

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY,  
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**COLLEGE OF SCIENCE**

DEPARTMENT OF THEORETICAL AND APPLIED BIOLOGY

**SEDIMENT CORE PROFILE OF HEAVY METALS IN LAKE AMPONSAH  
IN THE MINING DISTRICT OF BIBIANI, GHANA**

BY

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## DECLARATION

### Candidate's Declaration

I hereby declare that this work presented to the Department of Theoretical and Applied Biology in partial fulfillment for the award of MSc. Degree, is a true account of my own work except where particularly all sources of information have been acknowledged by means of reference.

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## ABSTRACT

The many years of gold mining in Ghana has generated huge environmental legacy issues, such as land degradation and environmental contaminations from heavy metals. The present study evaluated the contamination from arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg) and lead (Pb) at Bibiani, a historical gold mining town in Ghana. The study took a retrospective look at these contaminations by conducting sediment core analysis of heavy metals in sediments collected from Lake Amponsah in the Bibiani district. Sediment core was sampled to the depth of 30 cm applying a PVC corer and sliced into 5 cm segments. The concentration of As was analysed applying the Palintest (Wagtech) method, while Cd, Pb, Cu and Hg were determined applying the Anodic Stripping Voltammetry (ASV) method. The concentrations of the various metals in the sediment core ranged as follows – As: 21 – 97 mg/kg, Hg: 0.01 – 0.04 mg/kg, Cd: 0.09 – 0.74 mg/kg, Pb: 0.05 – 3.40 mg/kg, and Cu: 0.98 – 4.92 mg/kg. Generally, the concentrations of the metals were mostly greater in the upper portions of the sediment core relative to the bottom portions. This suggests greater impacts from anthropogenic activities in recent times in the Lake Amponsah watershed. Arsenic correlated strongly with Hg at the bottom half (15 – 30 cm) of the sediment core ( $r = 0.88$ ). The two metals however did not correlate in the upper half (0 – 15 cm) of the sediment core. It presupposes a historically relevant association between these two metals in the older bottom sediments, culminating from largely a single source factor. It provides evidence of historical application of Hg in gold extraction in the Lake Amponsah watershed, with As as a byproduct from the arsenopyrite ore. The absence of correlation between the two metals in the upper portions of the sediment core suggests that recent contaminations from these two metals originated from quite varied source factors, which may include activities related to small scale mining,

farming and leachates from waste dumps. Finally, it was established that Lake Amponsah was undergoing sedimentation at a rate of 1.76 cm/year.

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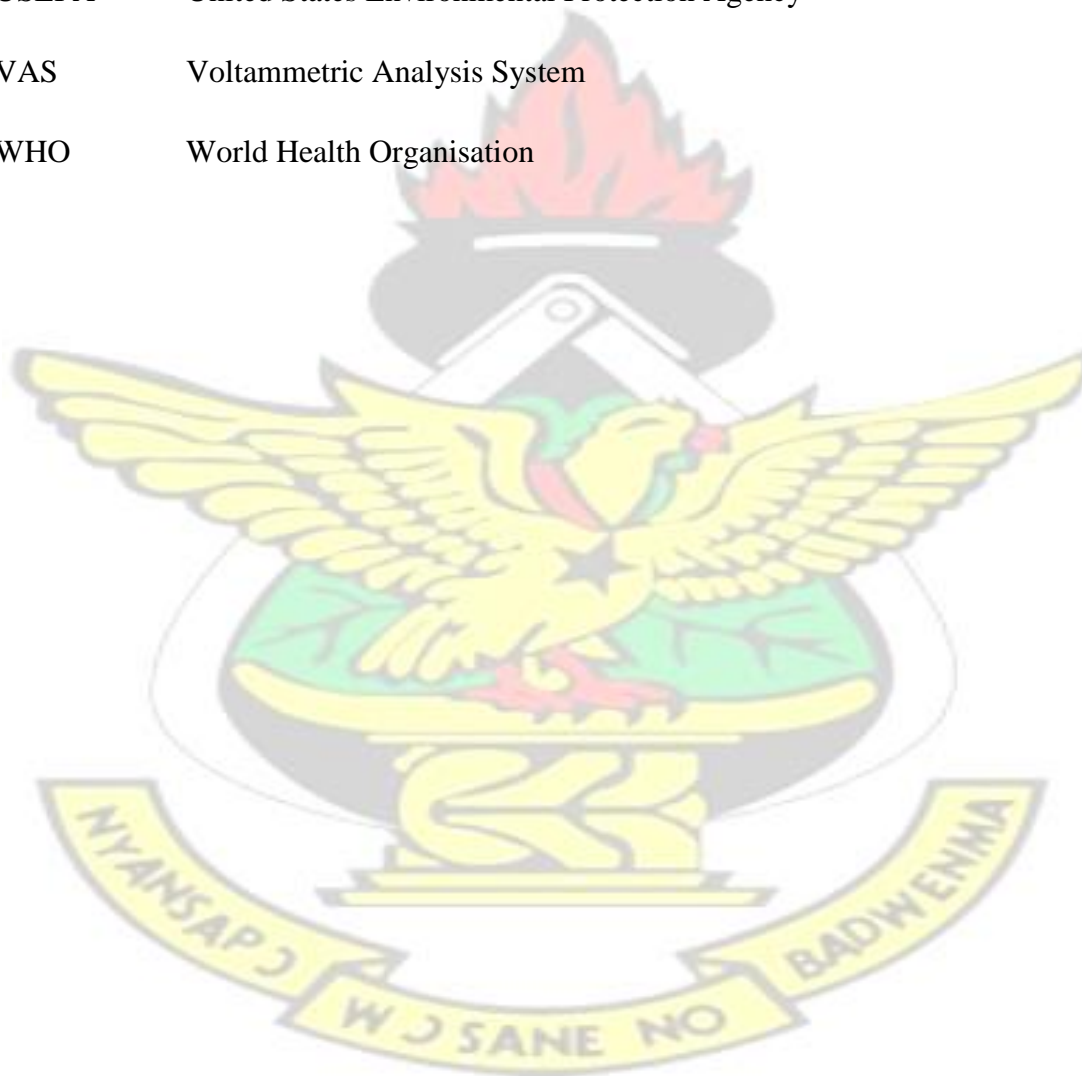
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## ABBREVIATIONS/ACRONYMS

AGBL	Ashanti Goldfields Bibiani Limited
AGCL	Ashanti Goldfields Company Limited
AMD	Acid Mine Drainage
ANZECC	Australian and New Zealand Environment and Conservation Council
ASM	Artisanal and small-scale mining
ASV	Anodic Stripping Voltammetry
ATSDR	Agency for Toxic Substances and Disease Registry
BABDA	Bibiani-Anhwiaso-Bekwai District Assembly
CAG	Central African Gold
CAGGL	Central African Gold Ghana Ltd
CAGL	Central African Gold Limited
CLAC	Chloride-Acetate Buffer Electrolyte
DWAF	Department of Water Affairs and Forestry
EAT	Environmental Affairs and Tourism
GAEC	Ghana Atomic Energy Commission
GEPA	Ghana Environmental Protection Agency
GLAMCO	Ghana Libya Gold Mining Company

IGR	International Gold Resources
IPCS	International Programme on Chemical Safety
MDH	Minnesota Department of Health
NGBL	Noble Gold Bibiani Limited
PVC	Polyvinyl Chloride
SBPA	Special Biological Protection Area
SQGs	Sediment Quality Guidelines
USEPA	United States Environmental Protection Agency
VAS	Voltammetric Analysis System
WHO	World Health Organisation





# CHAPTER ONE

## INTRODUCTION

### 1.1 BACKGROUND

Contamination from chemicals remains one of the serious environmental problems in Ghana. Activities linked to various segments of the Ghanaian economy have been implicated in episodes of these contaminations. For instance, mining operations in Ghana, which predates the 20<sup>th</sup> century, over the years, have caused contamination from heavy metals in the local environment (Bamford *et al.*, 1990; Amonoo-Neizer *et al.*, 1995; Ahmad and Carboo, 2000; Antwi-Agyei *et al.*, 2009; Nartey *et al.*, 2012). The applications of pesticides and fertilizers in agriculture, the use of various insecticides for agricultural and public health reasons, as well as poor waste management practices have all introduced one group of chemical contaminant or another into the environment in Ghana (Awumbila, 1996; ECDG, 2002; Ntow *et al.*, 2006).

One of the ultimate receivers of these chemical contaminants in the local environment are water bodies, especially via runoffs. So widespread has been the problems of chemical contamination in Ghana that many of the streams and rivers dotted across the country have been affected, with some virtually dying off (Down and Stocks, 1978; Asante *et al.*, 2007). Many of these receding water bodies are either located in the urban centres or within enclaves of mining activities. In Accra, the capital city of Ghana, there has been huge investment to dredge the Odaw River, for example, to bring it back to life (<http://graphic.com.gh>). This has however proved elusive due to recurrent inflows of large quantities of both chemical and biological stressors among other environmental pollutants. Similarly, the Densu River, which supplies parts of Accra with drinking water, is heavily polluted along its tributaries such that the Ghana Water Company has

complained of increased cost of treating drinking water from this source (<http://newsghana.com.gh>). In rural communities, the main threats endangering the sanctity of water bodies have emanated from mining and agricultural practices.

The pollution of rivers and lakes from chemicals leads to accumulation of these chemicals in sediment. Thus, sediments act as a major sink of chemical pollutants such as heavy metals (Mucha *et al.*, 2003). Sediments therefore contain an environmental record of pollutants that can be useful to help establish retrospectively the pollution history of an area (Wang *et al.*, 2007). Sediments build up gradually in a water body, such that older sediments are locked up in deeper layers while recent sediments are in upper layers. Potentially, past contaminations would remain buried with older sediments and recent contaminations associated with upper layer sediments. Provided a water body has not been dredged, a drilled sediment core could provide a good spectrum of pollution dynamics in a watershed (Spencer and MacLeod, 2002).

Many scientists have applied sediment core analysis to establish the pollution history of aquatic ecosystems and documented the importance of sediment contamination for ecosystem quality and the widespread incidence of sediment contamination (Burton 1991; Begum *et al.*, 2009). Especially, if dating of vertical segments of sediment cores could be achieved, it provides an insight into the environmental regulation regimes within which contaminations occurred. In this respect, the performance of various environmental regulations could be assessed. This principle was applied by Masunaga *et al.*, (1999) to establish the dioxin contamination from past pesticide use in Japan. It came out clearly that the least levels of dioxins in sediments in Japan coincided with periods when particular pesticides were banned. Sediment core profiling of pollutants such as heavy metals, even without dating is still useful, since the vertical variation of

contaminant concentrations provides evidence of recent and past trends of contamination.

## **1.2 PROBLEM STATEMENT AND JUSTIFICATION**

Gold mining in Bibiani dates back to the 1900s. Until now, there has been several remining and closure since 1913. Bibiani limited, one of the first mining companies to begin mining operations in the town, embarked solely on underground operations, and produced 2.2 million ounces of gold until shutdown in 1961. Between 1987 and 2013, several other mining companies including Ghana Libya Gold Mining Company (GLAMCO), International Gold Resources (IGR), Ashanti Goldfields Company Limited (AGCL), Central African Gold Limited (CAGL) and Noble Gold Bibiani Limited (NGBL) have had their spell at the Bibiani mines for comparatively different periods (CAG, 2007). Periodic closure of the mines stems from procurement challenges, depletion of economic reserves as deemed available at that time and other technical problems. Their activities for large-scale production of gold include exploration, drilling programmes, surface mining and retreatment of gold tailings from past mining operations ([www.nobleminres.com](http://www.nobleminres.com)) have had huge adverse effect on water bodies. Tailings from gold mining at Bibiani contains high levels of As. This is because geologically, arsenopyrite ( $\text{FeAsS}_2$ ), a compound containing As occur naturally in close association with gold in Bibiani north (Kesse, 1985). High levels of As in the top soil are worrying since it could accumulate into plants or be washed via runoff into surface reservoirs. Chemicals used during mining process cause pollution to the environment. During mining operations, chemicals such as sulfur, arsenic, mercury and cyanide, which were discharged into the environment, seep into ground water or are washed away by rainwater, ultimately collecting in rivers, lakes and aquifers. Indeed, mercury

pollution of water bodies, sediments, soil and mine workers in Ghana has already been reported (Donkor *et al.*, 2006, Ansong-Asante *et al.*, 2007; Abrefah *et al.*, 2011).

Until lately, fishing activity on Lake Amponsah in Bibiani had been a very vibrant business. A host of anthropogenic activities such as dumping of refuse, palm kernel extraction industry, small-scale mining (known locally as “*galamsey*”) among others operated close to the Lake have contributed in no small way to siltation in the Lake. This has affected aquatic lives within the Lake leading to some portions of the Lake body practically covered with weeds (Appendix: Plate A2). The activities of smallscale mining at Bibiani and its environs are threatening the environment and life in the District (BABD, 2006). Moreover, the use of mercury by small-scale miners to extract gold can pollute the water bodies. Mercury entering the human body may lead to health complications such as kidney problems, headaches, tremors and comas. Mercury exposure can take place directly through physical contact or indirectly through contaminated water or fish. People who consume such contaminated aquatic organisms are prone to serious health hazards. Besides gold mining, agriculture is also a major economic activity for the indigenes in Bibiani. Food crops such as cassava, plantain, cocoyam, maize etc. are largely cultivated in this area. Cocoa, a major cash crop in Ghana, is also cultivated in the Bibiani district (BABDA, 2006). All these activities can potentially introduce heavy metals into the Lake Amponsah watershed, which may be washed by runoffs into surface reservoirs and eventually accumulate in sediment.

### **1.3 AIM AND OBJECTIVES OF RESEARCH**

The aim of this study was to investigate the contamination profile of heavy metals in sediment core from Lake Amponsah, in the mining district of Bibiani, Ghana.



The specific objectives of this research were to:

1. evaluate the vertical profile of Hg, Cd, Pb, Cu and As in the sediment core;
2. assess the rate of sedimentation in the Lake;
3. identify the potential source factors of contamination in the Lake Amponsah watershed.



