COLLEGE OF HEALTH SCIENCE

SCHOOL OF PUBLIC HEALTH

UNIVERSITY OF GHANA

ASSESSMENT OF HEAVY METAL CONCENTRATIONS IN SEDIMENT, WATER AND FISH FROM THE ANKOBRA AND TANO RIVER BASINS IN GHANA

BY

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JULY, 2016.

DECLARATION

1, Gilbert Kofi Awuah, hereby declare that apart from references to other peoples' work, which have been duly acknowledged, this dissertation has been written independently by me and has not been submitted for the award of any degree in any institution.

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DEDICATION

To my wife Mrs. Catherine Elizabeth Awuah, with whose immense love, prayer and support I dare to dream, while making sure of the more important things in life! To my lovely children Kwaw Awuah, Kojo Awuah and Elizabeth Fiba Awuah for giving me the strength to face each day. To Mr Tuomo Pikkarainen of Aquaminerals Finland Ltd, for the encouragement throughout the entire programme.

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ABSTRACT

Background: Arsenic (As), mercury (Hg) and lead (Pb) are toxic heavy metals that occur naturally in the environment. However, their levels are on the rise due to anthropogenic activities posing threat to aquatic wildlife and humans.

Objectives: The aim of the study was to assess As, Hg and Pb concentrations in sediment, water and fishes from the Ankobra and Tano River in the Western Region of Ghana, where human activities; especially the artisanal gold mining have been suspected of grossly polluting the drainage systems.

Methods: An analytical cross-sectional study was conducted to determine the concentration of As, Hg and Pb in fish and aquatic media (water and sediment) from the Tano and Ankobra River basins of Jaway Wharf – Ellenda and Sanwoma respectively. As, Hg and Pb levels in the tissues (muscles) of different fish species "Ekpoke" *Ctenopoma kingsleyae,* "Ekpoke" *Sarotherodon galilaues*, "Ekpoke" *Sarotherodon melanotheron*, "Adwene" *Clarias gariepinus,* "Nzerma" *Pomadasys jubelini*, " Bile" *Parachanna obscura*, and "Senzeke" *Parapenaeus longirostris* (n=53), water samples (n=30) and sediment samples (n=25) were measured using the Atomic Absorption Spectrophotometer (AAS) Pinnacle 900T (Perkin Elmer, USA). Statistical analysis was done using Microsoft version 10 excel spread sheet and STATA software version 13 (StataCorps LP, Chicago, USA).

Results: Heavy metal concentration was in the order; Hg>As>Pb across the study sites. Overall, the mean concentrations of Hg and As were highest in fish (2.09 ± 1.29 mg/Kg) and (2.80 ± 1.52 mg/Kg), followed by sediment (1.40 ± 1.78 mg/Kg) and (0.61 ± 0.40 mg/Kg), and water (0.09 ± 0.36 mg/L) and (0.06 ± 0.05mg/L) respectively. Pb levels were highest in sediment (1.46 ± 4.26 mg/Kg), followed by water (0.14 ± 0.10 mg/L), and then fish (0.11 ± 0.11 mg/Kg) respectively. However, the variability of overall HM levels in sediment, water and fish were not significantly different (p=0.828, 0.570 and 0.978 respectively).

Generally, there were no significant differences in all the levels of As, Hg and Pb in water, sediment and fish in both Ankobra and Tano Rivers.

Conclusion: As and Hg levels in both Tano and Ankobra were above the WHO recommended levels for pristine freshwater ecosystems and may therefore pose a threat to aquatic wildlife and human health.

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LIST OF ABBREVIATIONS

As:	Arsenic
BDL:	Below detection limit
Cd:	Cadmium
EPA:	Environmental Protection Agency
FAO:	Food and Agriculture Organisation
Hg:	Mercury
HM:	Heavy metals
Pb:	Lead
WHO:	World Health Organisation

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Heavy metal (HM) contamination is an issue of global concern. It is the single major environmental problem posed by the mining industry worldwide, affecting most countries and all mining sectors. Environmental pollution has serious implications on water resources, aquatic ecosystems, food security, and human health (Taylor, 2012).

Heavy metals could leach into aquatic systems by natural means through weathering of rocks and be transported through surface runoff and by wind. However, human activities have led to increased contamination of the environment, including the aquatic environment. Excavation of soil and minerals as well as clearing of vast land for mining operations, have resulted in unlocking of chemical composition of bed rocks into water habitats (Wuana & Okieimen, 2011). Operational activities of mining companies such as crashing of rocks could release embedded heavy metals into the environment. Gold (Au) for example is extracted with toxic chemicals such as cyanide and mercury, which sometimes contaminate the environment. The waste generated after extraction (mostly called tailing damp) contains these toxic chemicals and is the single major environmental challenge faced by the mining industry worldwide, affecting most countries and all mining sectors (Cobbina et al., 2015). Tailing damps are huge containments found in all mining sites, and heavy metals from these tailing damps are sometimes released into the aquatic systems either unintentional or intentional through dike failure or release of excess water from the tailing damp (Cobbina et al., 2015).

In rural poor communities, mostly in developing countries in Africa, Asia and South America, rivers and streams are the main sources of drinking water, and for domestic usage (Rijsberman, 2006). Aquatic ecosystems are adversely affected as a result of changes in water chemistry due to introduction of excess dissolved anions and cations. In such conditions, the aquatic life forms are either move or killed in situations where organisms are unable to tolerate or make physiological adjustments. This leads to distortion in the trophic levels and eventually the collapsing of most aquatic ecosystem functions. As a result, communities who depend on the aquatic ecosystem within the mining environments are confronted with food security and health issue leading to malnutrition and abject poverty (Falkenmark & Lundqvist, 1998).

Heavy metal concentrations in the environment have increased seven-fold globally owing to a combination of anthropogenic activities and climate changes, with mining playing a major role. In Ghana, researchers have linked gold mining activities (mineral exploitation, disposal of tailings and waste waters, ore transportation, smelting, refining) with the persistent release of harmful and toxic metals such as mercury (Hg), lead (Pb), arsenic (As) and cadmium (Cd) among others into aquatic habitats (Cobbina et al., 2015).

Other possible sources of heavy metal contamination of water and sediments include increase in human activities; urbanization, agricultural runoff containing fertilizers and pesticides, leaching from landfills, industrial and sewage effluents (Akan et al., 2012). Heavy metals are non-biodegradable and therefore persist in the aquatic habitat. They are mostly deposited in sediments or/and assimilated by microorganisms, as well as concentrated in the tissues of sedentary organisms such as clams to a lethal level (Length, 2011).

Accumulations of heavy metals in aquatic organisms tend to increase from lower to higher trophic levels along the food chain. Fish is a major source of proteins, minerals, vitamins and omega-3 fatty oils, which are needed to improve health and prevent diseases (Basim & Khoshnood, 2013). However, fish could also be a source of HM contamination through their inherent ability to bioaccumulate. Heavy metals accumulated fish can be stored over a long period of time in their liver, gills and bones, and can finally be transferred to other animals including humans through the food chain (Asante et al., 2014).

HM contamination in fish is determined by the water pollution levels, food and sediments. Sediments also play a contributory role in determining HM contamination patterns in the aquatic systems, in that they behave both as carriers and sinks for the contaminants (Li, 2014) However, the level of accumulation in fish is dependent on the route of uptake, species of the fish concerned, and the kind of HM. These account for the reason why fish is sometimes used as a biomonitor in the assessment of bioaccumulation and biomagnification of HM within the ecosystem (Begum et al, 2009).

HM contamination in fish can predispose consumers to the various acute and chronic health effects of these toxic metals (Anim-Gyampo et al., 2013). There is growing evidence linking toxicants such as Hg, Pb, As, and Cd to the incidence of cognitive impairments, especially in children and all sorts of cancer with high incidence in upper gastrointestinal cancer rates, decreased immunological defenses, disabilities associated with malnutrition, intrauterine growth retardation, nervous system disease, kidney problems, reproductive disorders, skin lesions, vascular diseases, impaired psychological faculties, and endocrinal damage (Cobbina et al., 2015).

