

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

DEPARTMENT OF THEORETICAL AND APPLIED BIOLOGY

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**LEVELS OF HEAVY METALS IN WATER, FISH AND
SEDIMENTS IN PONDS AT YALE, A MINING COMMUNITY IN THE
TALENSI DISTRICT OF UPPER EAST REGION OF GHANA.**

**A THESIS SUBMITTED TO THE DEPARTMENT OF THEORETICAL
AND APPLIED BIOLOGY IN PARTIAL FULFILLMENT OF THE
REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE IN
ENVIRONMENTAL SCIENCE**

BY

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DECLARATION

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

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ABSTRACT

Unlike other Small scale gold mining (SSGM) and Artisanal gold mining (AGM) sites (Obuasi, Prestea, Tarkwa, Dunkwa-on-offin) found in Ghana, the severity of heavy metal contamination in water, fish and sediments at Yale has not been thoroughly examined to ascertain the extent of metal contamination, as well as the biogeochemical fate of released heavy metals.

Heavy metal (Pb, Fe, Mn, Hg and As) concentration in water, sediments and fish was analysed from a pond at Yale.

The pond at Yale is the main source of water for household and farming purposes in the town and surrounding communities.

In water Iron recorded high concentrations in both towns reading between 1.703mg/l and 1.760mg/l at Yale –Tarkwa and Yale-Obuasi respectively. Other heavy metals readings were Arsenic 0.084, Manganese 0.035, Lead 0.697, Mercury 0.027 and Arsenic 0.171, Manganese 0.060, Lead 0.062, Mercury 0.014mg/l for Yale-Tarkwa and Yale-Obuasi respectively. All the metals except Mn in water were above WHO standards for drinking water. Heavy metals levels in fish were all above WHO standards.

In sediment Arsenic recorded higher value than Iron and the rest of the metals tested for. The activities of small scale and artisanal gold mining is affecting the environment in so many ways, polluting the water bodies and causing land degradation. The concentration of heavy metals in water shows that the water is not safe for drinking. Measures need to be put in place to reduce these activities.

TABLE OF CONTENTS

DECLARATION	ii
ABSTRACT	iii
TABLE OF CONTENT	iv-vii
LIST OF TABLES.....	viii
LIST OF FIGURES.....	ix
LIST OF ABBREVIATIONS.....	x
DEDICATION.....	xi
ACKNOWLEDGEMENT	xii
CHAPTER ONE	1
1.1 Background to the Study	1
1.2 .1 Effects of heavy metals released during gold mining on humans.....	4
1.2.2 Mining and aquatic ecosystems	5
1.2.3 Malaria, Deforestation and Mining	5
1.3 Research Problem	6
1.4 Objective of the Study	6
1.5 Specific objectives.....	7
1.6 Justification	7
CHAPTER TWO	9
2.0 LITERATURE REVIEW	9
2.1 Brief history of gold mining in Ghana	9
2.2 Artisanal and Small- scale Gold mining (ASGM) in Ghana	10

2.3 Various Definitions of Artisanal and Small scale Gold Mining.....	12
2.4 Mining and processing of gold at small-scale and artisanal gold mining sites	14
2.5 Environmental Impact of Small scale Mining.....	17
2.6 General Properties of Heavy Metals	23
2.6.1. Sources of Heavy Metals (Fe, Mn, Pb, Hg and As).....	23
2.6.1.1 Mercury	23
2.6.1.2 Lead	25
2.6.1.3 Iron	26
2.6.1.4 Arsenic	27
2.6.1.5 Manganese	28
2.6.2 Effect of Heavy Metals	28
2.6.2.1. Mercury	29
2.6.2.2 Lead	31
2.6.2.3 Iron	31
2.6.2.4 Arsenic	32
2.6.2.5 Manganese	33
CHAPTER THREE	33
MATERIALS AND METHODS	33
3.1 Study area	34

3.1.1 Geographical location	33
3.1.2 Rainfall and Vegetation	34
3.1.3 Climate	35
3.1.4 Topology and Geology	35
3.1.5 Economy	36
3.2 Sampling	37
3.2.1 Sampling Containers	37
3.2.2 Sample Collection	37
3.2.2.1 Fish	40
3.2.2.2 Sediments	40
3.2.2.3 Water	40
3.2.3 Sample Preparation	41
3.2.3.1 Fish	41
3.2.3.2 Sediment	42
3.3 Sample Analysis	42
3.3.1 Determination of total As, Hg, Fe, Mn and Pb	42
3.3.1.1 Digestion	44
3.3.1.2 Measurement of total Fe, Mn and Pb using the Flame Atomic Absorption Spectrometer	46

3.3.1.3 Determination of As by HG-AAS	48
3.3.1.4 Determination of Hg by CV-AAS using sodium borohydride as reducing agent	51
DATA ANALYSIS.....	54
CHAPTER FOUR	55
4.0 RESULTS	55
4.1 Water	55
4.2 Sediments	57
4.3 Fish	58
CHAPTER FIVE	62
DISCUSSION	62
CHAPTER SIX.....	71
CONCLUSION AND RECOMMENDATION.....	71
CONCLUSION.....	71
RECOMMENDATION.....	72
REFERENCES	73
APPENDIX I.....	85
APPENDIX II.....	89
LIST OF TABLES	
Table 1: Description of sample collection sites.....	39
Table 2: Microwave digestion programme used for digestion of water samples.....	45
Table 3: FAAS conditions used for determination of Fe, Mn, and Pb.....	47

Table 4: Calibration of atomic absorption spectrometer.....	47
Table 5: Heavy metal concentration (mg/l) in water at Obuasi and Yale-Tarkwa.....	86
Table 6: Heavy metal concentration (mg/kg) in Sediment at Obuasi and Yale-Tarkwa.....	87
Table 7: Heavy metal concentration (mg/kg) in the muscles of fish at Obuasi and Yale-Tarkwa.....	87
Table 8: Heavy metal concentration (mg/kg) in the gills of fish Yale-Obuasi and Yale-Tarkwa.....	88
Table 9: Heavy metal concentration (mg/kg) in the head of fish at Yale Obuasi and Yale Tarkwa.....	88

LIST OF FIGURES

Figure 1: Artisanal gold miner washing gold obtained using the gravity method	15
Figure 2: Methods used by artisanal mining operators to extract gold	Figure 3: 16
Schematic flow diagram of the essential processes of gold extraction from alluvial gold deposits and gold-bearing river sediments (source: Field observation)	19
Figure 4: Map of the study area	33
Figure 5: Heavy metal concentration in water at Yale-Obuasi and Yale-Tarkwa	55
Figure 6: Operating platform at Yale	56
Figure 7: Open pits filled with water which serves as breeding ground for mosquitoes	56
Figure 8: Felt mats washing of suction gravel, mud, and rocks in Pond at Yale	57
Figure 9: Heavy metal concentration in sediment at Yale-Obuasi and Yale- Tarkwa	57
Figure10: Heavy metals concentration in muscles of fish at Yale-Tarkwa and Yale-Obuasi	58

Figure 11: Heavy metal concentration in head of fish

59

Figure 12: Heavy metal concentration in gills of fish

60

LIST OF ABBREVIATIONS



AAS	Atomic Absorption Spectrophotometer
ASGM	Artisanal and Small- Scale Gold Mining
ATSDR	Agency for Toxic Substances and Disease Registry
ANOVA	Analysis of Variance
CVAAS	Cold vapour atomic absorption spectrometry
ECA	Economic Commission for Africa
FAAS	Flame atomic absorption spectrometry
ILO	International Labour Organisation
LGDP	Local gross domestic product
WHO	World Health Organisation
UNIDO	United Nations International Development Organization
PNDC	Provisional National Defence Council Law
HG-AAS	Hydride generation atomic absorption spectrometry

DEDICATION

I dedicate this work to God, the Almighty, for His divine inspiration and guidance.

Without Him, this work could not have been a success.

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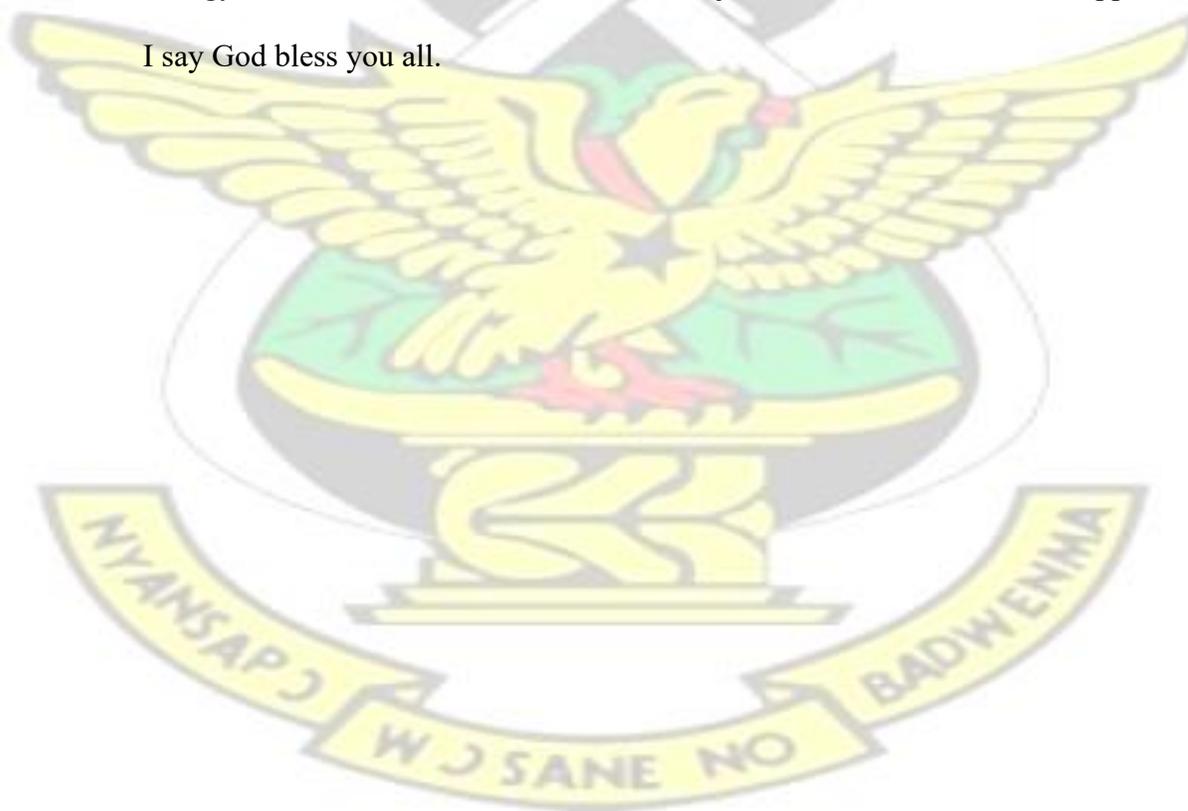
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CHAPTER ONE

1. INTRODUCTION

1.1 Background to the study

Gold mining accounts for a large proportion of foreign exchange earned by Ghana. Extensive small scale and artisanal gold mining play an important economic role and provides employment and livelihood for a large number of people. The economic gains are however, achieved at a great environmental cost. Mercury (Hg), the main chemical used for the gold extraction is widely considered to be among the highest priority pollutant which is of continuing concern globally. Concerns about mercury and other heavy metals released during the gold extraction process are based on their effect on the aquatic ecosystem and human health.

Small scale gold mining (SSGM) and Artisanal gold mining (AGM), popularly called ‘Galamsey’ has been a vibrant indigenous industry for many centuries in Ghana. Gold mining in the Talensi district date back to the colonial era, it was however, put to a stop in the 1930’s for political reasons (Agyemang, 2010). After the liberalization of small-scale mining in 1989, [following the enactment of the small-scale gold mining law (PNDC law 218 of 1989) and the Mercury law (PNDC law 217 of 1989)], the Talensi district have witnessed a rampant influx of migrants (Talensi-Nabdam District Report, 2010). Gold mining in the Talensi district is characterized by both small-scale and artisanal miners (Awumbila and Tsikata, 2010; Agyemang, 2010). There are only five registered concessions in the Talensi

and Nabdam areas (Hilson, 2008). The —Accral registered concession operated by Accra Small-scale Mining Group, —Kejetial operated by Unique

Mining Group, —Obuasill operated by Obuasi Mining Group, —Tarkwal and —Bantamal concessions also run by Nontaba and Yen YaYa Small-scale Mining Groups respectively (Hilson, 2008). These areas are also characterized by two main mining methods, the underground and surface mining.

Small-scale gold mining refers to the winning of gold dust by people whose activities are known to and overseen by government, whereas Artisanal gold mining refers to the winning of gold dust by people who do not have the sanction of the government (Adotey, 2003).

In Ghana, most of the gold bearing ores are known to be pyrites (FeS) and arsenopyrites, (FeSAs_2) (Kesse, 1985). Metals like cadmium, chromium, copper, manganese, arsenic, iron and zinc are natural components of gold-bearing sulphide and arsenopyrites ores (Kesse, 1985). During the gold recovery process, the miners use nitric acid (HNO_3). The miners have no system in place to recover the acid used; consequently, the acid used is released into the environment. In the environment, the acid leaches through rock piles and liberate metals, such as cadmium, lead, arsenic, copper, chromium, manganese, iron and zinc. The acid again leaches the heavy metals from the tailings which are released into water bodies during run-offs (source: field observation).

During processing of the ores for the gold metal, the separation processes does not extract all the minerals present. The tailings that accumulate in the environment

therefore contain quantities of heavy metals, as well as residues of the chemicals used for the extraction. The finely ground material from processing makes contaminants such as arsenic, cadmium, chromium, copper, iron and zinc, bound up in solid rock accessible to water. The tailings are released directly into rivers and this introduces large amounts of suspended solids and contaminants directly into aquatic habitats.

The miners add metallic mercury to the impure gold dust obtained to form a mercury-gold amalgam. Though the optimal mercury to gold ratio (Hg:Au) is about 1(^{v/v}), the miners add more mercury in order to be sure that they have amalgamated all the available gold (Essah, 2000). ‘Raw gold’ is recovered through the process of amalgam roasting in open fire.

The small-scale and artisanal gold miners have no system for recovering the mercury used; therefore all the mercury is released into the environment. Gravimetric material flow analysis studies show that between 20 to 30% of the mercury introduced is lost to soil tailings, stream and river sediment, and water bodies close to the processing sites, and between 70 to 80% of the mercury is lost to the atmosphere during the processing (van Straaten, 2000). Loss of mercury to the environment occurs during the process of amalgam roasting to recover the ‘raw gold’ or when the gold is refined by its buyer, in order to remove residual mercury (van Straaten, 2000).

The miners have refused to use simple mercury distillation retorts introduced by the Minerals Commission of Ghana, in collaboration with United Nations

International Development Organization (UNIDO), to recycle mercury safely by distilling the amalgam. The reasons vary from suspicion that some gold is lost in the distilled mercury, to resistance of gold buyers to purchase retorted amalgam (which tend to be darker than that heated in air), to traditional and indifference to mercury cast (Viega, 1997). The problem of mercury poisoning due to the activities of small-scale and artisanal gold mining compelled UNIDO, to include small-scale and artisanal gold mining, and mercury pollution among its priority programmes in the year 2000.

There are existing environmental impact regulatory procedures, which the miners are required to comply with. The provisions of the mercury and small-scale gold mining laws of 1989, basically require that good mining practices be observed and due regard paid to environmental protection. However, this has not been adhered to by the miners.

1.2 Effects of heavy metals released during gold mining on humans.

Heavy metals are toxic to living organisms because of their tendency to accumulate in selected tissues. Moreover, their presence is a causative agent of various sorts of disorders, including neuro-, nephro-, carcino-, terato-, and immunological (Zukowska and Biziuk, 2008).

The toxicity of heavy metals for humans is mainly caused by their persistence in the environment and hinged strongly upon the chemical form in which they are ingested (Zukowska and Biziuk, 2008). Several body organs could be affected by heavy metals, but tissues such as the kidney and liver and the central nervous system appear to be especially sensitive (Apostoli, 2002).

1.2.1 Mining and aquatic ecosystems

One of the most visually striking consequences of gold mining is the change that it has on aquatic ecosystems. All mining techniques used, disturb river and stream sediments, increase siltation rates, and may lead to radical changes in aquatic life. Mining operators can pollute streams and rivers through the uncontrolled run-off of tailings. Most far-reaching in its effects, however, is the widespread disturbance of river and stream sediment. The level of suspended particles increases to the point where streams and rivers have their colour altered to a muddy brown (see Fig. 1.1) and there are drastic declines in fish populations.