## **CHAPTER TWO**

### **LITERATURE REVIEW**

#### **2.1 HISTORICAL BACKGROUND OF GOLD MINING IN GHANA**

West Africa has for centuries, been one of the most important gold mining regions in the world. Presently, mining in Ghana comprises the extraction of gold, bauxite, manganese and diamond in commercial quantities. In 2004, gold mining, which is the most prominent, contributed about 93% of the exports made (Minerals Commission, Ghana, 2004). Ghana is one of the major gold producing countries ranking ninth globally for recognised gold deposits (Ghananewsagency.org). Commercial scale gold mining, however, is purported to have started in Ghana during the 19th century by the



British (Tsikata, 1997). Due to the reluctance of Ghanaians to work for the Europeans in the late 1920s, the British passed the Mercury Ordinance, which made it illegal for Ghanaians to own Mercury. After 1957, when Ghana gained independence from her colonial masters, the industry collapsed. Aryee (2001) revealed that the severe decline in gold production was due to many problems ensuing from the economic, financial, institutional and legal framework within which the sector operated.

The mining sector is undoubtedly an essential segment of the Ghanaian economy that has contributed notably to the country's socioeconomic development dating back to the colonial era (Aryee, 2001). Various hard rock deposits can be found and significant quantities have also been re-deposited in local water-bodies, alluvial gold.

In historical perspective, the mining sector's contribution to gross foreign exchange, particularly gold, has only been paralleled by the cocoa sector. In the advent of the country's structural adjustment programme in the early 1980s, intense policy reforms and restructuring has been witnessed in the mining sector (Akabzaa and Dariamani, 2001). The sector therefore, presents strong potential to generate substantial revenue and employment opportunities enough to provide economic benefits to the country and improved livelihood for the population. Nevertheless, an evaluation of the contribution of the mining sector to revenue generation, employment creation, net foreign exchange available in the national economy, social and environmental impact portray different picture (Aryee, 2001).

Almost all but one of the Ghanaian gold mines were nationalized around 1966. The industry experienced a continuous decline in gold production and the fast deterioration was the consequence of excessive state control. In the 1960s and 1970s,

Ghana developed one of the most centrally controlled economies outside Eastern Europe (Hilson, 2002a). This gave rise to an increase in illegal and uncontrolled artisanal mineral production and smuggling as well as declining mineral sector performance (Addy, 1998).

## **2.2 GOLD MINING AT BIBIANI**

Gold mining operations in Bibiani was initially recorded in early 1902 but experienced a temporary shutdown in 1913 after approximately 70,000 ounces of gold were recovered. Bibiani Gold limited, in 1927 took over the property and restarted an underground mine, which produced a total of 2.2 million ounces of gold. State Gold Mining Corporation in 1961 bought the property but sold it after seven years of operation (1968) following the depletion of economic reserves as deemed available at that time. Ghana Libya Gold Mining Company (GLAMCO) and International Gold Resource (IGR) each also took over the property between 1987 and 1996. In June-, 1996, Ashanti Goldfields Company Limited (AGCL) took over the Bibiani Gold project including its management and development which birthed the Ashanti Goldfields Bibiani limited (AGBL). In December, 2006 Central African Gold Limited (CAGL) took over the operations and management of the Bibiani mines but had to sell it after a short spell due to operational difficulties with an inappropriate mine plan, low metallurgical recoveries as a result of lack of process control and poor financial controls (CAG, 2007). Noble Gold Bibiani Limited then acquired the property in 2009, with its intention to acquire 100% of the CAGL subsidiary, Central African Gold Ghana Ltd (“CAGGL”), and has remained so to date.

## **2.3 ENVIRONMENTAL CONCERNS OF MINING OPERATIONS IN GHANA**

Mining operations normally require extensive and expensive waste treatment, and degradation of water resources can have long-term negative impacts on economic

opportunities in the surrounding areas. However, other ore and rock surround the material that is mined. Mining creates large amounts of mineral waste in the form of waste rock and tailings. The large and small-scale mining processes impact negatively on the environment and the socioeconomic status of the communities in which they operate (Encarta, 2002). The environmental impacts of both large-scale and smallscale gold mining in Ghana have been properly documented (Mireku-Gyimah and Suglo, 1993). Accompanying the pattern of socio-economic growth, resulting from mining operations in the country, however, have been increased environmental complications comprising, mercury pollution and land degradation. For instance, from 1947 until 1992, there was environmental degeneration, which resulted from effluents discharged into without the appropriate precautionary measures (Carboo, 1997; Tsidzi, 1993; Tufour 1997). In Ghana, gold is mined in fundamentally two different ways. Artisanal and small-scale mining (ASM) popularly referred to as ‘galamsey’ are mostly open pits operated by hand and the gold obtained are sold through regional marketers. On the other hand, large-scale (surface and underground mining enterprises) operate with industrialized production chains and direct ties to international markets. Small-scale mining and large-scale mining differ markedly in their environmental and social implications (Hilson 2002a, b).

### **2.3.1 Large Scale Mining**

Ghana has about 23 large-scale mining companies producing gold, diamonds, bauxite and manganese across the ten regions ([www.wikipedia.org](http://www.wikipedia.org)). Setting off on the economic premise that the environment is an asset, it remain a known fact that one of the world’s most valuable and precious minerals, gold, is found within it. Gold is a product of the environment and a gift of nature, although mining has widespread and drastic environmental and social effects on them. Large scale mining commence with

the exploration phase as a major step embarked upon to obtain knowledge of the extent and value of the mineral ore deposit, information about the location and value of the mineral ore deposit. The processes that take place during this phase include surveys, field studies, and drilling test boreholes and other exploratory excavations.

Large-scale mining operations, which involve open-pit mining techniques, can bring about significant deforestation by way of forest clearing and road constructions that expose remote forest areas to transient settlers, land speculators, and small-scale miners (rainforests.mongabay.com). While deforestation and chemical pollution from large-scale mining can affect the rainforest environment, downstream aquatic habitats fare worse. Increased sediment loads and reduced water flows can seriously affect local fish populations (<http://rainforests.mongabay.com>).

Surface mining results in the removal of massive amounts of top soil in order to gain access to the minerals, which can cause erosion, loss of habitat, and dust pollution (Habashi 1996; Akabzaa and Darimani 2001;-). Some of these mining activities transpire in the forest reserve areas in Ghana (Kusimi, 2008). For instance, the Atewa forest reserve, which protects the headwaters of the Birim and Densu rivers and declared by local and international conservation groups as a Special Biological Protection Area (SBPA) contains many plant species such as two unusual kinds of tree ferns and six butterfly species, which are found nowhere else on earth. Coincidentally, it is also the most mineralized of all the forest reserves in the country, hence, stands threatened from the activities of not just small-scale miners but large scale mining operators who have been given licenses to engage in surface mining.

Mine tailings (the residue of an ore that remains after it has been milled and the desired metals have been extracted with cyanide or sulfuric acid) need to be properly managed



because they constitute a potential heavy metals source in the environment. The separation processes used for most metals do not entirely extract all the minerals present. The tailings that accumulate in the environment may contain quantities of toxic metals and other minerals, as well as residues of the chemicals used for extraction. Some large-scale mining projects, however, encompass the reworking of waste piles (often tailings) from inactive or abandoned mines, or older waste piles at active mines. How a mining company disposes of this high-volume toxic waste material is one of the crucial questions that will determine whether a proposed mining project is environmentally acceptable. Gold mine tailings at Obuasi, for instance, contain very high amount of arsenic recording an average of 8305 mg/kg (Ahmad and Carboo, 2000). In recent times, concerns have been raised about the stability and environmental performance of tailings dams. The ability of these dams to hold tailings without significant intrusions of pollutants over time into adjoining soils have been questioned (Aucamp and van Schalkwyk, 2003). Inactive tailings impoundments also are receiving more attention due to the long-term effects of windblown dispersal, ground water contamination, and acid drainage (USEPA, 1994; Aucamp and van Schalkwyk, 2003)

### **2.3.2 Artisanal /Small Scale Mining**

Artisanal or small-scale mining (ASM) otherwise known by local folks as ‘galamsey’ was once a respected traditional vocation. It brought to the fore some challenges, when the government officially legalised the practice in the late 1980s by enacting the Small-scale mining law, PNDCL 218 (Anon, 1989; <http://ghananewsagency.org>).

This led to the establishment of the Small-scale Mining Project within the Ghana Minerals Commission. The Small-scale Mining Project (now Small-scale Mining Department) has the obligation of providing technical assistance to prospective and registered small-scale miners in Ghana and promoting their activities. Artisanal or



small-scale mining play a crucial role in poverty alleviation and rural development; most of those involved are poor rural folks and mining without doubt represents the most promising, if not the only, income opportunity available in some localities. However, the sector is also recognised for its high environmental costs, poor health, and safety record. Many are of the view that it is sordid, unprofitable and unsustainable (pubs.iied.org).

According to Hentschel *et al.* (2002), the small-scale mining produces negative impacts on the physical and social environment during the different stages of mining (exploration, exploitation, processing and closure). The most important environmental problems familiar to the sector comprises, erosion damage and deforestation, mercury and cyanide pollution, direct dumping of tailings and effluents into rivers and river damage in alluvial areas. Additionally, improperly constructed tailings dams, acid rock drainage, landscape destruction, garbage and solid waste, tropical diseases (malaria) and cultural damage due to invasion of sensitive tribal land have also contributed towards environmental degradation.

The advent of the Chinese investors in Ghana and their engagement in ASM sector contributed to the already worsened environmental challenges, especially the countries natural resources; water bodies, virgin forest etc. The New York Times (2013) reported that, Chinese state-owned companies came under criticism in the past for ignoring the social and environmental impact of their projects when investing in resource-rich African countries.

The conservation of forests is also a great concern as many artisanal mining operations transpire in and around forests that are home to vast amounts of biodiversity. An investigation reveals that almost three-quarters of active mining and exploratory sites

overlap with areas of high conservation value and high watershed stress (awsassets.panda.org). Report also indicates that some mining operations also work within environmental protected areas, for instance, forest reserves (Ingram *et al.*, 2011). Artisanal or small-scale mining operations often lead to felling of trees to create space for their camps, and it is a common thing for miners to engage in hunting, fishing, and collection of other forest resources for food and medicinal purposes or for purpose to supplement their income (Ingram *et al.*, 2011).

### **2.3.3 Acid Mine Drainage (AMD)**

Acid mine drainage (AMD) refers to the outflow of acidic water from a mining site. In most cases, this acid comes primarily from oxidation of iron sulfide ( $\text{FeS}_2$ , also known as pyrite or "fool's gold"), which is often found in conjunction with valuable metals. When large quantities of rock containing sulphide minerals are excavated from an open pit or opened up in an underground mine, it reacts with water and oxygen to create sulphuric acid. When the water reaches a certain level of acidity, a naturally occurring type of bacteria called *Thiobacillus ferrooxidans* may kick in, fasttracking the oxidation and acidification processes, leaching even more trace metals from the wastes.

Acid mine drainage is a global problem, leading to ecological destruction in watersheds and the contamination of human water sources by sulfuric acid and heavy metals, e.g. arsenic (As), copper (Cu) and lead (Pb). Acid mine drainage constitute a major problem with many hard-rock mines, including almost all mines where the metal ore is bound up with sulphur (metal sulphide mines). The metals dissolved by the acid drainage poison downstream waters, in many cases to the point where nothing other than microbes can survive. Although mining is by far the largest cause of this type of acid leaching, for instance, acid mine drainage in South Africa “threatens the scarce water

resources of South Africa, and as a result also human health and food security in mining areas” (EAT 2008). The process can also occur during non-mining land disturbances such as construction, or even naturally in some environments. The acid will leach from the rock as long as its source rock is exposed to air and water and until the sulphides are leached out to a process that can last hundreds, even thousands of years. Acid is transported from the mine site by rainwater or surface drainage and settles in nearby streams, rivers, lakes and groundwater.

The increased acidity caused by acid mine drainage has a range of negative effects on the environment depending on the enormity of the pH change. The acidification of the water has immediate injurious impact on aquatic ecosystems. Acid mine drainage severely degrades water quality, and can destroy aquatic life and make water virtually unusable. A direct effect is the conversion of all carbonate and bicarbonate into carbonic acid, below pH 4.2, which dissociates into carbon dioxide and water. This destroys the bicarbonate buffer system in the water, which acts as a control on acidity. Kelly (1998) submits that since many photosynthetic organisms require bicarbonate as their inorganic carbon source, their ability to photosynthesize is limited or altogether destroyed as bicarbonate decomposes and becomes less available. Additionally, nutrient cycling (decomposition) will be reduced and eventually cease in water bodies severely affected by acid inflow (Dallas and Day, 1993). Furthermore, acid waters kill some organisms, by destroying ionic balances, or damaging cell components or carbonate exoskeletons (Kelly, 1998).

#### **2.3.4 Erosion and Siltation**

Mineral development disturbs soil and rock in the course of constructing and maintaining roads, open pits and waste impoundments. In the absence of adequate

prevention and control strategies, erosion of the exposed earth may carry substantial amounts of sediment into streams, rivers and lakes. Minimising the disturbed organic material that ends up in nearby streams or other aquatic ecosystems represents a key challenge at many mines. Erosion from waste rock piles or runoff after heavy rainfall often increases the sediment load of nearby water bodies. In addition, mining may modify stream morphology by disrupting a channel, diverting stream flows, and changing the slope or bank stability of a stream channel. These disturbances can significantly change the characteristics of stream sediments, reducing water quality (Johnson, 1997. Quinton and Catt (2007) observed that water erosion on agricultural soils, which has received only agrochemicals, has enriched sediment metal concentrations to toxic levels, which breached many accepted standards for soils and sediments.

Siltation is the process whereby fine solid particles build up on the bed of a river or lake and is the result of an excessive load of suspended solids in a river or lake. Mining operations produce large quantities of dust and finely powdered rock, with much rock having been ground to particle sizes below 0.2 mm. Mining wastes can cause significant ecological destruction. Often, solid mine wastes are dumped into streams, destroying habitat and causing other contamination. Though the materials that are dumped after removal of the commodity being mined have fine particle size and reasonable physical characteristics that could permit plant growth and retain adequate amounts of water, these materials have been formed from hard unweathered material and so may not contain much of the finest clay material and lack organic or microbial activity. The result is that mine dumps may be very unstable, easily blown by wind, when, they are dry and eroded by heavy rain when wet. The action of rain and wind thus removes fine



particles into nearby water systems, leading to a build-up of suspended solids and ultimately siltation.