Regulation and control on the use of heavy metals are not fully enforced in most developing countries even though products such as paints and agro chemicals, which are known to have heavy metals, are widely used. Ghana is yet to have stringent laws for the use and disposal of hazardous waste, although Ghana is a signatory to “The International Convention on The Control of Trans boundary Movements of Hazardous Waste and their Disposal” known as the ‘Basal Convention’ (Dogbevi, 2009). The Food and Drug Law (PNDC Law 305 B), amended with an act of parliament, Act 523 are some measures intended to regulate usage of trace metals, but these laws are yet to be fully implemented. The EPA, Ghana, acceptable limits in water bodies have been set; Pb - 0.1mg/l, Zn - 10mg/l, Fe - 10mg/l and Cd< 0.1mg/l (Bannerman et al., 2003), but implementation regulations are frustrated by lack of man power and resources.

This study therefore assessed the bioconcentration levels of HM in some selected fish species and aquatic media (water and sediments) in the Ankobra and Tano river basins in the Western region of Ghana, where human activities, especially artisanal gold mining have contributed to aquatic pollution.

1.2 Statement of the Problem

The Ankobra and Tano river basins run through gold, manganese and diamond mining communities in the Western Region. The Ankobra river basin receives inflow from a network of streams and rivers, majority of which run through major agricultural lands and areas of heavy mining activities including a manganese mine at Nsuta and seven large-scale gold mines dotted around the Prestea, Tarkwa, Iduaprim, and Damang environments (Akabzaa, Jamieson, Jorgenson, & Nyame, 2009). Even more threatening is the drainage from several scattered small scale (artisanal) mining sites, locally called "galamsey" along the basin (Kortatsi, 2007). Sanwoma and Jaway Wharf – Ellenda are major fishing communities, which heavily depend on the consumption of fish from the Ankobra and Tano river basins respectively.

Heavy metal contamination is noted as a problem and a key determinant of poor quality of water, fish and sediments (Begum et al., 2009). Consumption of contaminated fishes from the Ankobra and Tano rivers could have serious health implications.. In the aquatic food chain, fish is known to bio-accumulate large amounts of HM (Anim et al., 2011).

Consumption of contaminated fishes with HM (Hg, As, Cd, Pb) above the acceptable levels have led to several detrimental health risks such as lung damage, coronary heart disease, neurologic and neurobehavioural disorders, dermatologic diseases, developmental anomalies, haematologic disorders, and high cumulative mortality rates due to cancers (Järup, 2003; Tchounwou et al., 2003). Hence there is the need to constantly monitor concentrations and distribution of HM in commercial fishes and their habitats.

1.3 Justification

Several researches have been conducted in to ascertain the levels of HM in aquatic ecosystems in Ghana largely affected by mining activities (Donkor, Nartey, Bonzongo, & Adotey, 2006; Hayford, Amin, Osae, & Kutu, 2008). Specifically, studies done in the Ankobra and Tano river basins have highlighted the presence of some HM (Bannerman et al., 2003). In the last decade especially, there has been significant increase in mining activities following the legalization of small–scale mining, together with illegal artisanal mining activities. There is therefore a a greater likelihood that HM contamination levels will increase above internationally accepted recommended levels within the catchment area of these mining activities; including Ankobra and Tano rivers (Donkor et al., 2006). A recent report submitted to the Water Resources Commission by the Water Research Institute on Groundwater Inventory and Hydro-geological Assessment on the Ankobra River Basin indicated the presence and levels of metals in water bodies within the basin are alarming (Myjoyonline, 2015). Meanwhile, it has been documented that the contribution of fish to the total animal protein consumption in Ghana is 60% (Nunoo et al., 2014). This however presents a worrying situation, since fish from these communities are transported and sold in major markets in the Western Region and eventually to other parts of Ghana. This undoubtedly poses a risk to human health and there is therefore a need to regularly monitor HM levels in affected river basins to protect human lives as well as the ecosystem. This could serve as basis for public health education on the health implications of eating contaminated fish and to guide good environmental management programs.

1.4 Objectives

1.4.1 General Objective

To assess heavy metal concentrations in fish, water and sediments from the Ankobra and Tano river basins.

1.4.2 Specific Objectives

- To determine the concentrations of Hg, Pb and As in tissues of fish caught from Ankobra and Tano river basins
- To determine the concentrations of Hg, Pb and As in water collected from the Ankobra and Tano river basins
- To determine the concentrations of Hg, Pb and As in sediments collected from the Ankobra and Tano river basins

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Introduction

A heavy metal (HM) is any metallic chemical element which has a relatively high density and is toxic or poisonous even at low concentration levels (Cobbina et al., 2015). The occurrence and concentration of many HM is increased as a result of human activities. The input of HM to the environment from anthropogenic activities is complicated; wastes from chemical and manufacturing industries containing heavy metals are directly or indirectly discharged into the aquatic ecosystem causing serious environmental pollution and even threatening human life (Das *et al.*, 2008). Naturally, HMs tend to concentrate in soils and sediments and artificially through anthropogenic factors (Anim-Gyampo et al., 2013) and are deposited into water bodies via chemical weathering of rocks and soils, agricultural runoffs, mining, industrial waste discharge, batteries, lead based paint, and gasoline and improper domestic waste discharge into water ways (Anim et al., 2011).

The major hazard to human health from HM are associated with exposure to the highly toxic elements which include Hg, Pb, As and Cd (Järup, 2003).

2.1.1 Sources of heavy metals release into the aquatic ecosystems

The release of heavy metal into aquatic systems is of two origins; the natural and the anthropogenic sources. The natural sources are mainly the eruption of volcanoes, landslides, surface runoffs and dust particles from the atmosphere attached with heavy metals discharged into the aquatic habitats. Human activities since the interception of the industrial era have tremendously increased the release of heavy metals from the earth's crust into surface water bodies. The man's ambitions to harness the deep natural riche minerals ores have resulted to tooth and knife approach in salvaging these resource without concern for the environment. Point and nonpoint contamination of water resources with heavy metal are on ascendency through the geological time frame as a result of alteration of volcanic and sedimentary rocks by hydrothermal processes and chemical reaction leading to formation of acidic rocks and soils. Further leaching of heavy metal into water bodies are caused by acid mine drainage (AMD) by dissolving the bond that holds these chemical together in the bed rock (Resongles et al., 2014). The chemical leaching of heavy metals into solution is also enhanced by increasing the surface area of particles sizes through the artificial pulverizing of huge bedrocks during the mining operation.

2.1.2 Acid mine drainage as source of heavy metals release into aquatic ecosystems

Generally, there are two types of mining operation depending on the geology and type of mineral resources; surface and underground mining (Adetunde et al., 2014). Surface mining is mostly practiced where mineral deposition occurred close to the surface of earth's crust. Surface mining includes; strip mining, open pit, dredging and hydraulic mining (Fuggle and Rabie, 1994). Underground mining involving up to about 50 m penetration of the ground, includes bord and pillar mining operations. The chemical reaction between water and rocks containing sulfur bearing minerals often results into metal rich solution called acid mine drainage (AMD) (Younger, 2001). The hydrogen bond between non-metal (sulfur) leads to formation of solution with low pH levels and depending on the geochemistry and physical characteristic of the bedrocks the ultimate solution are acidic. In most situations, pyrite (FeS_2)

compounds reaction with water molecules triggered the production of acid generation solution and metal dissolution in coal and hard rock sites. This could result in AMD system attaining temperature as high as 47^{o}C and pH low as 3.6 (Younger, 2001). The redox reaction is a slow process and the amounts of acid produce are contained by the buffering capacity of the water. However, under the mining conditions, the exposed surface area of the sulfur-bearing rocks are increased significantly due to pulverizing of the rocks leading to excess acid generation beyond the water's natural buffering capacities. The acidic nature of the AMD enhances the dissolution of heavy metals into the solution and makes the AMD a soup of toxic heavy metals and therefore become an environmental liability for mining company all over the world. In mining companies, where there are adherent to environmental management policies, the AMD and pulverized rocks materials are contained in dump sites normally referred to as tailing dumps. In this way, it is expected that, the toxic heavy metals will be neutralized with time. However, most of these toxic heavy metals are released either unintentional through dike failure or intentional through discharged by dilution of the AMD into the surface water systems. There is also a possibility of seepage of AMD into the ground water leading to contamination of groundwater and finally into drains and rivers systems. In situations where tailing materials are not contained, especially the case of small scale mining industries (galamsey), waste materials are continuously released into water bodies without a recall to consequences of the impact heavy metal pose to aquatic systems.

