DISTRIBUTION OF TOTAL MERCURY IN FISH, WATER AND SEDIMENTS FROM THE DENSU RESERVOIR AT WEIJA, ACCRA GHANA

BY

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DECLARATION

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

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DEDICATION

I dedicate this work to the Glory of God without whom man labours in vain.

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My utmost gratitude goes to the Almighty God for His grace, mercy and divine guidance throughout this program. I am grateful to my Archbishop and my parents for their care, support and love.

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ABSTRACT

Mercury is toxic and its ubiquitous nature makes it a global pollutant. Total mercury (THg) concentrations were determined in fish, sediments and water from the Densu Basin at Weija. Cold Vapour Atomic Absorption Spectrophotometry (CVAAS) technique using an automatic mercury analyser was used to determine total mercury after digestion of the samples. One hundred and sixty-five (165) fish samples comprising six (6) species; eighty-four (84) sediment samples and thirty (30) water samples were collected and analysed for total mercury. Mercury concentration in fish muscles ranged from 0.001 to 0.420 µg/g. *Hemichromis fasciatus* recorded the highest level of 0.420 µg/g whilst the lowest Hg concentration of 0.001µg/g was recorded in *Chrysicthys nigrodigitatus*. Mercury concentration (µg/g wet weight) in the muscle tissue of fish ranged from 0.014 to 0.420 (mean = 0.125±0.111) for *Hemichromis fasciatus*, from 0.022 to 0.385 (mean = 0.155±0.098) for *Tilapia zilli*, from 0.001 to 0.342 (mean = 0.096±0.094) for *Chrysicthys nigrodigitatus*, from 0.021 to 0.378 (mean = 0.181±0.115) for *Tilapia mariae*, from 0.010 to 0.367 (mean = 0.114±0.109) for *Clarias batrachus*, from 0.056 to 0.330 (mean = 0.114±0.076) for *Clarias gariepinus*. Mean mercury levels in sediment and water from Weija are 0.055±0.023µg/g and 0.0169±0.0077ng/L respectively. There was a significant correlation between Hg concentration in fish muscle and fresh weight of fish for *Hemichromis fasciatus* (r^2 = 0.5739). A good correlation between Hg concentration in fish muscle and total length of fish was also observed for *Hemichromis fasciatus* (r^2 = 0.6301). All the rest of the fish species showed poor correlation between Hg concentration in muscle and total length and fresh weight. Correlation between Hg concentration in fish and in sediment as well as fish and water was not significant. No correlation was observed between the total Hg concentration in the sediment and water. All the fish samples studied showed mercury concentrations below the World Health

organization (WHO) limit of 0.5µg/g wet weight. The results obtained from this study therefore showed that fish from the Densu River are unlikely to constitute a significant mercury exposure to the public through consumption. Levels of Hg in sediment and water suggest a relatively clean environment with regards to Hg.

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ABBREVIATION

CVAAS	Cold Vapour Atomic Absorption Spectrophotometry
IAEA	International Atomic Energy Agency
CRM	Certified Reference Material

CHAPTER ONE

1. INTRODUCTION

Mercury is a well-known pollutant that exists naturally in the air, water and sediment. It is one of the most serious and scientifically challenging contaminant in aquatic resources throughout the world. The increases in production and uses of mercury and the availability of many soluble species of this element have resulted in many contaminations in both aquatic and terrestrial ecosystems. Once mercury is released into the environment, it easily travels through environmental media in a variety of chemical forms. While there are three forms of mercury (elemental, inorganic, and organic), (Goldman and Shannon, 2001) the organic form, methyl mercury (MeHg), is the most toxic. Atmospheric deposition is normally in the form of inorganic mercury. Once mercury is deposited into water bodies, micro bacteria convert the inorganic mercury in the sediments into highly toxic methylmercury. This highly neurotoxic form accumulates in aquatic organisms, including fish (Lutter and Elisabeth, 2002). Methylmercury can easily accumulate at higher concentrations, and biomagnifies in aquatic and land-based organisms to concentrations that can easily adversely affect them.

Mercury content of fish is considered to be a good indicator of human exposure to methyl mercury (Yoshino, *et al*, 1966; Irukayama and Tsubaki, 1977). Because of the danger the metal posses to humans, it is therefore important to determine mercury levels in aquatic organisms, particularly the levels in edible fish. Extensive surveys have been carried out in a number of countries to evaluate the presence of mercury in the aquatic biota including fish, which has often been considered as a good indicator of aquatic pollution (Nixon *et al*., 1994; Rofhus and Fitzgerald, 1995; Nakagawa *et al*., 1997; Voegborlo *et al*., 1999; Love *et al*., 2003; Storelli *et al*.,

2003). The levels of mercury found in a fish are related to the level of mercury in its aquatic environment and its position in the food chain (Monteiro *et al*., 1999).

Methylmercury production occurs mainly in sediments and the rate depends on levels of Hg in sediment in addition to other factors like pH, DO (Dissolved Oxygen) and Organic matter content. Considerable data exist on the accumulation of mercury in sediments of numerous lakes (Koeman *et al*., 1975).

Mercury accumulation rates in sediments and water agree fairly well with limited measurements of atmospheric mercury deposition. Thus river sediments may be useful archives of historical, natural and anthropogenic inputs of mercury in rivers. In 1970, analysis carried out showed that more than 90% of the surface sediments in Onondaga Lake contained mercury at concentrations greater than 0.10 ppm. In that same year, mercury levels in fish were found to exceed 0.5 ppm, the maximum permissible levels established by WHO. (Hunter *et al*, 1987). Some fish had mercury concentrations as high as 3.6 ppm (Hunter *et al*., 1987). This thus confirms the fact that the toxicity of Hg in fish is very much related to the level of Hg in the river sediment.

Scientists have demonstrated that mercury and other metals in the bottom sediments of reservoirs, lakes, and estuaries can be moved into the overlying water through chemical and biological activities (U. S. Geological Survey, 2000). The rate that solutes, such as methylmercury, move in and out of sediments, known as the benthic flux, can be positive (into the water from bottom sediments) or negative (out of the water into bottom sediments). The magnitude and variability of the benthic flux determines whether or not methylmercury in the bottom of reservoirs represents a significant source of this toxic form of mercury to the environment. Furthermore, simultaneous collection and analysis of sediments, water and fish will

provide information on the extent of bioavailability of sediment-bound mercury compounds (Kannan et al, 1997).

Human exposure to methylmercury is therefore through the consumption of fish. The levels of methylmercury may reach hazardous levels in humans through repeated consumption of contaminated fish. Mercury toxicity is well established and its dangers to people have been well-known and several cases of Hg toxicity in the environment have been reported (US EPA, 2001). The most serious occurred in Minamata Bay area of Japan from 1953 – 1960 as a result of Hg, released into the bay from manufacturing plants. Mercury levels of 5 to 20 ppm were found in seafood eaten by 111 people diagnosed with "Minamata disease". Of these, 45 died as a result of an apparent poisoning (Yoshino *et al*., 1966; Irukayama and Tsubaki, 1977).

Methylmercury is highly toxic, and the nervous system is its principal target tissue. In adults, the earliest effects are non-specific symptoms such as paresthesia, malaise, and blurred vision. Furthermore with increasing exposure, signs appear such as concentric constriction of the visual field, deafness, dysarthria, ataxia, and ultimately coma and death (Harada, 1995). The developing central nervous system is more sensitive to methylmercury than the adult. Exposure to high levels of methylmercury during pregnancy gives a clinical picture which may be indistinguishable from cerebral palsy caused by other factors. The main pattern being microcephaly, hyperreflexia, and gross motor and mental impairment, sometimes associated with blindness or deafness (Harada, 1995; Takeuchi and Eto, 1999). In milder cases, the effects may only become apparent later during the development as psychomotor and mental impairment and persistent pathological reflexes (WHO/IPCS, 1990; NRC, 2000). Separate studies from one population exposed to methylmercury from fish also suggest an association with increased incidence of cardiovascular system diseases (Salonen *et al*., 1995, Rissanen *et al*., 2000).

An extensive body of literature documenting a positive relationship between fish mercury concentration and weight as well as length within an individual water body exist (Lange *et al*., 1994). Good correlation normally existed among carnivorous species while herbivorous species normally show poor correlation (Lange *et al*.,1994). Mercury in fish measured in Deep Creek pickerel in 1992 showed that the fish examined that was 48 cm long contained 0.98 mgHg/kg whereas those with length 20 cm long had average Hg concentration of 0.3 mgHg/kg (Gremillion *et al*., 2004)

Despite considerable works on mercury contamination of fish and fishery products in Ghana, information on mercury contamination of fish, water and sediments in freshwaters of Ghana are still not enough. Because mercury is a global pollutant that knows no national or continental boundaries and the cycling of mercury is very complex it is thus important to understand the effects of mercury contamination on our environment and to be aware of guidelines for fish consumption and other ways to reduce risk. This research ought to determine the levels of mercury in different fish species, water and sediments form the Densu Reservoir at Weija.

The Weija Dam is situated on the Densu River in the Ga South Municipality of Ghana. The Densu River is a 116 Km long river rising in the Atewa Range. It flows through an economically important agricultural region, supplies half the drinking water to the nation's capital city, and ends in an ecologically significant but environmentally threatened wetlands at the edge of the Atlantic Ocean. The population density of the Densu Basin is approximately 240 persons per square kilometer (River Basin Activities, 2008).

In this study, total mercury determined in different species of fish, water and sediments is anticipated to aid in generating data needed for the assessment of mercury intake from fish for

the development of consumption advisories for the general public. It could also be used as a baseline reference for future works.

1.1 Research Objectives:

The objectives of this research are:

- To determine total mercury in different species of fish, water and sediment in the Densu River Basin at Weija in Ghana.
- To determine if there is any correlation between total mercury concentration in fish and sediments, in fish and water, and in sediment and water.
- To determine if there is any correlation between total mercury concentration and weight as well as length of fish.
- To determine whether the levels of mercury in fish from the river are at levels of potential human health concern.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Sources of Environmental Mercury Pollution

The sources of environmental Hg pollution include natural occurrence and anthropogenic sources.

2.1.1 Natural Occurrence

Mercury is a naturally occurring element (around 80 µg/kg) in the earth's crust, rocks, minerals, and coal and base metal deposits according to Agency for Toxic Substances and Disease Registry in Atlanta (ATSDR, 2003). As with other components of the lithosphere, natural global cycling has always been a primary contributor to the presence of chemical elements in water, air, soils, and sediments. This process involves off-gassing of mercury from the lithosphere and hydrosphere to the atmosphere, where it is transported and deposited onto land, surface water, and soil. Areas of high mercury content associated with zones of instability and volcanic and thermal activity have been found over the globe. It also evolves from evaporation from soil and water surfaces, degradation of minerals and forest fires. Mercury in small, but varying concentrations can be found virtually in all geological media (UNEP, 2010) **.** Elemental and some forms of oxidized mercury are permanently coming to the atmosphere due to their volatility. High temperature in the earth mantle results in high mercury mobility and mercury continuously diffuses to the surface. In the zones of deep geological fractures these processes go on more intensively. Here are located so-called mercury geochemical belts where mercury concentrations in the upper layer appreciably exceed their average values. In some parts of

mercury belts the intensive accumulation of mercury resulted in the formation of extractable deposits (Jonasson and Boyle, 1971; Bailey *et al*., 1973). Regions with high concentrations in surface rocks are characterized by high mercury emissions to the atmosphere.

The natural mercury emissions are beyond control, and must be considered part of local and global living environment. In some areas of the world, the mercury concentrations in the earth's crust are naturally elevated, and contribute to elevated local and regional mercury concentrations in those areas (UNEP, 2010). Today's emissions of mercury from soil and water surfaces are composed of both natural sources and re-emission of previous deposition of mercury from both anthropogenic and natural sources. This makes it very difficult to determine the actual natural mercury emissions. For example, total estimates of re-emission from soil and water surfaces in Europe exist, but they include mercury originating from both natural and anthropogenic sources (Pirrone *et al.*, 2001). Attempts to directly measure natural emissions are ongoing (Coolbaugh *et al.*, 2002). Nonetheless, available information indicates that natural sources account for less than 50 percent of the total releases. Natural weathering of mercury-containing rocks is continuous and ubiquitous, allowing mercury to escape to air and to be washed into lakes and rivers. Volcanoes emit and release mercury when they erupt. Geothermal activity can also take mercury from underground and emit it to the atmosphere and release it to the deep oceans. Some recent models of the flow of mercury through the environment suggest that natural sources account for about 15% of the estimated 5500-8900 tonnes of mercury currently being emitted and re-emitted to the atmosphere from all sources. (UNEP, 2010).

2.1.2 Anthropogenic Sources

Since the industrial revolution of the late 18th and 19th centuries, anthropogenic sources have become a significant contributor to the environmental distribution of mercury and its compounds (ATSDR, 2003). Mercury is naturally present in coal and other fossil fuels, as well as in minerals like lime for cement production and soils (such as agricultural soils subject to acidification management) and metal ores including for example zinc, copper and gold ore. Coal-fired power production is today deemed the single largest global source of atmospheric mercury emissions (Pacyna and Pacyna, 2000). This is due to the increasing global power consumption, and also to the fact that emissions from intentional use of mercury are gradually diminishing in many of the industrialised countries. Point sources of anthropogenic mercury release, revolatilization from environmental media, sorption to soil and sediment particles, and bioaccumulation in the food webs contribute to further distribution and subsequent human exposure (ASTDR, 2003). The use of elemental mercury to capture gold particles as an amalgam has also contributed to the environmental burden of mercury and its compounds (Brito and Guimaraes, 1999; Grandjean *et al*., 1999). Dental amalgam fillings are the primary source of mercury exposure for the general population (Skare, 1995; Health Canada, 1997).

Large portion of the mercury present in the atmosphere today is the result of many years of releases due to anthropogenic activities. The natural component of the total atmospheric burden is difficult to estimate, although a study by Munthe *et al.*, (2001) has suggested that anthropogenic activities have increased the overall levels of mercury in the atmosphere by roughly a factor of 3. While there are some natural emissions of mercury from the earth's crust, anthropogenic sources are the major contributors to releases of mercury to the atmosphere, water and soil (UNEP, 2010).

Available global estimates of atmospheric emissions from waste incineration, as well as other releases originating from intentional uses of mercury in processes and products, are deemed underestimated and to some degree incomplete. Anthropogenic emissions from a number of major sources have decreased during the last decade in North America and Europe due to efforts put in place to reduce the production of mercury (UNEP, 2010).

The intentional use of mercury in products and processes is still deemed a significant source of mercury in the environment. The recorded global primary production of virgin mercury (commercial-grade mercury with 99.9% purity) is still large compared to current estimates of global atmospheric mercury emissions. When assessing the releases of mercury to the environment, it is generally difficult to quantify diffuse releases from the life cycle of mercury-containing products. These sources have not always been included fully in regional or global inventories for mercury releases to the environment. Some national studies do however give a certain insight in the contributions from this source category. The contribution from intentional mercury uses in a number of products in the European region was also assessed by Munthe and Kindbom (1997). They found that in the mid-1990's three dominating groups of intentional mercury uses in products contributed about 18 percent of the total mercury emissions to air in this region. Additional contributions from dental amalgam use were not included in the assessment.

2.2 Methylation of Mercury

Mercury methylation is the process whereby mercury is converted into methylmercury, the most toxic form of mercury. It has been estimated that the minimum lethal dose of methyl mercury for a 70-kg person ranges from 20 to 60 mg/kg (WHO, 1990 ; UNEP, 2010). Bacteria are largely for

this process, but man's activities can exacerbate the net amount of methylmercury in the environment. Methylmercury is also destroyed by bacteria, so it is necessary to look at both the creation and destruction mechanisms (US Geological survey, 2000).

This helps in the estimation of the concentration of methylmercury in a given aquatic organisms, for methylation and demethylation are key processes affecting concentrations of methylmercury in aquatic organisms in both grossly and lightly contaminated ecosystems (US Geological survey, 2000). This is illustrated in figure 2.1 below.

