STUDIES ON LEVELS OF MERCURY, CADMIUM AND ZINC IN FISH AND SEDIMENTS FROM RIVER OFFIN IN GHANA

by

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DECLARATION

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

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DEDICATION

I dedicate this thesis to my dear mother Miss Elizabeth Oti – Akenten. I am lucky to have you as my mother.

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To the Omnipotent God I humbly give thanks for his infinite mercy, grace and blessings He has showered on me from beginning till today. To God be the Glory!

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ABSTRACT

One hundred and forty eight fish samples covering twelve different species, twenty sediment samples and five soil samples were collected at five locations (Dominase, Nkotumso, Dunkwa-on-Offin, Buabenso, Awisam) along Offin River and analysed for total mercury, cadmium and zinc. Mercury was determined using the Cold Vapour Atomic Absorption Spectrometry employing an Automatic Mercury Analyzer (HG 5000 model). An Atomic Absorption Spectrometer (Unicam 929 model) was used for the determination of total cadmium and zinc. The fish species included *Oreochromis niloticus, Chrysichthys nigrodigitatus, Labeo coubie, Brycinus sp., Hepsetus odoe, Mormyrus sp., Papyrocranus afer, Heterobranchus sp., Tilapia zilli, Synodontis sp., Sarotherodon melanotheron,* and *Schilbe mystus*.

Total mercury concentration in fish ranged from 1.02 to 795.94 ng/g wet weight, from 68.73 to 1066.65 ng/g in sediments and from 44.61 to 137.80 ng/g in soil. Total cadmium concentration in fish ranged from below detection to 0.10 mg/kg wet weight and was below detection in all the sediments and soil sampled whereas total zinc concentration in fish ranged from below detection to 18.16 mg/kg wet weight, from 13.57 to 47.81 mg/kg in sediments and from 8.45 to 81.49 mg/kg in soil. *Synodontis sp.* recorded the highest concentration (mg/kg, wet weight) of Hg (0.79), Cd (0.10) and Zn (18.16) in all the fish samples analysed. About 37.5% and 18.8% fish species showed positive correlation between muscle tissue mercury concentration and fresh weight, and muscle tissue mercury concentration and total length of fish respectively. Generally, there was an

irregular distribution of these metals in fish as the river flows downstream towards river Pra.

Analytical results obtained showed that, cadmium and zinc concentrations in fish tissue were generally below the WHO maximum permissible limit; however, 3.4% of the fish samples analysed had tissue mercury concentrations above the WHO limit of 0.5 mg Hg/Kg. Though the results of the research indicates that consumption of fish from the Offin River is unlikely to constitute a health threat to consumers, the concentrations of Hg and Zn obtained were of elevated levels compared to those obtained in the year 2000 in River Offin. Continuous mining along the banks of Offin River coupled with long term bioaccumulation of heavy metals through food chain is of major concern. The study also revealed that *Synodontis sp.* (locally called Nkontro) has a good Hg, Cd and Zn accumulation potential and may serve as a biomarker for toxicological studies for these metals in the Offin River.

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ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometry
AOAC	Association of Official Analytical Chemists
CRM	Certified Reference Material
CVASS	Cold Vapour Atomic Absorption Spectrophotometry
DEFRA	Department for Environment Food and Rural Affairs
EA	Environment Agency.
EDXRF	Energy Dispersive X-ray Fluorescence
EPA	Environmental Protection Agency
F-AAS	Flame Atomic Absorption Spectrometry
GF-AAS	Graphite Furnace Atomic Absorption Spectrometry
IAEA	International Atomic Energy Agency
IARC	International Agency for Research on Cancer
ICP-AES	Inductively-Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
IOM	Institute of Medicine
IPCS	International Program on Chemical Safety
JECFA	Joint Expert Committee on Food Additives
NAA	Neutron Activation Analysis
ND	Not Detectable
XRF	X-Ray Florescence

CHAPTER ONE

1.0 INTRODUCTION

Small-scale mining brings several benefits to developing countries, manifested mainly as employment and revenue. Small-scale miners in Ghana are of two groups, those registered and licensed and those operating illegally (*galamseys*). Approximately two-thirds of Ghana's small-scale miners are engaged in the extraction of gold and are the fifth largest producer of gold. According to the Minerals Commission (2000), annual small-scale gold production has increased nearly tenfold over the past decade, rising from 17,234 oz in 1990 to 107,093 oz in 1997. Precious Minerals Marketing Corporation (PMMC, 2001) estimated that over US$117 million worth of gold has been obtained from small-scale mining operations since complete legalization of the industry in 1989. No precise small-scale mining employment figures can be found for Ghana, although it is estimated some 200,000 miners are involved directly in the extraction of gold and diamonds (Appiah, 1998), the great majority of which are *galamsey*. It is worth knowing that mining especially *galamsey* has eminent pollution problems associated with it which if not properly monitored can override the benefits that accrued from mining.

The Upper Denkyira District which lies within latitudes 5°.30' and 6°.02' north of the equator and longitudes 1° W and 2° W of the Greenwich Meridian has throughout the past years contributed its quota to mining in Ghana. The District covers a total land area of 1700 square kilometers, which is about 17% of total land area of the Central Region. The area falls under a forest-dissected plateau, rising to about 250 m above sea level.

There are pockets of steep sided hills alternating with flat-bottomed valleys. Dunkwa, the District Capital, has a series of high lands surrounding it.

The major river that drains the area is Offin. Large deposits of placer gold also referred to as 'alluvial gold' occur along the terrace, floodplain, channel and river bed of the Offin river, where large Birimian and Tarkwaian gold deposits have experienced several episodes of erosion and subsequent deposition (Hilson, 2001). The deposit material in the Offin placer is made up of silty clay overburden overlying sandy river gravels on soft decomposed green bedrock. The Offin gold placer which occurs freely is generally very fine-grained and of relatively high fineness (Debrah and Mireku, 1991).

Dunkwa Continental Goldfields, the only commercial large-scale dredge mining company in Ghana uses mercury in gold extraction and holds a mining lease to mine alluvial gold deposits that spans the banks of the Offin River in the district (Cheetham, 2000; Debrah and Mireku, 1991) (Picture 1-3, Appendix III). However the company is currently not operational and this has led to increased illegal mining activities along the banks of the Offin River. Currently there are no licensed small-scale mining concessions within the district. Interviews with some of the *galamsey* miners revealed that an initial huge capital is needed to acquire a plot of land along the Offin River from land owners. After prospecting, one has to consult local authorities, hire an excavator to remove the top soil to expose the gold bearing sandy river gravel, get water pump to get rid of the water that enters the open pit, hire workers to wash and process the gold and buy the gold at reduced price.

The artisanal or small scale mining (*galamsey*) scattered along the banks of Offin River uses amalgamation technique to recover gold from alluvial deposits. This technique involves bringing concentrated alluvial ore into contact with mercury, heating of the gold-mercury amalgam to vaporize and expel mercury in order to recover alluvial gold (Picture 4-7, Appendix III). This technique might cause mercury contamination in the aquatic environment since amalgamation is carried out along the river banks. Mercury (Hg) is one of the most important pollutants both because of its effect on aquatic organisms and it is potentially toxic to humans. Its major pathway to man is commonly accepted to be by ingestion of aquatic organisms, particularly fish (Fatoki and Awofolu, 2003). Large piscivorous fish from the Napo River, Ecuador, were found to be highly contaminated with mercury (up to 3 µg/g wet weight), while smaller herbivorous fish were generally below the WHO 0.5 µg/g health limit (Webb *et al*., 2004). Of the 65 fishes caught in the Barents Sea in 2006, 15 individuals representing 23.1% with weight exceeding 3 kg had mercury concentrations in their muscle tissue (skinless and boneless fillet) exceeding the WHO and European Union upper limit of 0.5 mg/kg (Kare *et al.*, 2006). The total mercury concentrations detected in the edible muscle tissue of tuna fish (*Auxis thazard thazard*) from the Gulf of Guinea, Ghana ranged from 0.044 to 0.201 µg/g (mean=0.108 µg/g) wet weight (Voegborlo *et al.,* 2007). Agorku (2006) reported that of all the 165 fishes sampled from Lake Bosomtwi, Kpong and Akosombo reservoirs in Ghana, only one sample of *Pelmatochromis guntheri* recorded a higher mercury concentration (1014.73 ppb) above the WHO acceptable limit for total mercury in fish. Surface sediment from the Upper Columbia River in Washington State were found to contain up to 2.7 µg/g (ppm) mercury (Johnson *et al*., 1990).

Disruption of the nervous system, damage to brain functions, kidney and DNA, negative reproductive effects such as birth defects and miscarriages are some of the health effects of mercury. Other health effects may include tremor, irritability, nervousness, memory loss, excessive shyness, insomnia, hallucinations and neuromuscular changes such as muscle atrophy and muscle weakness, headaches and decreases in cognitive function (ATSDR, 1999b; WHO, 2003).

Zinc though not toxic to life, is used to recover gold from cyanide solution at Ashanti Goldfields Limited in Obuasi. There is therefore the likelihood that zinc may leak from the Obuasi mine through their effluent into a tributary Jimi into the Offin River (Cheetham, 2000). Zinc in the aquatic environment is of particular importance because the gills of fish are physically damaged by high concentrations of zinc and can accumulate in freshwater animals at 51–1,130 times the concentration present in the water (EPA, 1987). A national contaminant biomonitoring programme to measure the concentration of some heavy metals in United State freshwater fish showed elevated levels of 168.1 µgZn/g fresh weight in 1978–1979, 109.2 µgZn/g fresh weight in 1980–1981 and 118.4 µgZn/g fresh weight in 1984 in the common carp, *Cyprinus carpio* (Schmitt and Brumbaugh, 1990). Sediment collected from streams in the Black Hills, South Dakota, an area impacted by gold mining operations, contained zinc at levels ranging from 3.8 to 250 µg/g dry weight (May *et al*., 2001).