2.1.3 Fate of heavy metals in aquatic ecosystems

Unlike trace metals, heavy metals in aquatic ecosystems are threat to aquatic life at all levels of concentrations. In the aquatic habitats, they are either deposited into the bottom sediment, absorbed by organisms or remain in suspension.

Sediment serves as a sink through which heavy metals re-enter the earth's crust. Fine sediment particles provide large surface area ratio to size for absorption of heavy metal from the water column, which settle out due to weight and buried into the sediment matrix. Microscopic phytoplankton organisms also carry out scavenging of heavy metals from water medium. Submerge weeds absorb significant quantity of heavy metal from the water into their systems and finally sequestered into the sediment. Macro invertebrates absorb heavy metals through feeding on detritus, which are mainly plants and animals parts. Particulate organic matters (POMs) also provide substrata onto which most suspended heavy metals in solutions are adsorbed which largely reflect prevailing condition within the water medium. The heavy metals enter the food when primary producers such as plankton are grazed on by zooplankton and in turn feed on by nektons. Sedentary organism such as bivalves, oysters and clams incorporates heavy metals into their body muscles through filter feeding. Heavy metal are non-digestible they are rather become lodged in the organs such as gills, gall bladder, stomach, liver, tissues as well as shell of shellfish and fins fish in contaminated aquatic habitats. Mobility of dissolved heavy metals through water, sediment and biota in an ecosystem becomes complex resulting in formation of complex compound that remain persistent. In the case of mercury, a sulfate reducing bacteria bind methyl group (organic) to mercury (inorganic) to form methyl-mercury (Gilmour et al., 1992). The reaction is enhanced under low pH and in the presences of dissolved organic compound at the water-sediment interface (Wright and Welbourn, 2002). Methylmercury is highly soluble in water and capable of crossing biological membranes and become deposited in fatty tissues of organisms. The high affinity of organic compounds for fatty tissues results in bioconcentration and biomagnifications of complex organic compound rich in heavy metals. Additional, the non-biodegradable of heavy metals result in their levels being comparable higher in organisms than in the water and the sediment. As such, mercury levels found in clams from contaminated environments are millions of times higher than in water or sediment, which they live in or feed on.

2.1.4 Impact of heavy metals on aquatic ecosystems

Metal extraction is an old industry that has evolved over the years into multi billon business and well-coordinated in developed worlds. On the other hand, in the less developed countries, metal extraction is fast glowing industry but in the hand of selected few if not fully operated by the expatriates. This has led to less monitoring, supervising and enforcement of the legislature per mining laws. As a result effluents and wastewater from mining companies loaded with high concentration of heavy metal are discharged into the aquatic ecosystems posing threat to aquatic wide life. The dissolved heavy metals in water are absorbed by fishes and other aquatic life via the gills and the skin by diffusion as well as feeding and predation. Since metals are non-biodegradable even the diluted forms of heavy metals are transformed into potential toxic concentration levels through bioconcentration. Metal toxicity produces adverse biological effect on the very survival of the aquatic organisms; their growth, metabolisms and reproduction are impaired through sub lethal effects (Wright and Welbourn, 2002).

2.1.5 Effect of heavy metal contamination on aquatic organisms

The physiology of aquatic wildlife evolved from simple to complex and varied significantly from species to species. As such, habitat becomes a limiting factor for aquatic organisms with different physiological requirement. Generally, there are two broad aquatic ecosystems based on salinity levels; marine and freshwater. Unlike terrestrial organisms, aquatic organisms are unable to transcend between the marine and freshwater ecosystems. Hence, in situations of excess contamination, aquatic ecosystems are pushed to edge of collapsing or extinction. The effect of heavy metal toxicity in water bodies are expressed in the growth rates, physiological functions, mortality and reproduction patterns of aquatic resources (Amundsen et al., 1997). Normally, dissolved heavy metals enter aquatic organisms at three levels; gills, digestive track and body surfaces (Beijer and Jernelove, 1986). Fish species of certain taxa have poisonous effect of chromium expressed in the body fluid as anemia, eosinophilia and lymphocytosis, bronchial and renal lesions as well as damages to the gills (Afshan et al., 2014). Exposure of aquatic organisms to cadmium and mercury have resulted into reproductive impair, kidney dysfunction, tumors, and hepatic dysfunctions (Mansour and Sidky, 2002). High level of lead in aquatic systems can cause generative damage in some aquatic life and cause blood and nervous defectiveness in animals and fishes (Kalay et al., 1999).

2.1.6 Effect of heavy metals on humans via intake of contaminated fish

The world fish consumption has doubled in the past 40 years and stand at 16 kg/year (WHO 2013). Fish protein is the most preferable form of animal diet due to its low cholesterol levels. Though world fish production is dwindling, fish consumption is projected to increase about 30 % fold between 210 and 2030 (WHO 2013). Since, there are high probabilities of bioconcentration and biomagnifications of heavy metals in the tissues of aquatic wildlife, it is therefore necessary to monitor the concentrations of heavy metals in commercial fish to ascertain the public health risk of human consumption. Ingestion of heavy metal through fish intake has resulted into ill health complication in humans' abnormal growth, reproductive defects and kidney failures.

2.1.7 Health implication of mining in Ghana

The increasing usage of HM such as arsenic and mercury in the mining industry over the years has brought in its wake serious environmental pollution through effluents and emanations (Anim et al., 2011). The situation would not get any better with artisanal and small-scale gold mining on the rise in many low- and middle income countries such as Ghana, which has witnessed its proportion of gold mining increased from 6% in 2000 to 23% in 2010 (Basu et al., 2015).

The main activities of the mining industries in Ghana are matters of concern as they negatively impact the environment. Their processing ore and methods of disposing off waste products are the main sources of HM pollution. Mine tailings are retained in sedimentation ponds and piled up for treatment; however these normally lead to siltation of nearby streams, destroying aquatic fauna and flora. There is eventual leach of elements such as mercury, arsenic, copper, chromium and zinc from acidic effluents, which then ends up polluting streams and rivers (Hayford et al., 2008).

Higher lead, zinc, and mercury levels have been found in the Ankobra and Tano river basins, with higher mercury levels detected in human blood (Baah, 2002). Ingestion of HM such as mercury through food (fish and water) may expose one to respiratory, neurologic and psychological diseases (Järup, 2003).

2.2 Heavy metals and their toxicity

2.2.1 Mercury

Mercury is an important element and its application span across various fields including science, agriculture, industry and dentistry and medicine. Mercury is used in thermometers, barometers, sphygmomanometers, compact fluorescent light bulbs, and control systems (Järup, 2003).

Mercury occurs naturally from the earth's crust, and from human (anthropogenic) activities such as mining. The emitted mercury both natural and anthropogenic is in an inorganic form, predominantly metallic vapour. The inorganic mercury is then converted to organic compounds such as methyl mercury in aquatic environment, which makes them prone to biomagnification in the food chains (Voegborlo & Adimado, 2010).

High concentrations of mercury has been identified in certain fish species and crustaceans (Abrefah et al., 2011), notably among them are shark, swordword fish and tuna (Järup, 2003). However, the size of the fish has been found to be a major factor of accumulation. There is a an association between the fish size and rate of accumulation of Hg, with accumulation levels recording high in bigger fish (Akoto et al., 2012). Therefore consumption of fish from fresh water contaminated with mercury is a significant health risk.

Health effects from mercury may include lung damage, neurological and psychological disorders, kidney damage, and congenital abnormalities (Järup, 2003) The international standards for acceptable levels of mercury in contaminated food is 0.5ppm, thus consumption above these maximum levels is a major health risk to the humans, (Australia New Zealand Food Standards Code, 2013; Choi, 2011; Jilai, 2014; Lagoon, 2011; Qwp, 2007).