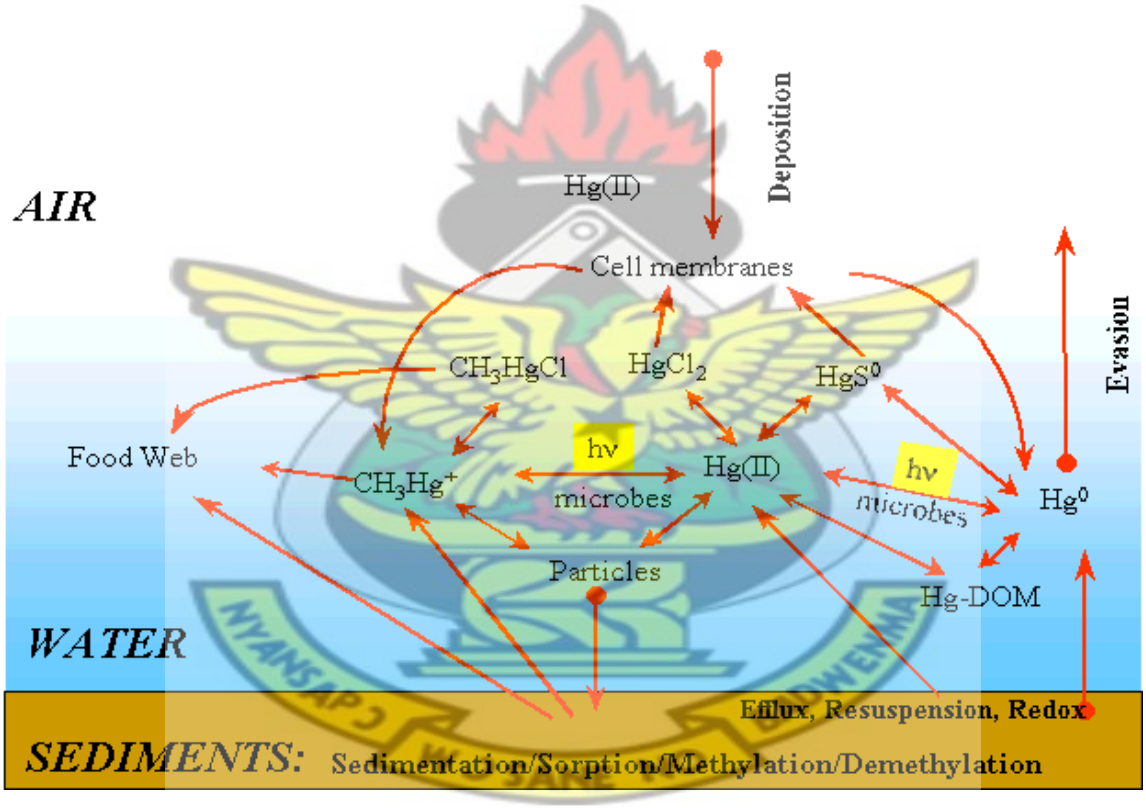

Figure 2.1 The aquatic Mercury cycle conceptual Model.

Source: http://www. usgs.gov/mercury.

The transformation processes for the various forms of mercury that apply in water also occur in soil and sediment. Formation and breakdown of organic mercury compounds appear to be dependent upon the same microbial and abiotic processes as in water (Andersson, 1979). The methylation of mercury is decreased by increasing chloride ion concentration (Olson *et al*., 1991), although the presence of chloride ions has been suggested to increase the rate of mercury release from sediments (Wang *et al*., 1991). In sediments, the complexing of elemental mercury with chloride ion and hydroxide ion to form various mercury compounds is dependent upon pH, salt content, and sediment composition.

The methylation of inorganic mercury in the sediment, is also a key step in the transport of mercury in aquatic food chains. Methylation was first demonstrated by Jensen and Jernelov, (1967) that microorganisms in lake sediments could methylate mercury. They later showed that the degree of methylation correlated well with the overall microbial activity in the sediment (Jensen and Jernelov, 1967). The following general conclusions have been drawn by Bisogni and Lawrence, (1973) concerning methylation by microorganisms:

a) mono-methylmercury is the predominant product of biological methylation near neutral pH,
b) the rate of methylation is greater under oxidising conditions than under anaerobic conditions,
c) the output of methylmercury doubles for a ten-fold increase in inorganic mercury,
d) temperature affects methylation as a result of its effect on overall microbial activity,
e) higher microbial growth rate increases mercury methylation,
f) methylation rates are inhibited by the addition of sulfide to anaerobic systems.

The formation of artificial lakes considerably increases the production of methylmercury, although this increase was found to be short-lived in new lakes in Finland (Simola and Lodenius, 1982; Alfthan *et al*., 1983). The is because the source of mercury in all of these artificial lakes appeared to be natural rather than anthropogenic in origin. Anaerobic conditions after the flooding of large amounts of organic material and the subsequent increase in microbial activity are thought to be the causes of the increased availability of mercury through methylation. The anaerobic conditions later reduce to normalcy in a short period of time. (Canada-Manitoba, 1987). A similar problem of increased mercury in new lakes, which was taken up by fish and fish-eating mammals, occurred in the scheme to divert the Churchill River in Manitoba, Canada (Canada-Manitoba, 1987). Methylation rates in one lake, which had been flooded 20 years previously, had returned to normal. Methylation rates in the new lake, which had flooded arboreal forest, were high and were expected to remain high for decades.

Methylation is also seen as a product of complex processes that move and transform mercury as depicted in Figure 2.2 below (U S Geological Survey, 2000). Atmospheric deposition contains the three principal forms of mercury, although inorganic divalent mercury (Hg(II)) is the dominant form. Once in surface water, mercury enters a complex cycle in which one form can be converted to another. Mercury attached to particles can settle onto the sediments where it can diffuse into the water column, be resuspended, be buried by other sediments, or be methylated (Figure 2.2). Methylmercury can enter the food chain, or it can be released back to the atmosphere by volatilization (U S Geological Survey, 2000).

Mercury and methylmercury exposure to sunlight (specifically ultra-violet light) has an overall detoxifying effect. Sunlight can break down methylmercury to Hg(II) or Hg(0), which can leave the aquatic environment and reenter the atmosphere as a gas.

The exact mechanisms by which mercury enters the food chain remain largely unknown and may vary among ecosystems. Certain bacteria play an important early role. Bacteria that process sulfate (SO_4^{2-}) in the environment take up mercury in its inorganic form and convert it to methylmercury through metabolic processes (U S Geological Survey, 2000). The conversion of inorganic mercury to methylmercury is important because methylmercury toxicity is greater and also organisms require considerably longer time to eliminate methylmercury. These methylmercury-producing bacteria may be consumed by organisms higher in the food chain, or the bacteria may excrete the methylmercury to the water where it can quickly be adsorb by plankton, which are also consumed by other organisms higher in the food chain as clearly depicted in Figure 2.2. Because animals accumulate methylmercury faster than they eliminate it, animals consume higher concentrations of mercury at each successive level of the food chain. Small environmental concentrations of methylmercury can thus readily accumulate to potentially harmful concentrations in fish, fish-eating wildlife and people. Even at very low atmospheric deposition rates in locations remote from point sources, mercury biomagnifications can result in toxic effects in consumers at the top of these aquatic food chains.

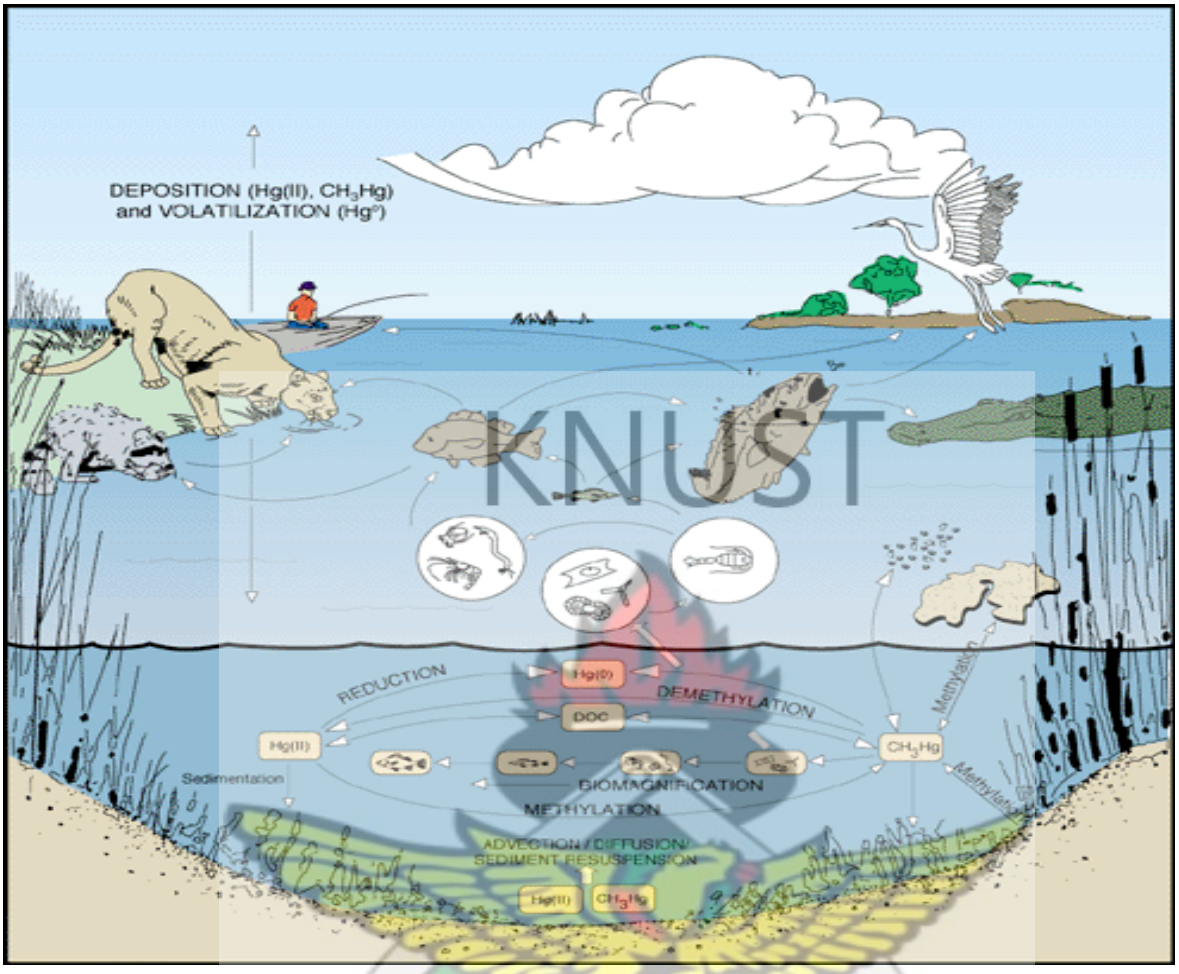

Figure 2.2 Factors affecting Methylation of Mercury.

Source: http://www.usgs.gov/themes/factsheet 146-00/index.html.

2.2.1 Mercury species transformations in aquatic environments

The formation of methylmercury in aquatic systems is influenced by a wide variety of environmental factors. The efficiency of microbial mercury methylation generally depends on factors such as microbial activity and the concentration of bioavailable mercury (rather than the total mercury pool), which in turn are influenced by parameters such as temperature, pH, redox potential and the presence of inorganic and organic complexing agents (Ullrich *et al*., 2001).

Certain bacteria also demethylate mercury and this tendency increases given increasing levels of methylmercury, thereby forming some natural constraints on build-up of methylmercury (Marvin-Dipasquale *et al.*, 2000; Bailey *et al.*, 2001). Since both methylation and demethylation processes occur at same time, environmental methylmercury concentrations reflect net methylation rather than actual rates of methylmercury synthesis. Numerous bacterial strains capable of demethylating methylmercury are known, including both aerobic and anaerobic species, but demethylation appears to be predominantly accomplished by aerobic organisms. Bacterial demethylation has been demonstrated both in sediments and in the water column of freshwater lakes. Degradation of methyl and phenyl mercury by fresh water algae has also been described (Ullrich *et al*., 2001). Purely chemical methylation of mercury is also possible if suitable methyl donors are present. The relative importance of abiotic versus biotic methylation mechanisms in the natural aquatic environment has not yet been established, but it is generally believed that mercury methylation is predominantly a microbially mediated process (Ullrich *et al.*, 2001).

Methylmercury is the predominant mercury species in fish, in most adult fish, 90 to 100 percent of mercury content is methylmercury (US EPA, 2001). As a consequence, the US EPA recommends that the cheaper total mercury chemical analysis be used for evaluation of risk from consuming local fish, and that results should be used as if mercury was present as 100 percent methylmercury in order to be most protective of human health.

Mason and Fitzgerald (1996; 1997) have reviewed aspects of the cycle of mercury in oceans and other waters. From this study, it is apparent that elemental mercury, dimethylmercury and, to a lesser extent, methylmercury are common constituents of the dissolved mercury pool in deep

ocean waters. In open ocean surface waters dimethylmercury is lacking, may be as a result of decomposition in the presence of light and an additional potential loss via evaporation from the water surface. Recent studies suggest that low oxygen conditions are not necessary for the formation of dimethylmercury in the open oceans. Studies in freshwater and estuarine environments have shown that methylation of mercury is primarily taking place under low oxygen conditions and mainly by sulphate-reducing bacteria. Here methylmercury is the product of methylation of ionic mercury. (U S Geological Survey, 2000).

2.3 Toxicity of Mercury

Mercury is one of the most toxic elements on the earth. Toxicity caused by mercury exposure is now becoming recognized as a widespread environmental problem and is continuing to attract a great deal of public attention. (The National Academies Press, 2007) Toxicity of mercury depends on its chemical form, and thus symptoms and signs are rather different in exposure to elemental mercury, inorganic mercury compounds, or organic mercury compounds such as alkylmercury compounds, methylmercury and ethylmercury salts, and dimethylmercury. (The National Academies Press, 2007). The sources of exposure are also markedly different for the different forms of mercury. For alkylmercury compounds, among which methylmercury is by far the most important, the major source of exposure is diet, especially fish and other seafood. For elemental mercury vapour, the most important source for the general population is dental amalgam. Release of mercury from amalgam fillings has been reviewed by Clarkson *et al*. (1988). It was concluded that amalgam surfaces release mercury vapour into the mouth, and this is the predominant source of human exposure to elemental mercury in the general population. Depending upon the number of amalgam fillings, the estimated average daily absorption of

mercury vapour from dental fillings vary between 3µg and 17µg mercury (WHO/IPCS, 1991; Clarkson et al., 1988). In rare cases the blood mercury levels due to dental amalgam may be as high as 20 µg/l (Barregard et al. 1995; Pirrone et al., 2001). For inorganic mercury compounds, diet is the most important source for the majority of people. However, for some segments of populations, use of skin-lightening creams and soaps that contain mercury; and use of mercury for cultural or ritualistic purposes or in traditional medicine, can also result in substantial exposures to inorganic or elemental mercury (UNEP, 2010). New findings during the last decade indicate that toxic effects may be taking place at lower concentrations than previously thought, and potentially larger parts of the global population may be affected (UNEP, 2010).

2.3.1 Toxicity of Methylmercury

Like other alkylmercury compounds, the toxicity of methylmercury is much higher than that of inorganic mercury. Methylmercury is a potent neuro-toxin, hence human exposure to methylmercury is clearly unwelcome and should be regarded with concern. It is present worldwide in fish and marine mammals consumed by humans (UNEP, 2010). Methylmercury is formed naturally by biological activity in aquatic environments, and it is bio-magnified in the food chain, resulting in much higher concentrations in higher predatory fish and mammals than in water and lower organisms. Most of the total mercury concentrations in fish are in the form of methylmercury (close to 100 percent for older fish), (UNEP, 2010). Most people are primarily exposed through the diet, mainly through the consumption of fish which is an extremely valuable component of the human diet in many parts of the world. In 1991, a joint committee from FAO and WHO revised guideline levels for mercury in fish aimed at human consumption. The

recommended dietary limit was set at 0.5 µg Hg/g wet weights for non predatory fish and 1.0 µg Hg/g wet weight for predatory fish (FAO/WHO, 1991).