1.2.2 Malaria, Deforestation and Mining

The excavations made by miners become ideal mosquito breeding grounds during the rainy season. This has resulted in the resurgence of malaria in these smallscale gold mining areas. The mobility of infected miners has aided the spread of the malaria parasites.

—Galamsey| make a significant contribution to the levels of deforestation in gold mining communities. The miners regularly clear vegetation if they are following a vein. Some deforestation occurs as a result of the cutting of forest paths by miners to facilitate mining operations on the forested banks of a pond.

1.3 Research Problem

Unlike other SSM and AGM sites (Obuasi, Prestea, Tarkwa, Dunkwa-on-offin) found in Ghana, the severity of heavy metal contamination in water, fish and sediments at Yale has not been thoroughly examined to ascertain the extent of metal contamination, as well as the biogeochemical fate of released heavy metals. In view of the continuing over-exploitation of the environment by the activities of small-scale and artisanal gold mining, contamination of water bodies in Yale and its catchment area may become critical; hence there is a need to acquire baseline data. The data generated shall be used as a scientific basis for further and future monitoring and assessment. Furthermore, the data generated will provide a greatly increased understanding of heavy metal contamination at gold mining sites within the Talensi district, for governmental agencies, environmental organizations (nongovernmental) and the general public.

1.4 Objective of the study

The study endeavors to assess the extent of heavy metal [mercury (Hg), arsenic (As), lead (Pb), manganese (Mn) and iron (Fe)] contamination of sediments, fish and water from gold mining ponds at Yale in the Talensi district of the Upper East Region, due to the activities of small-scale and artisanal gold miners.

1.5 Specific Objectives

1. To measure levels of heavy metals in water at Yale.
2. To measure levels of heavy metals in fish at Yale.
3. To measure levels of heavy metals in sediment at Yale.

1.6 Justification

Water and sediments are commonly used as indicators for the state of pollution of aquatic ecosystem (Aremu *et al.*, 2007), and provide a constant source of food for a number of aquatic organisms including fishes. Aquatic sediments consist of several different geochemical phases that act as reservoirs of heavy metals in the environment (Kheboian and Bauer, 1987).

Deterioration of water quality can have severe impacts on aquatic life and also on the lives of humans living either close or far from the discharge point, especially humans who use these waters for drinking and other domestic activities (Hollaway, 1997). Some pollutants reach aquatic environments through both direct discharge and transported into the waterways or indirectly through deposition from the air (van Straaten, 2000). This makes the analysis of the water in water bodies within the catchment area of mining communities imperative.

Fish is considered as one of the most significant indicators in freshwater systems for the estimation of metal pollution level (Rashed, 2001). The commercial and edible species have been widely investigated in order to check for those hazardous to human health (Begüm *et al.*, 2005).

Fishes accumulate heavy metals directly from water and through feeding processes and as a result, record high levels of heavy metals. The vulnerability of aquatic ecosystems to heavy metal contamination has been recognized as a serious pollution problem (Molina, 2011). The choice of mudfish (*Clarias gariepinus*) for this study is based on the availability, being a major source of protein for the local dwellers and the fact that, it feeds on sediment among other dietary sources. The ponds are main source of drinking water for humans and animals in the area. It is also used for irrigation purpose. However there are small- scale mining activities in and around the pond. There is therefore the need to ascertain the extent of pollution and how safe the water is for domestic purposes



CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 BRIEF HISTORY OF GOLD MINING IN GHANA

The Ghanaian small-scale mining industry is well over 2,000 years old. Vestiges of alluvial gold extraction and winning activities have been found that date as far back as the sixth century, and there is a wealth of evidence indicating that precious metals recovered from regional artisan activities were attracting Arab traders to certain areas of the country as early as the 7th and 8th centuries AD (Hilson, 2001). In fact, it was the rich gold deposits of the Western Sahara that were largely responsible for the wealth and strength of large ancient Ghanaian empires and cultures (Botchway, 1995), and by the 15th and 16th centuries, at the peak of European colonial exploration, Ghana was fittingly labeled the _Gold Coast (Hilson, 2001).

Small scale mining is an activity that is increasingly gaining momentum in Africa. It is largely practiced in rural areas by artisans who lack the requisite education, training, management skills and essential equipment (ECA, 2002).

Small-scale mining in Ghana, as in most developing countries, was for decades treated as an informal industrial sector, employing thousands of people but featuring largely rudimentary, unmonitored and uncontrolled practices. Until the 1980s, small-scale mining activities in Ghana remained largely unregulated and received little, if any, support from governmental bodies. This, however, changed with the implementation of the national Economic Recovery Plan (ERP), which, following years of careful planning, was finally launched in the mid-1980s. In a desperate move to revitalize a stagnating economy, the then Provincial National Defence

Council (PRDC) government consulted authorities from both the World Bank and International Monetary Fund (IMF) to assist in the drafting of national economic plan and policies. (Hilson, 2001).

In Ghana small-scale gold mining has contributed immensely to the national economy: between 1989, when it was officially legalised in the country, through to 2008, it accounted for the production over three million ounces of gold. This production accounted for over US\$500 million; the sector currently accounts for 16% of national gold output (Anon, 2009; Cleland, 2008). The rise in production in the sector has also resulted in increased use of mercury.

2.2 Artisanal and Small- scale Gold mining (ASGM) in Ghana

An artisanal miner or small-scale miner, often referred to as —*galamsey*,¹ in Ghana, are a group of people who are not officially employed by a mining company, but rather work independently, mining or panning for gold using their own resources. The name is derived from the English phrase —gather them and sell.¹ Small-scale mining includes enterprises or individuals that employ workers for mining, but generally working with hand tools.

According to Hilson (2001), no precise number of small-scale mining employment figures can be found for Ghana, although it is estimated that some 200,000 were involved directly in the extraction of gold and diamonds (Appiah, 1998), the great majority of which were *galamsey* operators.

The number of *galamseys* in Ghana is unknown, but it is believed that all people engaged in it have high rates of accidents and are exposed to mercury poisoning

from their crude processing methods. Many women are among the workers, acting mostly as porters for the miners.

In some cases, galamseys are the first to discover and work on extensive gold deposits before mining companies find out and take over. Galamsey workings are an indicator of the presence of gold.

Globally, an estimated 20 million people engage in artisanal mining, with nearly one-quarter of the world's gold output originating from small-scale mines. Most of these, roughly, one million independent miners operate illegally along the fringes of mining company lands where gold deposits are known. Despite the backbreaking work and dangerous conditions, the average miner can earn more than the national average, so mining is often viewed as attractive employment. Overall, mining is a huge part of foreign exports in Ghana, contributing nearly forty percent of the country's export revenue. Even though most work illegally in the shadows with constant threat of arrest, the galamsey continue to grow.

Artisanal mining can include activities as simple as panning for gold in rivers, to as complex as development of underground workings and small-scale processing plant.

They mostly operate in the southern part of the country where there are substantial reserves of gold deposits, within the environs of the larger mining companies. As a group, they are economically disadvantaged; galamsey settlements are usually poorer than neighboring agricultural villages.

2.3 Various Definitions of Artisanal and Small scale Gold Mining.

There are currently no universal definitions of artisanal or small-scale mining.

The definition of artisanal small scale mining varies from country to country (ECA, 2002).

Siduduziwe (2012), however, defines artisanal small scale mining as an activity that encompasses small, medium, informal, legal and illegal miners who use rudimentary methods and processes to extract mineral resources. These miners are unskilled, underequipped and not knowledgeable and have little appreciation of the environment.

The Southern African Development Community (SADC) Mining Co-ordinating Unit defined artisanal and small-scale mining operations by dividing them into three categories (Taupitz and Malago, 1993)

Micro-scale mining or manual mining with simple tools without using mechanical energy;

- Manual mining, well organized, using some mechanical energy and plant with required investment between \$10,000 and \$100,000; and
- Industrial small-scale mining or small mines using modern, adapted technology and with required investment of \$200,000 to \$3 million.

The world Bank defines artisanal mining as —a type of manual, low technology mining conducted on a small scale, predominantly in rural areas of the developing world (World Bank, 1995).

The International Labour Organization (ILO) contends that small-scale mining means different things to different people. To some, it is dirty, dangerous, and

disruptive and should be discouraged. To others, it is profitable and productive, or is simply the only way out of poverty (ECA, 2002).

According to the United Nations it uses the volume of material mined to establish the boundary between small- and large-scale mining. This boundary was set at 50,000 tons of ore per annum for underground mines and 100,000 tons per annum for open pits (Barnea, 1978).

In Ghana small-scale gold mining is defined as mining by any method not involving substantial expenditure by an individual or group of persons not exceeding nine in number or by a co-operative society made up of ten or more persons (Aryee *et al.*, 2003). Also, according to Leilanie (2012), small scale mining is a single unit mining operation with an annual production of unprocessed material of 50,000 tons or less. For the purposes of this research, such mines are individual enterprises or small family owned companies not affiliated to multinational companies as well as gold panners.

2.4 Mining and processing of gold at small-scale and artisanal gold mining sites

Generally the galamseys can dig only to a limited depth, far shallower and smaller than commercial mining companies. Under current Ghana law, it is illegal for

galamseys to dig on land granted to mining companies as concessions or licenses. Most galamseys find gold in free metallic dust form or they process oxide or sulphide gold ore using liquid mercury.

Alluvial gold is mixed with the sand and gravel of rivers, streams and lakes. Running water washes it from upstream and deposits it in the sand. The gold is usually in the form of fine grains or small nuggets. Galamsey operators mine gold from gold-bearing rocks through shallow underground mining in abandoned pits in industrial mines, and also through surface mining of alluvial gold deposits and gold-bearing river sediments. At Yale, the galamseys mine gold from gold-bearing ponds sediments and gold-bearing rocks.

The miners dig several meters down the earth using pick-axe and shovel. Pebbles and sand suspected to contain gold particles are collected, followed by hand sorting of undesirable pebbles and other unwanted materials. The residual ore obtained is mixed thoroughly with water (Pulp preparation).

The mixture is allowed to gently flow down an inclined 'sluice board' covered with hemp tissue or jute sack. As the mixture flows down the board, gold particles are trapped on the sack by the hand washing with water in a pan.

Further hand washing with water to separate the gold particles from the small amount of sand trapped together with the gold on the jute sack is done in a rubber container (the container is made of used inner tube of a car tyre). Liquid mercury is added progressively and in excess to the gold particles and hand-mixed thoroughly to form a homogenous Hg-Au amalgam (Fig. 1).



Figure 1: Artisanal gold miner washing gold obtained using the gravity method

The amalgam is wrapped in a piece of cloth and squeezed to eliminate residual water and unused mercury. To ensure that the gold obtained is of good quality, the galamseys expose the amalgam to piece of bar magnet, to attract iron and platinum metals. The amalgam is then placed in opened metallic containers. The containers are placed on opened fire to vaporize the mercury, leaving the raw gold. On the other hand, if the gold is mined from rocks, then it goes through the following steps.

The hard rock sample is passed through primary crushing in a hammer mill, followed by dry grinding in a disc mill.

The milled sample is sluiced and the rougher concentrate collected. After several batches of the material had been sluiced, the rougher concentrate was cleaned in a pan in order to estimate the free gold content (Amankwah *et al.*, 2010).

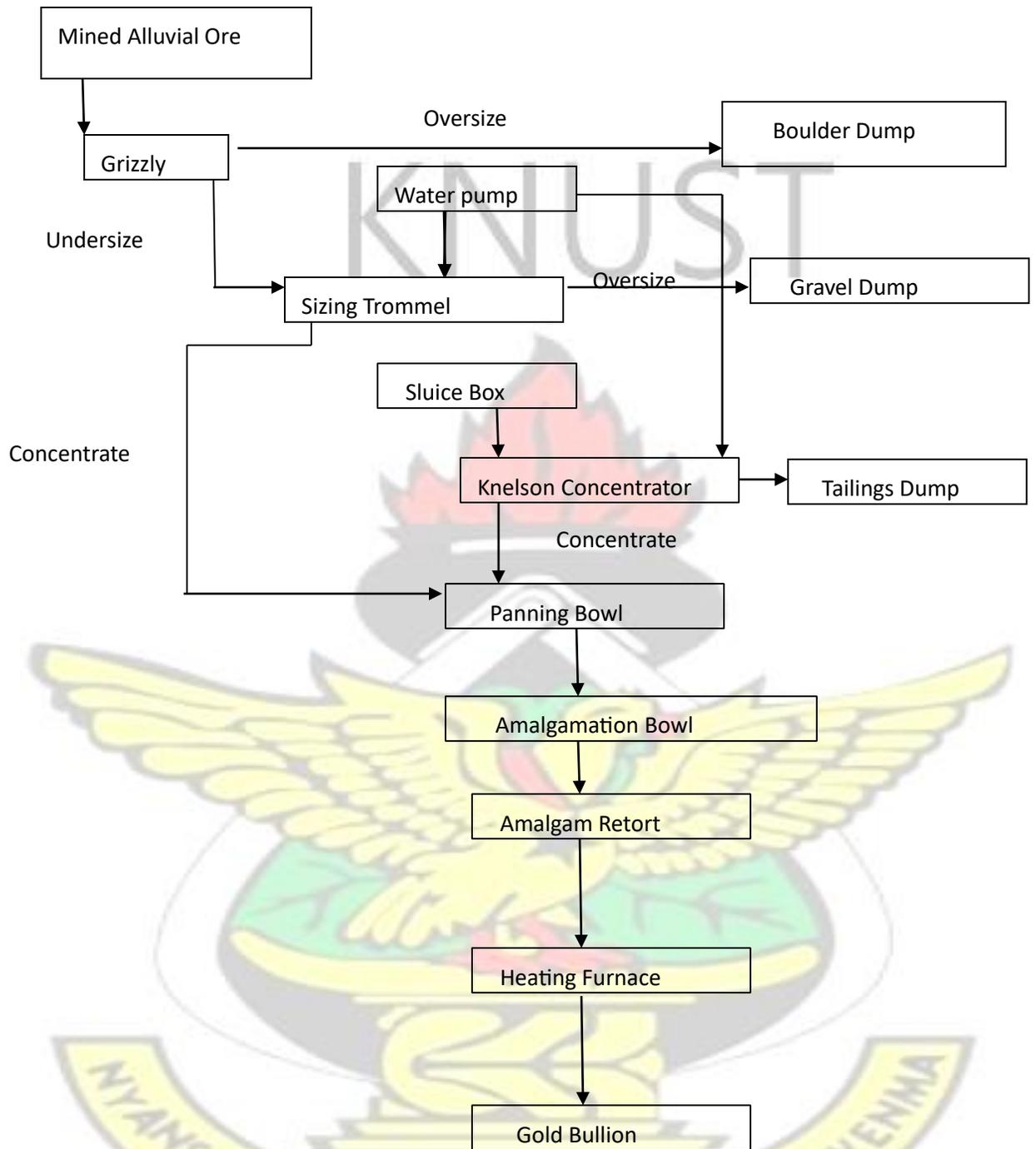


Figure 2: Methods used by artisanal mining operators to extract gold

Source: (Aryee *et al.*, 2003)