Zinc is a trace element that is essential for human health. A small amount of zinc in diet they can cause a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores and even birth defects (Heyneman, 1996; Nishi, 1996). Zinc deficiency

may increase the toxic effects of cadmium, arsenic and lead; thus an adequate amount of zinc can be considered protective against the toxicity of these elements. Although humans can handle proportionally large concentrations of zinc, too much zinc can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of zinc can affect the absorption and excretion of copper and iron in humans (ATSDR, 2005).

Cadmium occurs together with zinc in nature. Due to excavation works along the river banks, there is the likelihood that the levels of ubiquitous metal zinc and cadmium in the Offin River may be elevated. Cadmium has no essential biological function and is extremely toxic to humans. A recent study on heavy metal pollution of fish in Qua-Iboe river estuary revealed an elevated cadmium concentration of 0.38 mg/kg above WHO safety limit of 0.2mg/kg dry weight (Oze *et al*., 2006). Surficial sediments collected from 18 locations in three major tributaries to Newark Bay, New Jersey, had a mean cadmium concentration of 10±6 mg/kg (ppm) dry weight (Bonnevie *et al*. 1994).

Cadmium is known to accumulate in the body particularly in the kidneys causing renal failure, bone fragility and pains (itai-itai disease) (DEFRA and EA, 2002a) and cancer in humans (Williams *et al*., 1999). The study of cadmium is also important because of its synergistic reaction with zinc in the aquatic systems (Merian, 1991).

Mining operations release enormous metals into the environment, and their accumulation in the aquatic environment has direct consequences to man and the ecosystem. The

consumption of fish containing elevated levels of metals is a concern because accumulation of heavy metals can give rise to health problems. In Ghana, however, little work has been done to determine zinc, cadmium and mercury in fish and sediments from the Offin River basin. Due to lack of data, this project sought to determine levels of the Group IIB triad, zinc, cadmium and mercury released into the aquatic environment due to continuous mining in River Offin.

1.1 Research objectives

The objectives of this research are presented as follows:

- To determine the total metal concentrations of zinc, cadmium and mercury in fish and sediments from River Offin.
- To determine any correlation between metal levels in fish and sediments from the aquatic ecosystem.
- To evaluate the correlation between total mercury concentrations and factors such as size and length of fish.

1.2 Justification of objectives

Artisanal gold mining is widespread along the banks of River Offin and it has metamorphosed from the traditional hand dugging of mining pits to the use of Excavators that dig bigger and deeper wells in a matter of minutes. The pits are so close to the river that they constantly pump the river water that fills the pit back into the river thereby polluting the Offin River (Picture 8-11, Appendix III).

Fish is an extremely important component of the human diet in many parts of the world and it provides nutrients such as protein, omega-3 (n-3) fatty acids (that reduce cholesterol levels and the incidence of heart disease, stroke, and preterm delivery) and others that are not easily replaced (Anderson and Wiener, 1995; Burger *et al*., 2005; Daviglus *et al*., 2002; Patterson, 2002). Humans risk ingesting dangerous levels of mercury, cadmium and zinc when they eat contaminated fish. Since the metal poisons are odorless, invisible and accumulate in the meat of the fish, it is not easy to detect and can't be avoided by trimming off the skin or other parts (Williams *et al*., 1999).

Fishes have been used for many years to determine the pollution status of water, and are thus regarded as excellent biological markers of metals in aquatic ecosystems (Rashed, 2001). However analysis of sediment can be used in combination with fish to study heavy metals in aquatic environment (Clifton and Hamilton, 1979). It has been shown that sediments are an important sink for both mercury and methyl mercury in the aquatic environment (Mason and Lawrence, 1999) and mercury deposited to aquatic ecosystems can be converted to methyl mercury (MeHg) through the action of bacteria in sediments and other anaerobic habitats (Gilmour and Henry, 1991). Mercury absorption in fish are functions of feeding habits and food chain structure (Wiener and Spry, 1996)

There is an extensive body of literature documenting a positive relationship between Hg concentrations and fish size (Bidone *et al*., 1997; Lacerda *et al*., 2000; Lange *et al*., 1994; Ward and Neumann, 1999; Wiener and Spry, 1996). Analysis carried out on 65 individuals of Greenland halibut weighing from 0.81 kg to 7.1 kg, revealed lowest mercury concentration in muscle tissue of 0.019 mg/kg wet weight, in a fish that weighed 0.81 kg whereas highest mercury concentration measured in muscle tissue was 1.1 mg/kg

wet weight, for a fish that weighed 4.2 kg (Kare *et al*., 2006). Mercury in fish measured in Deep Creek pickerel in 1992 showed that the fish examined was 48 cm long and contained 0.98 mg Hg/kg wet weight whereas those with length 20 cm long had average mercury concentration of 0.3 mg/kg (Paul *et al*., 2004).

Cheetham (2000) determined the levels of mercury and zinc in water, sediment and fish from the Offin River and recommended that though the levels were less than the recommended EPA and WHO values, a longer and more regular period of study must be undertaken. This research seeks to determine the current levels of cadmium in addition to mercury and zinc in fish and sediments in River Offin.

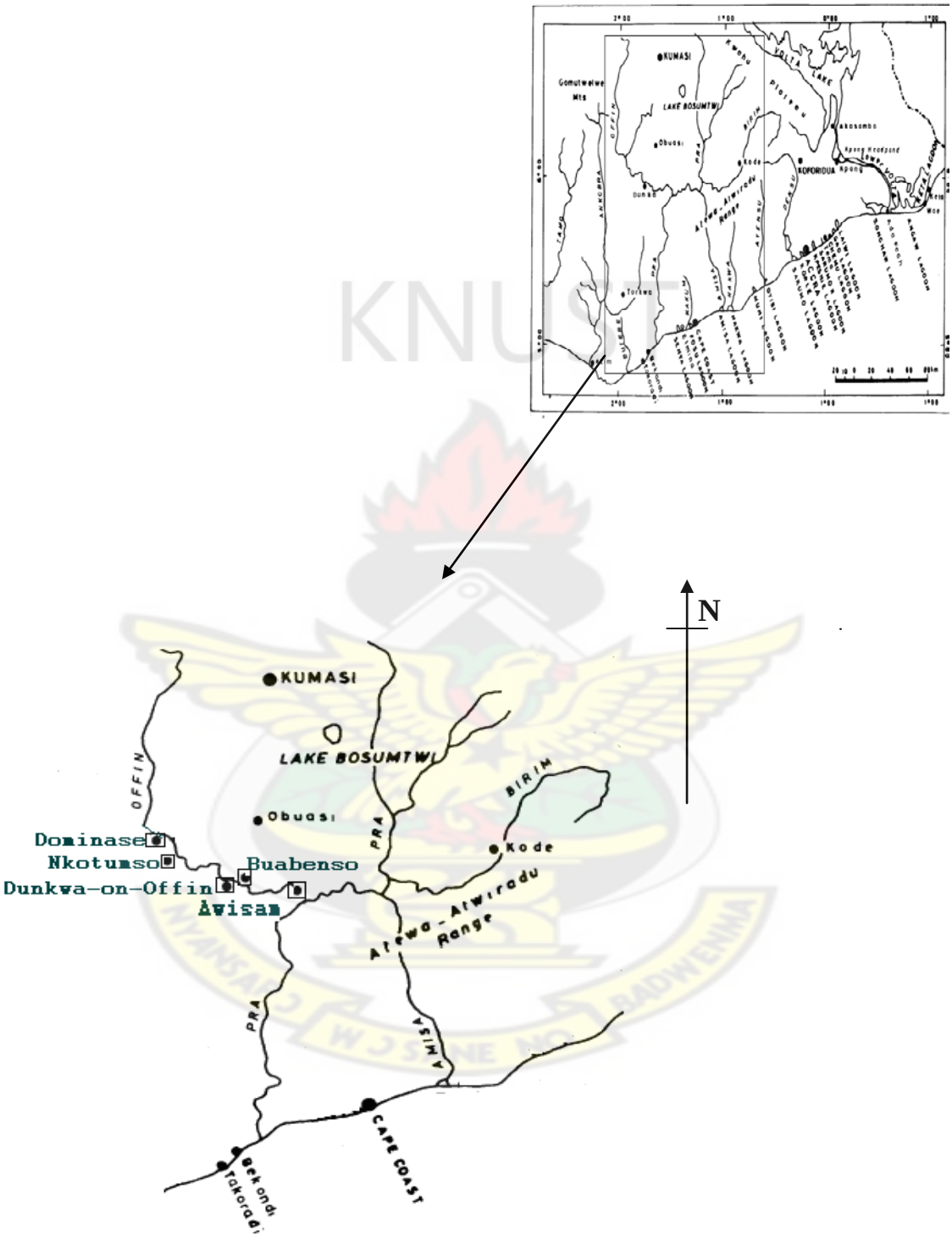

Fig. 1.0 Map of South-Western Ghana showing the various sampling sites.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 MERCURY

2.1.1 Introduction

Mercury is the only common metal that is a liquid at ambient temperatures and pressures (Boening, 2000). Mercury is sometimes called quicksilver. It rarely occurs free in nature and is found mainly in cinnabar ore (HgS) in Spain and Italy. It is a heavy, silvery-white liquid metal. It is a rather poor conductor of heat as compared to other metals but is a fair conductor of electricity. It alloys easily with many metals, such as gold, silver, and tin to form amalgams. Mercury can exist in 3 oxidation states (Elemental mercury (Hg^0), Mercurous mercury, (Hg^+) or Mercuric mercury, (Hg^{2+})). Mercurous and mercuric mercury can combine with other elements to form either organic or inorganic mercury compounds (Hu, 1998; IPCS, 1990). The distinction between elemental, inorganic and organic mercury is much more important than oxidation states in determining toxicity, as organic mercury compounds are the most toxic (William *et al*., 1999).