Mercury bioaccumulation in fish is influenced by physiological factors such as sex, age, size, growth rate or metabolic rate (Huckabee *et al*., 1979) and ecological factors such as trophic position or food chain length (Cabana *et al*., 1994; Kidd *et al*., 1995). Due to long-range atmospheric emission transport and ocean currents, methylmercury is also present in the environment far away from local or regional mercury sources. This implies that population groups particularly dependent on or accustomed to marine diets, such as the Inuits of the Arctic, as well as marine and freshwater fish dependent populations anywhere else on the globe, are particularly at risk due to methylmercury exposure(UNEP, 2010).

Methylmercury is highly toxic, and the nervous system is its principal target tissue. In adults, the earliest effects are non-specific symptoms such as paresthesia, malaise, and blurred vision; with increasing exposure, signs appear such as concentric constriction of the visual field, deafness, dysarthria, ataxia, and ultimately coma and death (Harada, 1995). The developing central nervous system is more sensitive to methylmercury than the adult. In infants exposed to high levels of methylmercury during pregnancy, the clinical picture may be indistinguishable from cerebral palsy caused by other factors. The main pattern being microcephaly, hyperreflexia, and gross motor and mental impairment. Sometimes it results in blindness or deafness (Harada, 1995; Takeuchi and Eto, 1999). In milder cases, the effects may only become apparent later during the development as psychomotor, mental impairment and persistent pathological reflexes (WHO/IPCS, 1990; NRC, 2000). Studies from one population exposed to methylmercury from fish also suggest an association with increased incidence of cardiovascular system diseases

(Salonen *et al.*, 1995; Rissanen *et al.*, 2000). From research on animals there is evidence of genotoxicity and effects on the immune system and the reproductive system (UNEP, 2010).

2.4 Mercury concentrations and transformations in surface waters.

Freshwater ecosystems are among the most sensitive to Hg pollution. Under conditions of high total Hg loading, MeHg production can vary widely, depending on the methylation efficiency of a particular ecosystem (Krabbenhoft *et al*., 1999). Mercury enters remote surface waters through direct atmospheric deposition and through soil water, wetland, or groundwater drainage. Streams and rivers can exhibit marked temporal variation in Hg concentrations, which is associated with variations in concentrations of dissolved organic carbon (DOC) or suspended matter. Large increases in Hg concentrations can occur during high flow events (Shanley *et al*., 2005). Some inputs of Hg to lakes are removed from the water column by the volatilization of Hg^0 and by sediment deposition. In freshwater lakes, photochemical processes are largely responsible for the reduction of ionic Hg to Hg^0 (Amyot *et al*., 1997). Microbial reduction (methylmercury degradation) has been observed in laboratory studies, but only at higher than ambient concentrations of Hg (Morel *et al*., 1998). Biogeochemical processes in lakes also result in net production of MeHg due to methylation in anoxic sediments and in the water column. Areas of elevated Hg concentrations in surface waters can be explained by high concentrations of DOC, as in the Adirondacks. High inputs of suspended solids, from rivers along Lake Champlain are related to high flow events caused by elevated atmospheric Hg deposition, as in lakes in Southeastern New Hampshire and Eastern Massachusetts. A large portion of the variation in total Hg and MeHg across the Adirondacks region can be explained by variation in DOC (Dennis *et al*., 2005). Areas with the highest mean surface water Hg concentrations also have the greatest

range in Hg concentrations. This variation may be attributed to heterogeneity in watershed characteristics or to high flow events (Shanley *et al*., 2005).

2.4.1 Mercury in Sediment

It has been estimated that sediment is an important sink for both Hg and MeHg in the aquatic environment (Mason *et al*., 1999) and after atmospheric deposition and runoff from surrounding catchments. Mercury can be converted to MeHg by bacteria in anoxic sediments and soils (Gilmour *et al*., 1992). The amount of MeHg in aquatic regions varies among ecosystems. Therefore, MeHg bioaccumulation in fish does not only depend on how much Hg enters the ecosystem, but also on the ability of the ecosystem to convert that Hg to MeHg (Heyes and Gilmour, 1999). For example, methylation of Hg has been found to be enhanced in wetlands but can be produced in other anoxic regions as well. Increased runoff from urbanized areas and as the result of impervious surfaces in and around the watershed may contribute to higher concentrations of Hg and MeHg in aquatic systems. Whereas MeHg has high affinity for particles and organic matter, the extent to which sediment is a source of MeHg to the fish largely depends on the size of particles and organic matter content of the sediment (Benoit *et al*., 1998; Mason, 2001).

In soil and water, mercury can exist in either the monovalent or divalent forms as inorganic compounds. The particular valence state in which mercury exists (Hg^0, Hg^+, Hg^{2+}) is dependent upon multiple factors, including the pH and redox potential of the medium as well as the strength of the ligands present. Mercury binds strongly to humic materials and sesquioxides, even at soil pH values greater than 4 (Blume and Brummer, 1991), although mercury sorption to soils generally decreases with increasing pH and or chloride ion concentration (Schuster, 1991).

Vaporization of mercury from soil has been associated with decreasing soil pH, with volatilization of soil mercury demonstrated at soil pH <3 (Warren and Dudas, 1992).

Most Hg^{2+} found in precipitation is bound to particulate matter (Meili *et al*., 1991), but its environmental transport and partitioning in surface waters and soils, once deposited, depend upon the specific mercury compound.

While in the soil or sediment, inorganic mercury may be adsorbed onto soil particles, where it is likely to remain bound unless consumed by organisms. Intake of elemental or inorganic mercury by aquatic microorganisms results in the biotransformation of those inorganic forms into methylmercury, which may be bioconcentrated in aquatic/marine animals. Bioaccumulation in aquatic species is influenced by the pH (Ponce and Bloom, 1991) and the dissolved oxygen content (Wren, 1992). Mercury concentrations in sediment and water, along with pH, sulfate, dissolved oxygen (DO), and organic matter were the best predictors of MeHg in sediment and water. The major control on MeHg production in both sediment and water appears to be the inorganic Hg concentration. Sulfate and pH accounted for significant additional variability in water column MeHg. Sulfate stimulates MeHg production through the action of sulfate-reducing bacteria. Acidity is also commonly identified as a correlate of MeHg in aquatic ecosystems, affecting methylation, partitioning, and bioaccumulation. These relationships support the idea that reduction in acid deposition to freshwater ecosystems – particularly sulfates – will reduce the net production of MeHg from inorganic Hg. Low DO in lake bottom waters was also strongly correlated with MeHg (Gilmour *et al*, 2008).

The sorption of mercury to soil is dependent upon the organic matter content of the particular soil or sediment (Blume and Brummer, 1991), and mercury has been shown to bind tightly to the

surface layer of peat (Lodenius and Autio, 1989). In water, both inorganic mercury and methylmercury bind tightly to organic particulates and may be distributed to other bodies of water or onto soils in a bound form. The mobilization of mercury from soil or sediment particles to which it is sorbed may occur by either chemical or biological reduction to elemental mercury or microbial conversion to dimethylmercury (Andersson, 1979; Callahan *et al*., 1979; US EPA, 1984). Elemental mercury has been shown to be able to move through the top 3–4 cm of dry soil at atmospheric pressure (Eichholz *et al*., 1988).

2.4.2 Movements of mercury in and between environmental compartments

Mercury is a natural component of earth. Research indicates that natural and anthropogenic activities can redistribute this element in the atmospheric, soil and water ecosystems through a complex combination of transport and transformations (U S Geological Survey, 2000).

Mercury is emitted to the atmosphere from a variety of sources and is dispersed and transported in air, deposited to the earth and stored in or redistributed between water, soil and atmospheric compartments. Therefore, mercury cycling and mercury partitioning between different environmental compartments are complex phenomena that depend on numerous environmental parameters (U S Geological Survey, 2000). Wet deposition was, until recently, assumed to represent the primary mechanism for transfer of mercury and its compounds from the atmosphere to aquatic and terrestrial receptors. However, studies by US EPA, have shown that dry deposition of divalent gaseous mercury species can be equal or greater than wet deposition, even in moist climatic areas such as the Florida Everglades and the Great Lakes Region (Rea *et al.,* 2000; 2001; Landis *et al.,*2002; Vette *et al.,* 2002).

The chemical and physical form of mercury in air affects the mechanisms by which it is transferred to the earth surface and ultimately influences the total depositional flux. An increase in ambient air concentrations of mercury will result in an increase of direct human exposure. Also an increase of mercury flux entering terrestrial and aquatic ecosystems leads to elevated concentrations of methylmercury in freshwater and marine biota. Extensive research conducted on mercury deposition in Boreal forests systems has shown that the main source of mercury and methylmercury to the forest floor is litter fall (Iverfeldt, 1991, Munthe *et al.*, 1995). This mercury and methylmercury mainly originate from the atmosphere and adsorbs on plants surfaces via dry deposition. In the environment, elemental mercury can combine with chlorine, sulfur, and other elements to form inorganic compounds. The most common naturally occurring forms of mercury found in the abiotic environment are metallic (elemental) mercury, mercuric sulfide, and the salts mercuric chloride and mercurous chloride. (ATSDR, 2003) Figure 2.3 illustrates pathway of mercury into the environment.

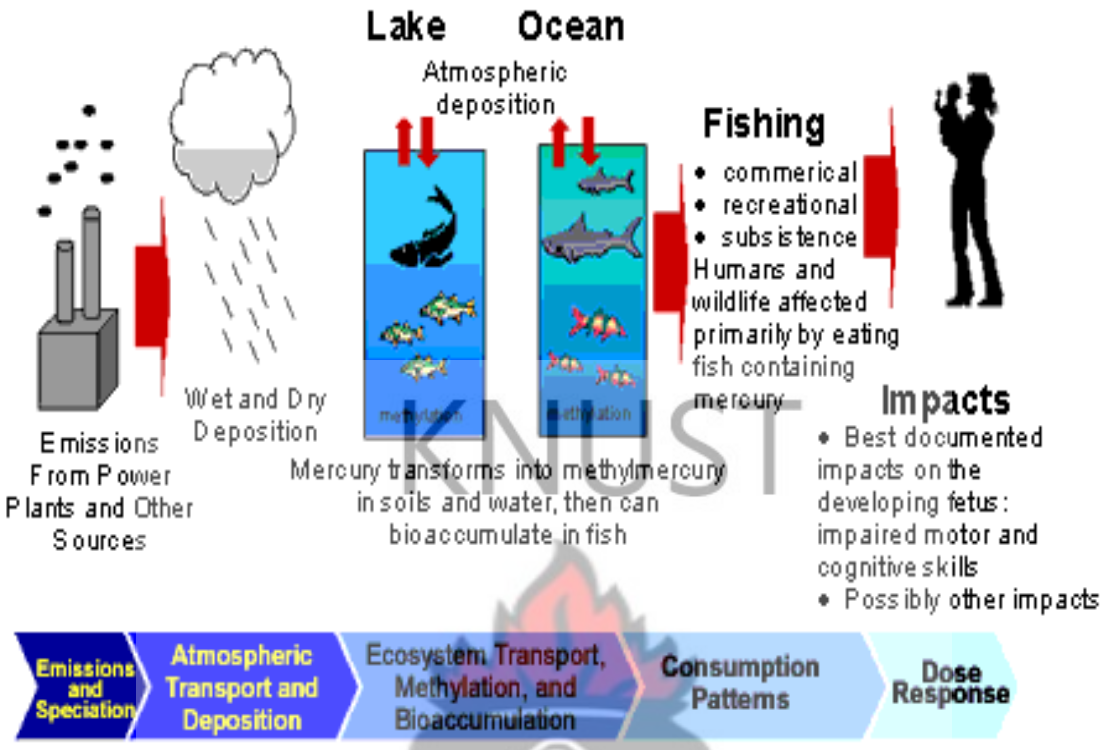

Figure 2.3 pathway of mercury into the environment

Source http://www.epa.gov/mercury/exposure.htm

2.5 Morphology of River Densu

River morphology is the shape or form of a river along its length and across its width. Transported materials are used in eroding a riverbed (degradation) and thus shaping its morphology. The transported materials are deposited (aggradation) either temporally or permanently along the course of a river when they can no longer be transported. Throughout geological history, rivers have altered their channels through erosion and deposition or human intervention, (Kusimi, 2008).

The Densu River system is one of the coastal drainage basins of Ghana. Its floodplain and river channel have been dramatically altered by building and construction, installation of a dam, salt

mining, grazing, channel incision and other fluvial processes. Like many other rivers, the Densu River channel is experiencing certain dynamics in its channel. The profile of the river is receding headward extending the lower section. In general the upper and middle sections are prone to degradational processes and the lower section by both aggradational and degradational processes (Kusimi, 2008). This has resulted in varied fluvial forms such as potholes, incised channels and irregular rapids in the upper and middle courses and meanders, ox-bow lakes and alluvial deposits in the lower section. The variation in channel morphology is attributed to the differences in gradient, fluvial processes (discharge) and physical elements such as vegetative cover and the underlying lithology of the river catchment, (Kusimi, 2008).

Akuffo reported that the Weija lake which is part of the Densu river is silting up at a rate of 2 % per year, giving it a lifespan of 50 years and is already 27 years old, meaning it has 23 years life left in it (Akuffo, 2003), if no stringent measures are taken to curb this situation. The degradation of the basin is attributed to the increase in the population of districts through which the river flows, particularly in the Greater Accra Region. For instance, the population of Accra has increased from 903,557 in 1970, to 1,431,099 in 1984 and 2,909,643 in 2000 (Ghana Statistical Service, 2002), and this has led to an increase in demand for housing, water, food and other resources of the basin. This accounts for the encroachment of the floodplain at Weija, a wetland declared as a RAMSAR site, for housing, farming and other human activities. The Weija Lake is also adversely affecting water discharge into the Sakumo Lagoon, causing it to disappear (Kusimi, 2009). The reservoir also accounts for the westward migration of the Densu mouth as discharge into the Gulf of Guinea is incapable of removing sand dunes deposited at its mouth by waves.

The river lies between latitudes 5°30'N to 6°20'N and longitudes 0°10'W to 0°35'W. The Densu River basin shares its boundary with the Odaw and Volta basins to the east and north, respectively, the Ayensu and Okrudu to the west and the Birim basin to the northwest the basin area is about 2488.41 km^2 with an average length of 225.6 km. Its main tributaries are the Kuia, Adaiso, Nsaki and Aprapon. The Densu Basin passes through three regions in Ghana namely Eastern, Greater Accra and Central Regions and falls under ten district administrations. The basin plays a critical role in the socio-economic development of the many towns and satellites villages dotted within it. Most of the urban centers such as Koforidua, Nsawam, Suhum (Fig 2.4) among others get treated water from the Densu River. From its reservoir at Weija, 91,000 m^3 of water a day is pumped to supply about 340,000 people in western Accra (Ghana Water Sewerage Company, 2003). Other small settlements also depend on untreated water from the Densu River and its tributaries.