Researches conducted in Ghana, reveal low concentration of mercury in fish species obtained from the Atlantic Ocean, along the coast of Ghana, which are less than the FAO/WHO limit of 0.5 µg/g, (FAO & WHO, 2011; Voegborlo & Adimado, 2010), an indication of low concentrations of mercury in marine environment.

2.2.2 Lead (Pb)

Lead (Pb) is a toxic metal that occurs naturally in the earth's crust and can be found in all parts of the environment. However, most lead concentrations are the result of human activities like mining, agriculture, burning of fossil fuels and manufacturing. The main source of Pb in most river basins comes from persistent release of Pb and other toxic substances through mining activities such as ore transportation, mineral exploration, smelting, refining, disposal of tailings, and wastewaters (Cobbina et al., 2015).

Concentrations of Pb have been found in to be higher in fish tissues such as bones, gills, liver, kidneys and scales, with gases moving via the gills to the blood stream as a major uptake mechanism (Akan et al., 2012). In the human body, Pb has been reported as a main hazard to human health. The toxic effect of Pb have been proven at low very low levels, with some studies even suggesting that there may be no level of exposure below which Pb is harmless (Ekpo et al., 2013). When Pb accumulates in the human body through such means as ingestion, it replaces calcium in bones, and can result in a myriad of health problems such as impairments to intellectual functioning, kidney failure, miscarriage, hypertension, lung cancer and even death (Jilai, 2014).

In Kenya, it has been reported that Pb concentrations in tilapia in the wet and dry seasons in the *Athi-Galana-Sabaki tributaries* respectively, were higher than prescribed by WHO in both seasons. Higher concentrations of Pb detected in the dry season was attributed to increased concentration in water as a result of evaporation. More so, higher temperatures may lead to higher activity and ventilation rates in fish, which may tend to lower the oxygen affinity of blood and consequently boost the pollutant accumulation rate (Nzeve et al., 2014)

In Nigeria, Pb levels detected in fish from Ogba, Warri and Ikpoba Rivers were lower than the WHO and FAO permissible limit (2.0mg/kg) which implied that fish from these rivers were safe to consume (Asante et al., 2014; Mohammadnabizadeh et al., 2014; Perera et., 2015)

2.2.3 Arsenic

Arsenic is widely distributed in natural waters and is often associated with geological sources, but in some locations anthropogenic inputs, such as the use of arsenical insecticides and the combustion of fossil fuels, can be extremely important additional sources. Inorganic arsenic is a known carcinogen and can cause cancer of the skin, lungs, liver and bladder (Yunus et al., 2011).

Fish is noted as the principal source of arsenic in the diet, and more than 90% of the arsenic found in marine fish is arsenobetaine (organic arsenic compound), which is considered non-toxic (Chen et al., 2009). However, Uneyama et al., (2007) noted that the organic arsenic in food and seafood appeared to be much less toxic than the inorganic forms. The study further showed that though most fishes had low concentration of arsenic, the higher bioaccumulation was found in the muscles (Vieira et al., 2011). Lower concentrations of As were detected in fishes from the north East coast of India (Kumar et al., 2012) than those from Gulf of Cambay in North West coast of India but higher concentrations were noted in fishes from Gresik coastal waters of Indonesia (Agoes and Hamami, 2007). Also, *Kwansa-Ansah et al., (2012)* reported a low mean concentration of 0.59 to 2.45 µg /g (wet weight (w.w)) of As in tilapia from the Volta Lake

CHAPTER THREE

3.0 METHODOLOGY

3.1 Type of study

An analytical cross-sectional study was carried out to determine levels of heavy metals in fishes and aquatic media (water and sediments) from the Ankobra and Tano river basins.

3.2 Study area

This study was done at Sanwoma and Jaway Wharf – Ellenda, in the Ellembelle and Jomoro districts respectively in the Western Region of Ghana.

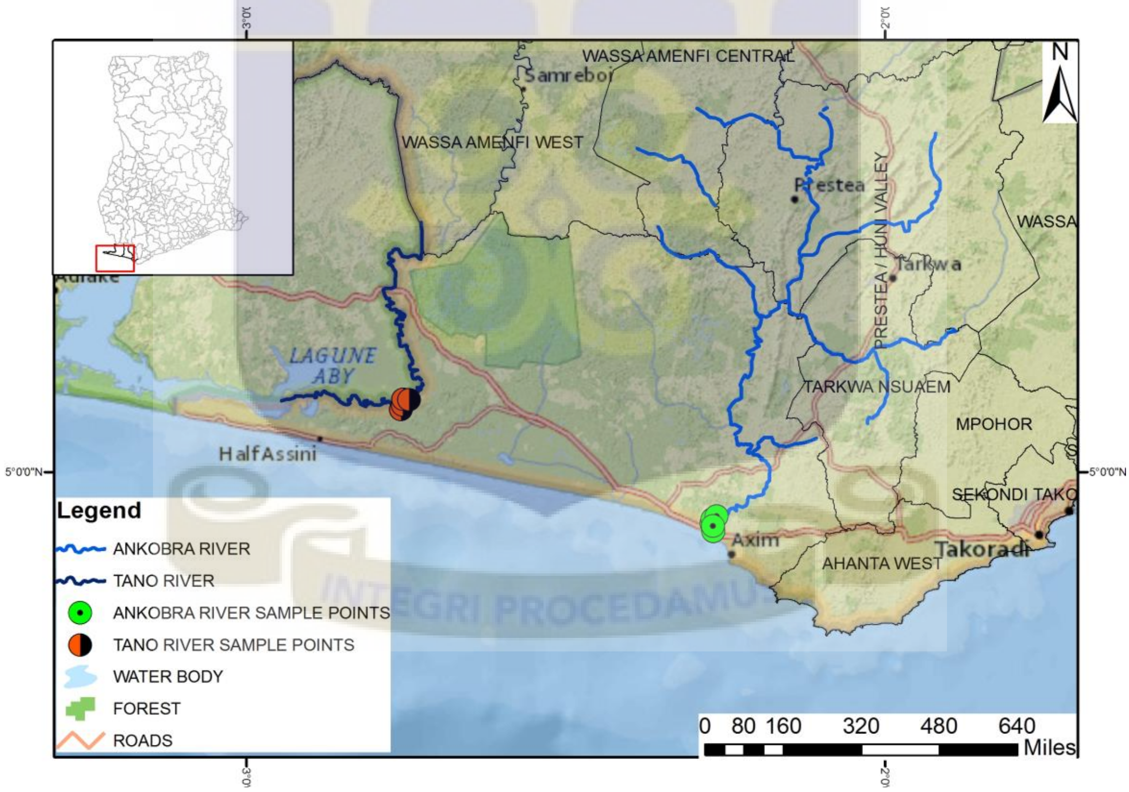

Figure 3.1: A Map Showing Tano and Ankobra Rivers Basins

Source: Centre for Remote and Geographic Information Systems (CERGIS, 2016)

Sanwoma

Sanwoma is drained and bounded on the East by the Ankobra River. It is bounded on the South by the Gulf of Guinea, West and North by Asanta and Nkroful respectively. Fishing is the major economic activity in the area mostly due to its strategic location at the estuary of the River Ankobra. Farming is also done but on a smaller scale. The georgraphical coordinates of the area of the Ankobra River that was used for the study covered; 4° 54' 11.14" N, 2° 16' 5.91" W to 4° 55' 51.00" N, 2° 14' 55.19" W.