Metallic mercury is a silver-white metal that is liquid at room temperature. Inorganic mercury compounds contain mercury as well as sulphur, oxygen or chlorine. They are mostly powders or crystals at room temperature. Organic mercury compounds consist of mercury and carbon, the most common one being methylmercury, a lethal pollutant found in rivers and lakes. The main source of mercury pollution is industrial wastes settling to the river and lake bottoms (Hu, 1998; Timbrell, 1995). Inorganic mercury can be methylated by microorganisms indigenous to soils, sediments, fresh water, and salt water,

to form organic mercury (methylmercury). Invariably, microbial processes can also lead to demethylation, where methyl mercury is reduced back to elemental mercury. This elemental mercury is believed to volatilize into the atmosphere (EPA, 1997).

Although most of the mercury in aquatic systems is in the inorganic form, about 95% of mercury accumulated by fish is in the form of methyl mercury (EPA, 1997). The high affinity of methyl mercury for sulfhydryl groups of proteins causes rapid absorption in living organisms. The rate of elimination of methyl mercury by fish is very slow relative to the rate of its uptake, allowing mercury to accumulate in their body (EPA, 1997; Laarman *et al*., 1975).

Mercury metal has many uses. Because of its high density it is used in barometers and manometers. It is extensively used in thermometers, thanks to its high rate of thermal expansion that is fairly constant over a wide temperature range. Its ease in amalgamating with gold is used in the recovery of gold from its ores. Industry uses mercury metal as a liquid electrode in the manufacture of chlorine and sodium hydroxide by electrolysis of brine. Mercury is still used in some electrical gear, such as switches and rectifiers, which need to be reliable, and for industrial catalysis. Much less mercury is now used in consumer batteries and fluorescent lighting, but its use has not been entirely eliminated. Calomel (mercurous chloride, Hg_2Cl_2) is used as a standard in electrochemical measurements and in medicine as a purgative. Mercuric chloride (corrosive sublimate, $HgCl_2$) is used as an insecticide, in rat poison, and as a disinfectant. Mercuric oxide is used in skin ointments. Mercuric sulphate is used as a catalyst in organic chemistry. Vermilion, a red pigment, is mercuric sulphide; another crystalline form of the sulphide

(also used as a pigment) is black. Mercury fulminate, Hg $(CNO)_2$, is used as a detonator (ATSDR, 1999b; EPA, 1997; IPCS, 1990).

Mercury has no known essential biological function and is highly toxic to humans (Williams *et al*., 1999). Depending on the chemical form and the dose received, mercury can be toxic to both humans and wildlife. In people, toxic doses of mercury can cause developmental effects in the fetus, as well as effects on the kidney and the nervous system in children and adults (EPA, 1997). The central nervous system is one of the most sensitive targets following an exposure to mercury, which may cause cognitive, personality, sensory or motor disturbances (WHO, 2003). The effects may include tremor, irritability, nervousness, memory loss, hallucinations and neuromuscular changes such as muscle atrophy and muscle weakness, headaches and decreases in cognitive function (IPCS, 1990; WHO, 2003). Exposure to high levels of methyl mercury results in central nervous system effects, including blindness, deafness, impaired level of consciousness, erethism (increased excitability), irritability, excessive shyness, insomnia, severe salivation, gingivitis, tremor and death (WHO, 1991). Long term exposure to mercury also affects the kidney and causes birth defects in humans (ATSDR, 1999b; IPCS, 1990; WHO 1991).

Mercury poisoning has been reported from ingestion of mercuric chloride (an inorganic compound which is used as a disinfectant), as well as from contaminated illegal drugs, for example amphetamines. Poisoning has also occurred from exposure to fungicides, some of which contain organic mercury compounds, and from industrial accidents in which mercury vapour was inhaled. Environmental discharges of mercury have also

occurred, by discharge of industrial waste, which contained contaminated fish, which were eventually eaten by humans (Matthew and Lawson, 1979). In recent years, there has been some concern that mercury contained in dental amalgams adversely affects human health, produces illnesses including multiple sclerosis and Alzheimer's disease, but this assertion has not been proven (Baldwin and Marshall, 1999; Hu, 1998).

2.1.2 Sources and Route of Human Exposure

Mercury occurs naturally and is widely distributed in the environment owing to natural and anthropogenic processes. The major natural sources of mercury in the environment are degassing from the earth's crust, emissions from volcanoes and evaporation from water bodies (IPCS, 1990). Mercury ore is found in all classes of rocks, including limestone, calcareous shales, sandstone, serpentine, chert, andesite, basalt, and rhyolite (ATSDR, 1999b). The normal concentration of mercury in igneous and sedimentary rocks and minerals appears to be 10–50 ng/g (ppb) (Andersson, 1979); however, the mineral cinnabar (mercuric sulfide) contains 86.2% mercury (Stokinger, 1981). Mining activities also result in losses of mercury through the dumping of mine tailings and direct discharges to the atmosphere. Other important man-made sources are the combustion of fossil fuels, the smelting of metal sulfide ores, the production of cement, and refuse incineration. Mercury also enters the environment from fertilizers, fungicides and from solid waste i.e. thermometers or electrical switches (DEFRA and EA, 2002b; IPCS, 1990). A recent study (Munthe *et al*., 2001) suggests that total mercury levels in the atmosphere have tripled as a result of anthropogenic activities.

Potential sources of general population exposure to mercury include inhalation of mercury vapours in ambient air, ingestion of drinking water and foodstuffs contaminated with mercury, and exposure to mercury through dental and medical treatments.

The general public is predominantly exposed to elemental mercury via inhalation of its vapour from amalgam using in dental fillings or from accidental spillages following breakages of thermometers, barometers or electrical switches (ATSDR, 1999b; IPCS, 1990). Naturally occurring elemental mercury in both ground and surface water is less than 0.5 μg L^{-1}. Mercury in drinking water is not considered a major source of exposure except when significant pollution occurs (WHO, 2005). Elevated concentrations of mercury in soil may lead to an increase in the mercury content in plants such as carrots, lettuce, mushrooms and apples, which, if grown in contaminated soil, may accumulate mercury. However, few data are available regarding the relationship between mercury concentration in the soil and the concentration in fruit and vegetables (DEFRA and EA, 2002b).

The major source of human exposure to mercury is through the diet, more specifically from the consumption of fish and fish products. Most of the mercury consumed in fish or other seafood is the highly absorbable methylmercury form (IPCS, 1990; WHO, 1990; WHO, 1991). People undergo exposure to inorganic mercury by ingestion due to the use of mercury salts in herbal remedies. Dermal exposure may also occur, as mercury salts were commonly used for their antiseptic, fungicidal and bactericidal properties (WHO, 2003). In addition, the use of skin-lighteners can result in significant exposure due to dermal absorption (IPCS, 1990).

Occupational exposure to mercury may be a major source of exposure. Individuals working in the production of electrical equipment, thermometers or barometers, those working in chemical processing plants or individuals living or working in buildings where mercury-containing latex paints have been used may all be exposed to elemental mercury vapour via inhalation of inorganic mercury (ATSDR, 1999b). Miners may also be exposed to elemental mercury vapour via inhalation as they burn the mercury-gold amalgam to recover gold. Dentists and dental assistants involved with dental amalgam may also be exposed to elemental mercury due to inhalation and to a lesser extent by skin contact. Mercury has been detected in blood, urine, human milk, and hair in individuals in the general population (ATSDR, 1999b; WHO, 2003).

2.1.3 Levels of Mercury in the Environment

2.1.3.1 Air

The average mercury level in the atmosphere currently is about 3 to 6 times higher than the estimated level in the preindustrial atmosphere (Mason *et al*., 1995; Munthe *et al*., 2001). Ambient air concentrations of mercury have been reported to average approximately 10–20 ng/m^3, with higher concentrations in industrialized areas (EPA, 1980a). Lindberg *et al*. (1987) and Pacyna (1987) estimated the total man-made global release of mercury to the atmosphere to be 2000-3000 tonnes/year. However, recent estimates of anthropogenic releases of mercury to the atmosphere range from 2,000–4,500 metric tons/year, mostly from the mining and smelting of mercury and other metal sulfide ores. The world-wide mining of mercury is estimated to yield about 10,000

tonnes/year, but this figure varies considerably from year to year, depending on the commercial value of the metal (IPCS, 1990; WHO 1990).

Other anthropogenic sources include industrial processes involving the use of mercury, such as chloralkali manufacturing facilities, combustion of fossil fuels, primarily coal, production of cement, and medical and municipal waste incineration and commercial/ industrial boilers (EPA, 1996; WHO, 1990; WHO, 1991). Anthropogenic emissions, mainly from combustion of fossil fuels, account for about 25% of mercury emissions to the atmosphere (WHO, 1990). The incineration of medical waste has been found to release up to 12.3 mg/m^3 of mercury into the atmosphere (Glasser *et al*., 1991).

2.1.3.2 Water

The earth's crust is an important source of mercury for bodies of natural water. Some of this mercury is undoubtedly of natural origin, but some may have been deposited from the atmosphere and may, ultimately, have been generated by human activities (Lindqvist *et al*., 1984). Natural weathering of mercury-bearing minerals in igneous rocks is estimated to release about 800 metric tons of mercury per year directly to surface waters of the earth (Gavis and Ferguson, 1972). Freshwaters without known sources of mercury contamination according to Gilmour and Henry (1991) generally contain less than 5 ng/L (ppt) of total mercury in aerobic surface waters and the baseline concentration of mercury in unpolluted marine waters has been estimated by Fowler (1990) to be less than 2 ng/L (2 ppt). Representative values for dissolved total mercury are: open ocean, 0.5-3 ng/litre; coastal sea water, 2-15 ng/litre; freshwater rivers and lakes, 1-3 ng/litre (Lindqvist *et al*., 1984).