## **2.4 HEAVY METAL CONTAMINATION FROM MINING ACTIVITIES**

Globally, industrialization has given rise to the degradation of environmental quality, resulting in long-term, adverse health effects (Vander Gaag *et al.*, 1991). Mining and industrial processing are among the main sources of heavy metals contamination in the environment. Mining activity brings about serious heavy metal pollution. Gold mining communities in Ghana have recorded contaminations of surface and ground water bodies (Davies *et al.*, 1994; Kuma and Younger, 2004; Obiri, 2007; Manu *et al.*, 2004). In spite of the numerous economic and social benefits derived from the mining sector, gold mining in recent times has become unpopular. It is regarded as a significant source of Hg, Pb and other heavy metal contamination of the environment due to activities like mineral exploitation, ore transportation, smelting and refining, disposal of the tailings and waste waters around mines (Essuman *et al.*, 2007; Hanson *et al.*, 2007; Koku and Balfor, 2007; Obiri, 2007).

Since gold mines are usually set up near rivers, excess chemicals are consequently discharged directly into waterways. Artisanal/small-scale gold miners mostly use mercury and other toxic chemicals, such as cyanide, in their operations. The use of mercury, for example, in gold mining in the Amazon Basin in Brazil eventually contaminated very large area of the Amazon River with about 200 tons being deposited annually in the basin (Malm *et al.*, 1990). Miners use mercury during the amalgamation process as an economical means to recover small gold particles from sediment. Once mercury and gold are combined to create amalgam, the amalgam is typically burned with a blowtorch or over an open flame to isolate the mercury from the gold. Once it settles in soil or water, mercury translates to methylmercury that can easily accumulate



in fish; which not only harms the fish but all other animals, including humans, who consume fish (Spiegel, 2009). Mine tailings is a major source of introducing heavy metals into environment (Liao *et al.*, 2008). Some scientific studies have elucidated that heavy metals constitute a substantial threat to the aquatic environment such as hindrance to fishing ; impairment of water quality and injury to living organisms (UNEP 1982, 1984); indirect effect on man through consumption of sea foods (Odiye, 1999).

#### **2.4.1 Lead (Pb)**

Lead (Pb) is a naturally occurring element that can be found in all environmental media: air, soil, sediment and water. Lead is defined by the United States Environmental Protection Agency (USEPA) as potentially hazardous to most forms of life, and is considered toxic and relatively accessible to aquatic organisms (USEPA, 1986). Lead is second on the Agency for Toxic Substances and Disease Registry's (ATSDR) top 20 List ([www.atsdr.cdc.gov](http://www.atsdr.cdc.gov)). The average concentration of Pb available in the earth's crust is around 13mg/kg, but there is considerable natural levels because of inputs from mineralised deposits of lead. However, a major feature of the environmental chemistry of Pb is the general diffuse pollution in top soils from a series of sources, including mining and smelting, recycling of sewage sludge and from motor vehicle exhausts.

Lead accounts for most of the cases of pediatric heavy metal poisoning (Roberts, 1999). Lead is bioaccumulated by benthic bacteria, freshwater plants, invertebrates and fish (DWAF, 1996). Every year, industries produce about 2.5 million tons of lead throughout the world for use in a variety of materials including paint, ceramics glaze, pesticides, batteries, plumbing, and PVC plastics pipes. Lead also commonly exists in ore containing other frequently mined materials, such as iron, copper, silver, and zinc.

Study conducted earlier recorded average lead concentration of 0.49 mg/kg in sediments and 0.17 mg/l in surface water from Lake Amponsah. The source of lead metal in the Lake was attributed to runoff associated with discharge from municipal wastewater, mining activities and lead emissions from gasoline-powered motor vehicles used by small-scale mining operators around the Lake (Owusu-Boateng and Kumi-Aboagye, 2013). Assimilation routes encompass the incorporation of plant material that is grown in contaminated soils (food chain), or the ingestion of contaminated soils directly (Basta and Gradwohl, 1998). Although adverse health effects of heavy metals have been known for a long time, exposures to heavy metals continue and are even increasing in some areas. The chronic effect of lead on man includes neurological disorders, especially in the foetus and in children. This can lead to behavioral changes and impaired performance in IQ tests (Needleman, 1987).

When lead (Pb) is released into the environment, it has a long residue time compared with most other pollutants (Jacobs, 1997). As a result, lead and its compounds tend to accumulate in soils and sediments where due to their low solubility and relative freedom from microbial degradation, they will remain accessible to the food chain and to human metabolism for the future. The WHO guideline value for Pb in domestic water supply is 0.01 mg/l (WHO, 2008).

#### **2.4.2 Mercury (Hg)**

Mercury is found in soil and rocks typically as an ore known as cinnabar, consisting of insoluble mercuric sulphide. Mercury abundance in the Earth's crust is very low being in the range 0.02 to 0.06 mg/kg, although it is likely to be more concentrated in argillaceous sediments and in coal (Kabata-Pendias and Mukherjee, 2007). In Ghana,

the existence of mercury in the environment may be imputed to the use of the metal in gold recovery processes where the inorganic form of the metal is either washed into rivers or is vaporized promptly into the atmosphere (Essumang *et al.*, 2007). Natural sources of atmospheric mercury include volcanoes, geologic deposits of mercury, and volatilisation from the ocean (Ferrara *et al.*, 2000). The WHO guideline value for total mercury in drinking is 0.001 mg/l (WHO, 2008).

According to the Ghana Atomic Energy Commission (GAEC), areas that contained high concentration of mercury are sites that experienced extensive illegal gold mining activities, showing that mercury concentration varied between 6.80mg/l and 19.82 mg/l for water, and 28.90 mg/kg and 84.30 mg/kg in sediment at sites with extensive small-scale mining activities (Ghanaian Chronicle, 2005). Mercury in sediment samples in the study area, Bibiani-Anhwiaso-Bekwai District, reportedly ranged between 0.17 and 1.74 mg/kg, while the corresponding stream/river water contained 0.13 to 1.341  $\mu\text{g/l}$  of Hg (Nartey *et al.*, 2011).

There are three forms of mercury: elemental (metallic), organic and inorganic mercury, and among these the most toxic one is the organic form, methylmercury (MeHg). Methylmercury undergoes microbiological transformation from inorganic mercury when it reaches aquatic environments, in water bodies or in soils (Zahir *et al.*, 2005). Inorganic and organic mercury are toxic to the human body in different ways, affecting different organs in different ways. Inorganic mercury can cause neurological and psychological symptoms, such as tremor, changes in personality, restlessness, anxiety, sleep disturbance and depression. These symptoms are however reversible after ending of exposure to inorganic mercury. Inorganic mercury is also an allergen, which may cause contact eczema. The kidneys are the organs that

accumulate the highest levels of mercury compared to brain and liver. This can cause kidney damage, which is reversible after the exposure has stopped (Zahir *et al.*, 2005).

Methylmercury toxicity is however not reversible as it is with inorganic mercury. According to the U.S. Environmental Protection Agency, the observed effects on animals exposed to high levels of methylmercury include mortality, reduced fertility, slower growth rates, and abnormal behavior that affect survival. Organic mercury affects the nervous system and the main symptoms of methyl mercury poisoning relate to damage of the nervous system. The earliest symptoms of poisoning are parestesias and numbness in the hands and feet. Later symptoms are coordination difficulties and concentric constriction of the visual (Järup, 2003). Other symptoms are memory loss, shortfall in attention and Alzheimer's disease like dementia (Zahir *et al.*, 2005).

Hock *et al.* (1998) conducted a study on whether environmental factors may influence the risk of getting Alzheimer's disease and found that Alzheimer's disease patients had a two-fold higher blood-mercury level than the control group and that in early onset Alzheimer's disease patients, blood-mercury levels were three-fold higher than the control group. Exposure of the foetus of humans to mercury can also cause late development of speech, late walking, memory shortfall in attention and autism (Zahir *et al.*, 2005). The general human population is primarily exposed to mercury via food, where fish is the major source of methyl mercury exposure (Järup, 2003).

Mercury has no necessary function in any living organism and is considered as a nonessential metal, is among the most toxic elements to man and many higher animals (Steinnes, 1995; Landner and Lindstrom, 1998). Mercury has caused more problems to the consumers of fish than any other inorganic contaminant. In extreme cases, consumption of mercury-tainted fish has led to the onset of a serious neurological



disease, termed Minamata disease. Victims of the disease are diagnosed as having a degeneration of their nervous systems. Numbness occurs in their limbs and lips. Their speech becomes slurred, and their vision constrict. Some people have serious brain damage, while others lapse into unconsciousness or suffer from involuntary movements. Furthermore, some victims are thought to be crazy when they begin to uncontrollably shout. In other cases, entire fisheries have been either restricted or significantly curtailed because of mercury contamination (Moore, 1991).

### **2.4.3 Cadmium (Cd)**

Cadmium occurs naturally in the environment at low levels usually with zinc, lead and copper ore deposits; however, the element is found in nature in mineral forms and obtained from cadmium ore, known as greenockite, which usually, is found in association with zinc ore. Commercial production of cadmium ore depends on the mining of zinc (ATSDR, 1999). Cadmium is commercially available as an oxide, chloride, or sulphide. The average natural abundance of cadmium in the earth's crust has usually been reported from 0.1 to 0.5 ppm. However, some rocks such as sedimentary rocks are known to contain about 0.1 to 29.25 ppm of cadmium. According to World Health Organization, cadmium levels in drinking water are usually less than 1 µg/l and consequently set a guideline value for cadmium as 0.003 mg/l drinking water (WHO, 2008).

Cadmium is more mobile in aquatic environments than most other heavy metals. Cadmium has a relatively long residence time in aquatic systems. In Lake Michigan, a mean residence time of 4-10 years was calculated for cadmium (Wester *et al.*, 1992). In polluted or organic-rich waters, adsorption of cadmium by humic substances and other organic complexing agents plays a dominant role in transport, partitioning, and remobilization of cadmium. Studies have indicated that concentrations of cadmium in



sediments are at least one order of magnitude higher than in the overlying water. Cadmium (Cd) concentration in the sediments of some surface reservoirs in some localities in Ghana ranged between 0.35 and 0.76 mg/kg was found to be 0.35 mg/kg at Tetrem and 0.57 mg/kg at Adobewora while 0.76 mg/kg was recorded at Gyeninso and 0.63 mg/kg was realized from Esaase (Agyarko *et al.*, 2014).

Food is the main source of daily exposure to cadmium (McLellan *et al.*, 1978). The effect of Cadmium (Cd) toxicity in man includes kidney damage and pains in bones (Friberg *et al.*, 1986). Of estimated 30- $\mu$ g cadmium ingested each day through food, about 5% of this exposure is absorbed by the digestive tract. Friberg *et al.*, (1986) and Nomiya (1976) have reviewed the fate of cadmium after chronic exposure by various routes. Cadmium is a toxic metal with no metabolic benefits to human and aquatic biota. Its presence in any compartment of the aquatic ecosystem indicates contamination (Opaluwa *et al.*, 2012). Exceptionally high Cd levels in drinking water may cause vomiting and diarrhoea, and occasionally death while taking lower levels over a long period will lead to kidney damage and fragile bones (Cleveland, 2008).

#### **2.4.4 Arsenic (As)**

Arsenic is a naturally occurring substance that can be present in soil, rocks, sediments and metals ores existing as oxyhydroxide, sulphide or compounds of various metals in most part of the world (Aronson, 1994). Arsenic is widespread in the environment, the average concentration in the earth's crust being approximately 2 mg/kg (DWAf, 1996). Arsenic is the most common cause of acute heavy metal poisoning in adults. Inorganic arsenic binds to haemoglobin after absorption, and is deposited in the liver, kidney, lungs, spleen, and skin. Arsenic levels in natural waters typically range between 1 and

2 µg/l, in spite of the fact that concentrations may be elevated (up to 12 µg/l) in areas containing natural sources (WHO, 2008).

Arsenic concentration in contaminated soils can reach values up to some hundreds of ppm in mining environments (Azcue *et al.*, 1995 and Garcia-Sanchez 2003). At Obuasi, the largest gold-mining area in Ghana, arsenic in drinking water from stream, shallow wells and boreholes ranged from <2 to 175 µg/L (Smedley *et al.*, 1996). This was attributed to mine pollution and natural oxidation of sulphide minerals, predominantly arsenopyrite.

The presence of arsenic in ground water is basically, the result of arsenic-bearing minerals shales, phosphorites, and iron and manganese ores but especially arsenopyrite (FeAsS), realgar (AsS), and orpiment (As<sub>2</sub>S<sub>3</sub>) dissolving naturally over time as certain types of rocks and soils are weathered. The gold in Ghana is associated with sulphide mineralisation particularly arsenopyrite (Griffis *et al.*, 2002). Arsenic can also dissolve out of certain rock formations when groundwater levels drop significantly allowing atmospheric oxygen to penetrate into the aquifer, and to oxidize arsenopyrite, leading to desorption of the adsorbed arsenic (Nickson *et al.*, 2000; Smedley and Kinniburgh, 2002).

Arsenic in surface and ground water is mostly a mixture of arsenite and arsenate.

Arsenic is widely distributed in food; particularly high levels are found in seafood (IPCS, 2001). It is reported that the main prospects of arsenic in Ghana occur at Kenyasi, Obuasi, Prestea, Tarkwa, Bibiani, and Bogoso with the gold occurring in close connotation with sulphide minerals, most significantly arsenopyrite (Smedley, 1996). For gold mining, mercury, arsenic and cyanide are normally the reported cases of

contamination. Asante *et al.*, (2007) reported high levels of arsenic comparable to other arsenic-endemic areas of the world in urine of inhabitants of Tarkwa and some villages near Obuasi in Ghana. Arsenic contamination has also been reported in groundwater in Obuasi and Bolgatanga (Smedley, 1996).