2.5 Environmental Impact of Small scale Mining

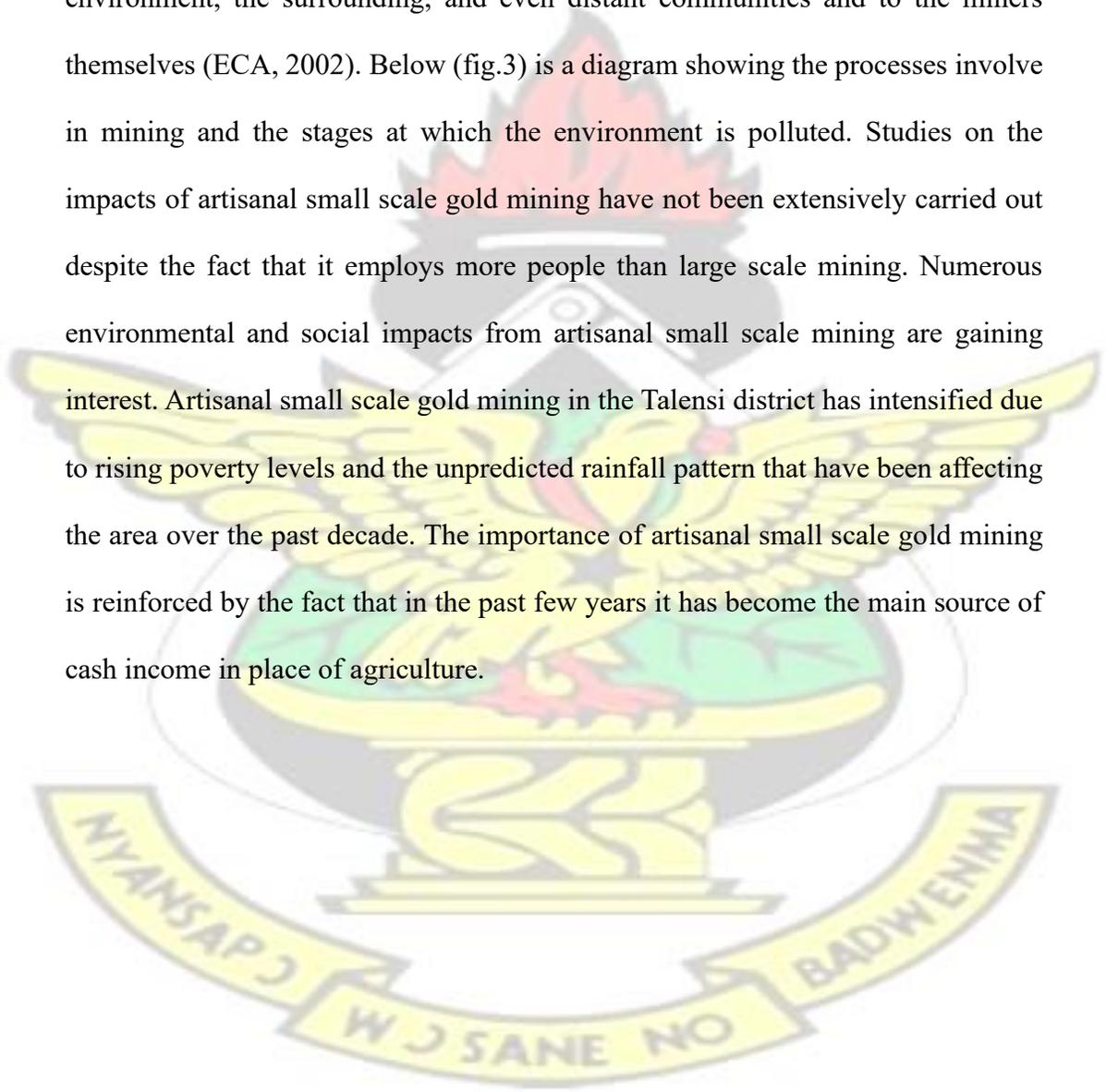
The research focuses on environmental and health problems caused by artisanal small scale (ASM) gold mining at Yale. Due to the inherent digging of soil and sluicing involved in artisanal mining, water siltation, erosion, and soil degradation can be an issue in rivers used for mining.

Rivers are also commonly diverted as a way to access mineral rich riverbeds. The digging of mines can also dig up and spread harmful materials, such as lead, that are located within the soil.

Other environmental issues can include formation of sinkholes, loss of biodiversity, and contamination of soil, groundwater and surface water by chemicals from mining processes. In some cases, additional forest logging is done in the vicinity of mines to create space for the storage of the created debris and soil. Contamination resulting from leakage of chemicals can also affect the health of the local population if not properly controlled Brook (2009).

Mining companies in most countries are required to follow stringent environmental and rehabilitation codes in order to minimize environmental impact and avoid impacting human health. These codes and regulations all require the common steps of Environmental Impact Assessment, development of Environmental Management plans, mine closure planning (which must be done before the start of mining operations), and environmental monitoring during operation and after closure. However, in some areas, particularly in the developing world, government regulations may not be well enforced.

Small-scale mining (SSM) is an activity that is increasingly gaining momentum in Africa. It is largely practiced in rural areas by artisans who lack the requisite education, training, management skills and essential equipment. Small-scale miners also lack financial resources with no access to bank loans (ECA, 2002). Very often, the mining operations are done haphazardly with severe consequences to the environment, the surrounding, and even distant communities and to the miners themselves (ECA, 2002). Below (fig.3) is a diagram showing the processes involve in mining and the stages at which the environment is polluted. Studies on the impacts of artisanal small scale gold mining have not been extensively carried out despite the fact that it employs more people than large scale mining. Numerous environmental and social impacts from artisanal small scale mining are gaining interest. Artisanal small scale gold mining in the Talensi district has intensified due to rising poverty levels and the unpredicted rainfall pattern that have been affecting the area over the past decade. The importance of artisanal small scale gold mining is reinforced by the fact that in the past few years it has become the main source of cash income in place of agriculture.



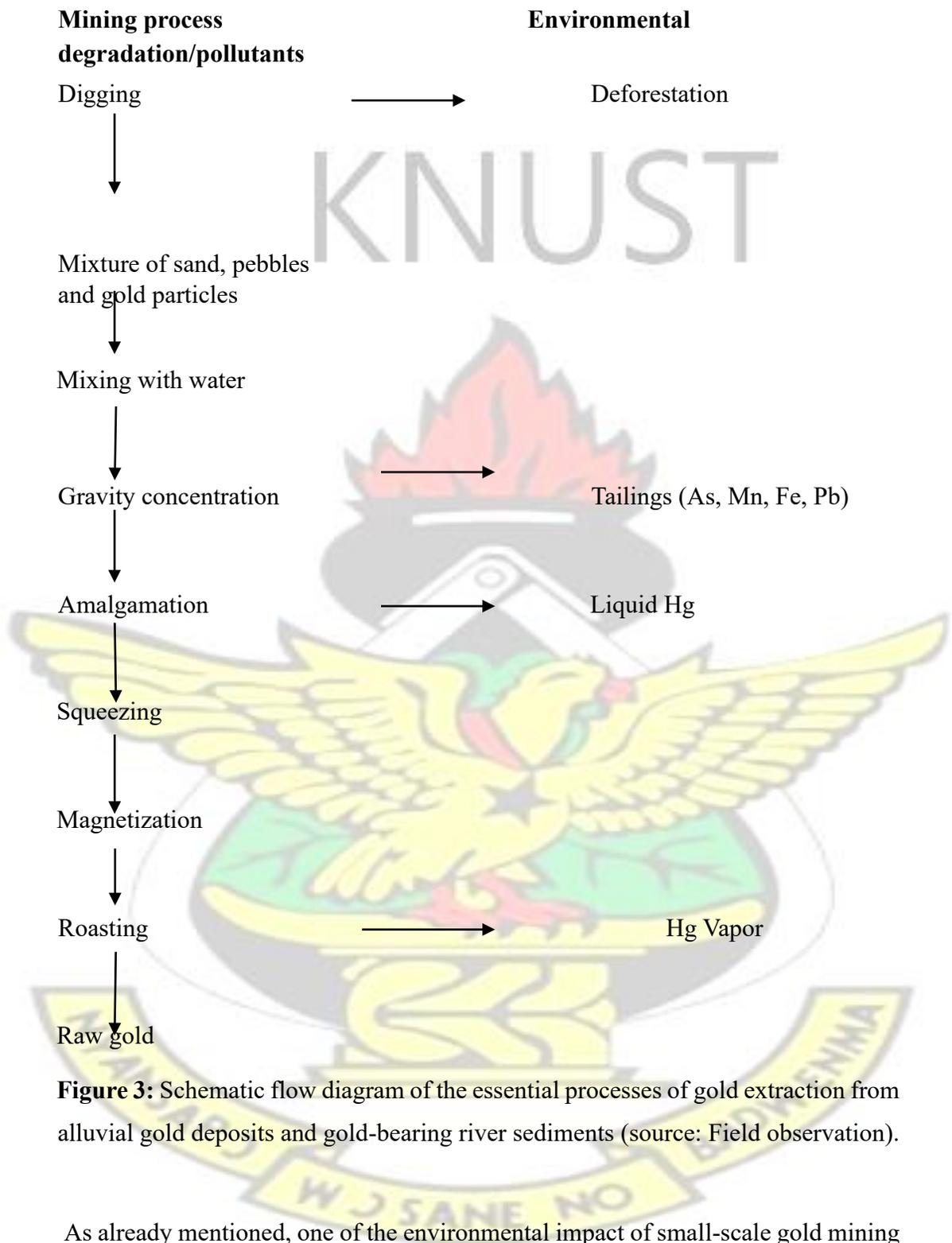


Figure 3: Schematic flow diagram of the essential processes of gold extraction from alluvial gold deposits and gold-bearing river sediments (source: Field observation).

As already mentioned, one of the environmental impact of small-scale gold mining in Ghana is land degradation — more specifically, clearing vast expanses of forest, digging trenches and the upturning of vegetation which in turn leaves land bare and

exposed to agents of erosion. Approximately 15,000 ha of land are potentially affected by small-scale mining activities (World Bank, 1995) and according to Hillson (2001), (Iddirisu and Tsikata, 1998) it is quite common for prospective sites to be stripped bare of vegetation topsoil, and where deep underground mining has occurred, and those pits are left uncovered and abandoned. Agyapong (1998), who conducted fieldwork in the Tarkwa region of Ghana, reports that vast tracts of the region were deforested as a result of smallscale gold mining.

Hilson, (2001) reported that Artisanal miners, who allegedly _clear the vegetation and then dig for mineral-bearing ore, have scarred the landscape with _excavated pits and trenches, which in turn renders the land unsuitable for any other purpose . As a result many of these pits have been filled with water and serve as breeding grounds for malaria-infected mosquitoes.

According to Hilson, (2001) the principal environmental problem caused by small-scale mining activity is mercury pollution from gold processing. In most developing countries, the mercury amalgamation technique is relied upon heavily as it is a cheap, dependable, portable operation for concentrating and extracting gold from low-grade ores (Hilson, 2001). It is now well known, however, that the chemical, in sufficient quantities, poses a serious threat to human health and is deleterious to a wide-range of ecological entities.

Once in the natural environment, mercury undergoes a change in speciation from an inorganic to a stable methylated state (MeHg) by non-enzymically and microbial action, and when ingested, eco-toxicological effects result.

An estimated five tons of mercury are released into the environment each year from small-scale gold-mining operations (World Bank, 1995).

Hilson reported that Research undertaken and reported by National Research Council (NRS) Consultants (1994) from Australia reveals that small-scale miners occupationally exposed to mercury, are, in fact, contaminated. According to Hilson, analysis of hair samples obtained from miners in Tarkwa and Accra shows a mean value of $7.4\mu\text{g/g}$; it is recommended by the World Health Organization that the average weekly intake of mercury should be no more than $5\mu\text{g/kg}$ of body weight, of which no more than $3.3\mu\text{g/kg}$ should be MeHg. Hilson again stated that two unpublished studies commissioned recently by UNIDO confirmed further that there is a mercury pollution problem — although with unknown dimensions — within certain small-scale gold-mining regions in Ghana.

The first study was conducted by (Rambaud *et al.*, 2001) involved analyzing hair, urine, blood and nail samples from 187 adults residing in an artisanal gold-mining community, some 40 per cent of whom claimed to have health problems (Hilson, 2001).

Clinical examinations identified 13 men as having slight neurological disorders (as a result of mercury overexposure), many gold washers having elevated concentrations of mercury in their bloodstreams, and that there is an exposure to mercury in the community through contaminated food.

Heavy metal pollution of surface and underground water sources results in considerable soil pollution and pollution increases when mined ores are dumped on the ground surface.

Most of the mercury released from human activities is released into air, through fossil fuel combustion, mining, smelting and solid waste combustion. Some forms of human activity release mercury directly into soil or water, for instance the application of agricultural fertilizers and industrial wastewater disposal. All mercury that is released in the environment will eventually end up in soils or surface waters (Karen, 2005).

Surface dumping exposes the metals to air and rain thereby generating much acid mine drainage. When agricultural soils are polluted, these metals are taken up by plants and consequently accumulate in their tissues. Animals that graze on such contaminated plants and drink from polluted waters also accumulate such metals in their tissues. Humans are in turn exposed to heavy metals by consuming contaminated plants and animals (Duruibe *et al.*, 2007).

Ore mills generate large amounts of waste, called tailings. These tailings can be toxic. Tailings, which are usually produced as slurry, are most commonly dumped into ponds made from naturally existing valleys.

442.6 General Properties of Heavy Metals

Although there is no clear definition of what a heavy metal is, density is in most cases taken to be the defining factor. Heavy metals are thus commonly defined as those having a specific density of more than 5 g/cm^3 (Järup, 2003).

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning.

Heavy metals are dangerous because they tend to bio accumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted.

2.6.1 Sources of Heavy Metals (Fe, Mn, Pb, Hg and As).

2.6.1.1 Mercury

Mercury is a hazardous environmental contaminant. In Japan, 2252 people have been affected and 1043 have died due to Minamata Disease for the past two decades, caused by elevated mercury pollution from a chemical plant (Kudo and Miyahara, 1991).

In the Mercury Study Report to Congress (USEPA,1997), sources of mercury emissions were placed in three categories: natural, anthropogenic, and re-emitted

sources. Mercury re-emission is the remobilization of settled mercury. The estimated global anthropogenic mercury emissions was 1913 metric tons in 1995 (Pacyna and Pacyna, 2002).

Natural and re-emitted mercury emissions into the atmosphere are very important factors in the mercury cycle (Wang *et al.*, 2004). The major naturally occurring mercury emission processes include: (1) degassing from mercury mineral deposits, (2) degassing from mercury contaminated aquatic and terrestrial systems (through reduction of Hg to Hg⁰), (3) volcanic emissions, and (4) forest fires (Nriagu, 1989; Lindqvist *et al.*, 1991; Nriagu, 1994; Camargo, 2002). The Mediterranean region has significant amounts of mercury mineral deposits (Bailey *et al.*, 1973). The natural emissions of mercury were estimated to be 110 metric tons per year in that region (Pirrone *et al.*, 2001). (Brunke *et al.*, 2001). One important characteristic of natural and re-emitted mercury emissions is their nonpoint and wide range sources. Therefore, it is difficult to estimate the emission amount accurately and apply efficient control methods.

The anthropogenic emission sources of mercury mostly result from: (1) solid waste incineration (municipal and medical wastes), (2) coal and oil combustion, (3) pyrometallurgical processes (iron, lead, and zinc), and (4) production of mercury and gold (Pirrone *et al.*, 1996). Among these sources, coal combustion and solid waste incineration account for more than half of the total global emissions (Pirrone *et al.*, 1996).

2.6.1.2 Lead

Lead has been used for at least 5000 years, early applications including building materials, pigments for glazing ceramics, and pipes for transporting water (Järup, 2003).

The general population is exposed to lead from air and food in roughly equal proportions. Earlier, lead in foodstuff originated from pots used for cooking and storage, and lead acetate was previously used to sweeten port wine (Järup, 2003).

Lead paint is another source of lead exposure and the major source of lead toxicity in children.

A review report by Lyn, (2006) said U.S. Department of Housing and Urban Development currently estimates that 38 million homes in the United States contain lead paint. Of those, 24 million are considered to contain significant leadbased paint hazards, including deteriorating paint and/or contaminated dust or soil outside the home (Jacobs *et al.*, 2002).

As lead paint deteriorates and airborne lead settles, it contaminates dust and soil (Farfel and Chisolm, 1991). Exposure to soil that contains particulate lead has been shown to be significantly hazardous for children, who are more commonly exposed by ingestion of house dust or soil than by paint chips.

Blood lead levels are more closely related to indoor dust exposure than to outdoor soil exposure (Lanphear *et al.*, 1998). Lead exposure can also occur during remodeling of a home built prior to 1978, when lead-based paints were still in commerce. According to (Lyn, 2006), in a population-based study, children who

lived in a home that had undergone some type of renovation, repair, or remodeling work in the prior year were at 1.3 times greater risk of having an elevated blood lead level than children not exposed to such activities (USEPA, 1999). The risk was even higher among children living in homes where practices, such as the removal of paint with heat guns, had been used.

Drinking water is also a major source of lead exposure, estimated to be responsible for approximately 20 percent of the total daily exposure experienced by the majority of the U.S. population (Russell Jones, 1989).

Occupational exposure to inorganic lead occurs in mines and smelters as well as welding of lead painted metal, and in battery plants. Low or moderate exposure may take place in the glass industry. High levels of air emissions may pollute areas near lead mines and smelters. Airborne lead can be deposited on soil and water, thus reaching humans *via* the food chain.