Atmospheric deposition of elemental mercury from both natural and anthropogenic sources has been identified as an indirect source of mercury to surface waters (WHO, 1991). Antarctic surface snow contained a mean mercury concentration of less than 1 pg/g (ppt) (Dick *et al*., 1990). Concentrations of mercury in rainwater and fresh snow in United States are generally below 200 ng/L (ppt) (EPA, 1984).

Mercury associated with soils can be directly washed into surface waters during rain events. Surface runoff is an important mechanism for transporting mercury from soil into surface waters, particularly for soils with high humic content (Meili, 1991).

2.1.3.3 Soil

In a review of the mercury content of virgin and cultivated surface soils from a number of countries, it was found that the average concentrations ranged from 20 to 625 ng/g (0.020 to 0.625 ppm) (Andersson, 1979). Atmospheric deposition of mercury from both natural and anthropogenic sources has been identified as an indirect source of mercury to soil and sediments (Sato and Sada, 1992; WHO, 1990; WHO, 1991). Wisconsin lakes contained higher mercury levels of 0.09-0.24 ppm at the top 15 cm of sediments relative to the lower levels recorded for the lower sediments. Rada *et al*. (1989) reported that since the lakes are not known to receive any direct deposition of mercury, it was postulated that the primary mercury source was atmospheric deposition. Surface sediment samples from the Upper Columbia River in Washington State were found to contain up to 2.7 µg/g (ppm) mercury (Johnson *et al*. 1990).

Mercury is released to cultivated soils through the direct application of inorganic and organic fertilizers (e.g., sewage sludge and compost), lime, and fungicides containing mercury (Andersson, 1979). Recently, Carpi *et al*. (1998) studied the contamination of sludge-amended soil with inorganic and methylmercury and the emission of this mercury contamination into the atmosphere. These authors reported the routine application of municipal sewage sludge to crop land significantly increased the concentration of both total mercury and methylmercury in surface soil from 80 to 6,1000 µg/kg (ppb) and 0.3–8.3 µg/kg (ppb), respectively.

2.1.4 Environmental Fate

The natural global bio-geochemical cycle of mercury, involves degassing of mineral mercury from the lithosphere and hydrosphere, long-range transport in the atmosphere, wet and dry deposition to land and surface water, sorption to soil and sediment particulates, revolatilization from land and surface water, and bioaccumulation in both terrestrial and aquatic food chains. This emission, deposition, and revolatilization make it difficult to trace the movement of mercury to its sources (WHO, 1990).

Over 95% of the mercury found in the atmosphere is gaseous mercury (Hg^0), the form involved in long-range (global) transport of the element. Its residence time in the atmosphere has been estimated to range from 6 days to 2 years (Andren and Nriagu, 1979; IPCS, 1990). This makes transport on a hemispherical scale possible and emissions in any continent can thus contribute to the deposition in other continents (IPCS, 1990; UNEP, 2002). In 1991, Glass *et al*. studied a 72-hour travel time trajectory for mercury

and showed that some mercury found in rain may originate from sources up to 2,500 km (1,550 miles) away. The remaining part of air emissions are in the form of gaseous divalent compounds (such as $HgCl_2$) or bound to particles present in the emission gas (Meili *et al*., 1991; UNEP, 2002). These species have a shorter atmospheric lifetime than elemental vapour and will deposit via wet or dry processes within roughly 100 to 1000 kilometers. However, significant conversion between mercury species may occur during atmospheric transport, which will affect the transport distance (Nater and Grigal, 1992; UNEP, 2002).

In soils and surface waters, mercury can exist in the mercuric (Hg^{2+}) and mercurous (Hg^{+}) states in a number of complex ions with varying water solubilities. Mercuric mercury, present as complexes and chelates with ligands, is probably the predominant form of mercury present in surface waters. Vaporization of mercury from soils may be controlled by temperature, with emissions from contaminated soils being greater in warmer weather when soil microbial reduction of Hg^{2+} to the more volatile elemental mercury is greatest (Lindberg et al., 1991). The bottom sediment of the oceans is thought to be the ultimate sink where mercury is deposited in the form of the highly insoluble mercuric sulfide (IPCS, 1990).

The process of methylation of inorganic mercury (Hg^{2+}) to methylmercury by microorganisms, which is highly bioavailable, is thus an important key to the fate of mercury in the environment (Beckvar *et al*., 1996; Berman and Bartha, 1986). Methylation is usually greatest at the sediment water interface, but also occurs in the

water column (Beckvar *et al*., 1996; Lindberg *et al*., 1991). Methylation is influenced by the availability of Hg [II], oxygen concentration, pH, redox potential, presence of sulfate and sulfide, type and concentrations of complexing inorganic and organic agents (Parks *et al*., 1989), salinity (Blum and Bartha, 1980), and organic carbon (Winfrey and Rudd, 1990).

Methylmercury in surface waters is rapidly accumulated by aquatic organisms. The concentrations in carnivorous fish such as large tuna, swordfish, shark, and mackerel at the top of both freshwater and marine food chains are biomagnified in the order of 10,000–100,000 times the concentrations found in their surrounding habitat (WHO, 1990; WHO, 1991). Humans absorb methyl mercury easily by consumption of contaminated fish and are especially vulnerable to its effects (IPCS, 1990).

2.1.5 Human Health Effects

The health effects of mercury depends on its chemical form (elemental, inorganic or organic), the route of exposure (inhalation, ingestion or skin contact), and level of exposure. Different forms of mercury have different effects in humans, because they do not all move through the body in the same way (ATSDR, 1999b).

2.1.5.1 Acute Effects

Acute (short-term) inhalation exposure to high levels of elemental mercury in humans results in central nervous system (CNS) effects, such as hallucinations, delirium, and suicidal tendencies. Gastrointestinal effects and respiratory effects, such as chest pains, dyspnea, cough, pulmonary function impairment, and interstitial pneumonitis have also

been noted from inhalation exposure to elemental mercury (IPCS, 1990). Such effects have been reported following exposure to 1.1 – 44 mg/m^3 elemental mercury (ATSDR, 1999b). The kidneys are also a major target organ following exposure to elemental mercury vapour due to the relatively high accumulation of mercury in the kidneys. Exposure to high concentrations of mercury has result in acute renal failure and degeneration of the proximal convoluted tubules (ATSDR 1999b; WHO, 2003).

Symptoms noted after acute oral exposure to inorganic mercury compounds include a metallic taste in the mouth, nausea, vomiting (may contain blood), swollen gums, excess salivation, diarrhoea (may contain blood), stomatitis (inflammation of the mouth) and severe abdominal pain. The acute lethal dose for most inorganic mercury compounds for an adult is 1 to 4 g or 14 to 57 mg/kg for a 70-kg person (ATSDR, 1999b; EPA, 1994c) Acute exposure to high levels of methyl mercury results in central nervous system effects, including blindness, deafness, impaired level of consciousness, and death. Ingesting large amounts of methylmercury also results in some of the mercury moving into the brain and affecting the nervous system. Inorganic mercury salts, such as mercuric chloride, do not enter the brain as readily as methylmercury or metallic mercury vapour. Damaged brain functions can cause degradation of learning abilities, personality changes, tremors, vision changes, deafness, muscle incoordination and memory loss (Hu, 1992; IPCS, 1990) .

It has been estimated that the minimum lethal dose of methyl mercury for a 70-kg person ranges from 20 to 60 mg/kg, but symptoms start when greater than 1.7 mg/kg has been ingested (WHO, 1990).

2.1.5.2 Chronic Effects:

The central nervous system is the major target organ for elemental mercury toxicity in humans. Effects noted include erethism (increased excitability), irritability, excessive shyness, insomnia, severe salivation, gingivitis, and a tremor. (WHO, 1991)

Chronic exposure to elemental mercury also affects the kidney in humans, with the development of proteinuria (ATSDR, 1999b; WHO, 1991). The primary effect from chronic exposure to inorganic mercury is kidney damage, primarily due to mercury-induced autoimmune glomerulonephritis (induction of an immune response to the body's kidney tissue) (WHO, 1991).

The primary effect from chronic exposure to methylmercury in humans is damage to the central nervous system. The earliest effects are symptoms such as paresthesia, blurred vision, and malaise. Effects at higher doses include deafness, speech difficulties, and constriction of the visual field (WHO, 1990). Acrodynia is a rare syndrome found in children exposed to mercury in any of its forms. It is characterized by severe leg cramps, irritability, paresthesia (a sensation of prickling on the skin), and painful pink fingers and peeling hands, feet and nose (ATSDR, 1999b).

2.1.5.3 Reproductive/Developmental Effects

Oral exposure to methylmercury has been observed to produce significant developmental effects. Infants born to women who ingested high concentrations of methyl mercury exhibited CNS effects, such as mental retardation, ataxia, deafness, constriction of the visual field, blindness, and cerebral palsy. Developmental delays and abnormal reflexes have been observed at low methylmercury concentrations (ATSDR, 1999b; WHO, 1990).

2.2 CADMIUM

2.2.1 Introduction

Cadmium, in its elemental form, occurs naturally in the earth's crust. Pure cadmium is a very soft, silvery-white metallic element. It is so soft that it can be cut with a knife and has no definite odour or taste. Cadmium is not usually found in the environment as a metal but as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulfur (cadmium sulfate, cadmium sulfide) (IPCS, 1992). Cadmium may change forms, but the cadmium metal itself does not disappear from the environment. Naturally-occurring isotopes are 106 (1.22%), 108 (0.88%), 110(12.39%), 111 (12.75%), 112 (24.07%), 113 (12.26%), 114 (28.86%), and 116 (7.50%) (Weast, 1974).