A study found out that most of the rivers in the mining areas of Obuasi and Tarkwa were polluted with elevated levels of hazardous chemicals, which were far above the World

Health Organisation (WHO) and Ghana Environmental Protection Agency's (GEPA) permissible levels. It allude to examples such as the river Nyam in Obuasi, which had arsenic concentration of 13.56 (mg/L) as against 0.01 mg/L required by the WHO and Ghana Environmental Protection Agency's (GEPA) permissible level of 1.0 mg/L. Arsine gas is a common byproduct produced by the manufacturing of pesticides that contain arsenic. Arsenic may also be found in water supplies worldwide, leading to exposure of shellfish, cod, and haddock. Heavy metal such as As concentration may accumulate to toxic level, which can cause a potential risk to human health. Arsenic exposure through drinking or bathing in contaminated water can cause among other illnesses or symptoms, cancer, abdominal pain, skin lesions, hypertension, cardiovascular disease, reproductive effects, and cancer at sites other than lung, bladder, kidney and skin (WHO, 2001, Carr and Neary, 2008).

#### **2.4.5 Copper (Cu)**

Copper is one of several heavy metals that are essential to life despite being as inherently toxic as non-essential heavy metals exemplified by lead and mercury (Scheinberg, 1991). Most copper (Cu) compounds found in air, soil and water are strongly attached to dust or embedded in minerals (MDH, 2006). Copper

concentrations in drinking water vary widely; usually range from  $\leq 0.005$  to  $>30$  mg/l, primarily because of the corrosion of interior copper plumbing (WHO, 2008). Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray (Cuzzocrea *et al.*, 2003).

People may be exposed to potentially harmful chemical, physical and biological agents in air, food, water or soil. Copper can be found in many kinds of food, in drinking water and in air. Because of that, we absorb eminent quantities of copper each day by eating, drinking and breathing. The absorption of copper is necessary, because copper is a trace element that is essential for human health. In humans, a small quantity of copper is necessary in diets to ensure good health (Vitosh *et al.*, 1994; MDH, 2006). Nevertheless, higher concentration of copper can result in adverse health effects in humans such as stomach cramps, vomiting, irritation of skin, nausea, diarrhoea, as well as affect the eyes and respiratory tract (Kegley *et al.*, 2009; MDH, 2006).

Copper has also been associated with liver damage and kidney disease (MDH, 2006). The absorption of copper is necessary, because copper is a trace element that is essential for human health (Cordano, 1998). Most copper compounds will settle and be bound to either, water sediments or soils particles. Soluble copper compounds form the largest threats to human health (Gaetke *et al.*, 2003). Usually water-soluble copper compounds occur in the environment after release through application in agriculture.

Metals are non-decomposable and accepted as main environmental contaminants causing cytotoxic, mutagenic and cancerous (carcinogenic) effects in animals (ALothman *et al.*, 2011). There are some reported cases of high copper contamination in mining areas of Ghana. Copper was estimated as 63.26 mg/kg in soil (Kpan *et al.*,



2014). The presence of copper in some small-scale mining areas are reported to be higher than the WHO guideline value due to the excavations made by panners in the course of prospecting for gold. Such activities lead to the weathering and leaching of this metal from waste rock dumps (AGC, 2001). When copper and copper compounds are released into water, the dissolved copper can be transported in surface waters either in the form of copper compounds or as free copper. Though copper binds strongly to suspended particles and sediments, there is evidence to suggest that some water-soluble copper compounds do enter groundwater. Copper that enters water finally hoards in the sediments of rivers, lakes and estuaries (ATSDR, 2004).

## **2.5 SEDIMENT AS A STORE OF POLLUTION RECORDS**

Sediment is a natural component of several aquatic systems derived from physical, chemical and biological components of watersheds. Sediment investigations in virtually all cases will involve measurement of chemical concentrations in the sediment. Sediments can emanate from the erosion of bedrocks and soil or from the decomposition of plants and animals. Sediments serves as important sink for a variety of pollutants, particularly heavy metals, and may serve as an enriched source for benthic organisms (Wang *et al.*, 2007) especially in estuarine ecosystems.

Continuous discharge of industrial and residential wastewater into water bodies is a potential source of environmental pollution. When heavy metals are discharged into surface reservoir, they rapidly become associated with particulates and are integrated into bottom sediments (Hanson *et al.*, 1983). The accumulation of metals from the overlying water to the sediment is dependent on a number of external environmental factors such as pH, ionic strength, anthropogenic input, the type and concentration of

organic and inorganic ligands and the available surface area for adsorption caused by the difference in grain size distribution (Davies *et al.*, 1991).

Heavy metal concentrations in the water column can be relatively low, but the concentrations in the sediment may be higher. Whereas low-level discharges of a contaminant may satisfy the water quality criteria, long-term partitioning to the sediments could result in the accumulation of high loads of pollutants. Davies *et al.*, (1991) has demonstrated that, the analysis of heavy metals in the sediments allows detection of pollutants that may either be absent or present in low concentrations in the water column. The impact of heavy metal contaminants in the sediment may be either acute or chronic (cumulative) on benthic organisms (Griggs *et al.*, 1977).

Pollutants have contaminated many of the sediments in our rivers, lakes, and oceans. Many of the contaminants were released years ago while other contaminants enter our water on daily basis. Some heavy metals flow directly from polluted runoff in urban and agricultural areas. Still other contaminants are carried through the air, landing in lakes and streams far from the factories and other facilities that produced them. Some contaminants accumulate in sediments via industrial and municipal waste dischargers, while others come from terrestrial runoff, disposal of liquid effluents, and leachate carrying chemicals springing up from numerous urban, industrial, and agricultural activities as well as atmospheric deposition (Harikumar *et al.*, 2009). Heavy metals from industrial and urban discharges are deposited in different components of the aquatic ecosystem, such as sediments, soils and biota. Comparatively, heavy metals are considered as one of the more serious pollutants in our natural environment stemming from their toxicity, persistence, and bioaccumulation problems (Loizidou *et al.*, 1992; Ramos *et al.*, 1999; Tam and Wong, 2002; Mucha *et al.*, 2003).

Higher sediment concentrations increase the turbidity of natural waters, reducing the light

Available to aquatic plants for photosynthesis (Ripley, 1996). In addition, increased sediment loads can smother benthic organisms in streams and oceans, eliminating important food sources for predators and decreasing available habitat for fish to migrate and spawn (Johnson, 1997). Higher sediment loads can also decrease the depth of streams, resulting in greater risk of flooding during times of high stream flow (Mason, 1997). Fine sediments can attract nutrients such as phosphorus and toxic contaminants such as pesticides, altering water chemistry (Carr and Neary, 2008).

#### **2.5.1 Sediment Core Analysis**

Sediment cores are an expensive and unique resource of immense scientific value, analysis of which can provide clues for a wide range of research comprising climate change, conditions in past lakes, dispositional history, sedimentary processes and environmental changes. Sediment cores have been used extensively over the past several decades to aid in the reconstruction and evaluation of impacts to aquatic ecosystems from a wide variety of disturbance events and processes (Engstrom *et al.* 1985; Von Gunten *et al.*, 1997; Brush, 2001). Some have concentrated on contaminants in general (Gearing *et al.*, 1991; Macdonald *et al.*, 2000; Gallagher *et al.*, 2004), while others have targeted the historical accumulation of Hg, primarily because of atmospheric deposition (Swain *et al.* 1992, Engstrom *et al.* 1994, Benoit *et al.* 1998, Lockhart *et al.* 1998, 2000, Heyvaert *et al.* 2000). During the last three decades a varied suite of new technologies have been developed to analyse sediment cores, often non-destructively, to produce high quality, closely spaced, co-located downcore

measurements characterising sediment physical properties, and composition in unprecedented detail (Rothwell and Rack, 2005).

In sediment core analysis, multiple cores are frequently collected and sub-sampled at a site for different groups of constituents, at either same or different depth intervals. This approach brings about considerable uncertainty in some cases in correlating information between the cores, including age estimates. It is preferable that all samples come from the same core to avoid uncertainty in extrapolating age estimates from one core to another and to aid in correlating trends in one group of constituents with another. In most lakes sampled after 1997, a single core was used to analyse all constituents for a given site (<http://pubs.usgs.gov>). Sampling intervals in cores may vary depending on objectives, sedimentation rate in the lake, and sample mass requirements.

In the study of sediment cores from the 78 meter, deep Lake Bosomtwe, Ghana (Koeberl *et al.*, 1997, 2007) has accrued a million years of sediment at the lake bottom and contains an excellent sediment record for the reconstruction of paleoclimatic patterns over the Sahel region of West Africa. Investigation into the influence of environmental factors on the apparent quality of age dating of the cores is undoubtedly important. In this light, the top of the core is assigned the sampling date and the bottom of the lake sediments assigned the reservoir construction date. Invariably, the sediments deposited during the accumulated period can be identified by concentrations of radioactive cesium-137 (<http://tx.usgs.gov>).

## **2.7 SEDIMENT QUALITY GUIDELINES**

Many studies have documented the importance of sediment contamination for ecosystem quality and the widespread incidence of sediment contamination (US Environmental Protection Agency, 1997; Burton, 1991). The last decade has



experienced an exponential growth in our understanding of contaminant in aquatic sediment. Generally, the basic purposes of sediment quality guidelines (SQGs) are to protect the aquatic biota from the harmful and toxic effects related with sedimentbound contaminants and useful tool for evaluating the potential for contaminants within sediment to induce biological effects (Spencer and Macleod, 2002).

Consequently, in Australia, as in many part of the world, sediment quality guidelines have recently been introduced, but detailed guidance on how to interpret and apply these guidelines is generally insufficient. Recent research has provided a quality comprehension of the science that corroborates standard quality guidelines. Moreover, this has been documented exhaustively in the proceedings of a recent international workshop on the subject (Wenning *et al.*, 2005). Verily, the limitations and uncertainties of current approaches need to be fully appreciated by the users, and these are discussed in details in a number of recent publications (Batley *et al.*, 2003; Simpson and Batley, 2003). Sediment quality guidelines for metals in use around the world differ over several orders of magnitude and are not centered on clear causeeffect relationships (Chapman *et al.*, 1999; Borgmann, 2003; Simpson and King, 2005).

The Australian approach was to introduce a tiered assessment framework so that exceedance of the interim guideline values led to additional studies to confirm or deny the possibility of biological impact (ANZECC/ARMCANZ, 2000; Environment Australia, 2002). The tiered assessment framework of the guidelines does not involve the assessment of benthic ecology or bioaccumulation (ANZECC/ARMCANZ, 2000), which are recognized as important indicators of sediment quality. The Australian and

New Zealand Environment and Conservation Council (ANZECC) acceptable guideline values for heavy metals such as Hg, Cd, Pb, Cu and As in sediment were given as 0.015, 1.2, 47, 34 and 20 mg/kg (Burton, 1991).

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## CHAPTER THREE

### MATERIALS AND METHODS

#### 3.1 THE STUDY AREA

The study was undertaken in Lake Amponsah Watershed in Bibiani, Ghana. Lake

Amponsah is situated in Bibiani-Anhwiaso-Bekwai District in the Western region of Ghana (Figure 1) (<http://www.statsghana.gov.gh>). Bibiani is a small city in Ghana with population of about 19,076 (BABDA, 2006). Bibiani is situated at 6.47° North latitude, -2.33° West longitude and 250 m above sea level (<http://www.mapstreetview.com>). The District has eighteen (18) towns and falls within the Equatorial Rain Forest Zone. The District shares boundaries with Atwima-Mponua District in the Ashanti Region to the north, to the south with Waasa-Amenfi West District, to the east with Upper Denkyira West District, and to the west with Sefwi-Wiawso District. The main commercial activities in the district stem from the industrial activities such as gold mines, artisanal mining (galamsey) and agriculture (farming activity).

Lake Amponsah, a man-made reservoir, was constructed around 1960 on purpose by then gold mining company known as State Gold Mining for domestic water use. It had a mean depth of an approximately 4.00 m, with the greatest depth of about 5.79 m (19 ft.). The Lake covers an area of 51,156.67 m<sup>2</sup> and has a storage capacity of about 168,205.40 m<sup>3</sup> (37 million gallons) of water. It also receives storm runoff from within its immediate catchment areas, notably; it is fed by the Amponsah stream. Nevertheless, during the entire period of the survey, its inlet had almost been silted up, thus affecting the normal inflow. The major activities around the Lake were smallscale mining including illegal gold mining popularly known as ‘galamsey’, palmkernel oil extraction industry and fishing.



Figure 1: The District Map of Sefwi Bibiani Anhwiaso Bekwai showing Bibiani

### 3.2 SAMPLE COLLECTION AND PREPARATION

Sediment core samples were collected with a PVC pipe corer from three (3) designated sampling points between the months of January and February 2014 (Figure 2). The sample collection was preceded by a familiarization visit and reconnaissance survey of the sampling site.





Figure 2: Bibiani township showing the location of Lake Amponsah and the specific sites (Sites 1, 2 and 3) where sediment cores were sample.

A Garmin GPS map 60CSx was used to determine the coordinates of the sampling points (Table 1).

**Table 1: Geographical locations of sampling points**

Sampling Code	GPS Readings
---------------	--------------

P1	N: 07.14257, E: 05.75565
P2	N: 07.14251, E: 05.75631
P3	N: 07.14287, E: 05.75687

### 3.2.1 Corer for Sampling

Sediment core samples were collected applying a corer made out of polyvinyl chloride (PVC) pipes of diameter 0.002 m and length 3 m (Appendix: Plate A5). Prior to the sampling, the PVC pipes that were used to form the corers were cleaned applying the following procedures to decontaminate them. The PVCs were first washed with detergent; rinsed with water to remove detergent and then with distilled water. This was followed with two successive one hour shaking treatment with nitric acid; rinsing with distilled water and then cleaning with acetone (to dry off water).

### Sample Collection and Preparation

Sediment cores were collected from all three designated sampling points (Figure 2). Each of the three sampling points were purposefully selected to correspond with points of discharge from a palm-kernel extraction location and inlet to the Lake from the Amponsah Stream (Site 1), a point of discharge of effluent from the small scale mining site (Site 2) and the portion with no direct anthropogenic activity and records the highest depth (Site 3). At each designated sampling site, a PVC coring pipe (diameter 0.002 m and height 3 m) (Appendix: Plate A5) was carefully drilled down to approximately 1 m into the Lake sediment (Plate 1).