2.6.1.3 Iron

Iron is the most abundant metal, and is believed to be the tenth most abundant element in the universe. Iron is a metal extracted from iron ore, and is hardly ever found in the free (elemental) state. Iron is the most used of all the metals, comprising 95 percent of all the metal tonnage produced worldwide. Its combination of low cost and high strength make it indispensable, especially in applications like automobiles, the hulls of large ships, and structural components for buildings.

2.6.1.4 Arsenic

Arsenic is a widely distributed metalloid, occurring in rock, soil, water and air. Inorganic arsenic is present in groundwater used for drinking in several countries all over the world (e.g. Bangladesh, Chile and China), whereas organic arsenic compounds (such as arsenobetaine) are primarily found in fish, which thus may give rise to human exposure (WHO, 2001).

Smelting of non-ferrous metals and the production of energy from fossil fuel are the two major industrial processes that lead to arsenic contamination of air, water and soil, smelting activities being the largest single anthropogenic source of atmospheric pollution (Chilvers and Peterson, 1987).

Concentrations in air in rural areas range from 1 to 4 ng/m³, whereas concentrations in cities may be as high as 200 ng/m³. Much higher concentrations (1000 ng/m³) have been measured near industrial sources. Water concentrations are usually 10g/l, although higher concentrations may occur near anthropogenic sources. Levels in soils usually range from 1 to 40 mg/kg, but pesticide application and waste disposal can result in much higher concentrations (WHO, 2001)

General population exposure to arsenic is mainly *via* intake of food and drinking water. Food is the most important source, but in some areas, arsenic in drinking water is a significant source of exposure to inorganic arsenic. Contaminated soils such as mine-tailings are also a potential source of arsenic exposure (WHO, 2001).

2.6.1.5 Manganese

Manganese is a very common compound that can be found everywhere on earth. Manganese compounds exist naturally in the environment as solids in the soils and small particles in the water. Manganese particles in air are present in dust particles. These usually settle to earth within a few days. Humans enhance manganese concentrations in the air by industrial activities and through burning fossil fuels. Manganese that derives from human sources can also enter surface water, groundwater and sewage water. Through the application of manganese pesticides, manganese will enter soils (Karen, 2005).

2.6.2 Effects of Heavy Metals

The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO (Järup, 2003).

Heavy metals have been used by humans for thousands of years. Although several adverse health effects of heavy metals have been known for a long time, exposure to heavy metals continues, and is even increasing in some parts of the world, in particular in less developed countries, though emissions have declined in most developed countries over the last 100 years (Järup, 2003).

The general population is primarily exposed to mercury *via* food, fish being a major source of methyl mercury exposure, and dental amalgam (WHO, 1990).

Although adverse health effects of heavy metals have been known for a long time, exposure to heavy metals continues and is even increasing in some areas. For example, mercury is still used in gold mining in many parts of Latin America and Africa. Arsenic is still common in wood preservatives, and tetraethyl lead remains a common additive to petrol, although this use has decreased dramatically in the developed countries.

2.6.2.1 Mercury

Acute mercury exposure may give rise to lung damage. Chronic poisoning is at relatively low levels of occupational exposure.

Metallic mercury is an allergen, which may cause contact eczema, and mercury from amalgam fillings may give rise to oral lichen. It has been feared that mercury in characterized by neurological and psychological symptoms, such as tremor, changes in personality, restlessness, anxiety, sleep disturbance and depression (Järup, 2003).

The two major, highly absorbed subspecies of mercury are elemental mercury (Hg^0) and MeHg. Silver dental amalgams contain over 50% Hg^0 , which is the only metal with a melting point below room temperature. Elemental mercury vapor is highly lipophilic and is efficiently absorbed through the lungs and oral mucosa.

After entering the blood, it rapidly passes the cell membranes including the bloodbrain barrier and placental barrier. Once inside a cell, Hg^0 is oxidized by catalase and becomes highly reactive Hg^{2+} (Ercal *et al.*, 2001).

When elemental mercury is inhaled, its vapour easily passes through pulmonary alveolar membranes and enters the blood, where it distributes primarily to the red blood cells, central nervous system, and kidneys. In contrast, less than 0.1% of elemental mercury is absorbed from the gastrointestinal tract after ingestion, so it has little toxicity when ingested. Only minimal absorption occurs with dermal exposure (Clarkson, 1997). Elemental mercury in contact with tissue oxidizes to mercuric ion, which does not cross the blood- brain barrier well. On the other hand when elemental mercury is converted to the mercuric form within the CNS, it is less able to diffuse out of the brain. Elemental mercury also crosses the placenta and concentrates in the foetus. In adults, the half- life of mercury is 60 days (Agency for Toxic Substances and Disease Registry, ATSDR, 2007).

The symptoms are reversible after cessation of exposure. Because of the blood– brain barrier there is no central nervous involvement related to inorganic mercury exposure. Metallic mercury may cause kidney damage, which is reversible after exposure has stopped. It has been feared that mercury in amalgam may cause a variety of symptoms. This so-called ‘amalgam disease’ is, however, controversial, and although some authors claim proof of symptom relief after removal of dental amalgam fillings (Lindh *et al.*, 2002) there is no scientific evidence of this (Langworth *et al.*, 2002).

Methyl mercury poisoning has a latency of 1 month or longer after acute exposure, and the main symptoms relate to nervous system damage (Weiss *et al.*, 2002).

2.6.2.2 Lead

Lead toxicity affects the central and peripheral nervous systems, renal function, and the vascular system. The toxic effects of lead vary greatly manifesting as subtle changes in neurocognitive function in low-level exposure or as the potentially fatal encephalopathy of acute lead poisoning (Needleman, 2004). As exposure progresses, symptoms of toxicity may manifest differently.

The symptoms of acute lead poisoning are headache, irritability, abdominal pain and various symptoms related to the nervous system (Järup, 2003). Lead encephalopathy is characterized by sleeplessness and restlessness. Children may be affected by behavioral disturbances, learning and concentration difficulties. In severe cases of lead encephalopathy, the affected person may suffer from acute psychosis, confusion and reduced consciousness. People who have been exposed to lead for a long time may suffer from memory deterioration, prolonged reaction time and reduced ability to understand.

Acute exposure to lead is known to cause proximal renal tubular Damage (WHO, 1995).

2.6.2.3 Iron

Iron is essential to all organisms, except for a few bacteria. It is mostly stable and incorporated in the inside of metalloproteins, because in exposed or in free form it causes production of free radicals that are generally toxic to cells. Iron binds avidly to virtually all biomolecules so it will adhere nonspecifically to cell membranes, nucleic acids, proteins etc. Iron distribution is heavily regulated in mammals. The

iron absorbed from the duodenum binds to transferrin, and carried by blood it reaches.

2.6.2.4 Arsenic

Inorganic arsenic is acutely toxic and intake of large quantities leads to gastrointestinal symptoms, severe disturbances of the cardiovascular and central nervous systems, and eventually death. In survivors, bone marrow depression, hemolysis, hepatomegaly, Melanosis, polyneuropathy and encephalopathy may be observed.

2.6.2.5 Manganese

In plants manganese ions are transported to the leaves after uptake from soils. When too little manganese can be absorbed from the soil this causes disturbances in plant mechanisms. Manganese can cause both toxicity and deficiency symptoms in plants (Karen, 2005). When the pH of the soil is low manganese deficiencies are more common.

CHAPTER 3

3.0 MATERIALS AND METHODS

3.1 Study area

3.1.1 Geographical location

Yale is located in the Talensi district of the Upper East Region (UER) of Ghana.

The district lies between latitude 10°15' and 10°60' north of the equator and longitude 0°31'.and 1°05' and west of the Greenwich meridian. The total land area is about 8,842 sq km, which translates into 2.7% of the total land area of the country (fig. 4)

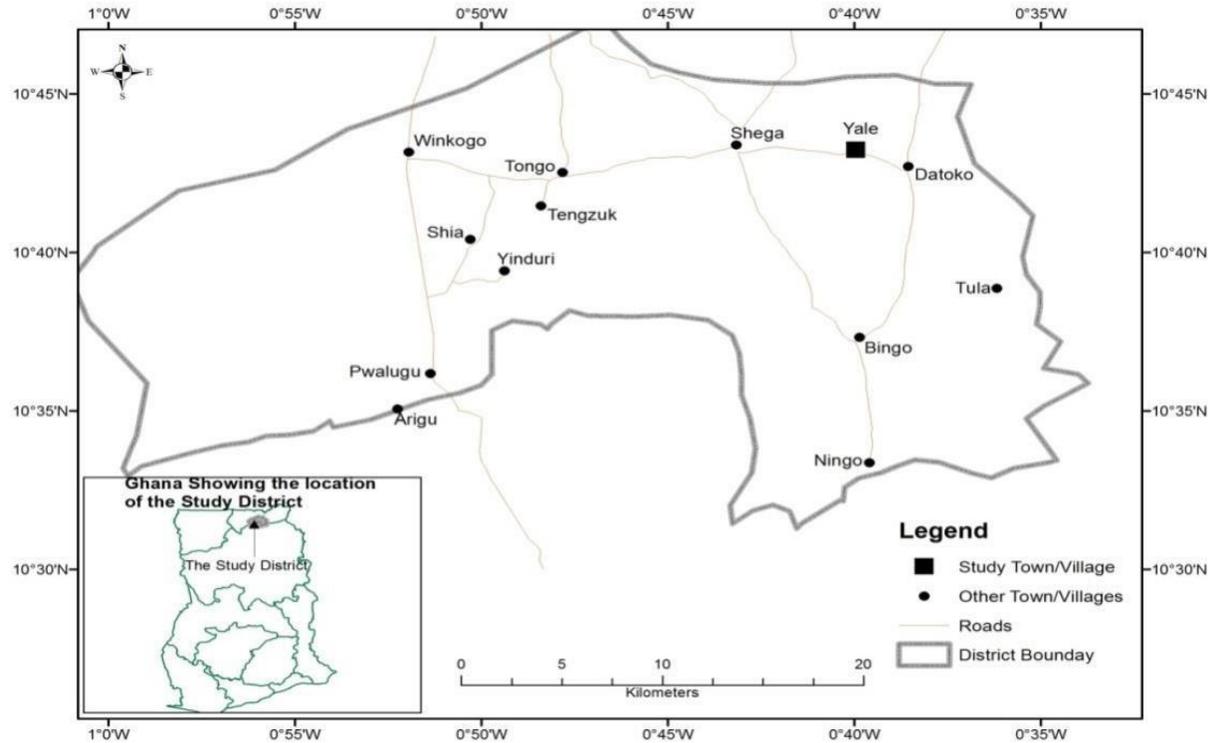


Figure 4: Map of the study area

The Talensi district was carved from the Talensi-Nabdam district in 2012. The Administrative capital of the district is Tongo. The Talensi district is bordered to the North by the Nabdam district, Bolgatanga Municipal to the West, East Mamprusi district (Northern region of Ghana) to the South East, West Mamprusi district (Northern region of Ghana) to the South West, and Bawku West district to the East.

The Upper East region is located in the north-eastern corner of Ghana and is the second smallest of 10 administrative regions in Ghana. (The region shares

boundaries with Burkina Faso to the north, Togo to the east, Upper West Region to the west, and the Northern Region to the south. It lies between longitude 0° and 1° west, and latitudes 10° 30'N and 11°N. The region is divided into 10 districts. The regional capital is Bolgatanga. (sometimes referred to as Bolga).

3.1.2 Rainfall and Vegetation

The area experiences a uni-modal rainfall pattern with mean annual rainfall figures ranging between 855 and 1269 mm (Atugbire *et al.*, 2010). The vegetation is savannah, consisting of short deciduous, widely spread fire resistance trees and shrubs. The grasses which vary in height are susceptible to bushfires. The district lies between latitude 10°15' relatively flat with a few hills to the East and southeast.

The natural vegetation is that of the savannah woodland characterized by short scattered drought-resistant trees and grass that gets burnt by bushfire or scorched by the sun during the long dry season. Human interference with ecology is significant, resulting in near semi-arid conditions. The most common economic trees are the *Butyrospermum* (sheanut), *Parkia biglobosa* (Dawadawa), *Adansonia digitata* (Boabab) and *Acacia nilotica* (Acacia).

3.1.3 Climate

The climate is characterized by one rainy season from May/June to September/October. The mean annual rainfall during this period is between 800 mm and 1100 mm. The rainfall is erratic spatially and in duration. There is a long spell of dry season from November to mid February, characterized by cold, dry and dusty harmattan winds. Temperatures during this period can be as low as 14 degrees

centigrade at night, but can go to more than 35 degrees centigrade during the daytime. Humidity is, however, very low making the daytime high temperature less uncomfortable. The region is entirely within the —Meningitis Belt of Africa. It is also within the onchocerciasis zone, but with the control of the disease, large areas of previously abandoned farmlands have been declared suitable for settlement and farming.

3.1.4 Topology and Geology

The topography of the district is dominated by relatively undulating lowlands gentle slopes ranging from 1% to 5% gradient with some isolated rock out crops and some uplands slopes at the Tongo and Nangodi areas.

The district falls within the Birimian, Tarkwanian and Voltarian rocks of Ghana. There are evidence of the presence of minerals especially gold. The district is drained mainly by the Red and White Volta and their tributaries

3.1.5 Economy

The main source of employment is crop Agricultural, through which about 90% of the population attain their livelihood. Other activities undertaken by the people are livestock rearing, poultry production, fuel wood extraction, food processing and mining.

Agriculture plays a major role in the local economy. It employs about two-thirds (2/3) of the labour force and accounting for about 75% of the local gross domestic product (LGDP). Agriculture serves as the source of cash crops, which comprise of

cereals, legumes and vegetables, and provide food stuffs and protein within these categories. It also provides inputs to satisfy the customary needs of people, a legitimate source of assets, and income of people, through the production, sale and ownership of livestock, notably cattle, small ruminant's animals and poultry. It also provides the raw material needs of indigenous industries within the agroprocessing sector; to be converted both as processed food and for further raw materials.

The quarrying that is carried out in the district is of two kinds, these are the industrial quarrying that depends on granite outcrops to produce granites and marbles and other aggregates like chipping and dust on one hand and the Artisanal stone quarrying and heaping activities that also produce stones for the construction industry.

Sand and gravel winning though vehemently discouraged in the district, is seriously a part of the district. It is however recognized as a necessary evil if infrastructural in the district is to development hence an aggressive environmental restoration package is attached to engagements in those activities. Similar to the above industry is the surface gold mining activities carried out in the district, the operation of which is unorganized, crude and a threat to the environment. However, it is noted as a very viable source of employment and revenue and for that matter, the assembly has recognized it as a sector to promote while taking steps to ensure environmental quality.

3.2 Sampling

3.2.1 Sampling containers

All polyethylene containers for sampling were immersed for at least 48 hours in a 10% (v/v) HNO₃ solution and thoroughly rinsed with double-distilled water before use (Mahapatra *et al.*, 2001; Bohrer *et al.*, 2007; Momen *et al.*, 2006).

3.2.2 Sample collection

Sediment, fish and water were collected at two villages within Yale for a period of three months. On the first two months, three samples of water, fish and sediment were taken. On the third month four samples were taken for water, fish and sediment. In all ten samples each was taken for water, fish and sediment for the three months. The towns in Yale have been named after the mining companies at Yale. Example the —Accra registered concession operated by Accra Small-scale Mining Group, is named after a town in Yale called Accra. The name Yale-Obuasi and Yale-Tarkwa will make it easy for readers to know the difference between the Obuasi and Tarkwa in Ashanti region and the in the western region respectively and the Obuasi and Tarkwa in Yale.