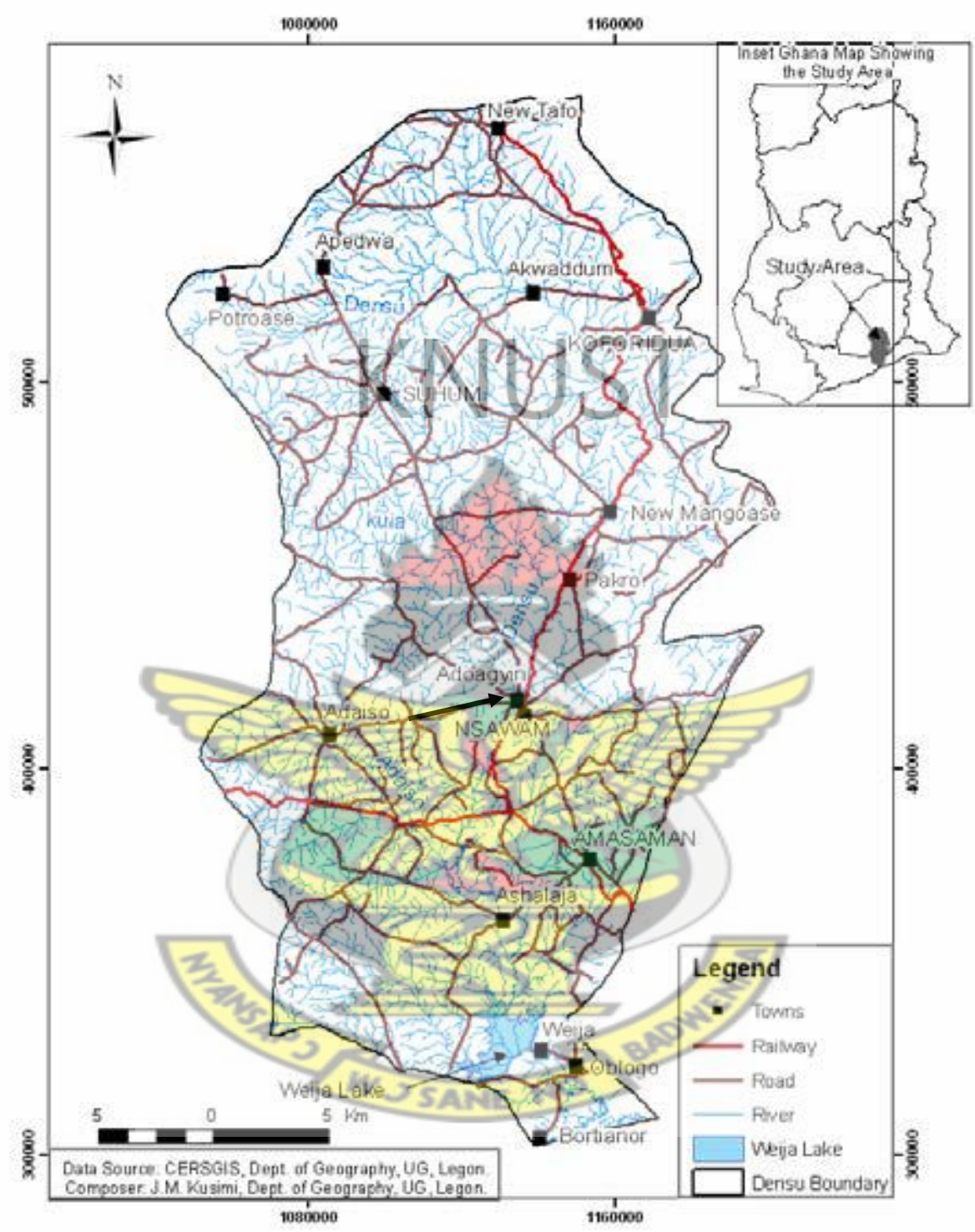

Fig 2.4 Map of the Densu Basin Source: Map data source

(Geological Survey of Ghana, 2008)

2.5.1 Anthropogenic activities in the Densu Basin

An impounded reservoir on the Densu river at Weija, a few kilometres before it discharges into the Atlantic Ocean, is an important source of water supply for the western part of the city of Accra. The major environmental concerns are erosion, siltation and pollution of the river, garbage, human wastes and excreta disposal, effluent from industries, motor garages and mechanical shops (Karikari and Ansa-Asare, 2004). The Densu Basin is also intensively used for the cultivation of both cash and food crops. Principal food crops cultivated within the basin are cassava, maize, yam, plantain, banana and cocoyam. Cash crops include cocoa, oil palm, pawpaw, pineapple, mangoes and citrus. Other land use activities include housing, sand winning, animal rearing, salt mining etc. These activities have seriously depleted the vegetative cover of the basin with hydrological and geomorphological implications such as flooding, soil erosion, siltation of the river channel and evaporation.

Industrial wastes from fruit processing factories, and other industries are discharged into the river. Agro-industries along the banks of the Densu River use the river as a source of water for their cultivation and so, the pollution of the river is expected. River Densu is the main source of water for the Accra metropolis and parts of the Eastern region of Ghana. It is also the main source of mudfish and tilapia for the communities along the river thus fishing is also one of the main anthropogenic activities.

The recipient downstream of the Densu River is the Weija reservoir which is one of the two main sources of water supply for the city of Accra. River Densu however, serves the communities along its catchment midstream to upstream where the water receives little or no treatment at all. 95 % of the basin is underlain by crystalline rocks, comprising five formations, namely Birimian, super group intruded by Granites, Togo series, and Dahomeyan and Accraian

sediments (Amuzu, 1975). At the source, it flows over metamorphosed lava, phyllites, schists tuffs and grey wacke (Fig 2.5). The dominant soils areochrosols, with patches of gleisols and lithosols (Amuzu, 1975). These geogene factors control the downstream evolution of the river chemistry.

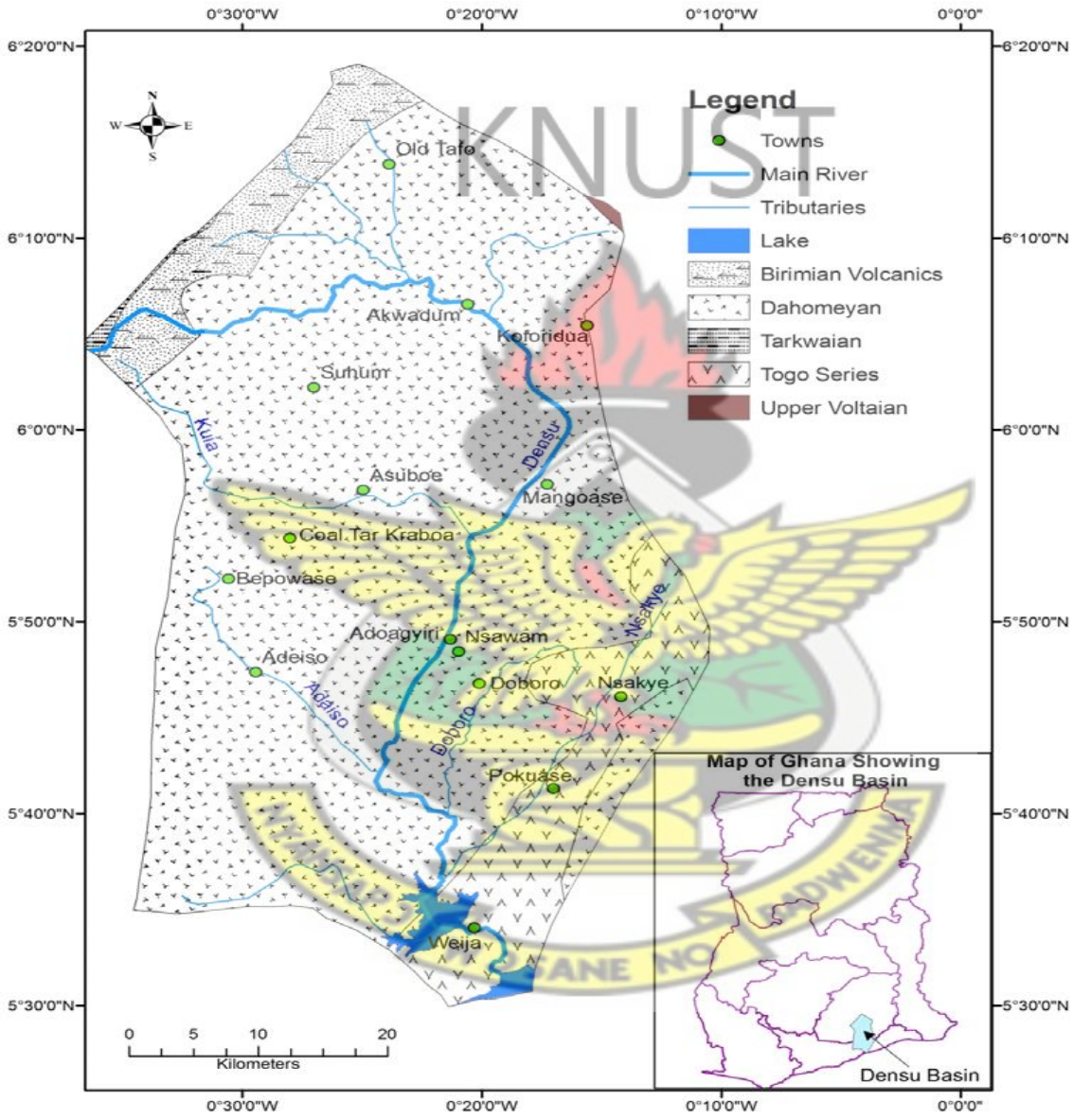

Fig 2.5: A Geological map of the Densu basin showing the Densu and the formations of the basin.

Source: (Geological Survey of Ghana, 2008)

The Densu River serving as a wide link among the villages and towns between Tafo and Accra is one of the largest terrestrials fresh water reservoir supplying Accra with drinking water. It plays an important role in the ecology, history and economy of the industrialized northeastern part of Ghana. The basin falls under two distinct climate zones characterized by two rainfall regimes with different intensities (Dickson and Benneh, 1980). The basin has by two rainfall maxima in a year, with the mean annual rainfall varying from about 900 to 1200 mm. The first rainfall season starts from May and ends in June and the second rainfall season starts from September and ends in October (Dickson and Benneh, 1980).

The highest mean monthly temperature of about 30 ºC occurs between March and April, and the lowest of about 26 ºC in August (Amuzu, 1975). The total population within the Densu River basin is estimated to be about 1.2 million people (Ghana Statistical Service, 2002). The main economic activity within the drainage basin is cash crop farming, but within its banks we have the cultivation of vegetables. There is also the rearing of livestock and fishing. With the ever-expanding population along the Densu basin, there is the need for proper conservation and efficient utilization of the freshwater body for sustainable development. This is necessary because there has been accelerated deterioration of water quality within the basin because of increased domestic, municipal and agricultural activities. Effluent discharge, urbanization and deforestation are the main causes of environmental degradation within the catchments of the Basin (Kakari and Ansa-Asare, 2004).

These activities have gained their roots because of lack of effective implementation and monitoring of water management and environmental policies by local government authorities in all the districts through which the Densu river flows. These practices have impacted very much

on the fluvial processes of the river (erosion and deposition), leading to much morphological changes in the channel pattern and form, braiding at the lower section and erosion at the middle course.

There is also that continuous run-off entrains sediments especially sand and silt into the river channel from exposed surfaces, resulting in the siltation of the river bed. Bed load analysis revealed that there was an inverse relationship between flow level and the concentration of sand and silt in the river channel. The concentration of sand and silt was high at low stages and minimal at high flows. Also, sediment discharge was found to be increasing from the source towards the mouth. The implication of sediment load and transport patterns in the river catchment is that it poses a great threat to the sustainability of the Weija Dam and water quality of the river in general. Also sediment load affects water turbidity. Turbidity determines the degree of scattering or absorption of light in the water and, thus, influences water temperature and the growth of aquatic plants and algae, which can increase water loss (evapo-transpiration) or cause eutrophication, (Kusimi, 2009). There is also the human contact which include the use of the water for bathing, washing, swimming, irrigation and gardening. These situations have resulted in siltation, pollution and prevalence of water-associated diseases (e.g. bilharzia, enteric infections and intestinal worms) in the area (Karkari and Ansa-Asare, 2004).

Anthropogenic activities thus introduce both inorganic and organic pollutants in the form of heavy metals and pesticides respectively into the water, sediment and biota of the basin (Kusimi, 2009). Some heavymetals like Pb, As, Cd and Hg even at low concentrations are toxic to life. As a result of these anthropogenic factors and geogene influences on the River Densu (as source of drinking water), it becomes imperative that regular reliable physico-chemical properties and levels of inorganic pollution of the Densu River is investigated.

CHAPTER THREE

MATERIALS AND METHODS

3.1 The Study Area

The Weija lake found in the Ga South Municipal district of Ghana is part of the 116km long Densu River in Ghana rising in the Atewa Range. The Densu river flows through an economically important agricultural region, supplies half the drinking water to the nation's capital city, and ends in an ecologically significant but environmentally threatened wetlands at the edge of the Atlantic Ocean. The Weija Dam is thus situated on the Densu River. On the south of the basin is the Weija lake, the sampling site, is shown in Figure 3.1 below.

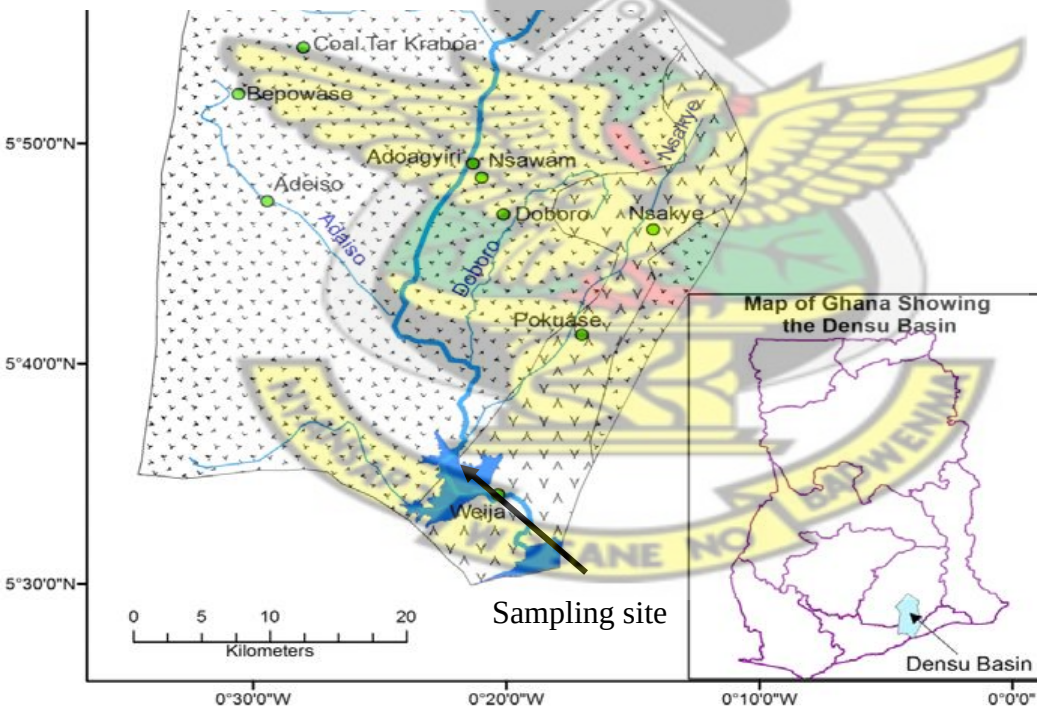

Fig. 3.1 A Geological map of the Densu Basin showing the sampling site, Weija.

Source: (Geological Survey of Ghana, 2008)

For the past two decades, the Densu River has been subjected to numerous environmental threats from farming, urbanization, logging and animal grazing along its banks particularly at Nsawam, Weija and Oblogo. Vegetables (e.g. okro), sugarcane, pawpaw and pineapples are extensively cultivated on commercial basis on the 35 m buffer zone regulation of the river. Various forms of fishing activities continue to pollute the river as it is also the main source of mudfish and tilapia for the communities along the river (Amuzu, 1975).

The 54.32 km^2 restricted zone demarcated under the Executive Instrument 130 of 1977 for the Weija lake has been seriously encroached upon according to the recent government committee report (Akuffo, 2003). These activities have reduced the vegetative cover, making soils more vulnerable to erosion into the river, which has serious implications on channel morphology, aquatic life and sedimentation of the Weija Reservoir. The river channel, especially the middle and lower courses are seriously experiencing erosion and siltation which is threatening the existence of the Weija Dam. Anthropogenic activities thus introduce both organic and inorganic pollutants in the form of pesticides and heavy metals (e.g mercury) respectively into the water, sediment and biota of the basin (Kusimi, 2009).

3.2 Apparatus and Glasswares

All glassware used were soaked in detergent solution overnight; rinsed with distilled water and soaked in 10% (v/v) HNO_3 overnight. They were rinsed with distilled water followed by 0.5% (w/v) $KMnO_4$ and finally rinsed with distilled water and dried before use. Automatic Mercury Analyzer Model HG-5000 (Sanso Seisakusho Co., Ltd, Japan), equipped with mercury lamp operated at a wavelength of 253.7 nm was used to measure Hg concentrations. Digestion tubes and a Clifton hot plate were used to digest the samples.