Soils and rocks contain varying amounts of cadmium, generally in small amounts but sometimes in larger amounts (for example in some fossil fuels or fertilizers). Cadmium ores are rare. Most cadmium is produced as a by-product from extraction of zinc, lead, or copper ores. Greenockite (CdS) is the only mineral of any consequence that contains cadmium (IPCS, 1992).

Cadmium does not corrode easily and has many uses in industry and consumer products, mainly in nickel-cadmium batteries, pigments used mostly in plastics, metal coatings, plastic stabilizers in polyvinyl chloride (PVC), and some metal alloys (Cook and Morrow, 1995; Thornton, 1992). Cadmium compounds are also used in printing, in textiles, in television phosphors, photography, lasers, as a neutron absorber in nuclear

reactors, in photovoltaic cells, and other semiconducting cadmium compounds in a variety of electronic applications (Chang, 2005; Elinder, 1985; OECD, 1994).

Cadmium has no essential biological function and is extremely toxic to humans. In chronic exposure, it accumulates in the body, particularly in the kidneys and the liver (Williams *et al*., 1999). These properties, along with its common usage make cadmium one of the commonest environmental metal poisonings. Acute poisoning from inhalation of fumes and ingestion of cadmium salts can also occur and at least one death has been reported from self-poisoning with cadmium chloride (Baldwin and Marshall, 1999).

2.2.2 Sources and Route of Human Exposure

Cadmium is widely distributed in the Earth's crust (0.1-0.5 mg/g), the atmosphere (1-5 ng/m^3), marine sediment (~1 mg/g) and sea water (~0.1 mg/g) (IPCS, 1992). Cadmium emissions arise from two major sources; natural sources and man-made or anthropogenic sources. Even though the average cadmium concentration in the earth's crust is generally placed between 0.1 and 0.5 ppm, much higher levels may accumulate in sedimentary rocks. Marine phosphates and phosphorites have been reported to contain levels as high as 500 ppm (Cook and Morrow, 1995; WHO, 1992) and are thus undesirable to use as fertilizers (Taylor, 1997). Weathering and erosion of parent rocks result in the transport by rivers of large quantities of cadmium to the world's oceans (OECD, 1994; WHO, 1992). Volcanic activity and forest fires have also been reported as natural sources of cadmium emissions (Nriagu, 1980). Large amounts of cadmium enter the environment from human activities such as mining and smelting operations, fuel combustion, disposal

of metal-containing products, and application of phosphate fertilizer or sewage sludges, cement production and waste incineration (Elinder, 1985; WHO, 1992).

Estimates of cadmium emissions to the atmosphere from human and natural sources have been carried out at the world-wide, regional, and national levels (IPCS, 1992). According to Nriagu (1979), about 10-15% of total airborne cadmium emissions arise from natural processes, the major source being volcanic action. Anthropogenic cadmium emissions to air arise, in decreasing order of importance, from the combustion of fossil fuels, iron and steel production, non-ferrous metals production and municipal solid waste combustion (Cook and Morrow, 1995; Van Assche and Ciarletta, 1992). Atmospheric cadmium occurs mainly in the forms of cadmium oxide and cadmium chloride which are ultimately dispersed by the wind (NTP, 1991).

Cadmium emissions to water arise, in decreasing order of importance, from phosphate fertilisers, non-ferrous metals production, and the iron and steel industry (OECD, 1994; Van Assche and Ciarletta, 1992). Mining represent a major source of cadmium release to the aquatic environment. Contamination can arise from mine drainage water, waste water from the processing of ores, overflow from the tailings pond, and rainwater run-off from the general mine area. The release of these effluents to local water-courses can lead to extensive contamination downstream of the mining operation (IPCS, 1992). Cadmium is however, a natural, usually minor constituent of surface and groundwater (ATSDR, 1999a). The atmospheric fall-out of cadmium to fresh and marine waters represents a major input of cadmium at the global level (Nriagu and Pacyna, 1988). Acidification of

soils and lakes may result in enhanced mobilization of cadmium from soils and sediments and lead to increased levels in surface and ground waters (WHO, 1986).

The application of phosphate fertilizers and atmospheric deposition are significant sources of cadmium input to arable soils in some parts of the world; sewage sludge can also be an important source at the local level (IPCS, 1992). Cadmium in soil tends to be more available when the soil pH is low. Cadmium is taken up and retained by aquatic and terrestrial plants and is concentrated in the liver and kidney of animals that eat the plants (Elinder, 1985).

Humans normally absorb cadmium into the body either by ingestion or inhalation. Dermal exposure (uptake through the skin) is generally not regarded to be of significance (Lauwerys, 1986). Human exposure to cadmium can result from consumption of food especially grain and leafy vegetables, which readily absorb cadmium from the soil (Williams *et al*., 1999), drinking water, or incidental ingestion of soil or dust contaminated with cadmium; from inhalation of cadmium-containing particles from ambient air; from inhalation of cigarette smoke, which contains cadmium taken up by tobacco; or from working in an occupation involving exposure to cadmium fumes and dust (Elinder, 1985). A daily intake of 2-4 mg cadmium was estimated from smoking one packet of cigarettes per day (WHO, 1992). For nonsmokers, ingestion of food is the largest source of cadmium exposures. Most drinking water contains only very low levels of cadmium and is usually not an important route of exposure, although water may leach cadmium from plumbing (ATSDR, 1997).

2.2.3 Levels of Cadmium in the Environment

2.2.3.1 Air

Ambient air cadmium concentrations have generally been estimated to range from 0.1 to 5 ng/m^3 in rural areas, from 2 to 15 ng/m^3 in urban areas, and from 15 to 150 ng/m^3 in industrialised areas (Elinder, 1985; OECD, 1994; WHO, 1992). Thornton (1992) suggested that coal and oil used in classical thermal power plants are responsible for 50% of the total cadmium emitted to the atmosphere.

Volcanic activity and forest fires has been estimated to release to the atmosphere 820 metric tons (Nriagu, 1980; OECD, 1994; WHO, 1992) and 1 to 70 metric tons per year (Nriagu, 1980) respectively. Emission rates of cadmium from solid waste incinerators have been found to range from 20 to 2,000 μg/m^3 from the stacks of traditional incinerators and from 10 - 40 μg/m^3 from advanced incinerators (IARC, 1993).

2.2.3.2 Water

Cadmium may enter aquatic systems through weathering and erosion of soils and bedrock, atmospheric deposition, direct discharge from industrial operations, leakage from landfills and contaminated sites, and the dispersive use of sludge and fertilisers in agriculture. Weathering and erosion of parent rocks result in the transport by rivers of large quantities, recently estimated at 15,000 metric tonnes per annum, of cadmium to the world's oceans (OECD, 1994; WHO, 1992).

Cadmium contamination can result from entry into aquifers of mine drainage water, waste water, tailing pond overflow, and rainwater runoff from mine areas (IARC, 1993). The upper Clark Fork River in Montana is contaminated with large amounts of cadmium from past mining activities between 1880 and 1972. While mining wastes are no longer released into the river, an estimated 14.5 million m^3 of tailings have been incorporated into the riverbed, floodplain, and reservoir sediments (Canfield *et al*., 1994). Some data shows that recent sediments in lakes and streams range from 0.2 to 0.9 ppm in contrast to the levels of generally less than 0. 1 ppm cited for fresh waters (Cook and Morrow, 1995). Surficial sediments collected from 18 locations in three major tributaries to Newark Bay, New Jersey, had a mean cadmium concentration of 10±6 mg/kg (ppm) dry weight (Bonnevie *et al*. 1994).

Rivers containing excess cadmium can contaminate surrounding land, either through irrigation for agricultural purposes, dumping of dredged sediments or flooding. It has also been demonstrated that rivers can transport cadmium for considerable distances, up to 50 km, from the source and is highly persistent in water, with a half-life of about 200 days (WHO, 1992). Atmospheric fallout of cadmium to aquatic systems is another major source of cadmium in the aquatic environment (IARC, 1993; Nriagu and Pacyna, 1988).

2.2.3.3 Soil

Cadmium in soils is derived from both natural and anthropogenic sources. The average natural abundance of cadmium in the earth's crust has most often been reported from 0.1 to 0.5 ppm, but some rocks such as sedimentary rocks are known to contain about 0.1 to

25 ppm of cadmium. Naturally, high levels of 200 to 14,000 ppm have been estimated for zinc ores and around 500 ppm for typical lead and copper ores. The raw materials for iron and steel production contain approximately 0.1 to 5.0 ppm, while those for cement production contain about 2 ppm of cadmium. Anthropogenic input of cadmium to soils occurs by aerial deposition and sewage sludge, manure and phosphate fertiliser application. The use of cadmium-containing fertilisers (10-200 ppm) and sewage sludge (1-1000 ppm) is most often quoted as the primary reason for the increase in the cadmium content of soils over the last 20 to 30 years in Europe (Cook and Morrow, 1995; Jensen and Bro-Rasmussen, 1992). Wet and dry deposition of cadmium from the atmosphere may also contribute sizable amounts of cadmium to soil in the areas surrounding sources of atmospheric emissions, such as incinerators and vehicular traffic, which may release cadmium from burned fuel and tire wear (EPA, 1985). Fossil fuels is known to contain 0.5 to 1.5 ppm cadmium (Cook and Morrow, 1995)

2.2.4 Environmental Fate

Cadmium emitted to the atmosphere from combustion processes is usually associated with very small particulates that are in the respirable range (<10 μm) and are subject to long-range transport with atmospheric residence time of about l-10 days before deposition occurs (Keitz, 1980). Indeed, it is often assumed that < 10% of such emissions are deposited locally, the remainder being available for long-range transport (Krell and Roeckner, 1988). Total deposition rates have been measured at numerous localities worldwide and values have generally been found to increase in the order: background < rural < urban < industrial (IPCS, 1992).