Table 3.1: Description of sample collection sites

Sampling point	Description of sampling site ¹	Sampling codes			
		Tarkwa		Obuasi	
		Sediment	Water	Sediment	Water
Point I	~5 m from Pond banks	YST 1	YWT 1	YOS 1	YOW 1
Point II	~ 10 m from Pond banks	YST 2	YWT 2	YOS 2	YOW2
Point III	~15 m from pond banks	YST 3	YWT 3	YOS 3	YOW3
Point IV	~20 m from pond banks	YST 4	YWT 4	YOS 4	YOW4
Point V	~25 m from pond banks	YST 5	YWT 5	YOS 5	YOW5
Point VI	~30 m from pond banks	YST 6	YWT 6	YOS 6	YOW6
Point VII	~35 m from pond banks	YST 7	YWT 7	YOS 7	YOW7
Point VIII	~ 40 m from pond banks	YST 8	YWT 8	YOS 8	YOW8
Point IX	~45 m from pond banks	YST 9	YWT 9	YOS 9	YOW9
Point X	~50 m from pond banks	YST 10	YWT 10	YOS10	YOW10
	YWT =	Water at Yale Tarkwa			
	YOS =	Sediment at Yale Obuasi			
	YOW =	Water at Yale- Obuasi			
	YTF =	Fish at Yale- Tarkwa			
	YOF =	Fish at Yale- Obuasi			

¹ The sampling sites descriptions applies to sediment and water

Key YST = Sediment at Yale Tarkwa

3.2.2.1 Fish

A number of fish were caught from each of the pond (Yale-Tarkwa and YaleObuasi) and put in a box. Three (3) individual mudfish, *Clarias gariepinus*, were selected from each box without looking into the box on each occasion. This was done each time sampling was done. In all a total of ten fish were taken to the laboratory. The fish samples were wrapped with thin polyethylene foils and stored in labelled hermetically-closed polyethylene bags. The bags were placed in a thermo-insulated container with ice packs and transported to the laboratories of the Ghana Atomic Energy Commission in Accra, for analysis.

3.2.2.2 Sediments

Sediments were collected at the bottom of the pond at intervals apart into precleaned polyethylene bags using acid-washed polyethylene shovel (Donkor *et al.*, 2006). Three samples were collected from three (3) different points in each of the pond and put into pre-cleaned polyethylene bags at each sampling location for each visit in a month. In all a total of ten bags of sediment were sampled. (Yale Tarkwa and Yale Obuasi) (Donkor *et al.*, 2006; Serfor-Armah *et al.*, 2004). The samples were placed in hermetically-closed polyethylene bags, stored in thermoinsulated containers with ice packs and transported to the laboratory for processing and analysis.

3.2.2.3 Water

The sampling bottles were pre-conditioned with 5% HNO₃ and later rinsed thoroughly with distilled water. A total of ten bottles of water samples were taken

from each pond at each sampling location (Yale-Tarkwa and Yale-Obuasi). On each sampling occasion three samples were taken from each sampling site. At each sampling site, the bottles were rinsed three times before sampling was done. The collection of the samples from the pond was done wearing hand gloves. The particles in the river disturbed by the feet were allowed to settle down before sampling. Pre-cleaned polyethylene sampling bottles were immersed about 10 cm below the surface of the water and filled with water. After sampling, each bottle was placed in a polyethylene bag with hermetic seals. The samples were then stored in a thermo-insulated container with ice packs and transported to the laboratory at the Ghana Atomic Energy Commission in Accra for analysis. On arrival at the laboratory, the samples were stored in a refrigerator at 4 °C till the next day.

3.2.3 Sample preparation

The processing and analysis was carried out at the Nuclear Chemistry and Environmental Research Centre of National Nuclear Research Institute, Ghana Atomic Energy Commission, Kwabenya, Accra.

3.2.3.1 Fish

The fish samples were rinsed three times using distilled water in each case. The standard length and body weight of each fish sample was taken.

Each fish sample was cut into muscle tissue, head and gills using a stainless steel knife and packed separately into pre-cleaned polyethylene bags. The sliced fish samples were transferred into labelled petri dishes and frozen at -20 °C. This was

followed by lyophilization (freeze drying) of the samples using the Christ Gamma 1-16 lyophilizer (Germany) for 72 hours (Donkor *et al.*, 2006). The lyophilized samples were pulverized and homogenized into powdery form and placed in polyethylene bottles (pre-cleaned). The bottles were placed in polyethylene bags with hermetic seals and stored at -20°C. Portions of the samples were taken for all analysis.

3.2.3.2 Sediment

At the laboratory, shelly fragments, leaves, roots and other debris were glovedhandpicked from the sediment samples (Serfor-Armah *et al.*, 2004) and frozen at 20 °C. This was followed by freeze-drying of the samples using the Christ Gamma 1-16 lyophilizer (Donkor *et al.*, 2006). The lyophilized sediment samples were then homogenized by sieving using a 64 µm-mesh (Fisher Scientific Company, USA) to obtain fine powdery samples. The lyophilized powdery samples were stored in 100 mL polyethylene containers, and placed in hermetically-closed polyethylene bags. The samples were kept in refrigerators at 4°C overnight. Aliquots of these samples were taken and used for the analysis.

3.3 Sample analysis

3.3.1 Determination of total As, Hg, Fe, Mn and Pb

Determination of the levels of As, Hg, Fe, Mn and Pb in fish, water and sediment samples was achieved by atomic absorption spectrometry. Hydride generation atomic absorption spectrometry (HG-AAS) was used for the determination of As,

cold vapour atomic absorption spectrometry (CVAAS) using sodium borohydride as reducing agent was used for the determination of Hg. Flame atomic absorption spectrometry (FAAS) was used for the determination of Fe, Mn and Pb. Prior to the determination, the samples were mineralized using microwave digestion.

Instrumentation

Varian AA 240FS fast sequential atomic absorption spectrometer equipped with a deuterium background corrector (VARIAN, Australia).

A VGA-77 vapour generator (Varian, Australia) equipped with a peristaltic pump to provide continuous flow vapor generation.

ETHOS 900 microwave digester (Milestone, USA) was used for digestion of water samples.

Quality control/Quality Assurance

Reference standards used for the elements of interest, blanks and duplicates of samples were digested the same conditions as the samples. These served as internal positive controls.

Reference standards used are from FLUKA ANALYTICAL, Sigma-Aldrich Chemie GmbH, product of Switzerland

BLANKS: They were to check contamination during sample preparation.

Duplicates: To check the reproducibility of the method used.

STANDARDS: To check the efficiency of the equipment being used

Chemicals

The under-listed commercially available stock standard solutions of Fe, Mn and Pb were used: $1000 \pm 4 \text{ mg Fe L}^{-1}$ in 2% (w/w) HNO_3 (Trace CERT[®], Fluka, Chemie, Switzerland), $1000 \pm 4 \text{ mg Pb L}^{-1}$ in 2% (w/w) HNO_3 (Trace CERT[®], Fluka, Chemie, Switzerland), Commercially available stock standard solution [$(1000 \pm 4 \text{ mg As L}^{-1}$ in 2% (w/w) HNO_3 , Trace CERT[®], Fluka Chemie, Switzerland)], Commercially available stock standard solution [$(999 \pm 4 \text{ } \mu\text{g Hg mL}$ in 1.4% (w/w) HNO_3 , Spectrascan, Teknolab AB, Sweden)], Sodium borohydride (NaBH_4), Sodium hydroxide (NaOH), Nitric acid (65% HNO_3), Hydrochloric acid (37 % HCl), Hydrogen peroxide (30%, H_2O_2)

The water used throughout the study was de-ionised distilled water (DDW) obtained by passing distilled water through a mixed bed ion-exchange column (Barnstead 9-034-3, Fischer Scientific Company).

3.3.1.1 Digestion

Water

Digestion of water samples was done according to the procedure described by Hoenig and de Kersabiec, (1998). The procedure is as follows:

6 mL of HNO_3 (65%), 3 mL of HCl (37%) and 0.25 mL of H_2O_2 (30%) were added to 5 mL of water sample in Teflon digestion tubes, the tubes were covered tightly and placed in the ETHOS 900 microwave digester. The water samples were digested using a four-step digestion procedure (Table 2). At the end of the digestion, the digest

was cooled, transferred into clean 25 mL volumetric flask and diluted to 20 mL with double-distilled water. This was followed by atomic absorption measurement.

Table 2 Microwave digestion programmer used for digestion of water samples

Digestion Step	Digestion Time (min)	Microwave			
		Power (W)	Pressure (bar)	Temperature 1 (°C)	Temperature 2 (°C)
1	5	250	100	400	500
2	1	0	100	400	500
3	10	250	100	400	500
4	5	450	100	400	500

Temperature 1 and temperature 2 represent the initial and final digestion temperatures

Fish

About 0.5 g of the lyophilized fish sample was weighed into Teflon beakers and 6 mL HNO₃ and 1 mL H₂O₂ added. The Teflon beakers were placed in the bomb and closed tightly. The bomb was placed at the center of a microwave oven (ETHOS 900 Microwave, Milestone) and digested for 26 min at full power. The completely digested samples were allowed to cool to room temperature and the volume made up to 20 mL. The digested samples were analyzed in triplicate, using an atomic absorption spectrometer.

Sediment

About 0.5 g of the lyophilized sediment sample was weighed and placed into the digestion bombs. This was followed by the addition of 10 mL of HNO₃-HCl (1:3 v/v). The samples were digested in the microwave system for 26 minutes (the detailed digestion programme is described above). After digestion the samples were left overnight to cool. This was followed by atomic absorption measurement.

3.3.1.2 Measurement of total Fe, Mn and Pb using the Flame Atomic Absorption Spectrometer

The instrumental conditions used for flame atomic absorption spectrometric determination of Fe, Mn and Pb were the following: the air-acetylene flame atomizer was made up of air as oxidant (flow rate: 13.50 L/min) and acetylene as fuel (flow rate: 2 L/min). The lamp current and wavelength of the hollow cathode lamps and the spectral slit width used for Fe, Mn and Pb determinations are presented on Table 3.

Table 3 FAAS conditions used for determination of Fe, Mn, and Pb

Element	Hollow cathode lamp		
Current (mA)	Wavelength (nm)	Slit width (nm)	
Fe	5.0	248.3	0.2
Mn	5.0	279.5	0.2
Pb	10.0	217.0	1.0

Calibration of atomic absorption spectrometer

The atomic absorption spectrometer was calibrated with the calibration standards for the element being determined. The absorbance obtained were used to plot calibration graphs for each element. After the calibration, each element was determined by measurement of the absorbance of the samples aspirated into the absorption cell. The calibration curve is used to calculate result from the AAS.

This is done to validate results and also to check the efficiency of the AAS,

Table 4 Calibration of atomic absorption spectrometer

Analyte	Concentration of calibration standard (mg/L)		
	Calibrant 1	Calibrant 2	Calibrant 3
Fe	2	5	10

Mn	2	5	10
Pb	2	5	10

Calculation of concentration

The concentration of each analyte in the water samples were calculated from the calibration curve for the analyte. In cases where there was dilution of the water sample, the concentration deduced from the calibration graph was multiplied by the dilution factor to give the actual concentration of the analyte in the sample.

Concentration of each analyte was calculated from their respective calibration regression lines. The actual concentration of the analyte in the sample was calculated using the relation:

$$C_{Sample} (\mu\text{g g}^{-1}) = \frac{C_{AAS} \times m D_f \times V_N}{m_{Sample}}$$

Where: C_{AAS} = Concentration of analyte obtained from calibration regression line (mg L^{-1}), D_f = Dilution factor, V_N = Nominal volume or sample volume (mL), C_{sam} = Actual concentration of analyte in sample ($\mu\text{g g}^{-1}$) and m_{sam} = Mass of homogenized sample measured for digestion (g).

3.3.1.3 Determination of As by HG-AAS

Hollow cathode lamps

The radiation sources were the hollow cathode lamp of As (wavelength 193.7 nm; spectral slit width 0.5 nm; lamp current 10 mA).

Reagents

For As determination, hydride generation was performed with a 0.6% (w/v) NaBH₄ in 0.5% (w/v) NaOH as the reductive solution with 6 M HCl as the carrier solution.

Standards

Calibration standards for As (0.2, 0.4, 0.6 mg L⁻¹) and Hg (0.1, 0.25, 0.5 mg L⁻¹) were prepared daily by appropriate dilution of the commercial stock standard solutions for As.

Reduction of As^V to As^{III}

To reduce all As^V to As^{III}, 4 mL of freshly prepared 5 M KI was added to the digest solution.



(3.7)

This was followed by hydride generation and subsequently by atomic absorption measurement.

Calibration

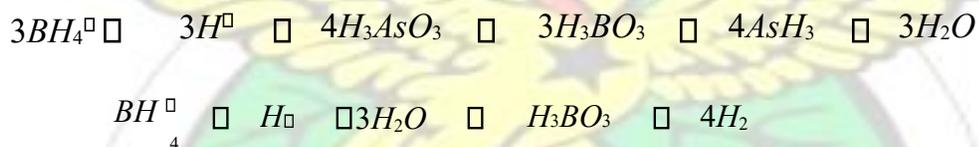
The HG-AAS system was calibrated with As standard calibrants (0.2, 0.4, 0.6 mg As L⁻¹) and the absorbance obtained were used for linear regression analysis (plot

of absorbance against the concentration of the calibrants). The concentration of As was deduced from the equation of the regression line.

Hydride generation and atomic absorption measurement

The continuous flow approach of an HG-AAS system was used to merge sample solution and reagents. The sample solution (flow rate 5 mL/45 sec) was mixed in a PEEK (polyetheretherketone) cross connector with both HCl (flow rate 5 mL/45 sec) and NaBH₄ (flow rate 5 mL/45 sec) solutions (both solutions pumped and added with the peristaltic pump) and pumped into the reaction coil. During the mixing, the tetrahydroborate ion, BH₄⁻ converts As(III) into the hydride (AsH₃).

Furthermore, the tetraborohydrate is hydrolyzed in the presence of HCl producing considerable hydrogen.



The gaseous hydride formed together with the hydrogen gas generated were separated from the liquid in the A-shaped gas-liquid separator component of the vapour generator, and transferred with a flow of argon gas into the Perma-pure dryer and dried by a stream of nitrogen gas. The liquid goes to waste and the gaseous hydride and excess hydrogen formed were swept out of the vapour generation vessel by the argon gas (flow rate 13.5 mL min⁻¹) into the AAS detection system. In the detection system, AsH₃ was atomized in the air-acetylene flame (also fed by the excess hydrogen generated) aligned in the light path of a As lamp in an atomic

absorption spectrometer. Absorbance measurements were recorded and the concentration deduced from the regression line.

Calculation of concentration

The concentration of As in each water sample was obtained from the equation of the regression line. The concentration of As in the sample (mg L^{-1}) was done using the relation:

$$C_{\text{Sample}} (\mu\text{g g}^{-1}) = \frac{C_{\text{AAS}} \cdot m_{\text{Sample}} \cdot D_f}{V_N}$$

Where: C_{AAS} = Concentration of analyte obtained from calibration regression line (mg L^{-1}), D_f = Dilution factor, V_N = Nominal volume or sample volume (mL), C_{sam} = Actual concentration of analyte in sample ($\mu\text{g g}^{-1}$) and m_{sam} = Mass of homogenized sample measured for digestion (g).

Where: D_f is dilution factor, and $\text{Conc}_{\text{calib}}$ is the concentration from calibration curve

3.3.1.4 Determination of Hg by CV-AAS using sodium borohydride as reducing agent

The radiation sources were the hollow cathode lamp of Hg (wavelength 253.7 nm; spectral slit width 0.5 nm; lamp current 4 mA) (Varian, Australia).

Calibration standards for Hg (0.1, 0.25, 0.5 mg L⁻¹) were prepared daily by appropriate dilution of the commercial stock standard solutions of Hg.

Reagents

- Hydride generation for Hg determination was performed using 0.3% (w/v) NaBH₄ in 5% (w/v) NaOH as the reductive solution and 5 M HCl as carrier solution.

Calibration

The CVAAS system was calibrated with As standard calibrants (0.2, 0.4, 0.6 mg As L⁻¹) and the absorbances obtained were used for linear regression analysis (plot of absorbance against the concentration of the calibrants). The concentration of As was deduced from the equation of the regression line.

The CVAAS system was calibrated with Hg standard calibrants (0.1, 0.25, 0.5 mg L⁻¹) and the absorbances obtained were used for linear regression analysis (plot of absorbance against the concentration of the calibrants). The concentration of Hg was deduced from the equation of the regression line.

Cold vapour generation and atomic absorption measurement

Cold vapor atomic absorption spectrometry (CVAAS) using sodium borohydride (NaBH₄) as the reducing agent, was employed to determine mercury concentrations. A brief description of the determination of Hg is as follows:

A peristaltic pump was used to merge sample solution and reagents. The sample solution (flow rate 5 mL/45 sec) was mixed in a PEEK (polyetheretherketone) cross connector with both HCl (flow rate 5 mL/45 sec) and NaBH₄ (flow rate 5 mL/45 sec) solutions (both solutions pumped and added with the peristaltic pump) and pumped into the reaction coil.

During the mixing, the tetrahydroborate ion, BH₄⁻ converts (reduction) Hg into the elemental state (Hg⁰).