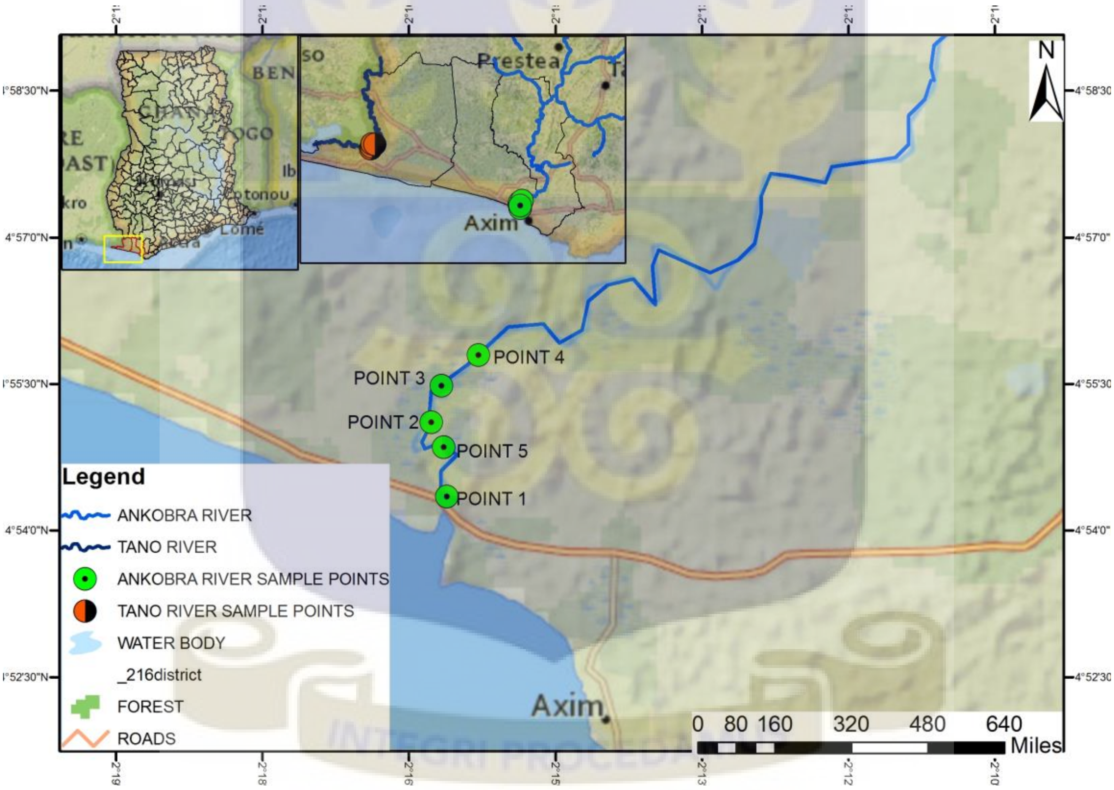

Figure 3.2: A Map Showing sampling Points at the Ankobra River

Source: (CERGIS, 2016)

Figure 3.3: Ankobra River at Sanwoma

Jaway Wharf- Ellenda

Jaway Wharf – Ellenda is a border town in the Jomoro District along the Tano River basin. It is noted for its vibrant market activities, which brings both Ghanaians and Ivoirians together for trading in all kinds of goods. Fishing in the Tano River is a major occupation and serves as a centre for the supply of tilapia to the Nzema communities of the Western region, as well as other parts of the country. The geographical coordinates for the Tano River area that was used for the study covered; 5° 6' 49.08" N, 2° 44' 37.24" W to 5° 6' 35.01" N, 2° 46' 13.55" W.

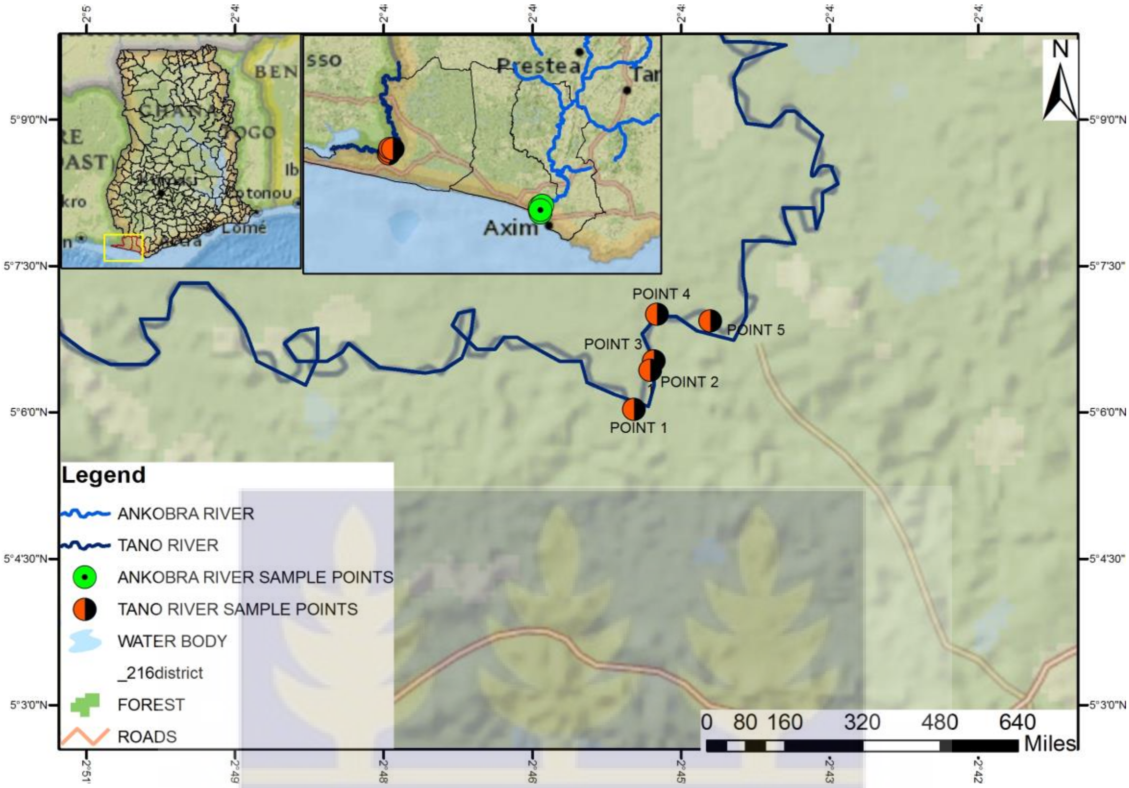

Figure 3.4: A Map Showing Sampling Points at the Tano River

Source: (CERGIS, 2016)

Figure 3.5: Tano River at Ellenda Jaway

3.3 Variables of interest

The variables of interest were the levels of heavy metal concentrations in fish, water and sediments.

3.4 Fish Sample Collection

The fish species collected were either freshwater or blackish water specimen.

In total, fifty-three (53) fish samples were collected by trap set overnight by local fishermen and used for analysis of As, Hg and Pb.

Sediments were collected from five (5) locations each in the Ankobra and Tano Rivers respectively (Figure 3.0). At each location in the Ankobra River, three (3) replicates of sediment samples were collected from five (5) different spots along the river, making a total of fifteen (15) sediment samples (Figure 3.1). Similarly, two (2) replicates of sediment samples were also collected at each location of the five (5) sites or spots across the river, making a total of ten (10) samples in the Tano River (Figure 3.3). In total, twenty five (25) sediments were sampled from the two river systems.

Similarly, water samples were collected from the five (5) locations in the Ankobra River at Sanwoma and Tano River at Jaway Wharf – Ellenda. At each point, three (3) replicates of water samples were collected at five (5) different spots along the river making a total of fifteen (15) water samples from each river. Over all, fifty-three (53) fishes, thirty (30) water and twenty-five (25) sediment samples were collected and analyzed from both river systems.

3.5 Sampling Method

A simple random sampling technique was employed to collect fresh fish directly from fishermen at the various landing sites of the study areas. Six (6) fishermen were contracted to set up fish traps randomly overnight within the lower, middle and upper sections of Rivers Ankrobra and Tano respectively. Sediments were collected from each location using Ekman grab onboard a local canoe. Water samples were also collected from the sub-surface of the same area in the two rivers.