Cadmium is more mobile in aquatic environments than most other heavy metals (e.g., lead). In polluted or organic-rich waters, adsorption of cadmium by humic substances and other organic complexing agents plays a dominant role in transport, partitioning, and remobilization of cadmium. Cadmium concentration in water is inversely related to the pH and the concentration of organic material in the water (Callahan *et al*., 1979). Cadmium has a relatively long residence time in aquatic systems. In Lake Michigan, a mean residence time of 4-10 years was calculated for cadmium (Wester *et al*., 1992). Studies have indicated that concentrations of cadmium in sediments are at least one order of magnitude higher than in the overlying water. Cadmium concentrates in freshwater and marine animals to concentrations hundreds to thousands of times higher than in the water (Callahan *et al*., 1979).

Rivers contaminated with cadmium can contaminate surrounding land, either through irrigation for agricultural purposes, by the dumping of dredged sediments, or through flooding (Forstner, 1980; Tsuchiya, 1978). Forstner (1980) reported soil cadmium concentration of 70 mg/kg in agricultural land adjacent to Neckar River, Germany, which received dredge sediments for soil improvement and Tsuchiya (1978) reported soil contamination due to irrigation in Japan.

The most important soil factors influencing plant cadmium accumulation are soil pH and cadmium concentration (Page *et al*., 1981; Herrero and Martin, 1993). Factors such as cation exchange capacity and the contents of the hydrous oxides of manganese and iron,

organic matter, and calcium carbonate also influence distribution of cadmium in soil and soil solution. Increases in these parameters result in decreased availability of cadmium to plants owing to a reduction of the level of cadmium in the soil solution (IPCS, 1992). Contamination of soil by cadmium is of concern because the cadmium is taken up efficiently by plants and, therefore, enters the food chain for humans and other animals (ATSDR, 1999a; IPCS, 1992).

2.2.5 Human Health Effects

Cadmium can enter the blood by absorption from the stomach or intestines after ingestion of food or water, or by absorption from the lungs after inhalation. However, once cadmium enters the body, it is very strongly retained and low doses may build up significant cadmium levels in the body if exposure continues. The amount of cadmium needed to cause an adverse effect in an exposed person depends on the chemical and physical form of the element. In general, cadmium compounds that dissolve easily in water (e.g., cadmium chloride), or those that can be dissolved in the body (e.g., cadmium oxide), tend to be more toxic than compounds that are very hard to dissolve (e.g., cadmium sulfide) (IPCS, 1992).

An acute intake of cadmium causes testicular damage and may affect female reproductive cycle. Within a few hours of exposure, there is necrosis and degeneration of the testes with complete loss of spermatozoa. This is due to a reduction in the blood supply to these organs (Timbrell, 1995). Acute inhalation of cadmium may initially cause irritation of the upper respiratory tract, although symptoms may be delayed for 4-8 hours. Dyspnea, chest pain and muscle weakness may also occur. Pulmonary oedema, bronchitis, chemical

pneumonitis, respiratory failure and death may occur within days of exposure. Long-term exposure may result in progressive pulmonary fibrosis and impaired lung function (WHO, 1992). Acute ingestion of cadmium produces severe gastrointestinal irritation, which is manifest as severe nausea and vomiting, abdominal cramps and diarrhoea. A lethal dose of cadmium for ingestion is estimated to be between 0.35 and 8.90 g (Hu, 1998).

Chronic oral exposure to cadmium leads to renal failure, characterised by proteinuria due to renal tubular dysfunction. The accumulation of cadmium in the kidney affects renal vitamin D metabolism, which subsequently disturbs calcium balance that may lead to osteomalacia and osteoporosis (DEFRA and EA, 2002a). This, as well as the increased excretion of calcium and phosphorus may result in bone disease characterized by bone and joint aches and pains, a syndrome, first described in Japan, where it was termed the itai-itai ("ouch-ouch") disease. Symptoms of this disease include weak bones that lead to deformities, especially of the spine, or to more easily broken bones. It is often fatal. (ATSDR, 1999a)

Long term exposure to cadmium can cause anemia, loss of sense of smell, fatigue and/or yellow staining of teeth. Chronic inhalation of cadmium causes loss of renal tubular function, leading to proteinuria and impairs lung function by causing bronchitis, obstructive lung disease and in some cases interstitial fibrosis (IPCS, 1992). Chronic obstructive airway disease has been associated with long-term high-level occupational exposure by inhalation (OECD, 1994; WHO, 1992). Cadmium (especially cadmium

oxide) is also known to be carcinogenic, and in studies has been linked with cancers in the lungs and prostate (Williams *et al*., 1999).

2.3 ZINC

2.3.1 Introduction

Zinc is one of the most common elements in the earth's crust. Zinc is found in the air, soil, and water and is present in all foods. In its pure elemental (or metallic) form, zinc is a bluish-white shiny metal. It is stable in dry air, but upon exposure to moist air, it becomes covered with a film of protective transparent layer of zinc oxide or basic carbonate (e.g. $ZnCO_3 \cdot 3Zn(OH)_2$) (ATSDR, 2005; IPCS, 2001) . A sheet of zinc looks very much like a sheet of aluminum, but zinc is more than twice as heavy, and does not bend easily. Zinc is not very ductile or malleable, especially when pure. Its naturally occurring isotopes are 64 (49%), 66 (28%), 67 (4%), 68 (19%) and 70 (0.6%) (Budavari, 1989).

There is no information on the taste and odor of metallic zinc. Powdered zinc is explosive and may burst into flames if stored in damp places. Metallic zinc has many uses in industry. A common use is as coating for iron or other metals through an electrolytic process known as “galvanizing” so that they do not rust or corrode. Metallic zinc is also mixed with other metals to form alloys such as brass and bronze. A zinc and copper alloy is used to make pennies in the United States (EU, 1996; Heiserman, 1992). Because zinc is easily die cast or molded into intricate shapes, it is often used to manufacture

automotive engine parts and electrical equipment. Metallic zinc is also used to make dry cell batteries (IPCS, 2001).

Zinc can also combine with other elements, such as chlorine, oxygen, and sulfur, to form zinc compounds. Most zinc ore found naturally in the environment is in the form of zinc sulfide. Zinc compounds are not explosive or flammable. Zinc sulfide is gray-white or yellow-white, and zinc oxide is white. Both of these compounds are used to make white paints, ceramics, and several other products. Zinc oxide is also used in producing rubber. Zinc compounds, such as zinc acetate, zinc chloride, and zinc sulfate, are used in preserving wood and in manufacturing and dyeing fabrics. Zinc chloride is also the major ingredient in smoke from smoke bombs. Zinc cyanide is used in electroplating and gold extraction. The primary uses of zinc phosphate are in preparation of metal coatings and as dental cement. Zinc compounds are also used by the drug industry as ingredients in some common products, such as sun blocks, diaper rash ointments, deodorants, athlete's foot preparations, acne and poison ivy preparations, dental cement and antidandruff shampoos (Budavari, 1989; Goodwin, 1998; Sax and Lewis, 1987; WHO, 2001).

Zinc is essential to sustain life and is found in almost every cell. An adult human of average weight contains about 2.5grams of zinc, most of which forms part of specialized enzymes and other proteins. It stimulates the activity of some enzymes, which are substances that promote biochemical reactions in the body (IOM, 2001). Zinc which supports the immune system (Solomons, 1998), is needed for wound healing (Heyneman, 1996), helps maintain the sense of taste and smell (Prasad et al., 1997), and is needed for

DNA synthesis (IOM, 2001). Zinc also supports normal growth and development during pregnancy, childhood, and adolescence (Fabris and Mocchegiani, 1995).

Too little zinc in the diet can lead to poor health, reproductive problems, and lowered ability to resist disease. Exposure to elevated levels of zinc is not as toxic to humans as some other metals; however, it has been shown to affect some biological functions. It inhibits the biological synthesis of adenosine triphosphate (the molecule that carries energy obtained from food), and it alters the permeability of some internal cell membranes to potassium (Guthrie and Perry, 1980). Although zinc is relatively nontoxic to humans, its ecological effects are of greater concern. Zinc has been shown to bioaccumulate in some saltwater species with steady state bioconcentration factors ranging from about 3.7 to 24,000. Zinc is also of concern for freshwater species because the gills of fish are physically damaged by high concentrations of zinc (EPA, 1987).

2.3.2 Sources and Route of Human Exposure

Zinc is a naturally occurring element found in the earth's surface rocks and ores containing zinc are widespread geologically and geographically. Because of its reactivity, zinc metal is not found as the free element in nature. There are approximately 55 mineralized forms of zinc. The source of most zinc is the sulphide, sphalerite, ZnS. Sphalerite is closely associated with galena, PbS, pyrites, FeS_2 and other sulphides in hypogene ore deposits, and must be separated from them in smelting. Transparent sphalerite is often green. Sphalerite also called zinc blende is cubic in crystal structure. ZnS crystallized in hexagonal crystals instead is called *wurtzite*. Hemimorphite is a

hydrated zinc silicate, $Zn_4Si_2O_7(OH)_2 \cdot H_2O$, fairly hard but light, and strongly pyroelectric. It is usually found in supergene enriched zones, together with smithsonite, $ZnCO_3$. Smithsonite is very easy to reduce to zinc. It is usually brownish, and often contains considerable cadmium (Hurlbut, 1952).

Sources of exposure to zinc include ingestion of food, drinking water, polluted air, tobacco products, and occupational exposure, with ingestion of food being the primary route of exposure (ATSDR, 2005). The RDA for zinc is 11 mg/day for men and 8 mg/day for women (IOM, 2002).