The elemental Hg formed was separated from the liquid in the gas-liquid separator component of the vapour generator, by a stream of the carrier gas, argon, (flow rate 13.5 mL min⁻¹) into the Perma-pure dryer and dried by a stream of nitrogen gas. The Hg⁰ then enters the atomic absorption cell. In the absorption cell, Hg⁰ aligned in the light path of the Hg lamp. Hg⁰ absorbs 253.7 nm light in proportion to the concentration of mercury in the sample. Absorbance measurements were recorded and the concentration deduced from the regression line.

Calculation of concentration

The concentration of Hg in the sample was obtained from the equation of the regression line. The concentration of Hg in the sample was done using the relation:

$$C_{Sample} (\mu\text{g g}^{-1}) = \frac{C_{AAS} \cdot m_{Sample} \cdot D_f}{V_N}$$

Where: C_{AAS} = Concentration of analyte obtained from calibration regression line (mg L^{-1}), D_f = Dilution factor, V_N = Nominal volume or sample volume (mL), C_{sam} = Actual concentration of analyte in sample ($\mu\text{g g}^{-1}$) and m_{sam} = Mass of homogenized sample measured for digestion (g).

3.3.1.5 DATA ANALYSIS

Statistical analysis for data in the study was performed using statistical software SPSS (Statistical Package for the Social Sciences) for the Paired Samples T-Tests.

A paired-samples T-test was conducted to compare the mean of metal concentration between Yale-Tarkwa and Yale-obuasi. In this test if the p value was less than 0.05 ($p < 0.05$) there was a statistically significant difference between the mean concentration. On the other hand if the p value is greater than 0.05 ($p > 0.05$) then there is no statistically significant difference between the mean concentration.

CHAPTER FOUR

4.0 RESULTS

The concentrations of the five heavy metals measured in water, fish tissue and sediment samples are presented in fig .5 below. The metals are Fe, Pd, As, Mn and Hg.

4.1 WATER

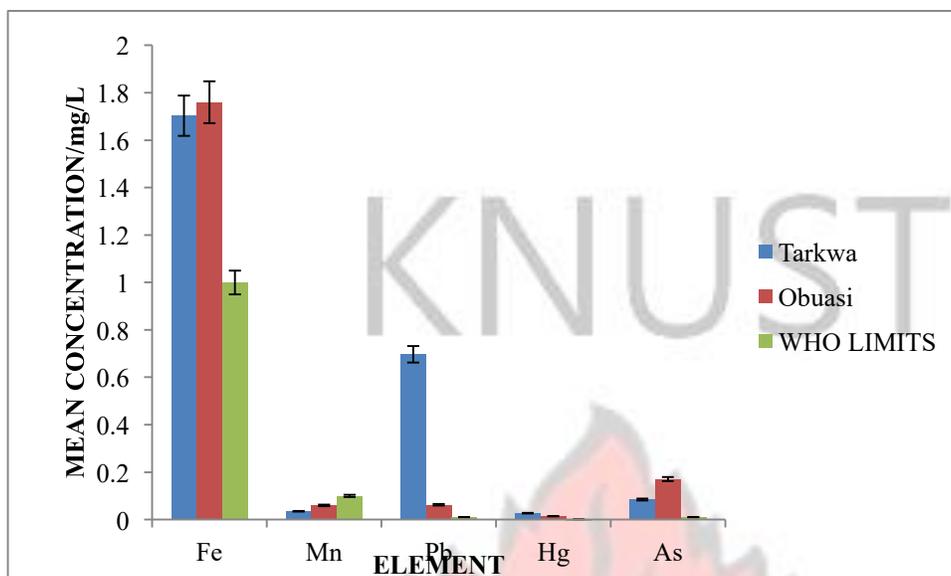


Figure 5: Heavy metals concentration in water at Yale- Obuasi and Yale-Tarkwa.

The mean concentration of iron was very high when it was compare with WHO (1997) standards of 1.0mg/L in both towns, 1.760mg/L and 1.703mg/L for YaleObuasi and Yale-Tarkwa respectively. There were no significant difference between the town ($p=125$)

Levels of maganese was very low in both towns when it was compared with WHO (2003) standards of 0.1mg/L, but the lowest was recorded at Yale-Obuasi.YaleObuasi recoded 0.035mg/L and Yale-Tarkwa recorded 0.060mg/L. There was no significant difference ($p=.15$) between the town Lead levels in both towns were

0.062mg/L and 0.697mg/L respectively forYale- Tarkwa andYale-Obuasi. There was no significant difference between the towns ($p=130$). Levels were above WHO (1997) standards of 0.01mg/L.

Levels of mercury concentration at Yale-Obuasi was 0.027mg/L and 0.014 at Yale-Tarkwa. The difference in concentration between the two towns was not significant ($p=65$). These levels were above WHO (2003) standard of 0.001mg/L.

Levels of arsenic was high at Yale-Tarkwa with a value of 0.171mg/L and 0.084mg/L at Yale-Obuasi. The difference in concentration was not significant ($p=745$). Levels were above WHO (2003) standard of 0.01mg/L.



Figure 6: Operating platform at Yale



Figure 7: Open pits filled with water which serves as breeding ground for mosquitoes.



Figure 8: Felt mats washing of suction gravel, mud, and rocks in Pond at Yale.

At Yale, the miners use a hydraulic suction hose and suction the gravel and mud as they move along the river. The gravel, mud, and rocks go through the tailings (pipes) and any gold fragments are collected on felt mats.

4.2 SEDIMENT

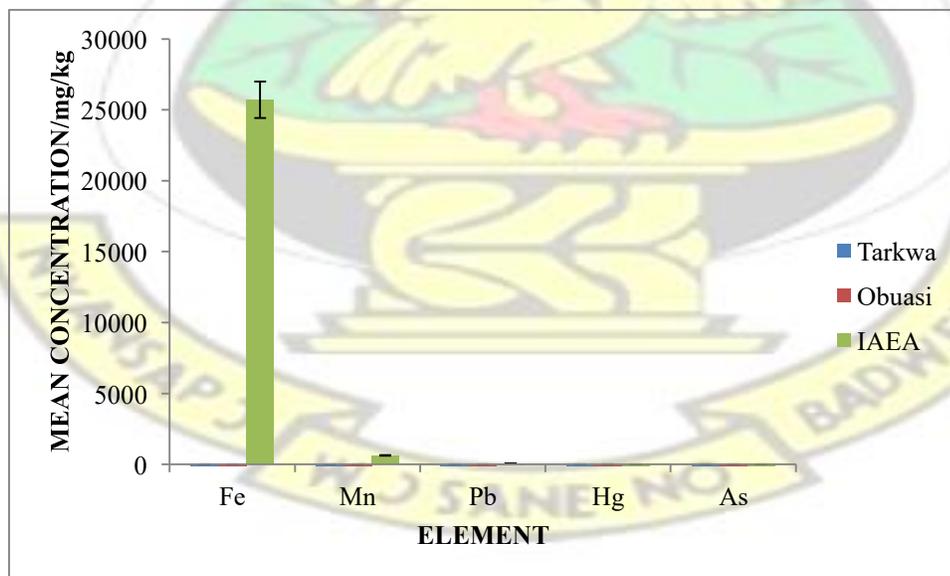


Figure 9: Heavy metal concentration in sediment Yale- Obuasi and Yale Tarkwa.

The levels of Iron in both towns were 0.954mg/kg for Yale-Obuasi and 0.978mg/kg for Yale-Tarkwa. The difference in concentration between the two towns was not significant ($p=274$). The levels are above International Atomic Energy Agency (IAEA) recommended limit for iron 25700mg/kg.

Level of Manganese at Yale-Obuasi was 0.194mg/kg and Yale-Tarkwa was 0.214mg/kg. There was no significant difference ($p=317$) in concentration between the towns. These levels were below IAEA recommended limits for manganese.

Lead level was 0.346mg/kg for Yale-Obuasi and 0.026mg/kg for Yale-Tarkwa. The difference in concentration between the town was significant ($p=001$). The levels are below IAEA recommended limit for lead.

Mercury levels were 0.039mg/kg and 0.013mg/kg for Yale-Obuasi and YaleTarkwa respectively. There was significant difference ($p=0.00$) between the town Levels were below IAEA recommended limit.

The levels of arsenic were 1.844mg/kg for Yale-Obuasi and 1.706mg/kg for YaleTarkwa. There was significant difference between the town ($p=001$). The levels in this work are below IAEA. The order for mean metal concentration at YaleObuasi is $Fe>Pb>As>Mn>Hg$ and the order at Yale-Tarkwa is $Fe>As>Pb>Mn>Hg$.

4.3 FISH

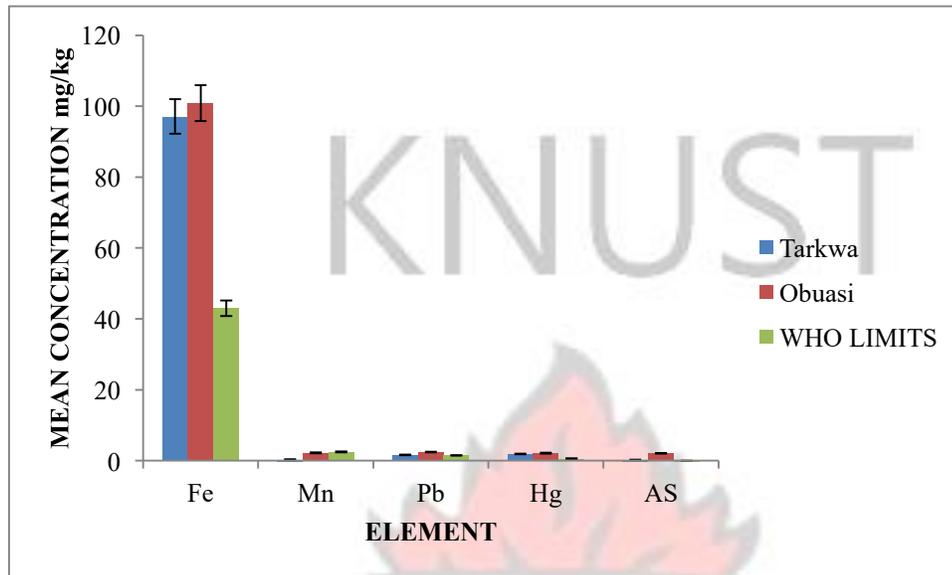


Figure 10: Heavy metals concentration in muscles of fish at Yale Tarkwa and Yale Obuasi.

Levels of iron in the muscle of fish at Yale-Obuasi were 97.100mg/kg and 100.911mg/kg for Yale-Tarkwa. There was no significant difference between the towns ($p=942$). These levels are above WHO/FAO (2011) standards of 43mg/kg.

The levels of manganese in the muscle of fish were 2.210mg/kg and 0.32mg/kg for Yale-Tarkwa and Yale-Obuasi respectively. There was no significant difference between the towns ($p=511$). These levels are below WHO (1997) standards of 2.5mg/kg.

Levels of lead in muscle were 2.423mg/kg for Yale-Tarkwa and 1.600mg/kg for Yale-Obuasi. There was no significant difference between the towns ($p=009$). Levels were above FAO/WHO (2011) of 1.0mg/kg.

There were high levels of mercury in the muscle of fish at both towns but Yale Tarkwa recorded the highest with a value of 2.112mg/kg and 1.920mg/kg from Yale-Obuasi. There was no significant difference between the towns ($p=355$). These levels were above FAO/WHO (2011) of 0.6mg/kg

Levels of arsenic in the muscle of fish from Yale-Tarkwa was 2.100mg/kg and Yale-Obuasi was 0.32mg/kg. There was no significant difference between the towns ($p=585$). These levels are above WHO/FAO (2011) standard for Arsenic 0.26mg/kg.

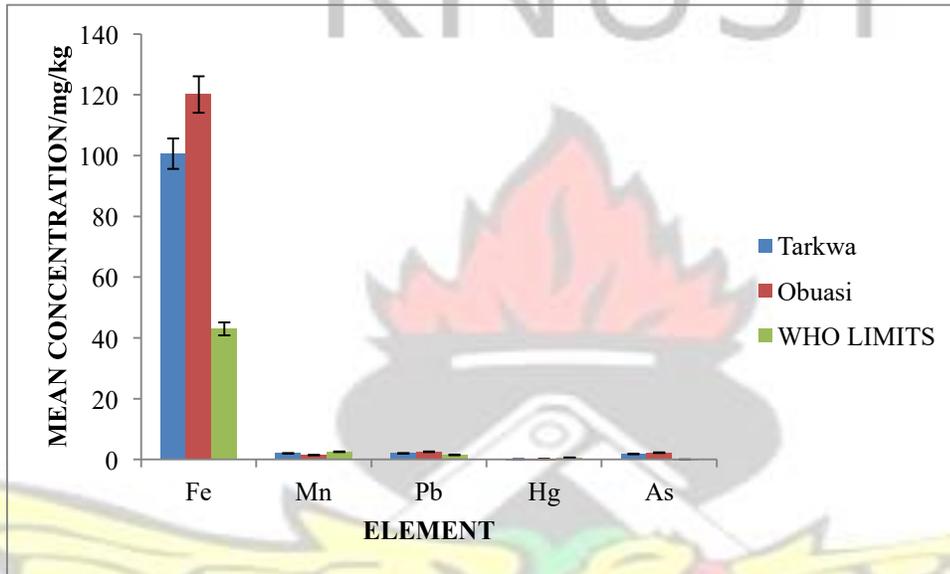


Figure 11: Heavy metal concentration in head of fish.

Levels of iron in the head of fish were 12.123mg/kg for Yale-Obuasi and 10.611mg/kg for Yale-Tarkwa. There was no significant difference between the towns ($p=216$).

Manganese levels in the head of fish at Yale-Tarkwa were 2.012mg/kg and 1.400mg/kg at Yale-Obuasi. There was no significant difference between the towns ($p=057$).

Levels of lead was very high in the head of fish from both towns. The value for Yale-Tarkwa was 2.013mg/kg and 2.500mg/kg for Yale-Obuasi. There was no significant difference between the towns ($p=009$).

Mercury levels were low as compared to other heavy metals. Yale-Tarkwa recorded 0.100mg/kg and Yale-Obuasi recorded 0.212mg/kg. There was no significant difference between the towns ($p=286$).

Arsenic recorded the highest concentration among all the metals. Levels at Yale-Obuasi was 2.230mg/kg and 1.800mg/kg at Yale-Tarkwa. There was no significant difference between the towns ($p=330$).

The order for metal concentration at Yale-Tarkwa is $Fe > Pb > Mn > As > Hg$ and the order at Yale-Obuasi is $Fe > Pb > As > Hg > Mn$.

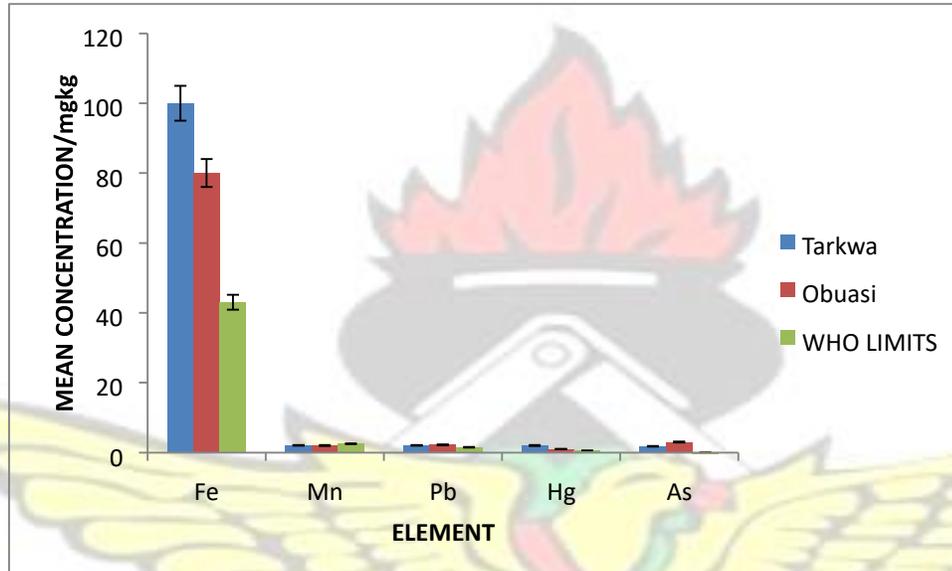


Figure 12: Heavy metal concentration in gills of fish

Levels of iron were very high in the gills of fish from both towns. Yale-Tarkwa recorded a value of 100.6mg/kg and 120.12mg/kg for Yale-Obuasi. There was no significant difference between the towns ($p=097$).