3.3 Reagents

All reagents used were of analytical reagent grade (BDH Chemicals Ltd, Poole, England) unless otherwise stated. Doubled distilled water was used for the preparation of all solutions. Mercury stock standard solution (1000 mg L^{-1}) ml was prepared by dissolving 0.0677 g of $HgCl_2$ in 14 ml of an acid mixture of HNO_3:$HClO_4$:H_2SO_4 (1:1:5) in a 50 ml digestion volumetric flask with heating on a hot plate at a temperature of 200 ^{0}C for thirty (30) minutes. Distilled water was added to make up to 50 ml. The working standard solutions were freshly prepared by diluting an appropriate aliquot of the stock solution through intermediate solutions using blank solution. Blank solutions were prepared by adding 1 ml of distilled H_2O, 2 ml of HNO_3 and $HClO_4$ (1:1) and 5 ml of H_2SO_4 in a digestion flask. The mixture was heated at 200 ^{0}C for 30 minutes. Distilled water was added to make up to 50 ml after the mixture was allowed to cool. Stannous Chloride solution (10% w/v) was prepared by dissolving 10 g of the salt in 1 M HCl solution to make a final volume of 100 ml . The solution was aerated with nitrogen gas at 50 ml min^{-1} for 30 min to expel any elemental mercury from it.

Sulphuric acid solution (10 M) was prepared by transferring about 100 ml of distilled water into 250 ml volumetric flask and 135 ml of concentrated (18.4 M) H_2SO_4 was added gradually while stirring in an ice bath. Distilled water was later added to make a final volume of 250 ml after it attained room temperature.

Potassium permanganate solution (0.5% w/v) was prepared by dissolving 0.5 g of $KMnO_4$ in distilled water to make a final volume of 100 ml.

Sodium hydroxide solution (10 M) was prepared by dissolving 200 g of NaOH in distilled water to make a final volume of 500 ml.

Hydroxylamine hydrochloride solution (10% w/v) was prepared by dissolving 10g of $NH_2OH.HCl$ in distilled water to make a final volume of 100 ml.

Ethylenediaminetetraacetate solution (EDTA) (10% w/v) was prepared by dissolving 10g of disodium salt of EDTA in distilled water to make a final volume of 100 ml.

Dithizone-toluene solution (0.01% w/v) was prepared by dissolving 0.01g dithizone in toluene to make a final volume of 100 ml.

3.4 Sampling and Sample preparation

3.4.1 Fish

The fish samples were collected from commercial catches made by the local fishermen. The samples obtained were of species meant for consumption. A total of 165 samples comprising of six species were obtained within 6 months (October, 2010 to March, 2011) from the Weija Dam. The six (6) species are, *Hemichromis fasciatus* (n=30), *Chrysichthys nigrodigitatus* (n=30), *Tilapia zilli* (n=30), *Tilapia mariae* (n=30), *Clarias batrachus* (n=30), *Clarias gariepinus* (n=15). The samples were placed in clean plastic bags and stored on ice in an ice chest. They were then transported to the laboratory, identified and kept in a freezer prior to preparation for chemical analysis. The fish samples were later taken from the freezer and allowed to defrost. They were washed with distilled water, dried on tissue paper and the length and body weight of each were taken. A portion of the edible muscle tissue was removed from the dorsal part of each fish, homogenized and stored in transparent polythene bags and kept in a freezer until chemical analysis.

3.4.2 Sediment

One sample was collected from each of 14 different locations each month at 5 m-25 m intervals along the banks of the river using the grab method. The samples were stored in polythene bags and kept cool during transportation to the laboratory. Sediment samples were air-dried and sieved through a 2 mm nylon sieve. A total of 84 sediments samples, (14 samples each month) were collected within 6 months (October, 2010 to March, 2011).

3.4.3 Water

Water was sampled into clean plastic 1.5 L bottles each month after rinsing the bottle with the water to be sampled from five different locations. Two bottles were filled with water from just below the water surface from each location. The two samples were combined together to form one composite sample and preserved with 7 ml concentrated HNO_3 /L and transported to the laboratory for chemical analysis. A total of thirty (30) water samples were collected within 6 months (October, 2010 to March, 2011).

3.5 Digestion Procedure for Fish and Sediment

The fish and sediment samples were digested for total mercury determination using the digestion tube method developed by Voegborlo *et al* (2010) followed by the procedure demonstrated in chart 3.1 below (Akagi and Nishimura, 1991). In the procedure, 0.5 g of homogenized fish, or 0.1 g of sediment was weighed into 50 ml digestion tube and 1 ml H_2O, 2 ml HNO_3:$HClO_3$ (1:1) and 5 ml H_2SO4 were added in turns. The mixture was then heated at a temperature of 200 ^{0}C for 30 minutes. The sample solution was then cooled and diluted to 50 ml with double distilled water.

Solutions of 25 µl and 50 µl and 100 µl of 1 µg ml^{-1} standard Hg solution were also subjected to the same digestion procedure. The concentrations of the standard solution digests obtained were 0.025 µg ml^{-1} , 0.05 µg ml^{-1} and 0.1 µg ml^{-1} respectively.

Sample (0.5 g fish or 0.1 g sediment in 50 ml digestion tube)

↓ H_2O, 1 ml

HNO_3: $HClO_4$ (1:1), 2 ml

H_2SO_4, 5 ml

Heat at 200 ^oC for 30 min

Digested Sample

Cool to room temperature

↓ H_2O,

Make up to 50 ml

Sample Solution, 5 ml

↓ 10% $SnCI_2$, 0.5 ml

CVAAS (Analyzer)

Chart 3.1 Analytical procedure for total mercury determination in fish and sediment samples

3.6 Extraction Procedure for Water

Extraction technique used for the water sample was developed at the National Institute for Minamata disease (NIMD) in Japan by Akagi and Nishimura (1991). In the procedure, one liter (1 L) of water sample was transferred into 1.5 L separatory funnel and 10 ml of 20 N H_2SO_4 and 5 ml of 0.5% $KMnO_4$ solution were added, mixed by shaking and was allowed to stand for 5 min. The solution was neutralized with 20 ml of 10 N NaOH, and 5 ml of 10% $NH_2OH.HCl$ solution was added and shaken. The mixture was allowed to stand for 30 minutes and 5 ml of 10% EDTA solution was added and shaken. Exactly 10 ml of purified 0.01% dithizone-toluene was added followed by vigorous shaking for 1 min. to extract mercury from the sample. The solution was allowed to stand for 1 hr, avoiding direct sunlight. This led to the formation of an aqueous phase and organic phase. The aqueous phase (lower phase) was discarded and the organic phase was transferred into a 10 ml conical centrifuge tube fitted with a glass stopper and centrifuged at 1200 rpm for 3 min with the glass stopper in place. When an emulsion was formed, 0.5 g of anhydrous sodium sulfate was added and the mixture shaken, followed by centrifugation to separate the phases. Exactly 7 ml of the organic phase was transferred into a 50 ml digestion tube. The solution was then evaporated to dryness in a water bath at 60 ^{0} C with a rotary evaporator. The residue was then subjected to wet digestion with the addition of 1 ml of H_2O, 2 ml of concentrated HNO_3:$HClO_4$ (1:1) and 5 ml of concentrated of H_2SO_4 in turns and heated on a hot plate at 200 ^oC for 30 min. The sample solution was allowed to cool and distilled water was added to make it up to a volume of 50 ml. Exactly 5 ml of the test solution was analysed using the mercury analyzer and the response was recorded in the form of a peak.

Water Sample, **1 L** (1.5 L capacity separatory funnel)

↓ Add 10 ml of 10 M H_2SO_4 and mix

Add 5 ml of 0.5% $KMnO_4$ solution and mix.

Let stand for 5 min.

Add 20 ml of 10 M NaOH and mix to neutralize

Add 5 ml of 10% $NH_2OH.HCl$ solution, mix, and allow standing for 20 min.

Add 5 ml of 10% EDTA solution and mix

Add 10 ml of purified 0.01% dithizone-toluene and vigorously shake for 1 min

Allow To stand for at least 1 hr.

Organic phase Aqueous phase

↓ (When an emulsion is formed, add 0.5 g of anhydrous $NaSO_4$ and shake.)

Centrifuge at 1,200 rpm for 3 min.

Organic phase, 7 ml (sample digestion tube)

↓ Evaporate to dryness

Residue

↓ Distilled water, 1 ml

HNO_3:$HCIO_4$ (1:1), 2 ml

H_2SO_4, 5 ml

Heat at 200 °C for 30 min.

Digested sample

↓ Allow to cool

Make up to 50 ml with distilled water

Test solution, a fixed volume (5 ml)

↓ 10% $SnCl_2$ solution, 0.5 ml

CV AAS

Chart 3.2 Analytical procedure for determining total mercury in water

3.7 Determination of mercury

Determination of mercury in all the digests was carried out by Cold Vapour Atomic Absorption Spectrophotometry using an Automatic Mercury Analyzer model HG-5000 (Sanso Seisakusho co., Ltd, Japan) developed at National Institute for Minamata Disease (NIMD). The analyzer is an instrument designed specifically for the measurement of mercury using the cold vapour technique. It makes use of the batch mercury cold vapour generating system. The analyzer consists of an air circulation pump, a reaction vessel, $SnCl_2$ dispenser, an acidic gas trap and a four-way stop-cock with tygon tubes to which is attached a ball valve. The operations of the ball valve and the air circulation pump are controlled by a microprocessor. A schematic diagram of the system is shown in Fig.3.3. During the determination, a known volume of the sample solution normally 5 ml is introduced into the reaction vessel using a micropipette (1-5 ml). The reaction vessel is immediately stoppered tightly and 0.5 ml of 10% (w/v) $SnCl_2$.2H2O in 1 M HCl is added from a dispenser for the reduction reaction. During this time, air is circulated through the four-way stopcock to allow the mercury vapour to come to equilibrium and the acidic gases produced by the reaction also swept into the sodium hydroxide solution. After 30 seconds the four-way stopcock is automatically rotated through 90^0 and the mercury vapour is swept into the absorption cell. This is connected to the computer from which the results of the various mercury levels are obtained and computed.

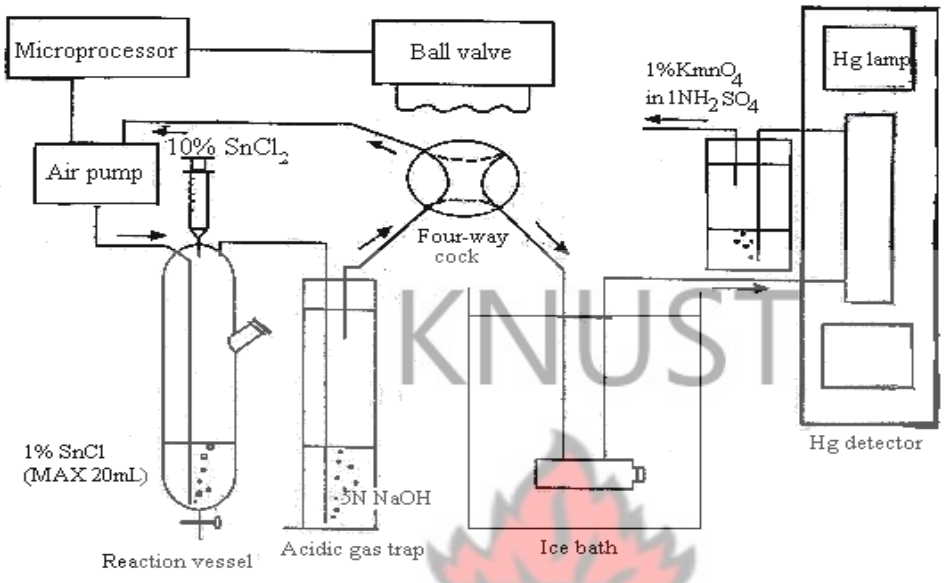

Fig. 3.2 A Schematic Diagram of the Authomatic Mercury Anayzer

3.8 Quality Assurance

The accuracy of the analytical method used was evaluated by performing recovery and analysis of certified reference material (CRM), IAEA-407 FISH HOMOGENATE.

3.8.1 Recovery of Mercury

3.8.1.1 Fish

Recovery of mercury from fish was determined by adding increasing amounts of mercury chloride solution to known weights of homogenized two different fish species namely *hemichromis fasciatus* and *tilapia zilli* which were taken through the digestion procedure.

3.8.1.2 Sediment

Recovery of mercury from sediment was determined also by adding increasing amounts of mercury chloride solution to one sediment sample which was taken through the digestion procedure.

3.8.1.3 Water

Recovery of mercury from water was determined by adding increasing amounts of mercury to distilled water which was taken through the extraction procedure. The resulting solutions were analysed for mercury concentration and the results obtained are reported in table 4.1 to 4.3.

3.8.2 Analysis of Certified Reference Material (CRM)

In the procedure, 0.01 g of the CRM was weighed into a 50 ml digestion tube. Four replicates of these were performed. All the samples were taken through the digestion procedure. The resultant solutions were analysed for Hg concentrations.

3.9 Statistical Analysis

The data obtained in this study were subjected to statistical analysis using Microsoft Excel and Statistical Package for Social Sciences (SPSS). Linear regression and correlation analysis were used to assess correlation between mercury concentration in fish, fish length and fish weight as well as sediment and water.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

Percent recovery was undertaken to ascertain the accuracy of the results and the results obtained indicated a very good recovery. Recoveries were 86 % to 103.6 %. The recovery results are reported in tables 4.1 to 4.3. The level of precision was also evaluated by calculating the mean and standard deviation for all samples and the results obtained indicated a good precision. These results are also tabulated below.

The accuracy of analytical procedure was also checked by analyzing the Certified Reference Material (CRM) IAEA-407 (Fish Homogenate). Recovery rates ranged from 78 to 96 %. The results are recorded in table 4.4 below.

Table 4.1 Recovery of mercury from fish

Sample	Hg added (ng)	Hg found (ng)	Hg recovered (ng)	% Recovered
Hemichromis	0	42.94	-	-
fasciatus	25	67.74	24.8	99.2
(0.57 g)	50	93.85	50.9	101.8
Tilapia	0	21.51	-	-
zilli	25	47.42	25.9	103.6
(0.56g)	50	70.49	48.98	98.0

Table 4.2 Recovery of mercury from sediment

Sample	Hg added (ng)	Hg found (ng)	Hg recovered (ng)	% Recovered
October	0	41.44	-	-
Sampling	25	66.24	24.8	99.2
Point 2 (0.1g)	50	92.43	51.0	102.0

Table 4.3 Recovery of mercury from distilled water

Sample	Hg added (ng)	Hg found (ng)	Hg recovered (ng)	% Recovered
Distilled	0	12.5	-	-
Water	25	36.5	24	96
(1000 ml)	50	55	43	86

Table 4.4 Results of CRM (IAEA – 407 FISH HOMOGENATE)

Samples (0.01 g)	Concentration obtained (µg/g)	Mean certified Concertration ± s.d	% Recovery (µg/g)
1	0.173	0.222±0.006	78
2	0.204	0.222±0.006	92
3	0.203	0.222±0.006	91.5
4	0.213	0.222±0.006	96

4.1 Total Mercury Concentrations in Fish, Sediments and Water

Total mercury (THg) concentrations were determined in fish muscle tissues, sediments and water from the River Densu at Weija Reservoir in the Ga South Municipality of the Greater Accra Region of Ghana. In all, a total of one hundred and sixty-five (165) fish samples covering six (6) species were analysed for total mercury. All the fish species analysed for total Hg are consumed by humans.

Summary of results of Hg concentrations, and weight of fish used in this study are presented in table 4.5. Mercury concentrations in water and sediments are presented in tables 4.6. The summary of total Hg concentrations (µg/g wet weight) in the edible muscle of fish ranged from 0.001 to 0.420. All the samples studied showed mercury concentrations below the World Health Organization (WHO/FAO) limit of 0.5 µg/g wet weight. Total mercury concentration in fish depends on the fish species and the concentrations also varied with factors such as total length of fish and fresh weight of fish. There was a significant variation between mercury concentrations, fish length and fish weight in this study. Although growth rate data of fish from the studied areas are not available, variations (e.g length and weight) suggest that all the fish species are not growing at the same rate.

