0042	0.035	0.179	**8.92**	**4.33**
P25	1.0016	0.023	0.000	**0.00**	**0**
P26	1.0041	0.021	0.000	**0.00**	**0**
P27	1.0038	0.017	0.000	**0.00**	**0**
P28	1.0047	0.012	0.000	**0.00**	**0**
P29	1.0027	0.013	0.000	**0.00**	**0**
P30	1.0026	0.016	0.000	**0.00**	**0**

P31	1.0041	0.028	0.057	**2.86**	**2.67**
P32	1.0023	-	0.000	**0.00**	**0**
P33	1.0042	0.019	0.000	**0.00**	**0**
P34	1.0037	0.017	0.000	**0.00**	**0**
P34	1.0035	0.013	0.000	**0.00**	**0**
P34	1.0035	0.007	0.000	**0.00**	**0**
P35	1.0021	0.003	0.000	**0.00**	**0**
P36	1.003	0.001	0.000	**0.00**	**0**
P37	1.0028	0.004	0.000	**0.00**	**0**
P38	1.0043	0.028	0.057	**2.86**	**2.67**
P39	1.0027	0.022	0.000	**0.00**	**0**
P40	1.0034	0.018	0.000	**0.00**	**0**
P41	1.0039	0.013	0.000	**0.00**	**0**
P42	1.0028	0.006	0.000	**0.00**	**0**
P43	1.0022	0.001	0.000	**0.00**	**0**
P44	1.0021	0.002	0.000	**0.00**	**0**
P45	1.0033	0.006	0.000	**0.00**	**0**
P45	1.0033	0.013	0.000	**0.00**	**0**
P45	1.0031	0.013	0.000	**0.00**	**0**
P46	1.0042	0.034	0.162	**8.05**	**4.18**
P47	1.0035	0.044	0.336	**16.72**	**5.24**
P48	1.0033	0.042	0.301	**14.99**	**5.1**
P49	1.0035	0.039	0.249	**12.39**	4.8
P50	1.0025	0.037	0.214	**10.67**	**4.59**
mean					**0.95**

APPENDIX 1E

Raw data of the analysis for copper metal

Points	Mass	Abs	Conc(ppm)	µg/g	*igeo*
P1	1.0029	-	-		**0**
P2	1.0019	0.0020	0.01	**0.48**	**-6.67**
P3	1.0023	0.0010	0.00	**0.18**	**-8.42**
P4	1.0014	0.003	0.02	**0.78**	**-6.67**
P5	1.0024	0.013	0.08	**3.75**	**-4.34**
P6	1.0032	0.008	0.05	**2.26**	**-5.08**
P7	1.0019	0.009	0.05	**2.56**	**-4.66**
P8	1.0019	0.005	0.03	**1.37**	**-5.67**
P9	1.0039	0.004	0.02	**1.07**	**-6.1**
P10	1.0023	0.002	0.01	**0.48**	**-6.67**
P11	1.0032	0.003	0.02	**0.77**	**-6.67**
P12	1.004	0.000	0.00	**0.00**	**0**
P13	1.0035	0.001	0.00	**0.18**	**-9.01**
P14	1.0033	0.001	0.00	**0.18**	**-9.01**
P15	1.0039	0.007	0.04	**1.96**	**-5.08**
P16	1.0019	0.011	0.06	**3.16**	**-4.34**
P17	1.0016	0.006	0.03	**1.67**	**-5.67**
P18	1.0011	0.004	0.02	**1.07**	**-6.67**
P19	1.0019	0.004	0.02	**1.07**	**-6.67**
P20	1.0019	0.003	0.02	**0.77**	**-6.67**
P21	1.0021	0.003	0.02	**0.77**	**-6.67**
P22	1.0038	0.000	0.00	**0.00**	**0**
P23	1.0023	0.003	0.02	**0.77**	**-6.67**
P24	1.0042	0.001	0.00	**0.18**	**-9.01**
P25	1.0016	0.000	0.00	**0.00**	**0**
P26	1.0041	0.000	0.00	**0.00**	**0**
P27	1.0038	0.001	0.00	**0.18**	**-9.01**
P28	1.0047	0.004	0.02	**1.07**	**-6.1**