Sediment cores up to 50 cm in length were retrieved from each of the three sampling points. Each sample was assigned an identifier in the field, which consisted of the site

name and number (Site 1, Site 2 and Site 3). The sediment cores held in the PVC core samplers were placed in transparent polyethylene bags and supported in a vertical position to allow water to gradually drain off. The cores were allowed to dry in ambient air for three days. The dried samples were then removed from the PVC corers and sliced into equal sections of approximately 5 cm each. That is, each core was sectioned into six equal parts labeled as follows: Site 1-A, Site 1-B, Site 1-C, Site 1-D, Site 1-E, Site 1-F (for sampling point Site 1), Site 2-A, Site 2-B, Site 2-C, Site 2-D, Site 2-E, Site 2-F (for sampling point Site 2) and Site 3-A, Site 3-B, Site 3-C, Site 3-D, Site 3-E, Site 3-F (for sampling point Site 3).

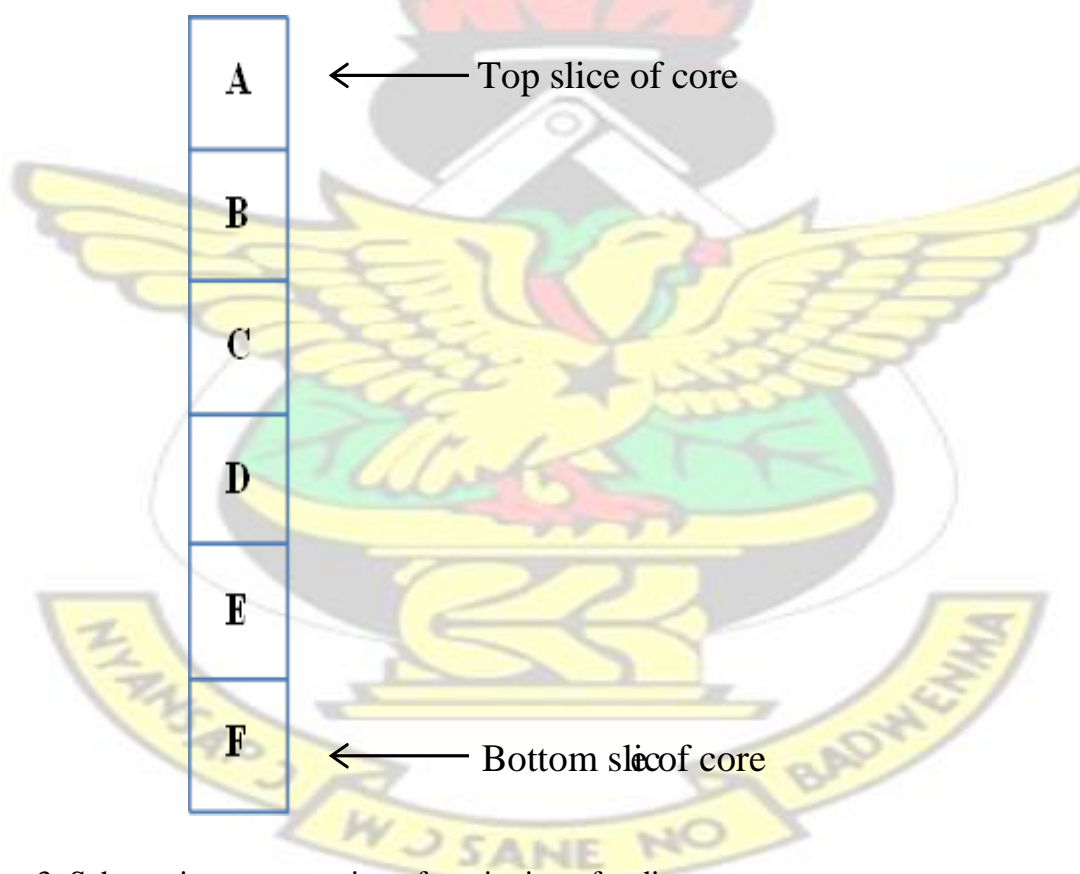


Figure 3: Schematic representation of sectioning of sediment core  
All the sediment core slices were stored in clean plastic bags (Plate 2) and kept frozen until required for digestion and laboratory analysis.





Plate 1: Sediment core sampling from Lake Amponsah for laboratory analysis



Plate 2: Sediment core slices stored in polyethylene bags

### 3.3 ESTIMATION OF SEDIMENTATION RATE IN THE LAKE

The rate of sedimentation in Lake Amponsah was estimated based on change in depth of the Lake with time. The average depth of the Lake was 4 m (400 cm) when it was constructed in 1960. The current average depth of the Lake was measured applying a



depth sounder device (Hondex Digital Depth Sounder). This device functions by sending laser beam from the surface of the Lake down to the Lake floor. The beam is then reflected back to the device and the distance travelled is estimated as depth. The depth measurement was taken at 50 different points across the Lake's surface and the average value estimated.

The annual rate of sedimentation in the Lake was then estimated as follows:

$$= (\text{Initial depth} - \text{Current depth}) / \text{Age of Lake}$$

Therefore:

$$\text{The annual rate of sedimentation} = (4 \text{ m} - \text{Current depth}) / (2014 - 1960)$$

### 3.4 LABORATORY ANALYSIS

Analyses of sediment samples for the content of specific heavy metals were performed at the Envaserv Research Consult, Accra, Ghana. To prepare the sediment for heavy metal analysis, the samples were air dried at room temperature for 4 h in the laboratory. With the aid of a mortar and pestle, each slice was ground into fine powder and sieved applying 2 mm mesh (Plate 3). The samples were then subjected to wet digestion (Jose *et al.*, 2005).



Plate 3: Samples ground into fine powder using mortar and pestle and sieved applying a 2 mm mesh

### 3.4.1 Sample Digestion

One (1) gram of the ground sediment sample was weighed into a 250 ml conical flask. Ten (10) ml of concentrated  $\text{HClO}_4$  (Perchloric Acid) (70%), 10 ml of concentrated  $\text{HCl}$  (Hydrogen Chloride) (38%) and 0.2 ml of  $\text{H}_2\text{O}_2$  (Hydrogen Peroxide) (30%) which served as a catalyst) were then added to the sample. The flask was swirled gently to obtain a uniform mixture, sealed with aluminium foil and heated on a hot plate for 1 hour at 100 °C. The digested mixture was allowed to cool to room temperature and then made up to 100 mL with de-ionize water (Plate 4).



Plate 4: Sample digestion process

### 3.4.2 Determination of Arsenic

Arsenic was determined applying the Palintest (Wagtech) method.

50 mL of the digest was transferred into a 200 mL conical flask. One (1) sachet of Wagtech A1 (contain sulphamic acid) and 1 tablet of A2 (contain sodium borohydride < 10%) was added to the solution and glassware corked immediately to avoid explosion due to pressure built up. Using an Arsenator (PTW 10010 Wagtech Potalab®, Palintest Ltd), (Plate 5) a blank was run with de-ionized water for 20 min for calibration purposes after which the sample was also run to determine the arsenic content.



Plate 5: Arsenator and kits for the determination of Arsenic

### 3.4.3 Determination of Cadmium, Lead and Copper

Cadmium, lead and copper were determined applying the Anodic Stripping Voltammetry (ASV) method, with PDV 6000 *plus* (Cogent/Modern Water Inc.) as the operational device (Plate 6). The device is interfaced to a computer via the VAS (voltammetric analysis system) software. Under this method, there were few important steps that were observed:

- preparation of electrodes



- creation of a method to run the samples
- preparation and run of a blank (calibration)
- preparation and run of a standard (calibration) and
- preparation and run of samples



Plate 6: PDV 6000 *plus* controller handset with the analytical cell in a waterproof case for determining heavy metals

#### 3.4.3.1 Reagents used

The following reagents were applied in the ASV method for determining Cu, Pb and Cd

- 50 mL Chloride-Acetate Buffer Electrolyte (CLAC)
- 1000 ppm Mercury Plating Solution (MPS) (contains Mercury nitrate <0.01%)
- 1000 ppm Copper, Lead and Cadmium Standards



- Electrode conditioning solution A (pnR-300-025ECS-01) (contains NaOH solution < 5%)

#### **3.4.3.2 Electrode Conditioning and Plating**

The ASV uses electrodes for the analysis. The electrodes consist of a reference, counter and working electrode. The reference electrode produces current to the cell. The working electrode collects the metals at the tip of the cells. The counter electrode measures the current being provided when the metals are being stripped off. The reference electrode is silver and coated to support the movement of the electrons to provide current. The metals collected are stripped back into the solution. All the electrodes were polished and conditioned, first with electrode conditioning solution A (contains < 5 % NaOH) and second in mercury plating/coating solution. The essence of the plating was to enhance the sensitivity of the detection of the metals in solution.

#### **3.4.3.3 Blank run**

10.0 mL of CLAC electrolyte and 10.0 mL de-ionized water were added in a clean analysis cup and placed in the cell assembly. Using the Run Configuration, this solution was analysed as a blank. By selecting, the “Display Graph” button, a blank voltammogram was displayed having no peak (no contaminants present). The range and the deposit time of 60 seconds were set based on the expected sample concentration.

#### **3.4.3.4 Standard run**

250  $\mu$ L of the 20 ppm stock standard solution was added to 20 mL CLAC electrolyte into a clean analysis cup. A standard of concentration 250 ppb (0.25 ppm) was created and covered to avert any possible evaporation and accidental contamination. At the end

of the analysis, a voltammogram was displayed with peak based on the standard used. This was to calibrate the instrument for a reliable analysis of the sample. The cell was rinsed repeatedly for 3 times with 20 mL de-ionized water.

#### **3.4.3.5 Sample run**

Five (5) mL of digested sample solution was pipetted and made up to 10 mL using deionized water. Ten (10) mL CLAC electrolyte was added to give a total volume of 20 mL in a clean analytical cup. The addition of the electrolyte was to ensure that the solution was sufficiently conductive to enhance plating processes and permitting the control of the electrode potential. Placing the electrode assembly over the analytical cup, the sample was run using VAS. By selecting the 'Display Graph' and 'Detect Peaks' options, the sample voltammogram was created showing peaks for Cd, Cu and Pb at the same time. The standard was re-run after analyzing every 5 samples so as to ensure validity of the data. The procedure was repeated to run the rest of the samples to generate the respective sample voltammogram.

### **Determination of Mercury**

#### **3.4.4.1 Reagents used**

- Standard: 20 mg/L Mercury Standard solution
- Electrolyte: Mercury/Chrome Electrolyte (product of Cogent/Modern Water, Inc.)
- Electrode Conditioning Solution A (pnR-300-025ECS-01) (contains NaOH solution, < 5%)

#### **3.4.4.2 Electrode conditioning**

The carbon electrodes were clean by firmly polishing the carbon surface for 30 s with the supplied kits after which the residual polishing fluid were rinsed with de-ionized

water. The electrodes thereafter were dipped into an electrode conditioning solution A (this product contains less than 5% of Sodium Hydroxide solution), produced by 'Modern Water Monitoring Ltd, UK', for briefly 20 seconds, rinsed with de-ionized water and returned to the analysis cell for reconnection. A clean analysis cup was filled with 20 mL of de-ionized water, placed in the cell assembly for rinsing the cell. Finally, 10 mL of the mercury/chrome electrolyte was injected into a clean analysis cup and added with enough mercury standards to get a concentration of 100 ppb and made up to 20 mL with de-ionized water. The solution was analysed 5 times using the Run configuration. The cell was then rinsed 3 times with 20 mL of de-ionized water.

#### **3.4.4.3 Blank run**

10 mL of mercury/chrome electrolyte and 10 mL of de-ionized water were added into a clean analysis cup. The cup was then placed in the cell assembly and the solution was analysed as a blank using the Run Configuration. The Run Configuration allowed for the selection of the deposit time (60 seconds) and range setting, which depends on the expected sample concentration. This process was done to calibrate the instrument.

#### **3.4.4.4 Standard run**

A standard mercury concentration of 200 ppb (0.2 ppm) was prepared. The solution was run using the run configuration to calibrate the instrument for the analysis of the 18 samples for the analyte (mercury). The solution was analysed several times until the peak height reproducibility was acceptable (within 5%). The cell was thereafter rinsed for 3 times with 20 mL de-ionized water.

#### **3.4.4.5 Sample run**

10 mL of the digested sample was added to 10 mL of mercury/chrome electrolyte in a clean analytical cup and placed in the cell assembly for analysis. The standard solution was re-run after analyzing every five (5) sample to ensure the validity of the standard used throughout the analysis.

### **3.4.5 Quality Assurance**

#### **3.4.5.1 Standard addition method**

In order to ensure that the results produced were scientifically acceptable, the normal laboratory regulations and procedures such as proper cleaning of apparatus, calibration of equipment, analysis of duplicates were strictly adhered to during the research. The VAS (voltammetric analysis system) provides an option for the use of the standard addition method, which serves the purpose of compensating for any possible matrix effect. This method is employed in situations where sample matrix also add to the analytical signal, thus, making it impossible to compare the analytical signal between sample and standard using the traditional calibration curve approach. With this method, the standard calibration is carried out in the same sample/electrolyte solution used to analyze the sample itself. The heavy metal concentrations in the blank solution were also analysed. The results revealed that heavy metals in the blanks were all below the detection limit ( $< 5.00$  mg/kg).

### **3.5 STATISTICAL ANALYSES**

The data obtained in this study were subjected to statistical analyses using ANOVA. Variation with  $p$ -value  $< 0.05$  was considered statistically significant. Linear regression



and correlation analysis were also conducted. The measures of central tendencies used in the analysis were the mean and standard error of the mean (SEM).