3.6 Data collection techniques and tools

Fresh fish obtained from the fishermen were immediately cleaned and sorted into similar kinds/species. The sorted specimens were then packaged into plastic ziplock bags, labelled, transferred into a cooler with ice packs and finally transported to the laboratory for further treatment and analysis. Sediments were transferred into ziplock bags labelled and placed in a cooler with ice packs. Water samples were collected into a pre-acid washed cleaned 250 ml sampling bottle. The water samples were acidified by addition of 1.5 ml concentrated analytical grade nitric acid as described by (Apha, 2008). The sample locations were geo-referenced using Gamine eTrex GPS (Garmin Ltd, Schaffhausen, Switzerland). The GPS coordinates of the various sampling points for the Ankobra and Tano River were recorded as shown in table 3.1 below;

Table 3.1: GPS COORDINATES

GPS COORDINATES				
ANKOBRA			TANO	
POINT	LATITUDE	LONGITUDE	LATITUDE	LONGITUDE
1	4° 54' 11.14" N	2° 16' 5.91" W	5° 6' 49.08" N	2° 44' 37.24" W
2	4° 54' 44.71" N	2° 16' 0.58" W	5° 7' 01.41" N	2° 45' 14.02" W
3	4° 55' 8.72" N	2° 16' 13.58" W	5° 6' 30.43" N	2° 45' 16.30" W
4	4° 55' 31.00" N	2° 16' 3.83" W	5° 6' 2.56" N	2° 45' 34.40" W
5	4° 55' 51.00" N	2° 14' 55.19" W	5° 6' 35.01" N	2° 46' 13.55" W

3.7 Laboratory Procedures

In the laboratory, the fish specimen were thawed and identified by species using the FAO fish identification guide in the Department of Marine and Fisheries Sciences. Six (6) fish species were identified belonging to six (6) families (*Clariidae*, *Anabantidae, Cichlidae*, *Channidae*, *Haemulidae*, *Paenaediae)* from the Tano River. The species included 'Ekpoke' *Ctenopoma kingsleyae sp*. (Gunther, 1896); 'Ekpoke' *Sarotherodon galilaues sp (*Linnaeus 1758*)*, 'Ekpoke' *Sarotherodon melanotheron sp*. (Ruppel, *1852)*; 'Adwene' *Clarias gariepinus sp*. (Burchell, 1822) *and* 'Bile' *Parachanna obscura sp*. *(*Gunther, 1861).

In the Ankobra River, four species were identified. The species from the Ankobra were from the freshwater and marine environment because of the Ankobra estuary. The freshwater species included, *"*Adwene" *Clarias gariepinus sp*. *(*Burchell, 1822), and "Bile" *Parachanna obscura sp*. *(*Gunther, 1861). The brackish species were 'Senzeke' *Parapenaeus longirostris* (Lucas, 1846) *and* 'Nzerma'. *Pomadasys jubelini* (Cuvier, 1830)

Laboratory analyses of Hg, As and Pb concentrations in fish (muscle), water and soil sediments were carried out using the Atomic Absorption Spectrophotometer Pinnacle 900T, (Perkin Elmer, USA) at the Ecological Laboratory, Institute of Environment and Sanitation (ISA), University of Ghana.

3.7.1 Fish Sample Preparation

Fish samples were further washed with de-ionised water to ensure they were free from contamination (Anim et al., 2011) and muscles were removed and prepared for HM analysis.

1. Five grams of fish sample was weighed into a macro-kjeldahl digestion flask.
2. 20 ml each of concentrated nitric acid and distilled water was added respectively. The volume of the mixture was reduced to 20 ml by boiling.
3. The mixture was cooled, and 10 ml of concentrated sulphuric acid was added and boiled. The mixture was further treated with addition of nitric acid till digestion of fish tissues.
4. The mixture was cooled, and 10 ml of saturated ammonium oxalate solution was added and boiled until copious white fumes were produced. The oxalate treatment assists in removing yellow colouration due to nitro compounds, such as fats to obtain a clear solution.
5. The solution was adjusted to 100 ml mark by addition of distilled water.
6. The solution was aspirated for heavy metals analysis using the Atomic Absorption Spectrophotometer Pinnacle 900T.

A blank solution was prepared by addition of nitric acid to distilled water as well as ammonium oxalate for quality control. Nitric acid, sulphuric acid, perchloric acid and hydrogen peroxide are commonly used oxidants. As each of them possesses inherent advantages, mixtures containing two or more of the above reagents were recommended. The procedure could be shortened considerably by the use of mixed oxidizing agents. The main advantage is that by oxidizing at less than 350 °C, the nitric acid is used more economically and there is little likelihood of loss of element by volatilization and the process does not require constant supervision.

3.7.2 Sediment Sample Preparation

Wet digestion of sediment samples were carried out using a mixture of nitric and perchloric acid solutions before aspirating with the Atomic Absorption Spectrophotometer Pinnacle 900T, Perkin Elmer for mercury, lead and arsenic.

1. 0.2 – 1.0 g of sediment samples (after oven-dry, 60°C to a constant) were weighed into a 125 ml Erlenmeyer flask.
2. 10 ml of ternary mixture (20 ml $HClO_4$: 500 ml HNO_3: 50 ml H_2SO_4) was added under a fume hood.
3. The contents were mixed and heated gently at low to medium heat on a hot plate under a perchloric acid fume hood.
4. Digestion of sediment samples continued until dense white fumes (fumes of sulphuric acid) appeared.
5. The mixture was then heated strongly (medium and high heat) for half a minute, and allowed to cool.
6. 40 – 50 ml distilled water was added, and boiled for half a minute and cooled.
7. The resulted mixture was filtered into 100 ml Pyrex volumetric flask and the volume was adjusted to the mark by addition of distilled water.

The solution was stored and heavy metal determination for mercury, lead and arsenic was carried out.

3.7.3 Water Sample Preparation

The acidified water samples were vigorously mixed and aspirated directly using Atomic Absorption Spectrophotometer Pinnacle 900T, (Perkin Elmer, USA) for determination of Hg, As and Pb levels.

3.8 Quality Control

Strict quality control measures were employed to ensure reliability of the results. All blanks and duplicates (samples) were analyzed after every 10 sample analyses to ensure precision and accuracy of analyses. The instruments were calibrated with standard solutions of the various metal, and all regents and standard stock solutions met the analytical-reagent grade (Bortey-Sam et al., 2015).

3.9 Data Processing and Analysis

Data obtained was coded and entered into Microsoft Excel version 13 (Microsoft Corporation, Washington, USA) for organization and analysis. Excel spreadsheet was further exported to STATA software version 13 (StataCorps LP, Chicago, USA) for the appropriate statistical analyses.

Means, standard deviation, ranges, p-values as well as percentages were used to describe data obtained. Graphical representation of data was done where appropriate using tables and bar charts. Kruskal-Wallis Test was used to find out differences in the concentration levels. This test was used because the nature or distribution of data did not satisfy the use of parametric tests such as T test an ANOVA. The data was thus heavily skewed. Qualitative data was summarized as text. Concentrations in micrograms per litres for sediment, fish, and water were converted to milligram per kilogram and microgram per litres respectively for an appropriate comparison with WHO recommended levels of HM in fish, water and sediments.

3.10 Ethical Consideration/Issues

The study was submitted to and approved by the Ethics and Research Committee of Ghana Health Service before embarking with the study.

Permission was sought from the chiefs, fishermen and assemblymen at Sanwoma and Jaway Wharf – Ellenda

CHAPTER FOUR

4.0 RESULTS

The summary of results for this study is presented in table 4.1 below, showing the mean concentrations, standard deviations and p-values for arsenic (As), mercury (Hg) and lead (Pb) in sediment, water and fish samples from the two study sites, Ankobra and Tano Rivers.

4.1 Concentration of heavy metals in sediment

The mean concentrations of As, Hg an Pb in sediment from the Tano and Ankobra rivers are presented in table 4.1. The mean concentration of HM in Tano were in the order; Pb (2.75 ± 6.68 mg/kg) > Hg (1.09 ± 0.73 mg/kg) > As (0.47 ± 0.29 mg/kg) whereas that of Ankobra was Hg (1.59 ± 2.21 mg/kg) > As (0.71 ± 0.46 mg/kg) >Pb (0.59 ± 0.30 mg/kg). Comparatively, mercury levels in sediments from Ankobra (1.59 ± 2.21 mg/Kg) were higher than that of Tano (1.09± 0.73 mg/Kg), but the difference was not statistically significant (p=0.828). Arsenic levels were also relatively higher in Ankobra (0.71 ± 0.46 mg/Kg) samples than in Tano (0.47 ± 0.29 mg/kg). Again, there were no significant differences between the levels recorded in the two rivers.