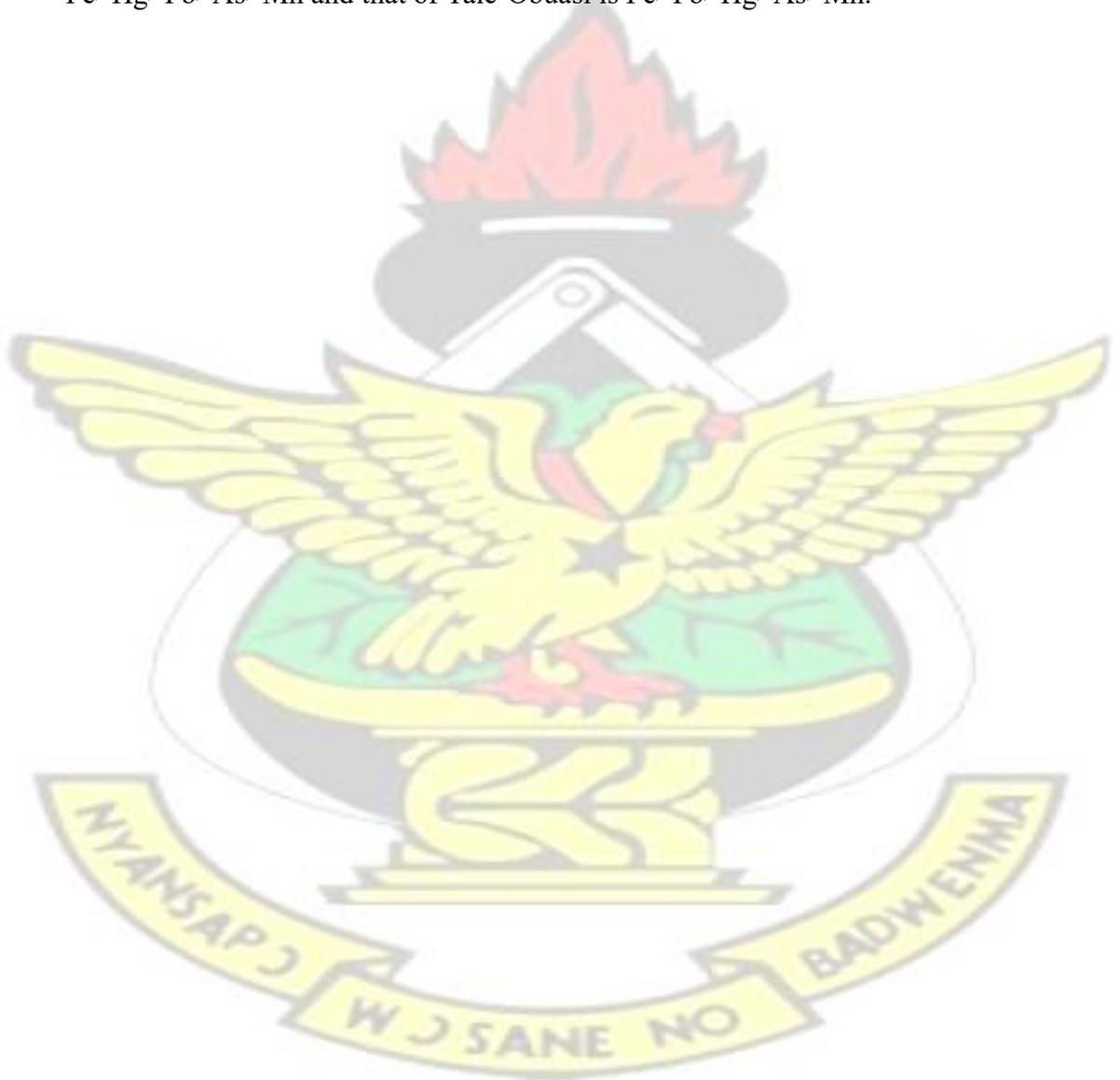
Levels of manganese was low in both town compared to levels of iron. Yale-Tarkwa recorded 2.012mg/kg and Yale-Obuasi recorded 1.400mg/kg in the gills of fish. There was no significant difference between the towns ($p=226$).

Levels of lead were 1.002mg/kg and 0.034mg/kg for fish from Yale-Obuasi and Yale-Tarkwa respectively. There was no significant difference between the towns ($p=017$). The levels were quite high at both towns.

Mercury concentration was high in fish from both towns. At Yale-Obuasi values of mercury read was 0.340mg/kg and that of Yale-Tarkwa was 0.212mg/kg. There was no significant difference between the towns ($p=0.77$).

Arsenic levels read 1.80mg/kg for fish in Yale-Tarkwa and 2.238mg/kg for fish in Yale-Obuasi. There was no significant difference between the towns ($p=1.65$).

The order for metal concentration in gills of fish from Yale-Tarkwa is $Fe > Hg > Pb > As > Mn$ and that of Yale-Obuasi is $Fe > Pb > Hg > As > Mn$.



CHAPTER FIVE

DISCUSSION

The ponds and dams are a common source of water for domestic activities in the upper East regions of Ghana. The pond at Yale is the main source of drinking water for human beings and animals, but illegal small scale mining activities in and around the pond might be one of the anthropogenic sources of heavy metal pollution of the pond.

Water

Level of Iron was 1.703mg/L and 1.760mg/L for Yale-Obuasi and Tarkwa respectively. The levels of iron are similar to result reported by Cobbina *et al* (2013) in water samples from Datuku in the Talensi-Nabdam district which ranged from 0.018mg/L in Yale-Obuasi abandoned pits (OAP) and 19.14mg/L down stream (DS). The levels recorded were also within the range of 0.4mg/L to 2.4 mg/L level found by Akabzaa and Darimani (2001) in three different streams polluted by mining activities in Tarkwa in the Western Region. The levels of iron in this work are above WHO (2003) permissible limit of 1.0 mg/L in drinking water.

High levels of iron cause staining in clothes and impart a bitter taste. Excess amounts of iron (more than 10 mg/L) causes rapid increase in pulse rate and coagulation of blood in blood vessels, hypertension and drowsiness (Patil and Ahmad, 2011).

Iron is the most abundant metal, and is believed to be the tenth most abundant element in the universe.

A report by National Research Council (1979), indicated that in remote areas, iron levels in air are about 50–90 ng/m³; at urban sites, levels are about 1.3µg/m³.

Concentrations up to 12 µg/m³ have been reported in the vicinity of iron- and steel producing Plants.

Level of Manganese at Yale-Obuasi was 0.035mg/L and 0.060mg/L for Yale-Tarkwa.. These levels are below findings by Cobbina *et al.* (2013) who reported values which varied from 0.036mg/L in samples taken from Accra borehole in Datuku to 2.24mg/L in samples taken from DS. Samir *et al.* (2008) also reported similar findings in water from Delta Lakes in Egypt (Edku, 0.024mg/L, Borollus, 0.194mg/L and Manzala, 0.084mg/L). Manganese in both town showed mean concentration above WHO (2003) recommended limit for drinking water quality. At levels exceeding 0.1 mg/l, manganese in water supplies causes an undesirable taste in beverages and stains sanitary ware and laundry. Concentrations below 0.1 mg/l are usually acceptable to consumers. Manganese is an essential element for humans and other animals. However there have been epidemiological studies that report adverse neurological effects following extended exposure to very high levels in drinking water (Singh *et al.*, 2007).

Lead levels at both study areas were high with Yale-Obuasi recording the highest value of 0.697mg/L and 0.062mg/L for Yale-Tarkwa. The levels were above WHO (1997) standards of 0.01mg/l for drinking water. Addo *et al.* (2011) also reported similar findings from Mokwe Lagoon with values ranging between

0.005mg/L and 0.016mg/L. Lead accumulated at soil surface may be taken up directly by grazing animals and by soil micro-organisms and so enter terrestrial food

chain (Denny *et al.*, 1987). Lead poisoning also causes inhibition of the synthesis of haemoglobin, dysfunctioning of kidney, joints and reproductive system, cardiovascular system and acute chronic damage to the central nervous system (Duruibe *et al.*, 2007).

Lead is a highly toxic metal to man since it causes brain damage, particularly to the young and induces aggressive behaviour (Ramadan, 2003). The high level of Pb in water could be attributed to the industrial and agricultural discharge as well as from spill of leaded petrol from engines boats used for pumping water and dust which holds a huge amount of lead from the combustion of petrol in automobile cars (Hardman *et al.* 1994). The high level of Pb in water could also be attributed to heavily travelled roads that run along the pond. Higher levels of Pb often occur in water bodies near highways and large cities due to high gasoline combustion (Banat *et al.*, 1998), small- scale mining activities in and around the pond could also be the result of high levels of lead.

Mercury levels from both towns were high. 0.027mg/L was recorded for YaleObuasi and 0.014mg/L for Yale-Tarkwa. The levels in this work are above WHO standards of 0.001mg/L. These levels are above what Cobbina *et al.* (2012) reported from their findings which varied from 0.0002mg/L for AB to 0.02mg/L for midstream (MS). Mercury is toxic and has no known function in human biochemistry and physiology. Poisoning by its organic forms includes neurological disorders, total damage to the brain and CNS and is also associated with congenital malformation. The general population is primarily exposed to mercury *via* food, fish being a major source of methyl mercury exposure (WHO, 1990), and dental amalgam. Several experimental

studies have shown that mercury vapour is released from amalgam fillings, and that the release rate may increase by chewing (Sallsten *et al.*, 1996). The presence of mercury could also be as a result of mining activities going on around the pond.

Concentration of arsenic in both towns was high with 0.084mg/L for Yale-Obuasi and Yale-Tarkwa had 0.171mg/L. The values reported in this work were above WHO standards of 0.1mg/L (Abbas *et al.*, 2010) for arsenic. Cobbina *et al.* (2012) recorded 0.004mg/L for AB and 0.002mg/L for DS. Ingestion of Arsenic is known to have caused skin tumours, lung cancer, liver dysfunction, peripheral neuropathy, hearing defects, and increased frequency of spontaneous abortions (Ercal *et al.*, 2001). Arsenic in mined rocks and ore stock piles heaped close to surface water bodies could be washed through runoffs into surface water bodies such as stream (Ravengai *et al.*, 2005).

Arsenic is carcinogenic in compounds of all its oxidation states and high level exposure can cause death (United States Department of Labor, 2004).

SEDIMENT

Iron levels in sediment at Obuasi and Tarkwa were almost the same. The value from Yale-Obuasi was 0.954mg/kg and Yale-Tarkwa was 0.194mg/kg. Similar work from the university of Cape Coast and its environment by Sarfo *et al* (2013), reported 13662±687.7 mg/kg for point B and 5954mg/kg for point A, which far exceeds the findings in this work. Research by Duodu *et al* (2011) on toxic metals in sediment of the weija dam recorded levels between 0.02048-0.00295mg/kg.

The levels of iron in this work are far below the International Atomic Energy Agency (IAEA) recommended values of 25700mg/kg.

Levels of manganese at Yale-Obuasi were 0.214mg/kg and 0.978mg/kg at Yale-Tarkwa. The value in this study is far below what Duodo *et al.* (2011) reported on Weija Dam which ranges between 433.61-60.71mg/kg. It is also below IAEA recommended limit of 631mg/kg.

Lead levels in both towns were high. The level for Yale-Obuasi is 0.346mg/kg and Yale-Tarkwa is 0.026mg/kg.

Comparing this work to similar work by Affum *et al.* (2011), on Assessment of Water Quality and Heavy Metal Levels in Water and Bottom Sediment Samples from Mokwé Lagoon and recorded values ranging between 0.50 and 29.2: g/g in sediment. The concentration levels were above findings in this present work. Reported Values in this work were below IAEA recommended limits of 60mg/kg.

Mercury levels in both towns were 0.039mg/kg and 0.013mg/kg for Yale-Obuasi and Yale-Tarkwa respectively. These levels were above IAEA recommended limits of 0.04mg/kg. A similar work was conducted by Agyarko *et al.* (2014) at three different mining localities in Ghana and recorded the following values for Esaase (18.72mg/kg), Tetrem (25.56mg/kg), Gyeninsò (46.60mg/kg) and Adobewora (20.50mg/kg).

Arsenic levels were 1.706mg/kg for Yale-Obuasi and 1.844mg/kg for Yale-Tarkwa. These values were above IAEA recommended limits of 13.4kg/kg.

Similarly Kofi Agyarko *et al.* (2014) recorded (107.50mg/kg) for Asaase,

(128.60mg/kg) for Tetrem, (60.10mg/kg) for Gyeninso and (49.68mg/kg) for Adobewora.

FISH

Iron levels in muscle of fish from Yale-Tarkwa were 97mg/kg and 100.9 for Yale-Obuasi. There was no significant difference between the towns ($p>0.05$).

Levels of Fe in gills for Yale-Tarkwa were 100.6mg/kg and 120mg/kg for Yale-Obuasi. There was no significant difference between the town ($p>0.05$)

Levels of Fe in Head were 100mg/kg for Yale-Tarkwa and 120mg/kg for Yale-Obuasi. There was no significant difference between the town ($p>0.05$)

The values in this work are above WHO/FAO (2011) permissible limit for iron.

Values reported by Sarfo *et al.* (2013) measured in the fish muscles for both point A (162.3 ± 23.57 mg/kg) and point B (383 ± 27.49 mg/kg) from university of Cape Coast and it environs. The high concentration of iron in gills could be attributed to the fact that water always passes through mouth and gill when the water is filtered, this is correlated with the findings of food and agricultural organization (Adeniyi *et al.*, 2007, Bryan 1971, Sreenivasa *et al.*, 2003). Research conducted by Tiimub and Dzifa (2013) recorded 44mg/kg for food samples. Iron is essential to most life forms and to normal human physiology. In humans, iron is an essential component of proteins involved in oxygen transports from the lungs to the tissues (Dallman, 1996). It is also essential for the regulation of cell growth and differentiation (Andrew, 1986).

Manganese levels in muscle at Yale-Tarkwa were 0.32mg/kg and 2.210mg/kg at Yale-Obuasi. There was no significant difference between the towns.

Levels of manganese in gills at Yale-Tarkwa were 2.012 and 1.400mg/kg for Yale-Obuasi. There was no significant difference between the towns.

Levels of manganese in head at Yale-Tarkwa were 3.012mg/kg and 1.400mg/kg for Yale-Obuasi. There was no significant difference between the towns.

The value in this study was below WHO standards of 2.5mg/kg (2008)

This work is similar to a research by Ishaq *et al.* (2011) who also reported 1.73mg/kg and 0.801mg/kg in the gill and tissue of *Clarias gariepinus* respectively. Accumulation level reported for Mn in the present study for muscles of *C. gariepinus* are also comparable to *Channaobscura* and *Tilapia zilli* respectively (Anim *et al.*, 2010).

Manganese is an essential trace element for both animals and man; necessary for the formation of connective tissues and bone, growth, carbohydrate and lipid metabolism, embryonic development of the inner ear, and reproductive function (WHO, 2011 and DWAF, 1996).

Lead levels in muscle were 1.600mg/kg for Yale-Tarkwa and 2.423mg/kg for Yale-Obuasi. There was no significant difference between the towns

Levels of lead in gills were Yale-Tarkwa 1.002mg/kg and Yale-Obuasi 0.034mg/kg. There was no significant difference between the towns.

Levels of lead in head were Yale-Tarkwa 4.013mg/kg and 2.500mg/kg for YaleObuasi. There was no significant difference between the towns. The values in this work are above WHO/FAO (2011) standards of 1mg/kg.

A research by Ishaq *et al.* (2011) reported lead concentration to be 1.28mg/kg and 0.607mg/kg for gills and tissue of *Clarias gariepinus* respectively.

Mercury levels in muscle at Yale-Obuasi 1.920mg/kg and, Yale- Tarkwa is 2.112mg/kg

There was no significant difference between the towns.

Levels of mercury in gills are Yale-Tarkwa 0.340mg/kg and Yale-Obuasi is 0.212mg/kg. There was no significant difference between the town.

Levels of mercury in head are Yale-Tarkwa 0.100mg/kg and Yale-Obuasi 0.212mg/kg. There was no significant difference between the town .

These levels are above WHO/FAO (2011) standards of 0.6mg/kg. The investigation in the present work is similar to what Ekpo *et al.* (2008) reported (0.002 – 0.008 mg/kg) for mercury levels in muscle of fish.

Arsenic levels in the muscle are at Yale-Tarkwa 0.31mg/kg and Yale-Obuasi 2.10mg/kg. There was no significant difference between the towns.