Table 4.5 Total Hg concentrations (µg/g) in fish muscle tissues from River Densu at Weija

Species Name	Sample Size (n)	Fresh weight Range (g)	Mean Weight (g)	Hg concentration Range (µg/g)	Mean Hg Concentration (µg/g) ± s. d.
Hemichromis fasciatus	30	14.26-162.1	67.4	0.014-0.420	0.125±0.111
Chrysichthys nigrodigitatus	30	34.41-143.5	87.0	0.001-0.342	0.096±0.094
Tilapia zilli	30	21.81-180.0	81.3	0.022-0.385	0.155±0.098
Tilapia mariae	30	19.17-191.3	89.4	0.021-0.378	0.181±0.115
Clarias batrachus	30	45.0- 401.4	153.6	0.010-0.367	0.114±0.109
Clarias gariepinus	15	47.26-290.2	145.2	0.056-0.330	0.114±0.076

s.d= standard deviation

Table 4.6 Mean Hg concentration in Water and Sediment from Weija

Month	Mean Hg (n=5) (Water) Concentration (ng/L)	Mean Hg (n=14) (Sediment) Concentration (µg/g)
October	0.023	0.065
November	0.011	0.057
December	0.011	0.050
January	0.021	0.052
February	0.023	0.053
March	0.010	0.054
Mean Hg concentration ± s.d	0.017±0.008 ng/L	0.055± 0.023 µg/g

s.d= standard deviation

Detailed results obtained including graphs showing relationships between total mercury concentration, total length, and fresh weight in fish as well as mercury concentration in sediment and water are presented in the Appendix. The level of mercury in fish ranged between 0.001 to 0.420 µg/g wet weight (table 4.5). The highest level of 0.420 µg/g wet weight was found in *Hemichromis fasciatus* and the lowest level of 0.001 µg/g wet weight was found in *Chrysicthys nigrodigitatus*. Mercury levels obtained showed that within the same aquatic environment, fish of the same species have significantly different levels of mercury. This could be due to physiological factors such as sex, age, size, growth rate, or metabolic rate since these are

important variables that determine level of mercury accumulation in fish according to Huckabee *et al*., (1979).

The range of mercury concentration (µg/g wet weight) in the muscle tissue ranged from 0.014 to 0.420 (mean = 0.125±0.111) for *Hemichromis fasciatus*, from 0.001 to 0.342 (mean = 0.096±0.094) for *Chrysichthys nigrodigitatus*, from 0.022 to 0.385 (mean = 0.155±0.098) for *Tilapia zilli*, from 0.021 to 0.378 (mean = 0.181±0.115) for *Tilapia mariae*, from 0.095 to 0.367 (mean = 0.114±0.109) for *Clarias batrachus*, and from 0.056 to 0.330 (mean = 0.114±0.076) for *Clarias gariepinus*.

Cabana *et al*., (1994) in their study on fish (*Lake trout*) from Ontario lake in Canada and Kidd *et al*., (1995) in their study on fish from Lango Manso, a reservoir in Brazil showed that mean mercury concentrations vary widely between species, which can be explained by trophic positions or food chain length in the food web. Further more in aquatic systems, mercury is converted to methylmercury which is taken up by biota and accumulated in the food chain, sometimes to levels that are many thousands of times greater than levels in the surrounding water (UNEP, 2010).

Thus fish from high trophic levels (carnivores) in a food chain usually have higher mercury concentrations than fish from lower trophic levels (herbivores) as a result of biomagnifications. In some cases in this study Hg concentrations also increased with trophic levels. For example from (table 4.5) *Chrysicthys nigrodigitatus* species recorded Hg concentration range of 0.001 to 0.342 µg/g wet weight (mean = 0.096±0.094) and fresh weight range of 34.41 to 143.5 g (mean = 87.0±36.8) whereas *Hemichromis fasciatus* at a higher trophic level recorded Hg concentration range of 0.014 to 0.420 µg/g wet weight (mean = 0.125±0.111) and fresh weight range of 14.26

to 162.1 g (mean=67.4±43.9). Furthermore there was also significant correlation between mercury concentration, fresh weight (r^2=0.5739) and total length (r^2=0.6301) for *Hemichromis fasciatus* (fig.4.11 and 4.12) whilst *Tilapia zilli* (fig. 4.1 and 4.2) showed poor correlation between mercury concentration, fresh weight (r^2=0.0029) and total length (r^2=0.0015). This observation can be due to the feeding habits of the fish species as *Hemichromis fasciatus* is a carnivorous fish which feeds on other fishes whereas *Tilapia zilli*, a herbivore feeds on aquatic plants.

Work done by Lange *et al*., (1994) also showed that mercury concentration varies with fresh weight of fish and total length. Good correlation between mercury concentration and total length and fresh weight of fish are normally observed among carnivorous species whereas poor correlations are observed among herbivorous species. Among the fish species studied at Weija, there was a poor correlation between Hg concentration and total length of *Tilapia mariae* (omnivore), *Tilapia zilli (*r^2=0.0015, herbivore*)*, *Clarias batrachus* (r^2=0.3753, benthic omnivore), *Clarias gariepinus* (r^2=0.0149, benthic omnivore), *Chrysichthys nigrodigitatus* (r^2=0.0466, omnivore). There was also a poor correlation between mercury concentration and total weight of *Tilapia zilli* (r^2= 0.0029), *Tilapia mariae* (r^2 = 0.0009), *Clarias batrachus* (r^2=0.3983), *Chrysichthys nigrodigitatus* (r^2=0.0318), *Clarias gariepinus* (r^2 = 0.0012).

Thompson (1985) observed lack of correlation between total length and mercury concentration for several fish species distributed along the Tasmanian continental shelf. Thompson (1985) concluded that use of correlation to estimate mercury content and define human consumption limit for a given species could not be done without proper knowledge of the species biology and the particularities of each environment it inhabited. Results of this study agree with this finding.

Poor correlation exist between mercury concentration and total length of *Tilapia mariae*, *Clarias batrachus* (r^2=0.3753) and *Clarias gariepinus* (r^2=0.0149) whereas good correlation was observed between mercury concentration and total length of *Hemichromis fasciatus* (r^2=0.6301). For instance, *Hemichromis fasciatus* with length of 24.4 cm and weight of 138.5 g had Hg concentration of 0.401 µg/g while *Tilapia mariae* with length and weight of 15.4 cm and 74.4 g respectively had Hg concentration of 0.085 µg/g. This finding agrees with that of Lathrop *et al*., (1991) which reports that length and age of fish species have been shown to be important factors determining mercury concentration in fish. Apart from diet and trophic level, differences in longevity, growth rate and other physiological and ecological factors can also lead to differences in mercury concentrations between species (Huckabee *et al*., 1979).

Mercury content in fish is considered to be a good indicator of human exposure to organic or methylmercury. Humans' health concerns arise when fish and wildlife from aquatic ecosystems are consumed by humans since fish accumulate high concentrations of methylmercury (Uchida *et al*., 1961) which can affect the nervous system, cause blurred vision, coma and ultimately death (Harada, 1995; Takeuchi and Eto, 1999). Therefore, diet consisting particularly of fish, could be the main source of human exposure to methylmercury.

The relatively low mercury levels found in the fish species studied from the Densu River could be attributed to the fact that, organic matter, pH, seasonal changes, regional variations and hydrologic conditions which are thought to be the most significant factors that control accumulation of mercury in fresh water fish as reported by Lindqvist *et al*., (1991) might be unfavourable. Agricultural activities that employ the use of mercurial compounds could be minimal. Atmospheric deposition of Hg which is another factor that increases Hg loads in freshwaters may be low.

Regarding direct mercury emissions to water bodies, the sediments represent a potential long term source of mercury to the aquatic system, particularly if the sediments are dredged or otherwise resuspended (Lindberg and Harriss, 1977). Contaminated sediments in aquatic environments can pose health risks to many types of organisms, including humans. Exposure to the contaminants occurs by several routes, including direct contact and consumption of organisms that have accumulated contaminants from the sediments. The potential adverse effects on human health and the environment are compelling reasons to seek to reduce exposure (The National Academies Press, 2007).

Mercury is unique among other toxic elements as it is the only metal which is consistently biomagnified within the aquatic food chain. (Linberg *et al*., 1987). Hamilton (1971) concluded that predators had an average MeHg concentration that was almost 15 times greater than algae eaters. Furthermore, studies have shown that only MeHg biomagnifies through successive trophic levels, with virtually all Hg present as MeHg in fish tissue (Watras *et al*., 1998; Bloom, 1992; Watras and Bloom, 1992).

Thus mercury concentrations are lowest in the smaller, non-predatory fish and can increase many-fold on the way up the food chain (AMAP, 1998). Apart from the concentration in food, other factors affect the bioaccumulation of mercury. Of most importance are the rates of methylation and demethylation by mercury methylating bacteria (e.g., sulphate reducers). When all of these factors are combined, the net methylation rate can strongly influence the amount of methylmercury that is produced and available for accumulation and retention by aquatic organisms (UNEP, 2010).

Furthermore mercury bioconcentration and methylation in aquatic food chains indicates that fish consumption is a major mercury pathway to man. (U S Geological Survey, 2000). This suggests that any potential large scale or long term releases of mercury to surface waters like the Densu river from contaminated waste storage areas or sediments must be closely monitored.

In addition, because Hg has capacity to become biomagnified upward in natural food chains, mercury monitoring in the Densu reservoir must also be directed toward predatory species at the highest trophic levels which will be exposed to the most elevated mercury levels within a particular ecosystem.

It has been reported that mercury concentrations in bed sediments are not necessarily correlated with concentration in fish tissue (Lourdes and Curvin, 1989 and Rose *et al*., 1999). This study agrees with this report. In this study, correlation between Hg concentration in different fish species and sediments at Weija was determined and reported as regression coefficient (r^2). All of the fish species showed poor correlation between Hg concentration in fish and sediment (table 4.7). The poor correlation between Hg concentrations and river sediments of all of the fish species could be attributed to the fact that Hg content in the fish muscle is not related only to the Hg content in the sediments, but also to the diet composition of the fish and to the other chemical and biological characteristics of the aquatic ecosystem (Huckabee *et al*., 1979).

Table 4.7 Correlation (r^2) between Hg concentration (µg/g) in fish and river sediments

Fish species and R^2 values					
Clarias batrachus	*Clarias gariepinus*	*Chrysicthys nigrodigitatus*	*Tilapia zilli*	*Tilapia mariae*	*Hemichromis fasciatus*
0.1619	0.297	0.1337	0.0974	0.1093	0.1088

In their study of selected fishes in Laguna lake in Philipines, Lourdes and Curvin (1989) observed no direct correlation between mercury levels in water and fish. This research agrees with that observation. For the correlation between Hg concentration in different fish species and water at Weija Site was also determined. All of the fish species showed poor correlation between Hg concentration in fish and water. The correlation between Hg concentration in *Clarias batrachus*, *Tilapia zilli* and *Hemichromis fasciatus* and water was relatively week with regression values of r^2=0.0102, 0.0374 and 0.0687 respectively. That for *Clarias gariepinus*, *Chrysicthys nigrodigitatus*, *Tilapia mariae* were 0.1103, 0.1971 and 0.1485 respectively.

Table 4.8 Correlation (r^2) between Hg concentration (µg/g) in sediment and water

Sampling Site	R^2 Values
Weija	0.230

Lourdes and Curvin, (1989) found no direct correlation between mercury levels in sediment and water in their study. This is also in line with this finding as there was no significant correlation observed, between the total Hg in the sediment and in the water. This however depicts that the total Hg concentrations in the sediment and water are independent of each other. This finding also agrees with the study of Harris and Bodaly, (1998) who reported that concentrations of total Hg or methylmercury (MeHg) in surface waters often do not correlate well with the Hg content of fresh water biota. Hg concentrations in sediment were below the International Atomic Energy Agency (IAEA) limit of 0.81µg/g.

The low Hg concentrations in sediments indicate that there has not been any local contaminating source in the studied area. This agrees with work done by Gilmour and Henry (1991) on non-contaminated sediments where low Hg levels were found. US EPA, (1997) reported that total Hg levels in lakes and streams are typically well under 20 ng/L, however, elevated levels may be found in lakes and streams thought to be impacted by anthropogenic Hg sources. This is consistent with this study, for Hg concentration range of 0.008 to 0.033 ng/L (mean = 0.0170±0.008) obtained were far below 20 ng/L and even the background level of 0.1µg/L.

CHAPTER FIVE

CONCLUSIONS

5.1 CONCLUSIONS.

From the analysis carried out, the following conclusions may be deduced from the results obtained.

- This study reports mercury levels in fish species from Densu reservoir at Weija. The concentration of total mercury (µg/g) in the edible muscle tissue of all the fish analysed from the reservoir ranged from 0.001 µg/g to 0.420 µg/g wet weight.
- The study also reported Hg level in sediments from the same site. The range of Hg concentrations in the river sediments were 0.009 µg/g to 0.131 µg/g (mean=0.055).
- The Hg level for water also ranged from 0.008 ng/L to 0.017 ng/L. Hg concentrations in fish are below the World Health organization (WHO) limit of 0.5 µg/g. Hg concentrations in sediment are below the International Atomic Energy Agency (IAEA) limit of 0.81 µg/g and Hg concentrations in water are below the WHO maximum contamination level of 1000 ng/L.
- The results obtained showed that water and fish species from the Densu Reservoir are unlikely to constitute a significant exposure of the public to Hg through consumption of fish.
- The low concentrations of mercury in sediments, fish species and water obtained in this study suggest a relatively clean aquatic environment, with regards to mercury.

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APPENDIX

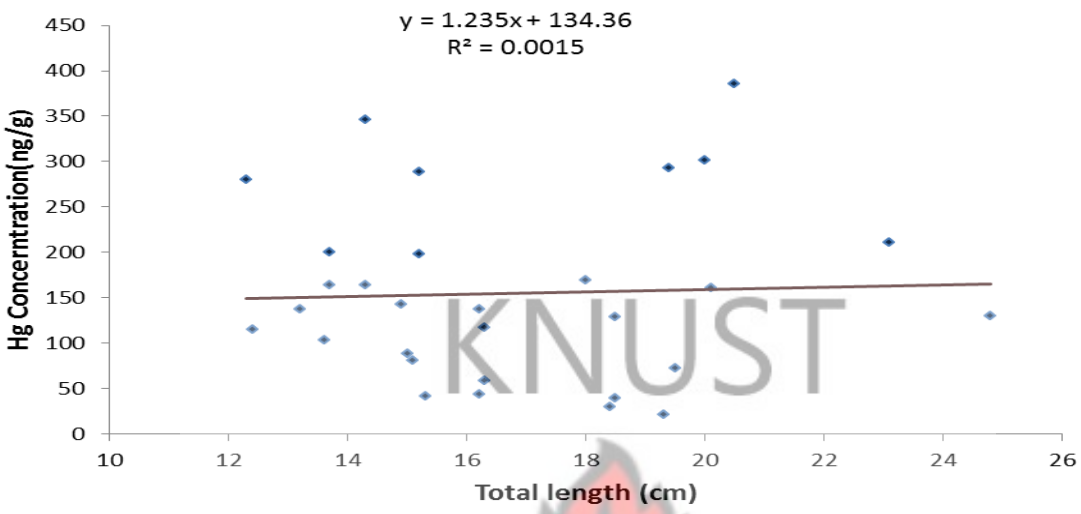

Fig. 4.1 Relationship between Hg concentration on wet weight basis and total length for *Tilapia zilli*

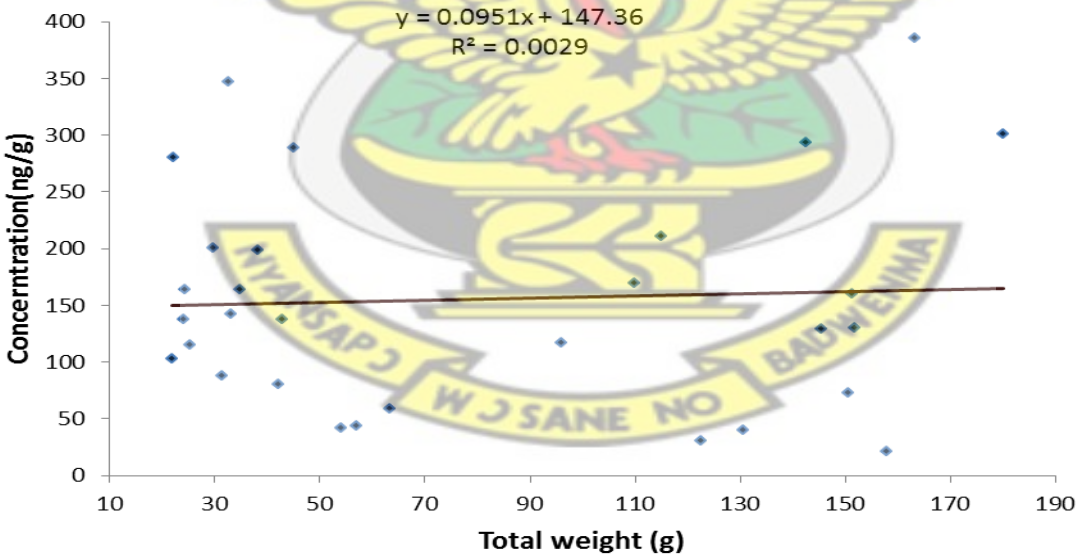

Fig. 4.2 Relationship between Hg concentration on wet weight basis and fresh weight for *Tilapia zilli*.