## **CHAPTER FOUR**

### **RESULTS**

#### **4.1 AVERAGE CONCENTRATIONS OF HEAVY METALS IN SEDIMENT CORE**

Sediment core samples were taken from Lake Amponsah at designated sampling points; Site 1, Site 2 and Site 3. The mean concentrations of the analysed heavy metals in the sediment cores at the respective sampling points are displayed graphically in Figure 4. Relatively high concentrations (mg/kg) of As were recorded at all the three sampling points (Site 1,  $56.83 \pm 3.50$ ; Site 2,  $72.00 \pm 12.39$ ; Site 3,  $44.50 \pm 11.22$ ), with mercury recording the least concentrations (Site 1,  $0.02 \pm 0.001$ ; Site 2,  $0.03 \pm 0.003$ ; Site 3,  $0.02 \pm 0.002$ ) (Appendix: Table A3). Cadmium concentrations were generally one order of magnitude greater than mercury concentrations. Lead and copper concentrations were within the same order of magnitude, but one order of magnitude greater than Cd concentrations and an order less than As concentrations. The variation in the concentrations of each metal among the three sampling sites was not statistically significant.

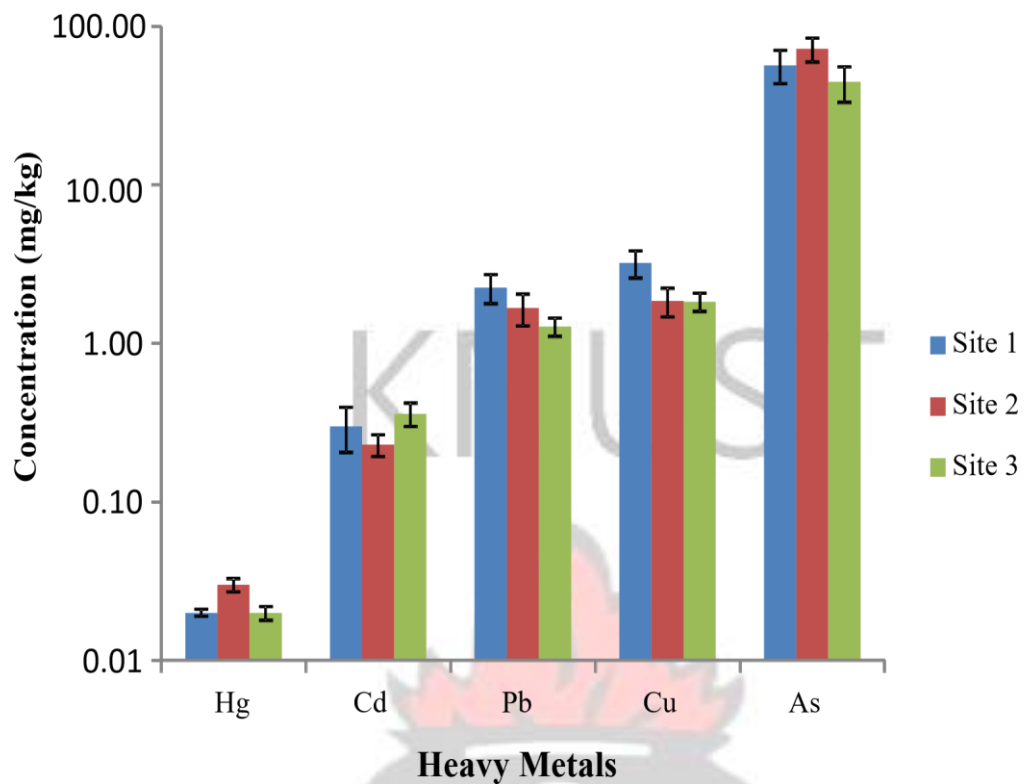


Figure 4: Mean concentrations of heavy metal at different sampling points

## 4.2 RATE OF SEDIMENTATION IN LAKE AMPONSAH

A depth sounder was applied to measure the depth of the Lake at 50 different points (Appendix: Table A5). From these measurements, the current average depth of Lake Amponsah was estimated as 10.01 ft. (305 cm). The rate of sedimentation per year was estimated as 1.76 cm. Thus, each 5 cm slice of sediment core corresponds to approximately 3 years of sedimentation. In effect, the 5, 10, 15, 20, 25 and 30 cm correspond to year 2011, 2008, 2005, 2002, 1999 and 1996 respectively.

## 4.3 DEPTH PROFILE OF HEAVY METALS IN SEDIMENT CORE

### 4.3.1 Mercury (Hg)

At sampling Site 1, Hg concentration exhibited a gradual decline with depth (from approximately 0.02 to 0.015 mg/kg), except at the 20 cm depth range, where there was a sharp increase in concentration to 0.025 mg/kg. At Site 2, the concentration of Hg varied between 0.01 and 0.04 mg/kg, with the highest concentration observed at the depth range of 30 cm. The depth profile of Hg appeared less varied at Site 3, ranging between 0.01- 0.02 mg/kg. The concentration of Hg was fairly, constant at 0.02 mg/kg between 10 and 25 cm depth range, while the surface sediment and the bottom sediment both recorded a low value of approximately 0.01 mg/kg (Figure 5).

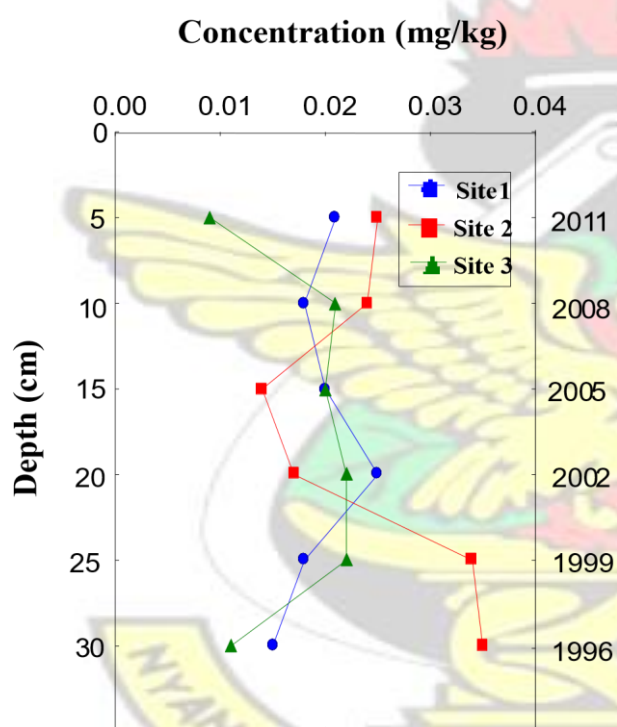


Figure 5: Depth profile of mercury in sediment core

#### 4.3.2 Cadmium (Cd)

Generally, the concentrations of Cd measured (with an average of 0.30 mg/kg) (Appendix: Table A2) decreased gradually with depth at all the sampling points (Figure 6). The depth profile of Cd varied between 0.09 and 0.74 mg/kg at Site 1, 0.15 and 0.37

mg/kg at Site 2, and 0.12 and 0.51 mg/kg at Site 3 (Table A1). Cadmium levels were highest at depth ranges of 5 cm, at Site 1, 10 cm at both Sites 2 and 3 (Figure 6). Apparently, cadmium recorded higher concentrations among the three sites than mercury.

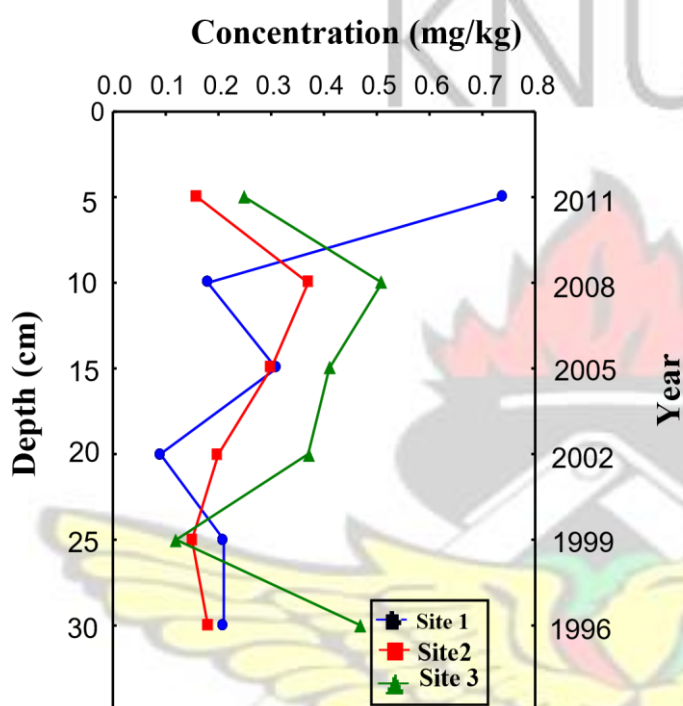


Figure 6: Depth profile of cadmium in sediment core

#### 4.3.3 Lead (Pb)

Similar to the depth profiles of Cd, Pb concentrations also generally decreased with depth at all the sampling points (Figure 7). The depth profiles of Pb varied between 0.6 and 3.4 mg/kg at Site 1, 0.5 and 2.9 mg/kg at Site 2, and 0.7 and 1.7 mg/kg at Site 3 (Appendix: Table A1). The average concentration (1.73 mg/kg) recorded for Pb (Appendix: Table A2) among the three sites was higher than that of Hg and Cd. At all the sampling points, highest concentrations of Pb were recorded in the top layer of the sediment core whilst the lowest were recorded at the bottom sediments.



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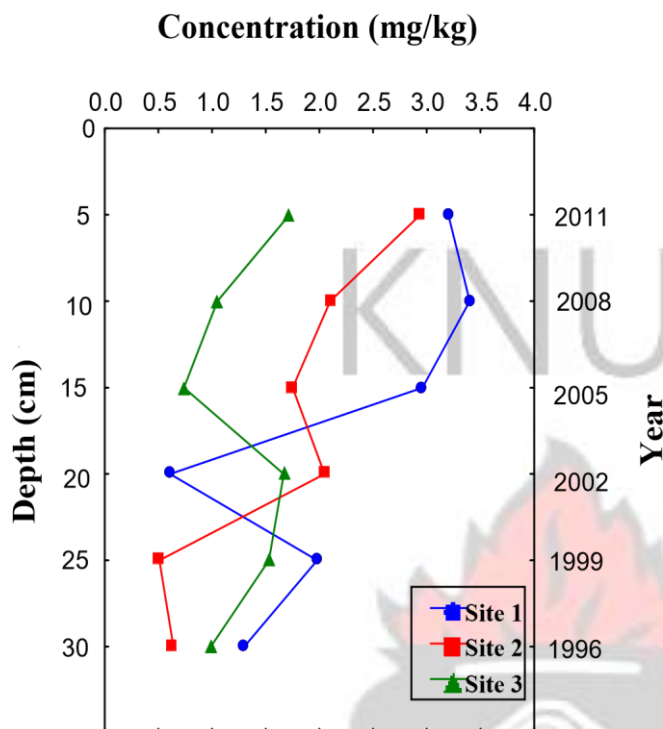
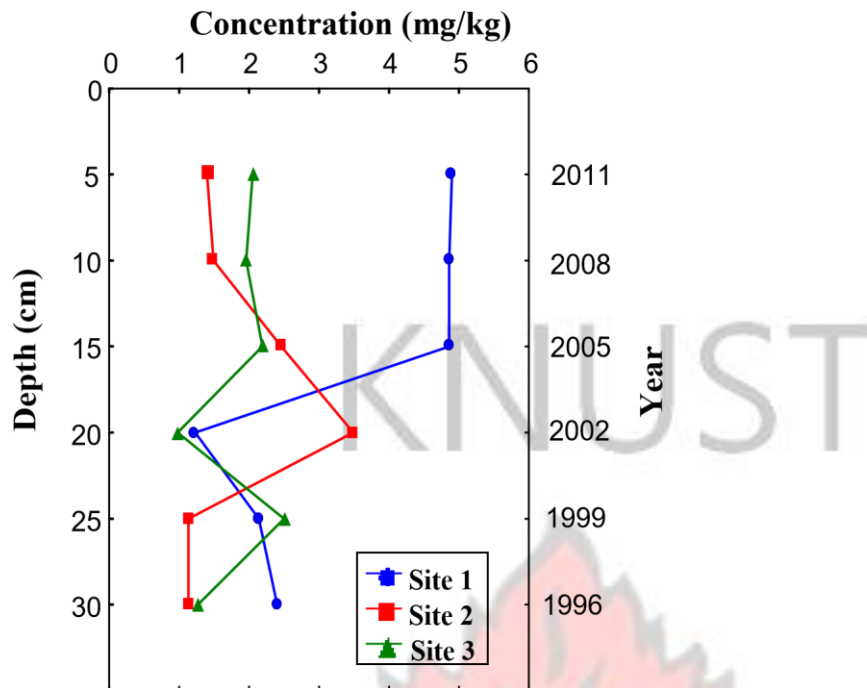


Figure 7: Depth profile of lead in sediment core

#### 4.3.4 Copper (Cu)

At sampling point Site 1, Cu concentration was fairly constant between 0 and 15 depth range and then decreased sharply (Figure 8). The depth profile of Cu at Site 2 showed gradual increase in concentration from the surface to a depth of 20 cm, after which Cu levels decreased sharply to a constant value of 1.13 mg/kg between 25 and 30 cm depth range. At Site 3, copper concentrations varied between approximately 1.0 and 2.5 mg/kg along the sediment core, with highest concentration occurring at 20 cm. The upper half of the sediment core recorded relatively greater concentrations of Cu compared to the bottom half at all the sampling points (Figure 8). Cu concentrations apparently, are higher than Hg, Cd and Pb at all the sampling sites



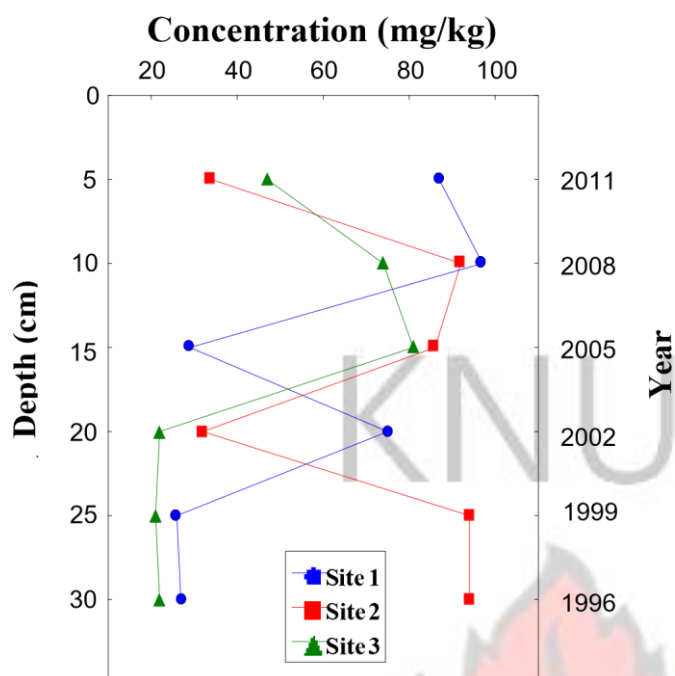
(Appendix: Table A2).