Levels of arsenic in gills were 1.33mg/kg for Yale-Tarkwa and 2.23mg/kg for Yale-Obuasi. There was no significant difference between the town.

Arsenic levels in head are Yale-Tarkwa 1.800mg/kg and Yale-Obuasi 2.23mg/kg. There was no significant difference between the town.

A research by Kumar *et al.* (2011) on the assessment of human health risk for heavy metals in collected fish from tropical wetland in India reported values ranging between 0.82-1.22g/g for catlacatla, below detected limit (BDL)-1.02g/g for Oreochromisnilotica and BDL-0.73 for Labeorohita. The level is above WHO/FAO (2011) standards of 0.26mg/kg



CHAPTER SIX

CONCLUSION AND RECOMMENDATION

6.1 CONCLUSION

Artisanal small scale gold mining in the Talensi district has intensified due to rising poverty levels and the unpredicted rainfall pattern that has been affecting the area over the past decade. The importance of artisanal small scale gold mining is reinforced by the fact that in the past few years it has become the main source of cash income in place of agriculture. The use of chemicals containing heavy metals for the extraction of gold has become a worrying issue globally.

The following conclusions were made from the research:

Iron, lead, mercury, arsenic and manganese were the following metals considered for this research.

The result showed that there were heavy metals in all the samples analyzed. The levels of iron were above WHO permissible limit of 1.0 mg/L for drinking water.

Lead levels recorded in water samples were above the permissible limit of 0.01 mg/L by WHO. The high level of Pb in water could be attributed to the industrial and agricultural discharge as well as from spill of leaded petrol from engines boats used for pumping water.

Mercury levels in water samples were above WHO permissible limit of 0.001mg/L for drinking water. The presence of mercury could also be as a result of mining activities going on around the pond.

Levels of manganese were below WHO permissible limits 0.1mg/L.

Arsenic levels were above WHO permissible limits of 0.01.

6.2 RECOMMENDATION

The following recommendations are made to help people have an understanding of the effects of heavy metals on the health of people, water bodies and the environment as a whole.

- Government agencies like Minerals Commission and EPA should monitor the activities of Small Scale gold miners along the ponds at Yale to minimize pollution.
- Constant monitoring and education by agencies like Environmental Protection Agency, Minerals Commission in order to protect the pond from further contamination and its adverse health effects.
- Mining policy design should be done in a participatory manner. Consultations should involve different stakeholders including miners, relevant government institutions, rural development experts, local communities, NGOs, the private sector, international development agencies and other interested parties.
- Policy makers should come together with the local people who are agents and sufferers of environmental related problems. This is important as environmental protection depends not only on government policies and regulations but the people who live in the environment.

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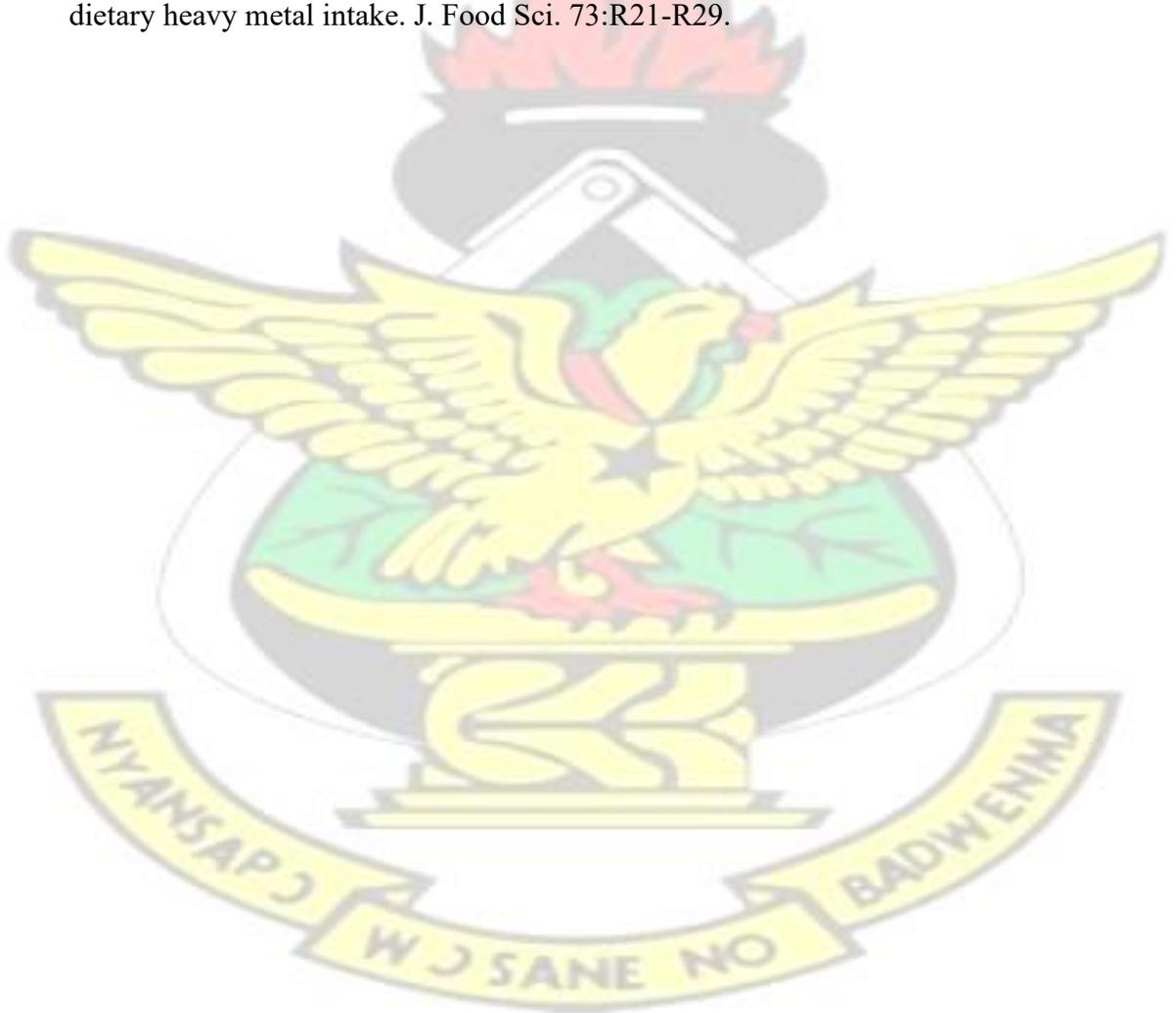
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APPENDIX I



Figure 9: Operating platform at Yale



Figure10: Open pits filled with water which serves as breeding ground for mosquitoes



Figure 11: Felt mats washing of suction gravel, mud, and rocks in Pond at Yale.

At Yale, the miners use a hydraulic suction hose and suction the gravel and mud as they move along the river. The gravel, mud, and rocks go through the tailings (pipes) and any gold fragments are collected on felt mats.

Table 5: Heavy metal concentration (mg/l) in water at Obuasi and YaleTarkwa

ELEMENT	MEAN CONCENTRATION (mg/l)		% RECOVERING		% RALATIVE STANDARD DEVIATION		PERMISSIBLE LIMITS(FAO/ WHO)
	TARKWA	OBUASI	TARKWA	OBUASI	TARKWA	OBUASI	
Fe	1.703	1.76	99.88	99.88	0.062	0.062	1.0
Mn	0.035	0.06	99.95	99.95	0.385	0.11	0.1
Pb	0.697	0.062	99.88	100	0	0.099	0.01
Hg	0.027	0.014	97.56	97.57	5.233	5.149	0.001
As	0.084	0.171	78.94	78.94	2.932	2.3	0.01

Table 6 Heavy metal concentration (mg/kg) in Sediment at Obuasi and YaleTarkwa

ELEMENT	MEAN CONCENTRATION (mg/KG)		% RECOVERING		% RALATIVE STANDARD DEVIATION	
	TARKWA	OBUASI	TARKWA	OBUASI	TARKWA	OBUASI
Fe	0.978	0.954	99.88	99.88	0.107	0.462
Mn	0.194	0.214	98.95	99.95	0.099	0.207
Pb	0.026	0.346	99.88	100	0.028	0.014
Hg	0.013	0.039	97.56	97.56	3.822	6.043
As	1.844	1.706	77.94	78.94	6.734	3.44

Table 7: Heavy metal concentration (mg/kg) in the muscles of fish at Obuasi and Yale-Tarkwa

ELEMENT	MEAN CONCENTRATION (mg/kg)		% RECOVERING		% RALATIVE STANDARD DEVIATION		PERMISSIBLE LIMITS(FAO/WHO)
	TARKWA	OBUASI	TARKWA	OBUASI	TARKWA	OBUASI	
Fe	97.1	100.9	99.9	99.88	0.03	0.107	
Mn	0.32	2.21	98.88	98.95	0.021	0.099	2.5
Pb	1.6	2.423	90.9	99.88	0.032	0.028	1.5
Hg	1.92	2.112	96.9	80	0.022	2.822	
As	0.31	2.1	95.87	77.7	0.012	4.734	

Table 8: Heavy metal concentration(mg/kg) in the gills of fish Yale-Obuasi and Yale-Tarkwa

ELEMENT	MEAN CONCENTRATION (mg/kg)		% RECOVERING		% RALATIVE STANDARD DEVIATION		PERMISSIBLE LIMITS(FAO/WHO)
	TARKWA	OBUASI	TARKWA	OBUASI	TARKWA	OBUASI	

Fe	100.6	120.12	99.88	99.99	0.01	0.002	
Mn	2.012	1.400	98.95	97	0.099	0.123	2.5
Pb	1.002	.034	99 87	97.89	0.023	0.034	1.5
Hg	0.340	0.212	99.77	98.88	3	1.023	
As	1.800	2.230	78.9	89	1	2.034	0.02(1985)

Table 9: Heavy metal concentration (mg/kg) in the head of fish at Yale Obuasi and Yale Tarkwa

ELEMENT	MEAN CONCENTRATION (mg/kg)		% RECOVERING		% RALATIVE STANDARD DEVIATION		PERMISSIBLE LIMITS(FAO/WHO)
	TARKWA	OBUASI	TARKWA	OBUASI	TARKWA	OBUASI	
Fe	100	120.12	99.88	99.99	0.01	0.002	43 (2011)
Mn	3.012	1.400	98.95	97	0.099	0.123	2.5
Pb	4.013	2.500	99 87	97.89	0.023	0.034	1.5
Hg	0.100	0.212	99.77	98.88	3	1.023	0.6(2011)
As	1.800	2.23	78.9	89	1	2.034	0.02(1985)

APPENDIX II

Water

Fe

Paired Samples Test

		Paired Differences			t	df	Sig. (2tailed)
Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				

				Lower	Upper			
Pair Obuasi - 1 Tarkwa	- .09670	.18075	.05716	-.22600	.03260	- 1.692	9	.125

There is no significant difference

Mn

Paired Samples Test

	Paired Differences					t	df	Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair Obuasi - 1 Tarkwa	.283000	.298014	.094240	.069814	.496186	3.003	9	.015

There is no significant difference

Pb

Paired Samples Test

	Paired Differences					t	df	Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair Obuasi - 1 Tarkwa	-.368700	.698833	.220991	-.868615	.131215	-1.668	9	.130

There is no significant difference

Hg

Paired Samples Test

	Paired Differences					t	df
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	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference		t	df	Sig. (2tailed)
				Lower	Upper			
Pair Obuasi - 1 Tarkwa	.422000	.636480	.201273	-.033311	.877311	2.097	9	.065

There is no significant difference

As

Paired Samples Test

	Paired Differences					t	df	Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair Obuasi - 1 Tarkwa	.052100	.491625	.155465	-.299587	.403787	.335	9	.745

There is no significant difference

Sediment

Fe

Paired Samples Test

	Paired Differences					t	df	Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair Obuasi - 1 Tarkwa	-.199000	.540626	.170961	-.585741	.187741	1.164	9	.274

There is no significant difference

Mn

Paired Samples Test

	Paired Differences					t	df	Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair 1 Obuasi - Tarkwa	1.032530E1	30.794528	9.738085	32.354378	11.703778	1.060	9	.317

There is no significant difference

Pb

Paired Samples Test

	Paired Differences					t	df	Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair 1 Obuasi - Tarkwa	.541300	.323701	.102363	.309738	.772862	5.288	9	.001

There is significant difference

Hg

Paired Samples Test

	Paired Differences					t	df	Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			

Pair Obuasi -	-	-	-	-	-	-	-	-
1 Tarkwa	.934000	.284613	.090002	1.137600	.730400	10.377	9	.000

There is significant difference

KNUST



As

Paired Samples Test

	Paired Differences							Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference		t	df	
				Lower	Upper			
Pair Obuasi - 1 Tarkwa	-.426300	.295287	.093378	-.637536	-.215064	4.565	9	.001

There is significant difference

Fish Fe

Muscle

Paired Samples Test

	Paired Differences							Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference		t	df	
				Lower	Upper			
Pair Obuasi - 1 Tarkwa	-.011600	.487806	.154258	-.360555	.337355	-.075	9	.942

There is no significant difference

Gill

Paired Samples Test

	Paired Differences							Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference		t	df	
				Lower	Upper			

There is no

					Lower	Upper			
Pair Obuasi -									
1	Tarkwa	.344800	.588027	.185950	-.075849	.765449	1.854	9	.097

significant difference

Head

Paired Samples Test

		Paired Differences							
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference		t	df	Sig. (2tailed)
					Lower	Upper			
Pair Obuasi -									
1	Tarkwa	.224200	.532948	.168533	-.157048	.605448	1.330	9	.216

There is no significant difference

Mn
Muscle

Paired Samples Test

		Paired Differences							
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference		t	df	Sig. (2tailed)
					Lower	Upper			
Pair Obuasi -									
1	Tarkwa	.042100	.194416	.061480	-.096977	.181177	.685	9	.511

There is no significant difference

Gill

Paired Samples Test

Paired Samples Test

	Paired Differences					t	df	Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair Obuasi - 1 Tarkwa	-.051000	.135847	.042959	-.148179	.046179	-1.187	9	.266

There is no significant difference

Head

	Paired Differences					t	df	Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair Obuasi - 1 Tarkwa	.226600	.327913	.103695	-.461175	.007975	-2.185	9	.057

There is no significant difference

Pb

Muscles

Paired Samples Test

	Paired Differences					t	df	Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			

There is no

Pair Obuasi - 1 Tarkwa	.326000	.310102	.098063	.104167	.547833	3.324	9	.009
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There is no significant difference

Gill

Paired Samples Test

	Paired Differences					t	df	Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair Obuasi - 1 Tarkwa	.435400	.471324	.149046	.098235	.772565	2.921	9	.017

significant difference



Head

Paired Samples Test

	Paired Differences					t	df	Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair Obuasi - 1 Tarkwa	.012800	.250616	.079252	-.166480	.192080	.162	9	.875

There is no significant difference

Hg

Muscle

Paired Samples Test

	Paired Differences					t	df	Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair Obuasi - 1 Tarkwa	-.031000	.100608	.031815	-.102971	.040971	-.974	9	.355

There is no significant difference

Gill

Paired Samples Test

	Paired Differences					t	df	Sig. (2tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			

There is no

Head

				Paired Samples Test					
				Lower	Upper				
Pair	Obuasi -								
1	Tarkwa	.010700	.016932	.005354	-.001412	.022812	1.998	9	.077

significant difference

		Paired Differences								
				95% Confidence Interval of the Difference						
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper	t	df	Sig. (2tailed)	
Pair	Obuasi -									
1	Tarkwa	.024900	.069488	.021974	-.024809	.074609	1.133	9	.286	

There is no significant difference

As
Muscle

		Paired Differences								
				95% Confidence Interval of the Difference						
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper	t	df	Sig. (2tailed)	
Pair	Obuasi -									
1	Tarkwa	.001760	.009836	.003111	-.005277	.008797	.566	9	.585	

There is no significant difference

Gill

		Paired Samples Test								
		Paired Differences					t	df	Sig. (2tailed)	

Head

Paired Samples Test

	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference		t	df	Sig.
				Lower	Upper			
Pair Obuasi - 1 Tarkwa	.043700	.091343	.028885	-.109043	.021643	-1.513	9	.165

significant difference

Paired Differences

	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference		t	df	Sig. (2tailed)
				Lower	Upper			
Pair Obuasi - 1 Tarkwa	-.003200	.009818	.003105	-.010224	.003824	-1.031	9	.330

There is no significant difference

There is no