Table 4.1: Mean concentration, standard deviation and p-values of mercury, arsenic and lead in sediment, water and fishes from the Tano and Ankobra rivers

	Mercury concentration			Arsenic concentration			Lead concentration		
Source	Mean	SD	p-value	Mean	SD	p-value	Mean	SD	p-value
Sediment (mg/Kg)									
Tano	1.09	0.73	0.828	0.47	0.29	0.570	2.75	6.68	0.978
Ankobra	1.59	2.21		0.71	0.46		0.59	0.30	
Water (mg/L)									
Tano	0.01	0.01	0.680	0.07	*	0.527	0.11	0.07	0.610
Ankobra	0.15	0.47		0.06	0.06		0.15	0.11	
Fish (mg/Kg)									
Tano									
Ctenopoma kingsleyae	2.51	1.28		2.72	1.33		0.1194	0.1014	
Sarotherodon galilaeus	1.73	1.14		3.86	1.29		ND	ND	
Clarias gariepinus	2.66	1.02	0.524	3.48	1.78	0.825	ND	ND	NA
Parachanna obscura	2.96	0.80		3.54	1.68		ND	ND	
Sarotherodon melanotheron	3.71	2.01		2.86	1.97		ND	ND	
All species	2.72	1.36		3.36	1.52		0.1196	0.1014	
Ankobra									
Pomadasys jubelini	1.24	0.48		1.73	1.70		ND	ND	
Parapenaeus longirostris	2.32	1.95		2.07	1.04		ND	ND	
Clarias gariepinus	1.08	0.69	0.720	2.22	2.22	0.749	ND	ND	NA
Parachanna obscura	0.98	0.86		2.71	1.38		0.1024	*	
All species	1.45	1.21		2.15	1.54		0.1024	*	

* Only one value recorded

4.2 Concentration of heavy metals in water

The mean concentration of As, Hg and Pb in water samples from the Tano and Ankobra rivers are shown in table 4.1. The mean concentration of HM in water from Tano were in the order; Pb (0.11 ± 0.07 mg/L) > As (0.07 mg/L) > Hg (0.01 ± 0.01 mg/L), and Hg (0.15 ± 0.47 mg/L) > Pb (0.15 ± 0.11 mg/L) > As (0.06 ± 0.06 mg/L) in the Ankobra River. Higher levels of Hg were measured in water from the Ankobra (0.15 ± 0.47 mg/L) than Tano River (0.01 ± 0.01 mg/L), although the difference was not statistically significant (p=0.680). Low, but detectable levels of As were measured in water samples from Tano (0.07 mg/L) and Ankobra (0.06 ± 0.06 mg/L) respectively. The mean concentration of Pb in water samples from Ankobra (0.15 ± 0.11 mg/L) was slightly higher than that of Tano River (0.11 ± 0.07 mg/L), suggesting that Pb pollution in Ankobra water could be of much concern than the levels determined in the Tano River. However, there was no significant difference (p=0.680) between the two rivers.

4.3 Concentration of heavy metals in fish

Overall, the mean concentration of Hg, As and Pb in the Tano and Ankobra rivers were; (2.72 ± 1.36 mg/Kg), (3.36 ± 1.52 mg/Kg) and (0.12 ± 0.10 mg/Kg) and (1.45 ± 1.21 mg/Kg), (2.15 ± 1.54 mg/Kg), and (0.10 mg/Kg) respectively as shown in table 4.1. Although fish from Tano had relatively higher HM levels, there was no statistical difference in HM levels between the two rivers.

4.4 Concentration of heavy metals in different fish species

The concentration of Hg in the different fish species from the Tano were; "Ekpoke" *S. melanotheron* (3.71 ± 2.01 mg/Kg) > "Bile" *P. obscura* (2.96 ± 0.80 mg/Kg) > "Adwene" C. *gariepinus* (2.66 ± 1.02 mg/Kg) > "Ekpoke" *C. kingsleyae* (2.51 ± 1.28

mg/Kg) > "Ekpoke" *S. galilaues*.(1.73 ± 1.14 mg/Kg) whereas As was in the order; "Ekpoke" *S. galilaues* (3.86 ± 1.29 mg/Kg) > *"Bile"* *P. obscura* (3.54 ± 1.68 mg/Kg) > *"Adwene"* *C. gariepinus* (3.48 ± 1.78 mg/Kg) > "Ekpoke" *S. melanotheron* (2.86 ± 1.97 mg/Kg) > "Ekpoke" *C. kingsleyae* (2.72 ± 1.33 mg/Kg) as shown in Table 4.1. The variability of mercury and arsenic levels in different fish species were not significantly different (p=0.524 and 0.8250 respectively). The levels of Hg in different fish species from the Ankobra River were; "Senzeke" *P. longirostris* (2.32 ± 1.95 mg/Kg) > "Nzerma" *P. Jubelini* (1.24 ± 0.48 mg/Kg) > "Adwene" *C. gariepinus* (1.08 ± 0.69 mg/Kg)> "Bile" *P. obscura* (0.98 ± 0.86 mg/Kg) and that of As was in order of "Adwene" *C. gariepinus* (2.22 ± 2.22 mg/Kg) > "Senzeke" *P. longirostris* (2.07 ± 1.04 mg/Kg) > "Bile" *P. obscura* (2.71 ± 1.38 mg/Kg) > "Nzerma" *P. Jubelini* (1.73 ± 1.70 mg/Kg). There was no significant difference in Hg levels between different fish species in the Ankobra river (p=0.7200). Comparatively, As levels were higher than Hg for three of the four fish species from the Ankobra except "Senzeke" *P. longirostris* where Hg levels were higher than the As as shown in table 4.1.

4.5 Comparative analysis of HM concentration in fish from fresh and brackish water the Ankobra estuary.

The concentrations of Hg (1.78. ± 1.21 mg/Kg) and (1.03 ± 0.77 mg/Kg), and As (1.90 ± 1.36 mg/Kg) and (2.47 ± 1.81 mg/Kg) in brackish and freshwater fishes from the Ankobra estuary are presented in table 4.2 below.

Table 4.2: Mean concentration, standard deviation and p-values of mercury and arsenic in Brackish and Freshwater fishes from the Ankobra rivers estuary.

	Mercury Concentration (mg/Kg)			Arsenic Concentration (mg/Kg)		
Source	Mean	SD	p-value	Mean	SD	p-value
Ankobra						
Blackish	1.78	1.21	0.338	1.90	1.36	0.621
Freshwater	1.03	0.77		2.47	1.81	

Comparatively, there were higher levels of Hg in brackish than freshwater, whereas As levels in freshwater were higher than brackish. However, there was no statistical difference in HM levels between the two waters in the estuary (p= 0.338 and 0.621).

4.6 Comparative analysis of HM concentration in sediment, water and fish from the Tano and Ankobra rivers

A comparative analysis of HM concentrations in total sediment, water and fish from the Tano and Ankobra rivers is presented in table 4.3 below.

Table 4.3: Average concentration, standard deviation and p-values of mercury, arsenic and lead in sediment, water and fishes for the two rivers, Tano and Ankobra

	Mercury concentration			Arsenic concentration			Lead concentration		
Source	Mean	SD	p-value	Mean	SD	p-value	Mean	SD	p-value
Tano & Ankobra									
Soil (mg/Kg)	1.40	1.78	0.828	0.61	0.40	0.570	1.46	4.26	0.978
Water (mg/L)	0.09	0.36		0.06	0.05		0.14	0.10	
Fish (mg/Kg)	2.09	1.29		2.80	1.52		0.11	0.11	

Overall, the mean concentrations of Hg and As were highest in fish (2.09 ± 1.29 mg/Kg) and (2.80 ± 1.52 mg/Kg), followed by sediment (1.40 ± 1.78 mg/Kg) and (0.61 ± 0.40 mg/Kg), and water (0.09 ± 0.36 mg/L) and (0.06 ± 0.05mg/L) respectively. Lead levels were highest in sediment (1.46 ± 4.26 mg/Kg), followed by water (0.14 ± 0.10 mg/L), and then fish (0.11 ± 0.11 mg/Kg) respectively. However, the variability of overall HM levels in sediment, water and fish were not significantly different (p=0.828, 0.570 and 0.978 respectively).