P29	1.0027	0.008	0.05	**2.26**	**-5.1**
P30	1.0026	0.005	0.03	**1.37**	**-5.67**
P31	1.0041	0.003	0.02	**0.77**	**-6.67**
P32	1.0023	0.005	0.03	**1.37**	**-5.67**
P33	1.0042	0.001	0.00	**0.18**	**-9.01**
P34	1.0037	0.004	0.02	**1.07**	**-6.1**
P34	1.0035	0.002	0.01	**0.48**	**-6.67**
P34	1.0035	0.004	0.02	**1.07**	**-6.1**
P35	1.0021	0.001	0.00	**0.18**	**-9.01**
P36	1.003	0.000	0.00	0.00	**0**
P37	1.0028	0.000	0.00	0.00	**0**
P38	1.0043	0.004	0.02	**1.07**	**-6.1**
P39	1.0027	0.007	0.04	**1.96**	**-5.1**
P40	1.0034	0.003	0.02	**0.77**	**-6.67**
P41	1.0039	0.004	0.02	**1.07**	**-6.1**
P42	1.0028	0.002	0.01	**0.48**	**-6.67**
P43	1.0022	0.000	0.00	**0.00**	**0**
P44	1.0021	0.001	0.00	**0.18**	**-9.01**
P45	1.0033	0.000	0.00	**0.00**	**0**
P45	1.0033	0.000	0.00	**0.00**	**0**
P45	1.0031	0.000	0.00	**0.00**	**0**
P46	1.0042	0.004	0.02	**1.07**	**-6.1**
P47	1.0035	0.007	0.04	**1.96**	**-5.1**
P48	1.0033	0.009	0.05	**2.56**	**-4.66**
P49	1.0035	0.006	0.03	**1.67**	**-5.67**
P50	1.0025	0.004	0.02	**1.07**	**-6.1**
Mean					**-5.17**

APPENDIX 1F

Raw data of the physicochemical parameters

BLK1=22.1
BLK2=23.1
AVG=22.6
%OC=T*0.2*0.3/0.5
%OM=%OC*1.72

POINTS	pH	EC		%OM
P1	8.55	122	15.8	1.4
P2	8.82	163.4	10.7	2.4
P3	8.7	163.4	9.9	2.6
P4	8.74	174.6	8.1	3
P5	8.68	170.1	7.5	3.1
P6	8.5	109.2	14.9	1.6
P7	9.01	112.8	12.4	2.1
P8	8.77	154.4	9.2	2.8
P9	8.95	174.6	8.5	2.9
P10	8.8	158.9	4.9	3.6
P11	8.89	130	11.1	2.4
P12	8.79	119.1	10.6	2.5
P13	9.04	109	11.2	2.3
P14	9.11	64	14.5	1.7
P15	9.12	101.1	16	1.4
P16	8.83	100.5	14.8	1.6
P17	9.1	107.1	12.9	2
P18	8.99	92.3	11.5	2.3
P19	8.84	106.8	9.4	2.7
P20	9.3	117.1	10.4	2.5
P21	9.25	106.1	5.7	3.5
P22	9.34	75.6	9.2	2.8

P23	9.14	75.5	10.8	2.4
P24	8.98	109.3	11.2	2.3
P25	8.89	121.2	13.3	1.9
P26	9.17	98.4	13	2
P27	8.92	71.5	11.1	2.4
P28	8.94	80.2	12	2.2
P29	9.09	110.5	8.2	2.9
P30	9.32	96.9	10.2	2.5
P31	8.99	105.6	9.7	2.7
P32	9.01	102.8	8.5	2.9
P33	8.7	193.3	10.8	2.4
P34	9.58	123.8	8.5	2.9
P34	9.59	119	8.1	2.9
P34	9.55	117.4	8.3	2.9
P35	9.45	119	8.9	2.8
P36	9.16	107	9.7	2.6
P37	9.14	73.3	11.6	2.3
P38	8.98	88.9	11.5	2.3
P39	8.79	79	14.2	1.7
P40	8.95	80.1	13.9	1.8
P41	9.28	64	13.1	1.9
P42	9.23	80.9	13.4	1.9
P43	9.27	78.7	10	2.6
P44	9.14	188.1	10.2	2.5
P45	9.51	135.1	10.2	2.5
P45	9.5	130.3	10.4	2.5
P45	9.53	135.1	10.3	2.5
P46	9.41	103.9	8.7	2.9
P47	9.17	97.1	8.6	2.9
P48	9.28	89.4	10.2	2.5
P49	9.37	70.1	11.9	2.2
P50	9.13	48.4	12.7	2