Zinc is present in most drinking water. Based on a body weight of 70 kg, the mean daily intakes of zinc in drinking water for residents of homes with galvanized and copper pipe plumbing systems in Seattle, Washington, were estimated to be 0.017–0.028 and 0.002–0.006 mg/kg/day, respectively (Sharrett *et al*., 1982).

Zinc is widespread in commonly consumed foods but tends to be higher in those of animal origin, particularly some seafoods (e.g., one serving of oysters will more than meet the daily dietary requirements of zinc) (NAS/NRC, 1979). Meat products contain relatively high concentrations of zinc, whereas fruits and vegetables have relatively low concentrations. Meats, fish, and poultry contained an average of 24.5 mg zinc/kg, whereas grains (or cereal products) and potatoes contained 8 and 6 mg/kg, respectively (Mahaffey et al., 1975). Nonvegetarians absorb a higher percentage of zinc (3.7 mg/day) than vegetarians (2.4 mg/day) (Hunt, 2003).

Zinc is found in human tissues and body fluids. Body tissue and fluid samples were collected from two nonoccupationally exposed individuals living in the Los Angeles, California area (Krishnan and Hee, 1992). Ear wax, blood plasma, sweat, and skin from these individuals contained zinc at levels of 88–103, 0.79–1.7, 0.50–1.58, and 15.6–1,000 μg/g dry weight, respectively. Hayashi *et al*. (1993) reported that human fingernail samples from Japanese individuals had higher mean levels of zinc in the spring (145–149 μg/g) compared to winter (122–136 μg/g). A recent study of breast milk in lactating mothers showed an average zinc concentration of about 5.65 mg/L. This average did not vary much depending on the age of the mother (Honda *et al*., 2003).

Exposure to airborne zinc is largely occupational through the inhalation of industrial dusts or fumes. Individuals occupationally exposed to metallic zinc and zinc compounds are those involved in galvanizing, smelting, welding, or brass foundry operations. Inhalation of zinc oxide particles (0.2–1.0 μm) and fumes by workers can result in metal fume fever (Martin *et al*., 1999).

2.3.3 Levels of Zinc in the Environment

2.3.3.1 Air

Natural phenomena such as volcanic eruptions, forest fires, dust storms, and sea spray all contribute to the continuous cycling of zinc in air. Zinc is also released into the air by soils as they erode in wind and rain. The WHO in 2001 estimated 915,000 tonnes/year of zinc released into the environment due to erosion. Volcanic release of zinc into the

atmosphere has been estimated by Lantzy and Mackenzie (1979) to be around 35,800 tonnes annually, based on the average zinc concentration in soils and andesites with sea salt sprays estimated to be 440 metric tons/year by Nriagu (1989). Thus, total annual emissions of zinc to air from natural sources are estimated at about 45 000 tonnes/year (Nriagu, 1989).

Zinc released by human activities comes mainly from mines, steel mills, brass works, smelters, industrial boilers that burn coal, incinerators that burn refuse and sewage sludge, and sewage plants that discharge treated waste. In general, levels of zinc in air are relatively low and fairly constant. The average concentration of zinc in air (as fine dust particles) is typically less than 1 microgram per cubic meter ($\mu g/m^3$), although concentrations of 5 $\mu g/m^3$ have been measured near industrial sources. Deposition of airborne zinc is strongly dependent on particle size and meteorological factors, primarily wind speed and humidity. Wet deposition predominates with estimated values for zinc removal from air of 60–90% (Ohnesorge and Wilhelm, 1991).

2.3.3.2 Water

Rain, snow, ice, sun, and wind erode zinc-containing rocks and soil. Wind and runoffs carry minute amounts of zinc to lakes, rivers, and the sea, where some zinc remains dissolved in water or as fine suspended particles, others settles to the bottom in association with heavier particles. Average concentrations range from 0.02 to 0.05 milligram per liter (mg/L) in surface water and 0.01 to 0.1 mg/L in drinking water (EPA, 1980b). For various rivers worldwide, Holland (1978) reported average values of 5–45

µg/litre. Drainage from active and inactive mining areas may be a significant source of zinc in water. Gonzales *et al*. (1985) reported zinc levels of up to 4 mg/litre in surface water collected near a mine. Elevated zinc levels of up to 175 µg/litre were found in Birch Creek, a heavily mined river, compared to <10 µg/litre in an unmined stream (LaPerriere *et al*., 1985). On an annual worldwide basis, an estimated 77,000–375,000 metric tons of zinc are discharged into water from anthropogenic sources (Nriagu and Pacyna, 1988).

One of the consequences is that zinc polluted rivers are depositing zinc-polluted sludge on their banks. Zinc may also increase the acidity of waters. However environmental toxicity of zinc in water is dependent upon the concentration of other minerals and the pH of the solution, which affect the ligands that associate with zinc (Paquin *et al*., 2002).

Zinc has been shown to bioaccumulate in some saltwater species with steady state bioconcentration factors ranging from about 3.7 to 24,000. Zinc is also of concern for freshwater species (EPA, 1987).

2.3.3.3 Soil

Zinc is the 17th most common element in the earth's crust and most rocks contain zinc in varying amounts. Zinc generally remains in the upper layers bound to soil particles, but it can leach to groundwater depending on soil characteristics. It moves more readily in sandy soil. Concentrations of zinc in sandy soil particles are about 200 times higher than in the water between the soil particles. The concentration ratios are even higher (over 1,000) in both loam and clay soils (ATSDR, 2005). Zinc concentrations in igneous and

sedimentary rocks were reported to be 48–240 mg/kg for basaltic igneous rock, 5–140 mg/kg for granitic igneous rock, 18–180 mg/kg for shales and clays, 34-1500 mg/kg for black shales and 2–41 mg/kg for sandstones (Thornton, 1996). For non-contaminated soils worldwide, Adriano (1986) reported average zinc concentrations of 40–90 mg/kg, with a minimum of 1 mg/kg and a maximum of 2000 mg/kg. Low levels are found in sandy soils (10–30 mg/kg), while high contents are found in clays (95 mg/kg). Sediment samples collected from streams in the Black Hills, South Dakota, an area impacted by gold mining operations, contained zinc at levels ranging from 3.8 to 250 µg/g dry weight (May *et al*., 2001).

On a worldwide basis, an estimated 1,193,000–3,294,000 metric tons of zinc per year are released to soil from anthropogenic sources (Nriagu and Pacyna, 1988). Wet and dry deposition, mine tailings, the use of zinc compounds as fertilizers and the application of municipal sludges and manure to cropland are considerable sources of zinc in soils (ATSDR, 2005; Chang *et al*., 1987). When the soils of farmland are polluted with zinc, animals will absorb concentrations that are damaging to their health and only a limited number of plants have a chance of survival. Water-soluble zinc that is located in soils can contaminate groundwater (ATSDR, 2005).

2.3.4 Environmental Fate

Due to natural erosion processes like the weathering and abrasion of rock, soils and sediments by wind and water, a small but significant fraction of natural zinc is continuously being mobilised and transported in the environment. Volcanic eruptions, forest fires and aerosol formations above seas also contribute to the natural transport of

zinc. These processes causes cycling of zinc in the environment, resulting in natural background levels in the air, surface waters and soil.

Zinc present in air is mostly adsorbed on fine dust particles and are small enough to be in the respirable range (Dorn *et al*., 1976). Zinc bound to soil particulates may be transported to the atmosphere as wind-blown dust (Perwak *et al*., 1980). This dust eventually settles over land and water. Rain, snow, gravitational settling and deposition on water and soil surfaces aid in removing zinc from air (Golomb *et al*., 1997).

In water the free zinc ion is thought to coordinate with six water molecules to form the octahedral aquo ion $[Zn(H_2O)_6]^{2+}$ in the absence of other complexing or adsorbing agents. In typical river waters, 90% of the zinc is present as aquo ion and the remainder consists of $ZnHCO_3^+$, $ZnCO_3$, $ZnSO_4$ and unstable organozinc complexes that dissociate to liberate Zn^{2+} (Spear, 1981). Most of the zinc introduced into aquatic environments eventually is partitioned into the sediments and for this reason, top sediment layers usually mirror the zinc levels in the overlying water. Zinc mobility in aquatic ecosystems is a function of the composition of suspended and bed sediments, dissolved and particulate iron and manganese concentrations, pH, salinity, concentrations of complexing ligands, and the concentration of zinc (EPA, 2003). In natural waters, complexing agents, such as humic acid, can bind zinc. Zinc bioavailability and toxicity to aquatic organisms are highest under conditions of low pH, low alkalinity, low dissolved oxygen, and elevated temperatures (Weatherley *et al*., 1980). Aquatic populations are frequently decimated in zinc-polluted waters (Everall *et al*., 1989).

In the soil, zinc is bound to the soil complex (clays, organic matter, etc), depending on different physicochemical soil factors such as pH and organic matter content. These factors determine the solubility of zinc in soil, and consequently, its bioavailability for uptake by organisms. Humic and fulvic acids are important for the speciation of zinc in soil and aquatic systems. For example, 60–75% of zinc in soil solution has been reported to be bound by fulvates (Geering and Hodgson, 1969). Zinc may be taken up by animals eating soil or drinking water containing zinc.

2.3.5 Human Health Effects

Zinc is an essential element in our diet, but too little or too much can be harmful. Zinc deficiency most often occurs when zinc intake is inadequate or poorly absorbed, when there are increased losses of zinc from the body, or when the body's requirement for zinc increases (Prasad, 1996). The World Health Organization (1996) estimated that one-third (33%) of the world's population is at risk of inadequate zinc intakes. Signs of zinc deficiency include growth retardation, hair loss, diarrhea, delayed sexual maturation and impotence, eye and skin lesions, and loss of appetite (IOM, 2001). There is also evidence that weight loss, delayed healing of wounds, taste abnormalities, and mental lethargy can occur (Heyneman, 1996; Nishi, 1996). Zinc deficiency may increase the toxic effects of arsenic, copper, cadmium and lead; thus an adequate amount of zinc can be considered protective against the toxicity of these elements (ATSDR, 2005).