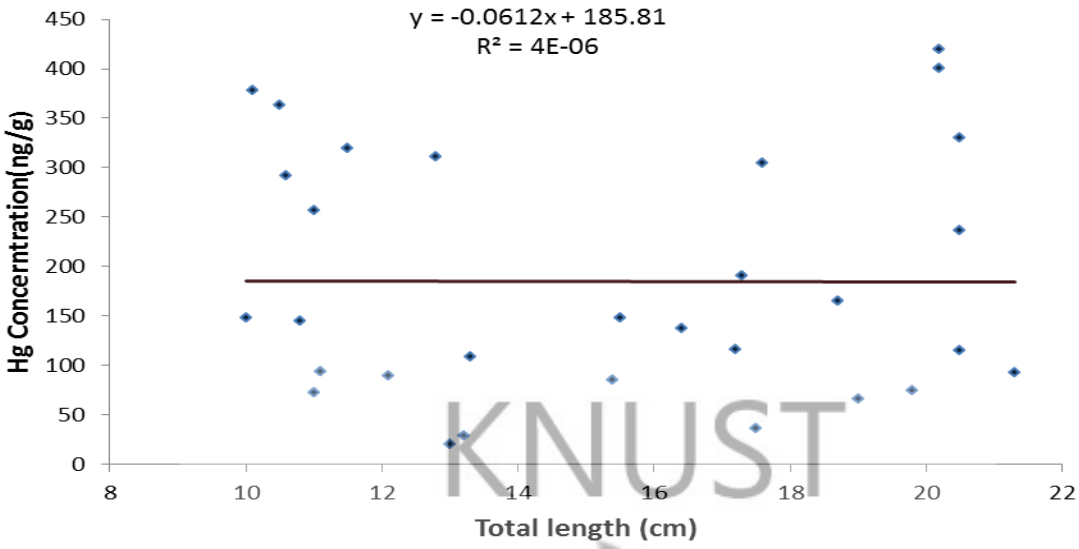

Fig. 4.3 Relationship between Hg concentration on wet weight basis and total length for *Tilapia mariae*.

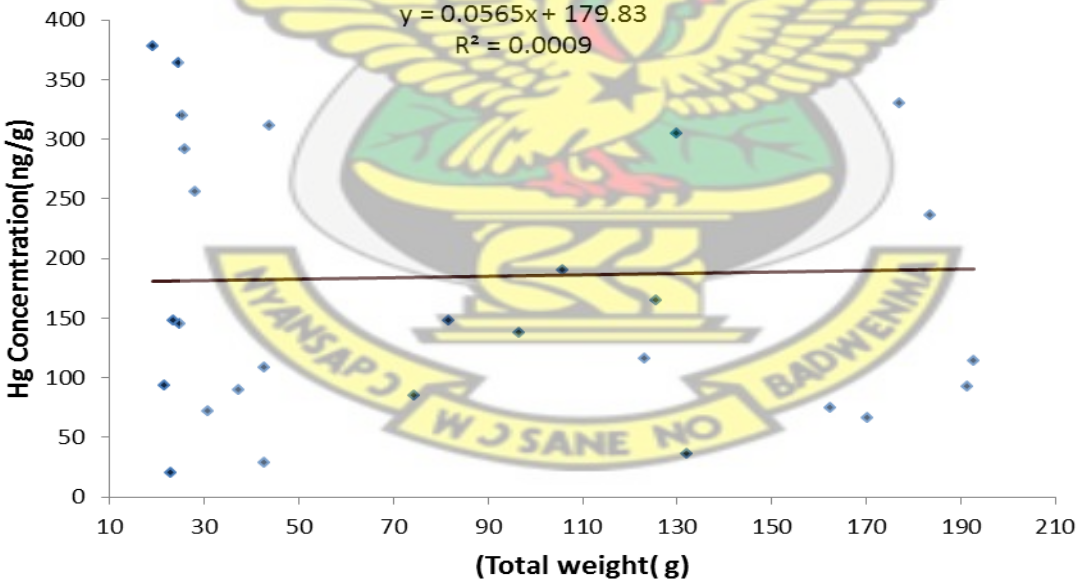

Fig. 4.4 Relationship between Hg concentration on wet weight basis and fresh weight for *Tilapia mariae*

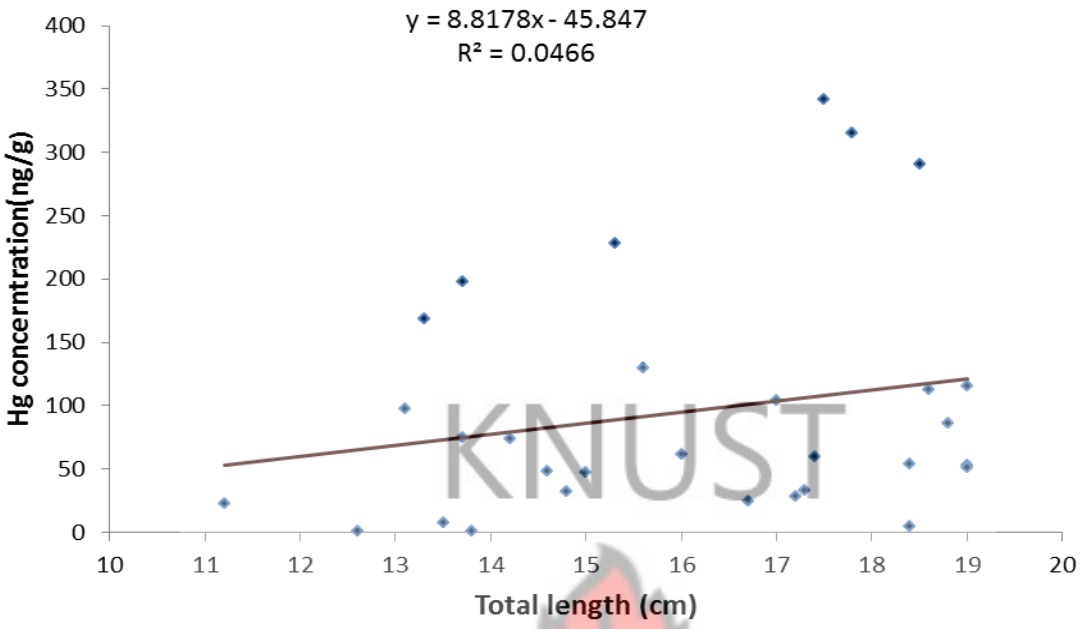

Fig. 4.5 Relationship between Hg concentration on wet weight basis and total length for *Chrysicthys nigrodigitatus*.

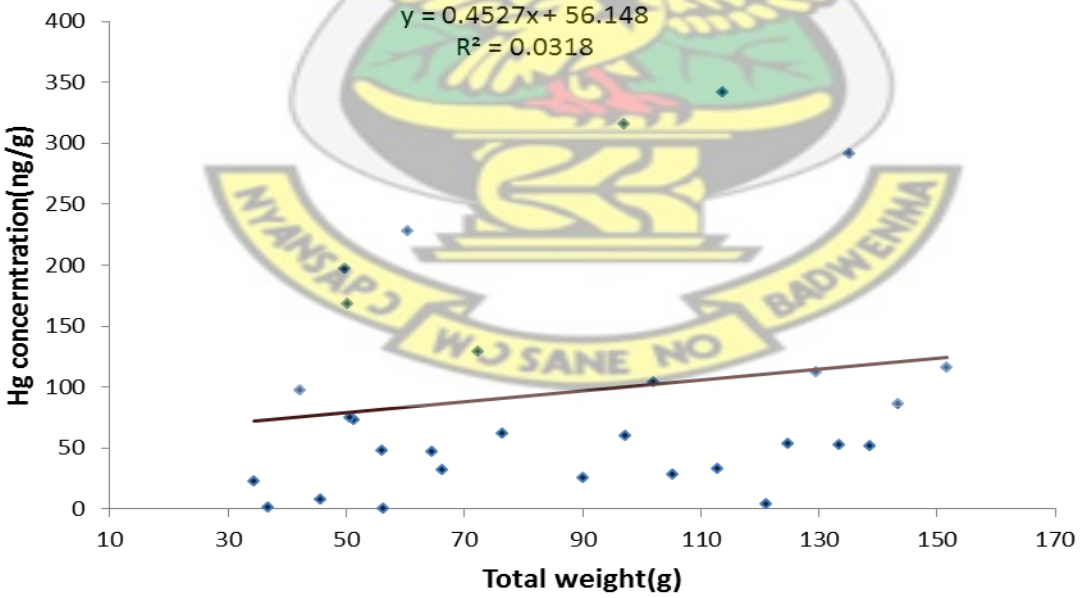

Fig. 4.6 Relationship between Hg concentration on wet weight basis and fresh weight for *Chrysicthys nigrodigitatus*.

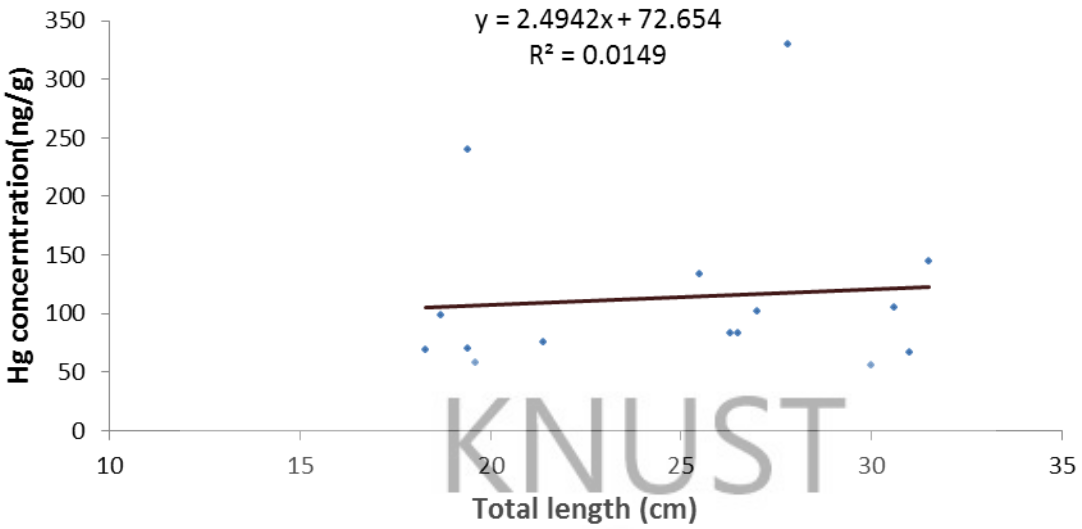

Fig. 4.7 Relationship between Hg concentration on wet weight basis and total length for *Clarias gariepinus*.

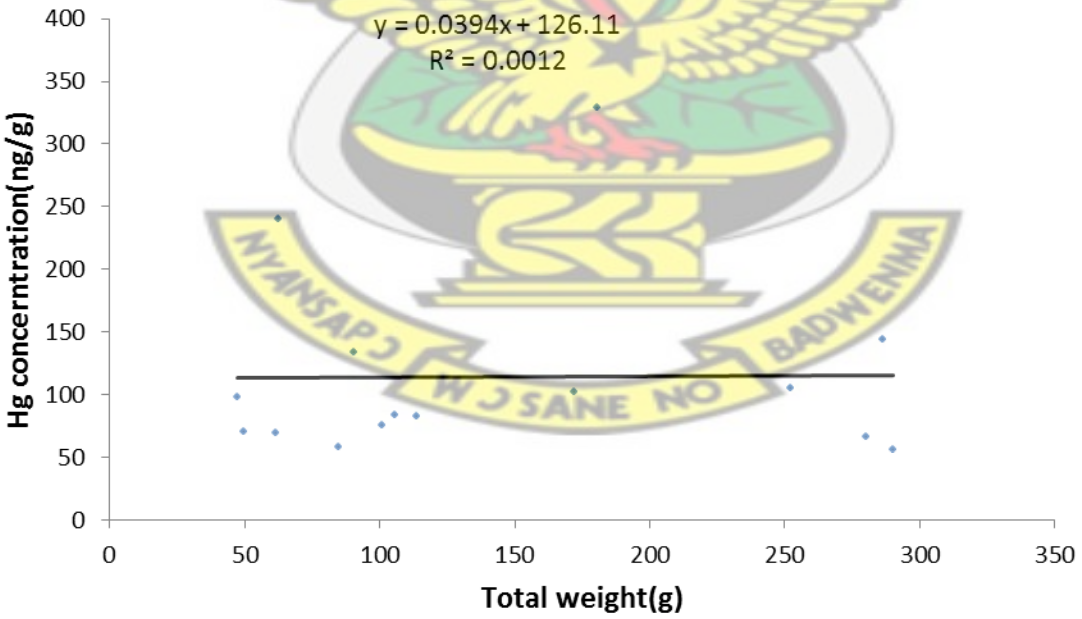

Fig. 4.8 Relationship between Hg concentration on wet weight basis and fresh weight for *Clarias gariepinus*.

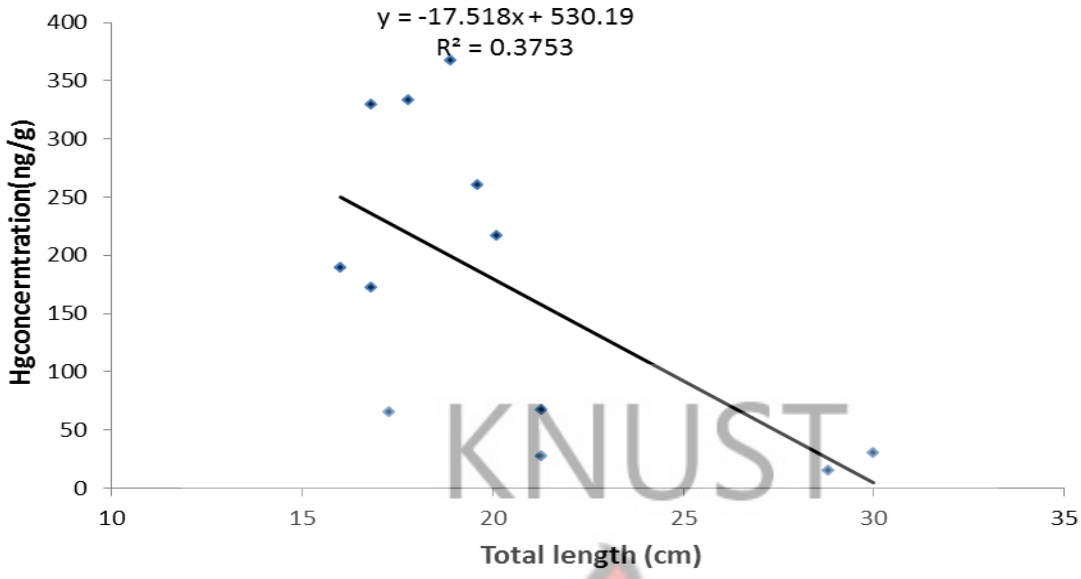

Fig. 4.9 Relationship between Hg concentration on wet weight basis and total length for *Clarias batrachus*.