Figure 8: Depth profile of copper in sediment core

#### 4.3.5 Arsenic (As)

The depth profile of As was quite haphazard at all the sampling points (Figure 9). It though appeared that As concentrations were relatively reduced in the bottom layer at sampling locations Site 1 and Site 3. Noticeably, the highest concentration value (97 mg/kg) among the three studied stations, at depth 10 cm, was recorded in depth profile for Site 1 (Figure 9). At Site 2 however, As recorded a highest concentration (94 mg/kg) in the bottom layer between 25 and 30 cm depth range. Arsenic (As) resulted with a highest concentration of 81 mg/kg at depth 15 cm with a minimum concentration of 21 mg/kg at depth 25 cm recorded for Site 3 (Figure 9).

Figure 9: Depth profile of arsenic in sediment core



#### 4.4 CORRELATIONAL ANALYSIS

Correlation matrix of the metals is presented in Table 2. With the exception of arsenic, the other metals, cadmium, lead, and copper negatively correlated with mercury. However, two notable correlations were apparent, considering the correlation coefficients ( $r$ ). Lead correlated strongly with Cu ( $r = 0.74$ ), while moderate positive correlation was observed between Hg and As ( $r = 0.44$ ) (Table 2). Following this observation, the relationships between Pb and Cu, and Hg and As were each analysed separately for the top half (i.e. 0-15 cm) of the sediment core, as a well as the bottom half (i.e. 15-30 cm) of the core.



**Table 2: Correlation matrix of various metals in sediment core**

	<i>Hg</i>	<i>Cd</i>	<i>Pb</i>	<i>Cu</i>	<i>As</i>
Hg	1.00	-	-	-	-
Cd	0.25	1.00	-	-	-
Pb	-0.26	0.20	1.00	-	-
Cu	-0.30	0.27	0.74	1.00	-
<u>As</u>	<u>0.44</u>	<u>0.15</u>	<u>0.10</u>	<u>0.06</u>	<u>1.00</u>

The correlation between As and Hg was much pronounced and relevant at the bottom half (15-30 cm) of the sediment core ( $r = 0.88$ ) (Figure 10). Arsenic and Hg did not correlate at the top half (0-15 cm) of the sediment core.

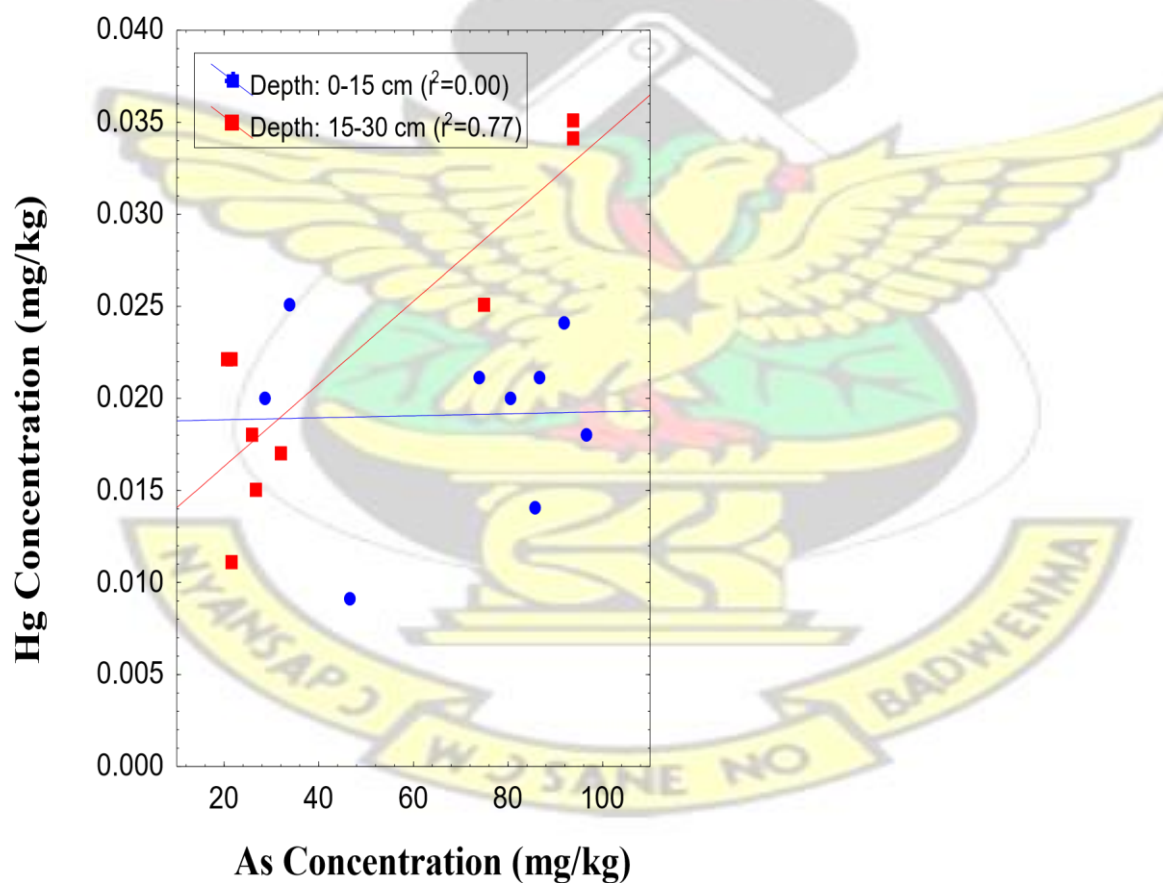


Figure 10: Regression between mercury and arsenic at the top (0-15 cm) and down (15-30 cm) portions of the sediment core.

Lead and copper, on the other hand, strongly correlated at both the top and bottom halves (with approximately,  $r = 0.7$  in each case) of the sediment core (Figure 11).

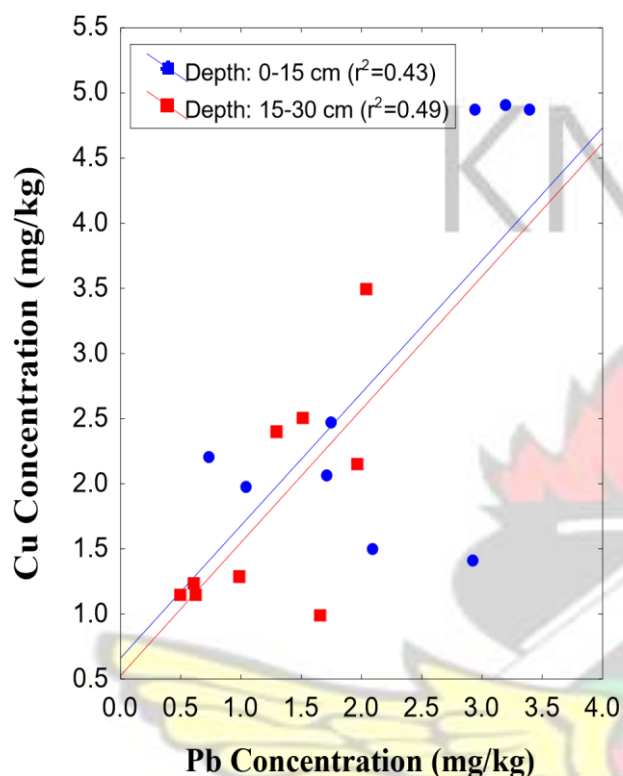


Figure 11: Regression between copper and lead at the top (0-15 cm) and down (15-30 cm) portions of the sediment core. (15-

## CHAPTER FIVE

### DISCUSSION

#### 5.1 SEDIMENT QUALITY

##### 5.1.1 Average Concentration of Heavy Metals in Sediment Core

For each sediment core, the average sediment concentration of heavy metals was estimated and compared among the three studied sites (Figure 4). Among the various metals, Hg had the lowest average concentration, while As had the highest. The average concentration of As (57.78 mg/kg) was three orders greater than that of Hg (0.02 mg/kg) (Figure 6). The general trend in heavy metals concentrations investigated in the study was  $Hg < Cd < Pb < Cu < As$  (Figure 4).

##### 5.1.1.1 Mercury (Hg)

Average Hg concentration was highest at Site 2 whiles the levels at both Sites 1 and 3 were comparable (Figure 5). The differences among the sites were not statistically significant. The relatively high average concentration ( $0.03 \pm 0.003$  mg/kg) (Table A3) of Hg at Site 2 was probably because it received a lot of untreated effluent discharged directly from the illegal mining activity. Even though Hg is banned in Ghana, illicit application of this chemical for gold extraction reportedly existed in Ghana and implicated in water and sediment pollution of local reservoirs (Donkor *et al.*, 2006). Mercury is heavily relied upon for small-scale (illegal) gold extraction in Ghana. For the illegal gold miners, the use of Hg is economical, reliable, and allowed-portable operation for concentrating and extracting gold from low-grade ores. The use of mercury in gold mining by the Artisanal Small Scale Miners constitutes a point source of contamination. Mercury poses a serious threat to human health and a wide-range of

ecological groupings. It has the tendency of weakening one's immune system, life expectancy, government's expenditure on healthcare and subsequently the

productivity of the country's labour force. Mercury accumulated in bottom sediment could be released into the Lake environment through flux exchanges between sediment and overlying water (Jackson and Jackson, 1995; Li, *et al.*, 2009). The recorded average concentration (0.02 mg/kg) of Hg was however, within acceptable guideline value 0.15 mg/kg recommended by the Australian and New Zealand Environment and Conservation Council (ANZECC), (Appendix: Table A4). The present study also confirmed a previous work by Owusu-Boateng and Kumi-Aboagye (2013) that attributed the presence of mercury in sediment of Lake Amponsah to effluent discharged from small-scale mining activities directly into the Lake.

#### **5.1.1.2 Cadmium (Cd)**

The variation in the average concentrations of Cd among the various sites was not statistically significant. Cadmium and mercury are elements that occur naturally at low concentrations in the environment (MCPA, 1999). Cadmium adsorbs strongly to sediments and organic matter. In the present study, a highest value of  $0.36 \pm 0.060$  mg/kg recorded for Cd was observed for Site 3. Unlike Hg and As, Cd recorded a lower average value ( $0.23 \pm 0.036$  mg/kg) at Site 2 compared to other sites (Appendix: Table A3). This suggests no direct anthropogenic inputs from illegal mining activities happening around the Lake (Appendix: Table A2). However, the most likely anthropogenic source of Cd in the Lake sediment is fossil fuel combustion from vehicular movements across the roads close to the Lake and anthropogenic loads from residential areas. The recorded average concentration of Cd (0.29 mg/kg) was below the guideline limit of 1.2 mg/kg recommended by Australian and New Zealand



Environment and Conservation Council (ANZECC) (Appendix: Table A4). In a related study at Akoti and Etwebo mining communities within Bibiani district, Oppong-Kyekyeku in 2011, observed that Cd in sediment was higher than Hg, Pb and As. Comparatively, Cd concentration recorded at Suraw River was clearly, higher than that of the present study.

#### **5.1.1.3 Lead (Pb)**

Of the various sampling location, Site 3 recorded the lowest concentration ( $1.28 \pm 0.167$  mg/kg) of Pb, whereas the highest concentration ( $2.25 \pm 0.465$  mg/kg) was observed at Site1 (Appendix: Table A3). The variation in Pb concentrations among various sites was however not statistically significant. This variation in Pb concentrations is probably due to the presence of major sources of metal pollution, intensive anthropogenic activity and runoff from waste dumpsite (Plate 7) and industrial effluents (from palm-kernel extraction industry) (Appendix: Plate A1) from neighbouring communities around the Lake. The results from this work showed an average Pb concentration of 1.73 mg/kg, which was lower than the limit recommended by Australian and New Zealand Environment and Conservation Council (ANZECC) (47 mg/kg) (Appendix: Table A4). Findings from many studies on sediment samples have reported high concentrations of Pb but the range has been suggested to be between 6.10 - 10.60 mg/kg in mining communities such as Esaase, Tetrem, Gyeninso and Adobewora in Ghana (Agyarko *et al.*, 2014). In comparison, it was found that the average concentration observed for the present work was lower.



Plate 7: Rubbish dump sited close to Lake Amponsah

#### 5.1.1.4 Copper (Cu)

The highest concentration for Cu ( $3.21 \pm 0.62$  mg/kg) was observed for Site 1, while the lowest level ( $1.83 \pm 0.24$  mg/kg) of the metal was detected in Site 3 (Appendix: Table A3). This is probable because Site 3 was further away from the road and again received very little effluent from the waste dumpsite (Plate 7) and the communities around the Lake. There is a slight variation in metal concentration between Sites 2 and 3; nonetheless, the variation in concentration among the three sampling sites was not statistically significant, indicating there are possibly common origins of metal contamination. Copper can be released into the environment by natural sources (Cuzzocrea *et al.*, 2003) and human activities. The presence of copper in the study area is probably due to release from brakes of vehicles that ply the road everyday across the Lake, and discharge of effluent from the waste dumpsite because of improper disposal

of copper wire by the inhabitants around the Lake. Other sources of Cu are runoffs from the agricultural farmlands around the Lake. Evidently, Cu compounds are used as fungicides, algacides, insecticides, wood preservatives and, are added to fertilizers, and likewise as food additives (Abbasi *et al.*, 1998; Eaton, 2005). The comparatively high prevalence of Cu levels in Site 1 could be attributable to its close proximity to the waste dumpsite.