CHAPTER FIVE

5. 0 DISCUSSSION

The aim of this study was to determine levels of heavy metals (Arsenic, Mercury and Lead) in sediment, fish and water from the Ankobra and Tano River basins in the Western Region of Ghana. According to Akabzaa and Darimani, (2001) the area spanning the basins of Tano and Ankobra are noted for mining operations since the 15th century, and industrial effluent including HM are likely to discharge into the streams that feed the Tano and Ankobra River. Levels of HM in aquatic media and fish were compared to other findings as well as USA EPA, WHO and US FDA standards and recommended levels respectively.

Overall, mean Hg and As levels were highest in fish; (2.09 ± 1.29 mg/Kg), (2.80 ± 1.52 mg/Kg) followed by sediment; (1.40 ± 1.78 mg/Kg), (0.61 ± 0.40 mg/Kg) with water recording the lowest concentrations (0.09 ± 0.36 mg/L), (0.06 ± 0.05 mg/L) respectively. In contrast, Pb levels were highest in sediments (1.46 ± 4.26 mg/Kg) and similar in water (0.14 ± 0.10 mg/L) and fish (0.11 ± 0.11 mg/Kg) (Table 4.3).

This is in agreement with the fact that biota, are better accumulators of trace metal than any other medium (Anim et al., 2013). The higher levels of As and Hg measured in fish tissues, compared to sediment and water is not surprising since fishes are known to bio accumulate toxic metals (Voegborlo & Adimado, 2010). The high levels of Pb in sediment than in fish and water could possibly be due to the fact that Pb has a high affinity for sediment (Abouelnasr and Dana, 2009). The relatively higher levels of As and Hg in fish from Tano than in Ankobra is reflected in the fact that Tano seem to be more polluted than the Ankobra River (table 4.1). This is consistent with the finding by Kyereme et al. (2015), where the Tano River was found to be loaded with higher levels of HM, and attributed this to a possible dilution effect in the Ankobra river which has many tributaries. Comparatively, the levels of As and Hg were above the recommended level of 1 mg/Kg for seafood for Australia and UK respectively (Neff, 1997; Edmonds and Francesconi, 1993) and of 1.0 mg/Kg mercury for fish and shellfish for U.S. FDA (USA EPA, 1985) respectively.

With regards to different fish species in Ankobra, As levels in fish tissues were in the order "Bile" *P. obscura* > "Adwene" *C. gariepinus* > "Senzeke" *P. longirostris* > "Nzerma" *P. jubelini*. This is reflected also in an increase in As levels from "brackish" water environment towards freshwater environment since *P. longirostris* and *P. jubelini* that are diadromous species, and therefore do migrate between estuarine and marine environments. This is in agreement with the report by Voegborlo & Adimado (2010), who found low levels of HM in marine environment along the coast of Ghana. However, *P. obscura* and *C. gariepinus* are mainly freshwater species and can only survive in freshwater. This therefore suggests that the fresh water end of the Ankobra is more contaminated with As than the brackish environment. On the other hand, the levels of Hg in the fish tissues are inconsistent and do not show any patterns. The exceptionally high level of Hg in *P. longirostris* could possibly be due to its association with sediment since it is a dermesal fish species (feed on detritus), which may contain high levels of mercury (Johnson and Battram 1993).

Again arsenic (As) levels were generally high in fish tissues than Hg levels recorded in the Tano River table 4.1. This could be due to the fact that the fishes are better accumulators of As than Hg from both water and sediment (Wayah and Gadima, 2015). Comparatively, the levels of As and Hg in the Tano river were above the recommended levels as above.

In water, As (0.06 ± 0.06 µg/L), Hg (0.15 ± 0.47 µg/L) and Pb (0.15 ± 0.11 µg/L) levels in Ankobra were higher than that of Tano; As (0.07 µg/L), Hg (0.01 ± 0.01 µg/L) and Pb (0.11 ± 0.07 µg/L) as shown in table 4.1. This could be due to inflow of highly contaminated effluent by gold mining activities especially artisanal (Galamsey) gold mining through its many tributaries into the Ankobra River basin (Esumang, 2009). The contaminated levels of Hg far exceeded the recommended level for pristine fresh water ecosystem (0.005 µg/L (ATSDR, 1997) and drinking water (2 µg/L, WHO 2004). Also, As levels exceeded WHO recommended levels of (50 µg/L) for drinking water (IPCS/WHO, 1992).

In sediments, Tano recorded a higher level of Pb (2.75 ± 6.68 mg/Kg) as compared to Ankobra (0.59 ± 0.30 mg/Kg), although Hg and As levels were marginally higher in Ankobra (table 4.1). There was however, no significant difference in the mean concentrations of Hg, As and Pb (p-0.828, 0.570 and 0.978) in sediments from both river systems. Similar results were obtained by Kyereme et al. (2015) for Hg in the Tano and Ankobra.

The findings from this study concerning Hg, As and Pb above recommended levels from both study sites are rather disturbing because a significant proportion of fish consumed in Ghana are caught from the Ankobra and Tano Rivers.

The elevated levels of Hg in fish are known to cause serious neurotoxic and genotoxic effects (Hibbeln et al, 2007). High intake of mercury appears to hamper a baby's brain development, as well as causes chest pain, shortness of breath, coughing up blood, parestesias and numbness in the hands and feet. Moreover, consumption of foods contaminated with mercury has detrimental impacts on the gastrointestinal tract and may induce kidney toxicity if ingested (Järup, 2003) . In addition, higher Hg levels are known to have direct effects on fishes ranging from reduced reproduction, impaired growth and development, behavioural abnormalities, altered blood chemistry, reduced oxygen exchange and sometimes death (Folmar, 1993)

Consumption of As contaminated foods above recommended levels has also been linked to an increased risk of skin cancer and other skin lesions, such as hyperkeratosis and pigmentation changes. The recent WHO evaluation concludes that arsenic exposure via drinking water is causally related to cancer in the lungs, kidney, bladder and skin, the last of which is preceded by directly observable precancerous lesions (WHO, 2004) . In the wake of these developments, it could be speculated that arsenic in the environment could play a possible role in Buruli Ulcer pathogenesis (Gyasi et al., 2012) . Furthermore, there is relatively strong evidence for hypertension and cardiovascular disease, long-term neurological effects, and cancer at sites other than lung, bladder, kidney and skin (Järup, 2003).

Exposure to higher Pb levels has been known to cause symptoms of acute lead poisoning such as headache, irritability, abdominal pain and various symptoms related to the nervous system. In severe cases, Lead encephalopathy can occur and is characterized by acute psychosis, confusion and reduced consciousness sleeplessness and restlessness. Affected children may manifest be affected behavioural disturbances, learning and concentration difficulties. In less serious cases, the most obvious sign of Pb poisoning is disturbance of haemoglobin synthesis, and eventually anaemia in the long term.

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

In general, the study showed that the levels of heavy metal load in the Ankobra and Tano Rivers known to traverse several industrial and artisanal mining areas had higher levels of heavy metals above WHO recommenced values for sediment, water and fish. Comparatively, the mean As, Hg and Pb load in the Tano River was relatively higher, compared to that of the Ankobra River. This also reflected in a higher metal load in sediment from the Tano than Ankobra River. This implies that the health of aquatic lives in these rivers are threatened since these HM are considered toxic and can cause ill-health of fishes and other aquatic lives. Also the health of the communities who depend on these water bodies for domestic and other uses are at risk.

6.2 Recommendations

1. Future works should be focused on periodic assessment and monitoring of fishes, sediment and water from the various tributaries that flow directly into the Tano and Ankobra River basins to identify point of contamination.
2. Other heavy metals such as Cd, Cr, Cu, Zn and Ni should be considered for future studies.
3. The various stakeholders in Ghana such as the Environmental Protection Agency (EPA), Water Research Institute (WRI), The Minerals Commission, Ministry of Environment Science Technology and Innovation should collaborate to finding the most appropriate remediation technologies for addressing the heavy metal pollution in the Tano and Ankobra River basins.

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APPENDIX