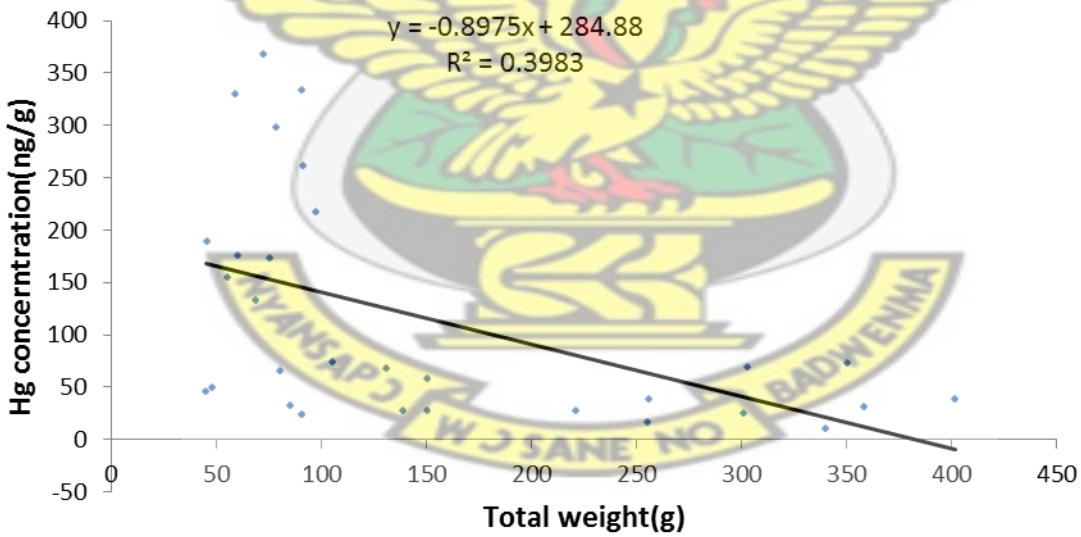

Fig. 4.10 Relationship between Hg concentration on wet weight basis and fresh weight for *Clarias batrachus*.

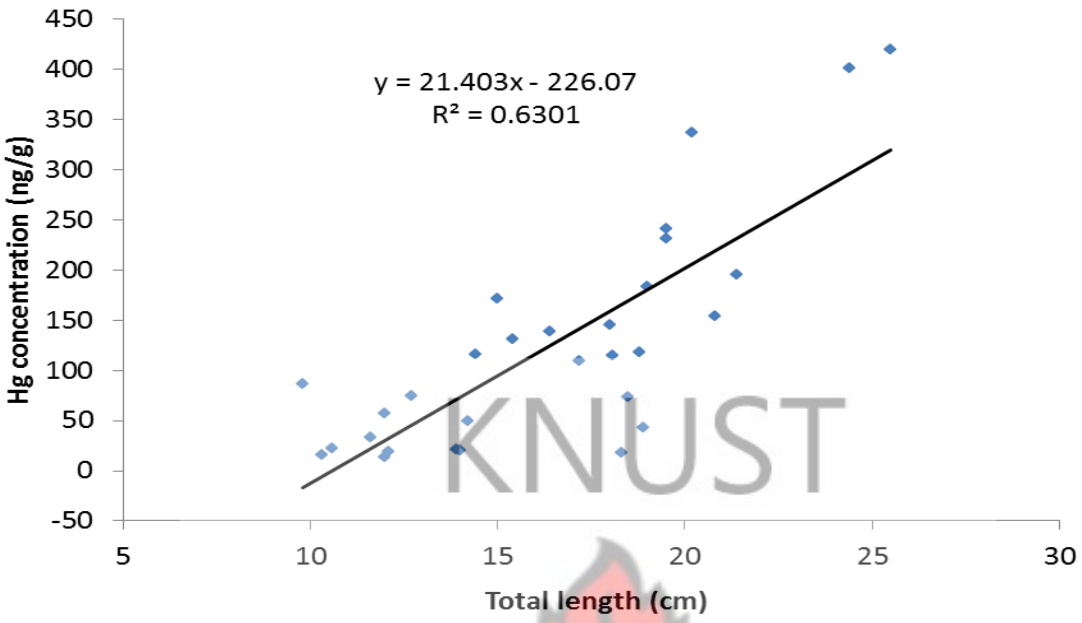

Fig. 4.11 Relationship between Hg concentration on wet weight basis and total length for *Hemichromis fasciatus*.

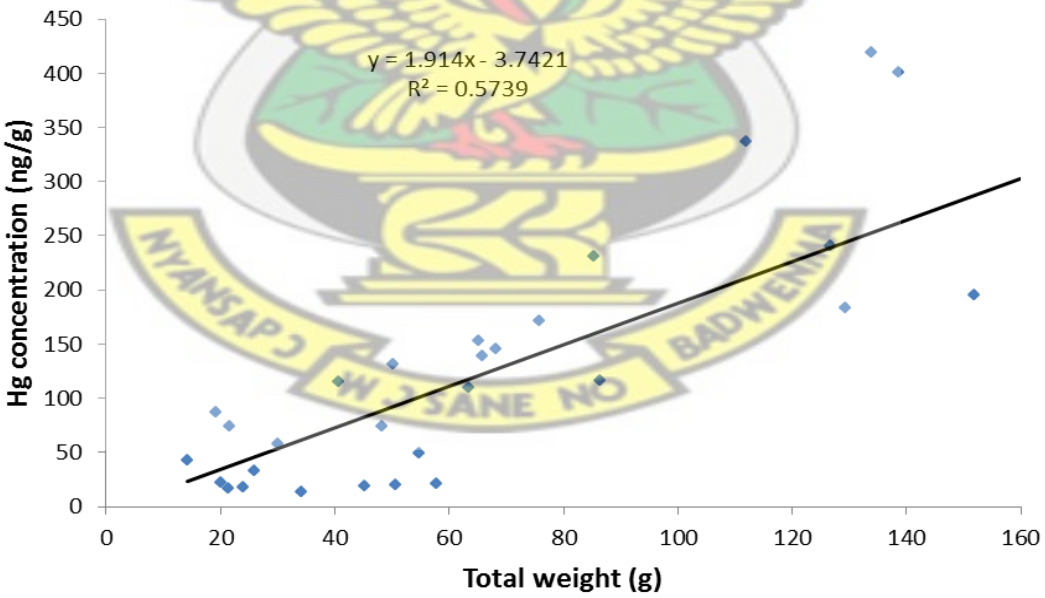

Fig. 4.12 Relationship between Hg concentration on wet weight basis and fresh weight for *Hemichromis fasciatus*.

Table 4.9 Results for *Clarias gariepinus*

Sample code	Total length (cm)	Total weight (g)	T-Hg concentration (µg/g)
MA1	27	172.11	0.102
MA2	19.4	49.71	0.070
MA3	18.3	61.51	0.069
MA4	18.7	47.26	0.098
MA5	19.4	62.45	0.240
MA6	26.3	113.83	0.083
MA7	27.8	180.78	0.330
MA8	30	290.18	0.056
MA9	31	280	0.067
MA10	25.5	90.5	0.133
MA11	21.4	101	0.075
MA12	19.6	85	0.058
MA13	26.5	105.81	0.083
MA14	31.5	286.4	0.144
MA15	30.6	252.2	0.105

MA=*Clarias gariepinus*

Table 4.10 Results for *Tilapia zilli*

Sample Code	Total length (cm)	Total weight (g)	T-Hg concentration (µg/g)
TA1	19.3	157.84	0.022
TA2	20.5	163.36	0.385
TA3	20	179.96	0.301
TA4	19.5	150.47	0.073
TA5	18.5	130.69	0.040
TA6	18.5	145.51	0.129
TA7	16.3	95.85	0.117
TA8	20.1	151.22	0.160
TA9	18.4	122.58	0.030
TA10	19.4	142.43	0.293
TA11	18	109.84	0.170
TA12	16.3	63.42	0.059
TA13	16.2	42.93	0.138
TA14	14.3	32.59	0.347
TA15	15.1	42.04	0.081
TA16	16.2	57.02	0.044
TA17	15.3	53.94	0.041
TA18	14.9	33.16	0.142
TA19	13.7	24.25	0.164
TA20	24.8	151.88	0.130

TA21	23.1	114.86	0.211
TA22	15	31.45	0.088
TA23	15.5	38.15	0.199
TA24	14.3	34.73	0.164
TA25	13.7	29.58	0.201
TA26	15.2	44.94	0.288
TA27	12.3	22.22	0.280
TA28	13.2	24	0.137
TA29	12.4	25.31	0.115
TA30	13.6	21.81	0.103

TA=*Tilapia zilli*

Table 4.11 Results for *Tilapia mariae*

Sample Code	Total length (cm)	Total weight (g)	T-Hg concentration (µg/g)
TB1	13	22.83	0.021
TB2	18.7	125.68	0.165
TB3	17.3	105.92	0.190
TB4	15.4	74.49	0.085
TB5	17.6	130.02	0.305
TB6	17.2	123.24	0.116
TB7	16.4	96.48	0.137
TB8	17.5	131.93	0.036

TB9	19.8	162.43	0.075
TB10	20.2	160.72	0.317
TB11	20.5	192.72	0.115
TB12	19	170.29	0.067
TB13	21.3	191.27	0.093
TB14	20.5	177.05	0.330
TB15	20.2	162.34	0.373
TB16	20.5	183.5	0.236
TB17	15.5	81.68	0.148
TB18	13.3	42.62	0.108
TB19	13.2	42.7	0.029
TB20	12.8	43.86	0.310
TB21	11.5	25.23	0.320
TB22	10.6	25.91	0.292
TB23	11	28.17	0.256
TB24	11	30.73	0.072
TB25	10.8	24.81	0.145
TB26	11.1	21.53	0.094
TB27	10	23.58	0.148
TB28	12.1	37.16	0.089
TB29	10.5	24.45	0.364
TB30	10.1	19.17	0.378

TB=*Tilapia mariae*

Table 4.12: Results for *Chrysicthys nigrodigitatus*

Sample code	Total length (cm)	Total weight (g)	T-Hg concentration (µg/g)
TD1	14.2	51.42	0.073
TD2	13.7	49.89	0.198
TD3	13.3	50.13	0.168
TD4	13.1	42.23	0.097
TD5	12.6	36.88	0.001
TD6	13.8	56.27	0.001
TD7	15	64.61	0.047
TD8	13.7	50.63	0.075
TD9	13.5	45.74	0.008
TD10	11.2	34.41	0.022
TD11	14.6	55.98	0.048
TD12	14.8	66.36	0.032
TD13	17.2	105.28	0.029
TD14	19	133.53	0.053
TD15	17.3	112.84	0.033
TD16	18.4	124.73	0.054
TD17	16.7	90.06	0.025
TD18	16	76.52	0.062
TD19	15.3	60.41	0.228
TD20	17.5	113.7	0.341

TD21	18.8	143.45	0.086
TD22	17.8	96.96	0.315
TD23	19	138.57	0.051
TD24	17	101.93	0.104
TD25	18.6	129.55	0.113
TD26	18.4	121.14	0.004
TD27	18.5	135.23	0.291
TD28	19	151.7	0.116
TD29	17.4	97.21	0.060
TD30	15.6	72.39	0.129

TD=*Chrysicthys nigrodigitatus*

Table: 4.13 Results for *Hemichromis fasciatus*

Sample Code	Total length (cm)	Total weight (g)	T-Hg concentration (µg/g)
TC1	18.9	14.26	0.043
TC2	18.5	21.54	0.074
TC3	18.8	162.07	0.118
TC4	24.4	138.54	0.401
TC5	19.5	126.73	0.241
TC6	13.90	57.85	0.021
TC7	18.30	24.06	0.018
TC8	20.80	65.20	0.154

TC9	15.40	50.20	0.131
TC10	18.09	40.75	0.115
TC11	12.70	48.28	0.074
TC12	19.00	129.32	0.183
TC13	21.40	151.76	0.195
TC14	10.30	21.37	0.016
TC15	14.20	54.72	0.050
TC16	12.00	30.10	0.057
TC17	14.00	50.55	0.020
TC18	12.10	45.29	0.019
TC19	11.60	25.92	0.033
TC20	12.00	34.09	0.014
TC21	17.20	63.42	0.110
TC22	16.40	65.80	0.139
TC23	9.80	19.11	0.087
TC24	18.00	68.20	0.145
TC25	20.20	111.90	0.336
TC26	19.52	85.4	0.231
TC27	10.60	20.00	0.023
TC28	15.00	75.80	0.172
TC29	14.4	86.40	0.116
TC30	25.50	133.89	0.419

TC=*Hemichromis fasciatus*

Table 4.14 Results for *Clarias batrachus*

Sample Code	Total length /cm	Total weight /g	T-Hg concentration µg/g
MB1	16.00	45.81	0.189
MB2	18.90	72.69	0.367
MB3	21.30	131.01	0.067
MB4	16.80	75.44	0.172
MB5	28.80	255.35	0.016
MB6	19.60	91.55	0.261
MB7	17.30	80.22	0.065
MB8	20.10	97.49	0.217
MB9	30.00	358.41	0.030
MB10	17.8	90.58	0.334
MB11	16.80	58.93	0.330
MB12	21.30	138.92	0.027
MB13	30.5	150.6	0.027
MB14	32	401.4	0.038
MB15	14.5	48	0.048
MB16	25.6	105.4	0.073
MB17	32	340	0.010
MB18	28.8	301	0.024
MB19	19.6	68.8	0.132
MB20	30.4	302.75	0.069

MB21	31	350.6	0.072
MB22	18	55.5	0.154
MB23	24.4	78.8	0.297
MB24	24.6	90.6	0.023
MB25	29.8	85.4	0.032
MB26	32	150.68	0.058
MB27	16	60.5	0.175
MB28	15.8	45	0.045
MB29	32.8	256.02	0.038
MB30	28	221.24	0.027

MB=*Clarias batrachus*

Table 4.15 Mercury concentration in Water

Sampling site	Months					
	October	November	December	January	February	March
Weija	0.033 0.019 0.022 0.023 0.016	0.012 0.010 0.011 0.011 0.011	0.012 0.019 0.014 0.011 0.011	0.026 0.033 0.017 0.016 0.014	0.020 0.016 0.017 0.032 0.032	0.008 0.012 0.008 0.012 0.009
Average Hg Concentration (ng/L)	0.023	0.011	0.011	0.021	0.023	0.010

Table 4.16 Results for Hg Concentration in sediment

Sampling site	Months					
	October	November	December	January	February	March
Weija	0.041 0.043 0.054 0.049 0.036	0.053 0.067 0.035 0.045 0.054	0.031 0.090 0.021 0.011 0.028	0.058 0.045 0.031 0.050 0.081	0.079 0.076 0.061 0.015 0.027	0.072 0.027 08.93 0.084 0.038

	0.057	0.069	0.035	0.061	0.084	0.034
	0.040	0.067	0.048	0.051	0.024	0.070
	0.088	0.048	0.022	0.057	0.038	0.067
	0.080	0.064	0.078	0.039	0.042	0.041
	0.094	0.047	0.096	0.032	0.035	0.070
	0.084	0.045	0.078	0.070	0.028	0.055
	0.048	0.073	0.047	0.009	0.079	0.080
	0.064	0.059	0.066	0.068	0.077	0.024
	0.131	0.068	0.047	0.072	0.076	0.077
Average Hg Concentration (µg/g)	0.065	0.057	0.050	0.052	0.053	0.054