Evidently, Site 1 of the Lake received high amount of domestic effluents and sewage from nearby communities as well as runoff from waste dumpsite through the canal conveying the Amponsah stream that joins the Lake. The average concentration of Cu in the sediment (2.30 mg/kg) was far less than guideline limit recommended by the Australian and New Zealand Environment and Conservation Council (ANZECC) (34 mg/kg) (Appendix: Table A4). The average copper concentration recorded in the present study was far lower than the concentration recorded in the sediments from some mining communities such as; Esaase, Tetrem, Gyeninso and Adobewora which ranged 24.28 - 101.15 mg/kg (Agyarko *et al.*, 2014).

#### **5.1.1.5 Arsenic (As)**

Arsenic showed highest concentrations among all sampling sites compared to the other metals analysed for, in this work, thus, confirming the report by Quarshie *et al.*, (2011) who recounted high levels of arsenic, prevalent in illegal mining (galamsey) areas or regions with history of illegal mining. The highest average concentration ( $72.00 \pm 12.39$  mg/kg) of As was at Site 2 while the lowest average concentration ( $44.50 \pm 11.22$  mg/kg) was observed at Site 3 (Appendix: Table A3). Variation in As concentrations among sites was not statistically significant possibly the source of As contamination may be common among the sites. The measured average concentration of As (57.78 mg/kg)



in the Lake sediment exceeded guidelines value of 20 mg/kg recommended by the Australian and New Zealand Environment and Conservation Council (ANZECC) (Appendix: Table A4).

Geological setting of Bibiani mining area reveals arsenopyrites (FeAsS) as the main gold bearing ores found in the area. Arsenic in (Lake Amponsah) sediment is probably from natural source of gold ore (arsenopyrite) in Bibiani north (Figure 4). The existence of arsenic as an impurity in gold ore (Eisler, 2004) might have contributed to the high contamination of As in the Lake sediment. In general, As was found to be in the highest concentration among the five elements studied (Hg, Cd, Pb, Cu and As) which is consistent with preceding reports on Obuasi as a severely As contaminated area (Kumi-Boateng, 2007; Smedley *et al.*, 1996; Smedley, 1996). In addition, As concentration reported for the present work is within the range 49.68 - 128.60 mg/kg observed for As in mining areas such as Esaase, Tetrem, Gyeninsio and Adobewora in Ghana (Agyarko *et al.*, 2014).

## **5.2 SEDIMENTATION RATE IN LAKE AMPONSAH**

From the results (Appendix: Table A5), the Lake has experienced some level of sedimentation after supposedly fifty-four (54) years in existence. The average depth of the Lake at the time of construction was 400 cm but has reduced to approximately 305 cm as a result of factors such as erosion and siltation. The wastewater from the residential areas close to the Lake, runoff from agricultural farmlands and effluent discharged from local industrial activities such as small-scale mining and palm-kernel extraction facility sited around the water body, might have carried substantial amount of sediment load to the Lake. The portion of the Lake that receives effluent from the



Amponsah stream (Site 1) was the worst hit area. Weeds covered this part of the Lake (Appendix: Plate A2), which was adjacent a waste dumpsite. Domestic and industrial solid wastes from the dumpsite (Plate 7) probably were washed via runoffs into the water body during rainfall.

### 5.3 CORRELATION OF HEAVY METALS

When pollutants correlate, it presupposes that their sources of contamination might be similar. From the correlation matrix, it is evident that arsenic correlated positively with mercury ( $r = 0.44$ ) (Table 2), which suggests similar source factors for these two metals. It is significant that these two metals correlated. It probably reflected activity involving the use of mercury for the extraction of gold from arsenopyrite bearing gold ore (Valdes *et al.*, 2005; Quarshie *et al.*, 2011). Figure 10 elucidated further that the correlation between Hg and As was much pronounced in the bottom layers of the sediment core ( $r = 0.88$ ), with no significant correlation registered in the top sediments. It presupposes a historically relevant association between these two metals in the Lake Amponsah watershed, considering that historically Hg was applied to extract gold in that region. Strong positive correlations was also observed between Cu and Pb ( $r = 0.74$ ) (Table 2). The strong correlation recorded between the two metals was observed in both the top and bottom fractions of the sediment core (0-15 cm and 15-30 cm) ( $r \approx 0.7$  in each case) (Figure 11). The sources of these two metals were presumably similar. Their inputs into the Lake may be via runoffs from agricultural activities happening around Lake Amponsah (Appendix: Table A3).

### 5.4 DEPTH PROFILE OF HEAVY METALS IN SEDIMENT

Depth profiles for Cu, As and Pb indicated relatively higher concentrations at the top sediment than in the bottom sediment, which may indicate increased impacts from recent human activities ranging from agricultural practices, exploitation of natural resources and leachate from waste dumpsite (Ajayi and Osibanjo, 1981). Mercury and cadmium did not follow any particular trend; their depth profile was variable and perhaps attributable to various anthropogenic occurrences, which finds its way into the Lake via the canal carrying the Amponsah stream and effluent from illegal mining activity.

Generally, the sampling Site 3 recorded the least contamination from heavy metals probable because it was further away from the illegal mining site as well as received no direct domestic effluent from nearby settlement and other major human activities along the bank of the Lake. The highest contamination from heavy metals was observed at Site 1, which received direct domestic effluent from the residential areas and leachate from a waste dumpsite.

## **CHAPTER SIX**

### **CONCLUSION AND RECOMMENDATION**

#### **6.1 CONCLUSION**

This study evaluated the vertical profile of Hg, Cd, Pb, Cu and As in the sediment core and provided a perspective on source factors of these pollutants in Lake Amponsah as well as the sedimentation rate in the Lake. Trends in heavy metals profile in the sediments revealed variations in the distribution of the metals, with respect to the top sediment and the bottom sediment. Most of the metals (Pb, Cu and As) decreased in

concentration relatively with depth, which connotes increased contamination from current anthropogenic activities such as effluent discharge from small-scale or artisanal mining operations, domestic waste discharged from residential areas close to the Lake and runoffs from agricultural farmlands around the Lake.

The investigation again revealed that the source of mercury in Lake Amponsah could be direct Hg input source through activities of artisanal gold miners operating around the Lake over the years. The exceptionally high concentration of As could be attributable to the geology of Bibiani in general which is known to consist of arsenopyrite, which contains arsenic and the activities of small-scale miners around the Lake Amponsah. In spite of the ongoing small-scale mining activities happening around the Lake, the correlation between Hg and As was more pronounced in deeper sediments of the Lake, which indicated a highly common source of contamination in the past.

Finally, it was estimated that Lake Amponsah was undergoing sedimentation at an average rate of 1.76 cm/year.

## **6.2 RECOMMENDATIONS**

The following recommendations were suggested base on the outcome of the research:

- Further study should be pursued regarding dating of the various layers of the sediment core in order to establish more precisely the historical record of heavy metals input into the Lake sediment.
- Contamination from organic compounds should also be studied to help understand the extent of general pollution in Lake Amponsah.

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## APPENDIX

**Table A1:**

Raw data of heavy metal concentrations of mercury, cadmium, lead, copper and arsenic in lake sediment at three sampling sites in Lake Amponsah

Sample	Hg	Cd	Pb	Cu	As
Code	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Site1 A1	0.021	0.74	3.20	4.92	87.00
Site1 B1	0.018	0.18	3.44	4.86	97.00

Site1 C1	0.020	0.31	2.96	3.71	79.00
Site1 D1	0.025	0.09	0.61	1.23	75.00
Site1 E1	0.018	0.21	1.98	2.14	26.00
Site1 F1	0.015	0.21	1.30	2.40	27.00
Site2 A2	0.025	0.16	2.94	1.40	34.00
Site2 B2	0.024	0.37	2.10	1.49	92.00
Site2 C2	0.014	0.30	1.75	2.46	86.00
Site2 D2	0.017	0.20	2.05	3.49	32.00
Site2 E2	0.034	0.15	0.51	1.13	94.00
Site2 F2	0.035	0.18	0.64	1.13	94.00
Site3 A3	0.009	0.25	1.72	2.05	47.00
Site3 B3	0.021	0.51	1.05	1.96	74.00
Site3 C3	0.020	0.41	0.74	2.19	81.00
Site3 D3	0.022	0.37	1.67	0.98	22.00
Site3 E3	0.022	0.12	1.53	2.50	21.00
<u>Site3 F3</u>	<u>0.011</u>	<u>0.47</u>	<u>0.99</u>	<u>1.27</u>	<u>22.00</u>

Site 1 (A1 -F1) - represent segments cores in sediment at Site 1; Site 2 (A2-F2) – represent segments core in sediment at Site 2. Site 3 (A3-F3) – represent segments cores in sediment at Site 3

**Table A2:**

Summary of average concentration of heavy metals in Lake Amponsah

Station Codes	Mean Concentration (mg/kg)				
	Hg	Cd	Pb	Cu	As
Site 1	0.02	0.30	2.25	3.21	56.83
Site 2	0.03	0.23	1.67	1.85	72.00
Site 3	0.02	0.36	1.28	1.83	44.50
<b><u>Mean</u></b>	<b><u>0.02</u></b>	<b><u>0.30</u></b>	<b><u>1.73</u></b>	<b><u>2.30</u></b>	<b><u>57.78</u></b>



**Table A3:**

Mean  $\pm$  standard error concentration (mg/kg) in Lake sediment

Station Codes	Mean Concentration (mg/kg)				
	Hg	Cd	Pb	Cu	As
Site 1	0.02 $\pm$ 0.001	0.30 $\pm$ 0.094	2.25 $\pm$ 0.465	3.21 $\pm$ 0.622	56.83 $\pm$ 13.502
Site 2	0.03 $\pm$ 0.003	0.23 $\pm$ 0.036	1.67 $\pm$ 0.381	1.85 $\pm$ 0.384	72.00 $\pm$ 12.394
Site 3	0.02 $\pm$ 0.002	0.36 $\pm$ 0.060	1.28 $\pm$ 0.167	1.83 $\pm$ 0.237	44.50 $\pm$ 11.215

**Table A4:**

Comparison of heavy metal (Hg, Cd, Pb, Cu, As) concentrations in sediment of Lake Amponsah with ANZECC (Burton, 2002) sediment quality guidelines.

Concentration (mg/kg)		
METAL	ANZECC	AVERAGE VALUES FROM CURRENT STUDY
Hg	0.15	0.02
Cd	1.2	0.29
Pb	47	1.73
Cu	34	2.30
As	20	57.78

Australian and New Zealand Environment and Conservation Council (ANZECC) (Burton, 2002)

### Average depth readings of Lake Amponsah

<u>POINTS READINGS (FT)</u>		<u>POINTS READINGS (FT)</u>	
PT 1	4.1	PT 26	10.8
PT 2	5.5	PT 27	11.2
PT 3	5.9	PT 28	11.5
PT 4	6.4	PT 29	12.1
PT 5	7.0	PT 30	13.0
PT 6	6.6	PT 31	13.3
PT 7	5.9	PT 32	13.5
PT 8	7.1	PT 33	14.2
PT 9	8.2	PT 34	14.1
PT 10	8.4	PT 35	14.0
PT 11	8.5	PT 36	13.9
PT 12	8.2	PT 37	13.6
PT 13	7.4	PT 38	13.2
PT 14	5.6	PT 39	12.2
PT 15	7.1	PT 40	8.1
PT 16	4.6	PT 41	8.0
PT 17	9.0	PT 42	13.1

PT 18	10.2	PT 43	13.5
PT 19	10.3	PT 44	13.0
PT 20	10.4	PT 45	11.6
PT 21	10.5	PT 46	10.0
PT 22	10.6	PT 47	11.6
PT 23	10.4	PT 48	12.6
PT 24	10.0	PT 49	14.0
PT 25	10.5	PT 50	13.8

AVERAGE DEPTH

10.00731707

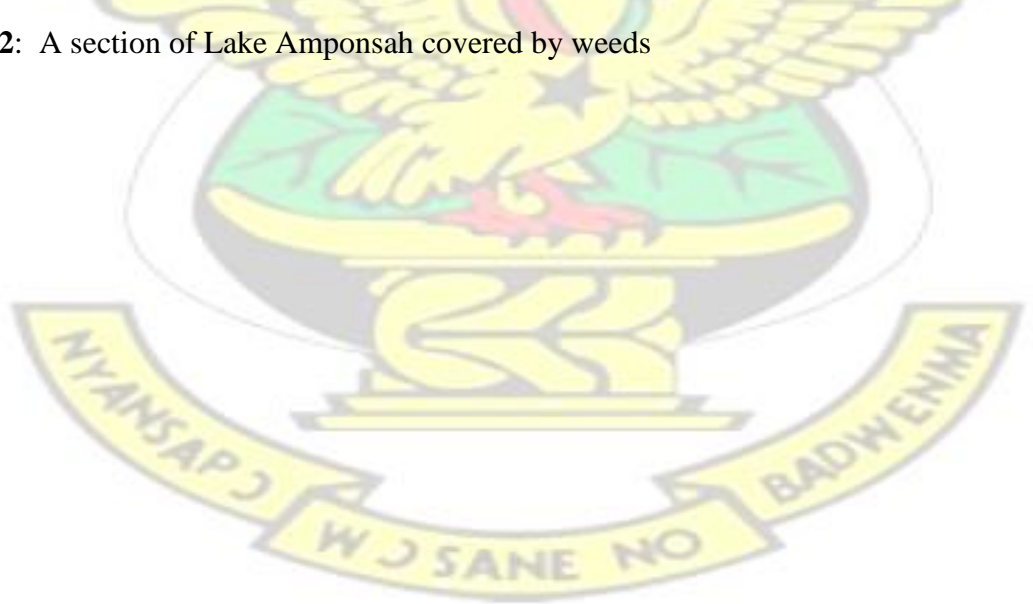


**Plate A1:** Palm-kernel Extraction Industry sited around Lake Amponsah





**Plate A2:** A section of Lake Amponsah covered by weeds







**Plate A3:** Small-scale (Galamsey) site around Lake Amponsah





**Plate A4:** Using a depth sounder device (Hondex Digital Depth Sounder) to determine current depth in Lake Amponsah



**Plate A5:** PVC corer of diameter 0.002 m and height 3 m