Large doses of zinc (10-15 times higher than the RDA) taken by mouth even for a short time may cause stomach cramps, nausea, and vomiting. Ingesting high levels of zinc for

several months may cause anemia, damage the pancreas, and decrease levels of high-density lipoprotein (HDL) cholesterol (the good form of cholesterol) (ATSDR, 2005).

Zinc toxicity has been seen in both acute and chronic forms. Intakes of 150 to 450 mg of zinc per day have been associated with low copper status, altered iron function, reduced immune function, and reduced levels of high-density lipoproteins (Hooper *et al*., 1980). One case report cited severe nausea and vomiting within 30 minutes after the person ingested four grams of zinc gluconate (570 mg elemental zinc) (Lewis and Kokan, 1998).

Inhaling large amounts of zinc (as zinc dust or fumes from smelting or welding) can cause a specific short-term disease called metal fume fever. This is believed to be an immune response affecting the lungs and body temperature. Very little is known about the long-term effects of breathing zinc dust or fumes (ATSDR, 2005).

High exposure to zinc dust can cause cough with phlegm. Skin irritation will probably occur in people exposed to some zinc compounds. Metal particles can irritate the eyes and zinc has not been classified for human carcinogenicity (ATSDR, 2005).

2.4 ANALYTICAL METHODS FOR MERCURY DETERMINATION IN FISH

Numerous methods have been used to determine mercury levels in biological and environmental samples. Most methods have used atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), or neutron activation analysis (NAA). In addition, methods based on mass spectrometry (MS), spectrophotometry, gas chromatography and anodic stripping voltammetry (ASV) have also been tested. Of the available methods, cold vapor (CV) AAS is the most widely used.

All the above techniques represent a considerable improvement on the original "dithizone" method. This dithizone method was widely used up to the advent of atomic absorption spectrometry in the late 1960s. Basically it involved the formation of a coloured complex with dithizone after all the mercury in the sample had been converted to Hg^{2+} ions by oxidation in strong acids. After neutralization of excess oxidant with a reducing agent, usually hydroxylamine, the coloured complex is extracted into a non-polar solvent. After washing the extract, the colour intensity is measured on a spectrophotometer and the amount of mercury estimated from a standard curve. The dithizone procedure has an absolute sensitivity of about 0.5 µg of mercury. The quoted recovery rates for the dithizone procedure from foodstuffs and tissues are in the range of 85-99% and the reproducibility can yield a coefficient of variation of as low as 2%.

Procedures for neutron activation analysis of total mercury have been reviewed by Wallace (1971), Swedish Expert Group (1971) and Burrows (1975). The method is based on the principle that when natural mercury (a mixture of stable isotopes) is exposed to a high flux of thermal (slow) neutrons, it is converted to a mixture of radioactive isotopes, principally ^{197}Hg and ^{203}Hg, which have decay half-lives of 65 hours and 47 days, respectively. After the sample has been irradiated with neutrons, a precise weight of carrier mercury is added and the sample subjected to digestion and organic destruction. On completion of digestion, mercury is isolated by electrodeposition on a gold foil and the radioactivity is determined with a gamma counter. The use of carrier mercury corrects for any losses of mercury during the digestion, extraction, and isolation procedures. The

limit of detection is 0.1-0.3 ng of mercury. The sample size is 0.3 g giving a concentration limit of 0.3-1 µg/kg in most biological samples. The neutron activation procedure is regarded as the most accurate and sensitive procedure and is usually used as the reference method (WHO, 1976).

The "Magos" selective atomic-absorption method (Magos, 1971; Magos and Clarkson, 1972) has found wide application. It can determine both total and inorganic mercury and, by difference, organic mercury. The apparatus is inexpensive, portable, and does not require sophisticated facilities. The technique has a sensitivity of approximately 0.5 ng of mercury. The relative standard deviation was 2% and the recovery rates were quoted as being close to 100%.

The gas chromatography method is usually used when there is a need to selectively measure methylmercury or other organic species. It has been widely used for the measurement of methylmercury in fish tissues. Gas chromatography is used to determine methylmercury directly (detection limit, 1.0 ng/g sample). Of the available methods, Cold Vapour-AAS is the method of choice (Baxter and Frech, 1990; Munaf *et al*., 1991) and the method recommended by EPA and AOAC (AOAC, 1984; Beckert *et al*., 1990; EPA, 1994a). The CVAAS was used for analyzing total mercury in fish and sediments in this study. The technique and procedure is discussed below.

2.4.1 The Cold Vapour (CV) Atomic Absorption Technique

Mercury is unique among other heavy metals. Hg has a high pressure at ambient temperature (0.61 Pa at 20^0C). This uniqueness of Hg allows its determination to be exploited. The traditional methods for the determination of Hg include flameless AAS, AFS and ICPAES, all of which exhibit poor sensitivity. The high vapour pressure of Hg at ambient temperature enables the metal to be determined by AAS without the use of an atomizer. During the determination, Hg is reduced to metallic mercury from its compounds and is transferred at the vapour phase. This is achieved by a simple chemical reduction reaction used to generate the gaseous mercury species. The process is known as Cold Vapour Atomic Absorption Spectrometry (CVAAS). The CVAA process has two primary advantages. First, mercury (the analyte), is removed from sample matrix, which reduces the potential for matrix interferences. Second, the detection limits are improved because the entire mercury sample is introduced into the absorption cell within a few seconds. Therefore, the density of mercury in the cell during data collection (absorption, fluorescence or emission depending on the detection technique) is greatly enhanced as compared to typical sample introduction. Two reducing agents usually employed for CV analysis are tin (II) chloride ($SnCl_2$) and sodium borohydride ($NaBH_4$).

$$Hg^{2+} + Sn^{2+} \leftrightarrow \ Hg^0 + Sn^{4+}$$

2.5 ANALYTICAL METHODS FOR CADMUIM AND ZINC ANALYSIS

- Inductively-coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (F-AAS, GF-AAS), ICP-mass spectrometry (ICP-MS), X-ray fluorescence (XRF), and electroanalytical techniques, such as polarography

or stripping voltammetry, and neutron activation analysis are commonly used instrumental techniques for zinc and cadmium determination (ATSDR, 1999a; IPCS, 2001).

Inductively-coupled plasma atomic emission spectrometry (ICP-AES) is considerably more sensitive than F-AAS, and detection of 2 µg/L is possible by direct analysis (Greenberg *et al*., 1992), although with the latest axial plasma instruments with ultrasonic nebulization, the limit is as low as 0.2 µg/litre. This technique offers adequate sensitivity for zinc in contaminated waters or for acid digests of soil, sediment and biological samples. The multi-element capability offered by ICP-AES is a considerable advantage over AAS methods (AOAC, 1998; EPA, 1994b; NIOSH, 1994).

- Flame AAS has been used to determine zinc concentrations in natural waters. AAS is a rapid method of measuring zinc, with a detection limit of 0.005 ppm (Fishman, 1966; Hunt & Wilson, 1986). Flame AAS, coupled with microwave digestion and GF-AAS, has been used to determine the concentration of zinc in food and shellfish samples. Limits of detection ranged from 0.12 to 0.24 ppm, with recoveries ranging from 80 to 113% (AOAC, 1984; McCarthy and Ellis, 1991; Morales-Rubio *et al*., 1992). GF-AAS was also used to determine low levels of zinc in beer. Recovery (94–106%) and precision (4.2% CV) were excellent. Sensitivity was not reported (Wagner *et al*., 1991).
- ICP mass spectrometry (ICP-MS) offers excellent sensitivity. The technique is ideally suited to digests of soils, sediments and biological samples; the greater

sensitivity means that any difficulties due to a high content of solids are overcome by dilution. In addition, because of its mass resolution, ICP-MS enables isotopic ratio analysis ($^{67}Zn/^{68}Zn/^{70}Zn$) or isotope dilution studies using ^{65}Zn (Ward, 1987). ICP-MS has been used to determine the concentration of zinc in water. Detection limits have been reported to be as low as 0.017 µg/L using ^{66}Zn isotope. Recoveries range from 99 to 117% (APHA, 1998).

- A relatively new XRF procedure based on polarized X-rays has a detection limit for zinc of 0.1 mg/kg in biological materials (Heckel, 1995). Another technique, energy dispersive x-ray fluorescence (EDXRF,) has been used to detect zinc in dried food samples with better precision (e.g., detection limit, 0.8 ppm) than AAS methods (Nielson *et al*. 1991).
- Neutron activation analysis (NAA) is a useful technique for the non-destructive analysis of solid samples, and requires a minimum of sample preparation (Fredrickson, 1989; Heydorn, 1995). Its main advantage is its multi-element capability; the great disadvantage is its limited availability, and long analysis time. It has largely been superseded by ICP-MS, which offers a similar capability and is more widely available. For zinc, the sensitivity of NAA is poor (IPCS, 2001).

The most commonly used methods, at present, are atomic absorption spectrometry, electrochemical methods, and neutron activation analysis. Other methods are colorimetry, atomic emission spectrometry, atomic fluorescence spectrometry, and proton-induced X-ray emissions (PIXE) analysis. Analytical methods for cadmium have been reviewed by Friberg *et al*. (1986).

The AAS techniques appear to be most sensitive, with recoveries ranging from 94 to 109% (Bruhn and Franke, 1976; Muys, 1984). A method used to isolate cadmium by first extracting with bismuth diethyldithiocarbamate (Bi[DDC]) and then with zinc diethyldithiocarbamate ($Zn[DDC]_2$) in chloroform and then measuring by Radiochemical neutron activation analysis (RNAA) showed 94-106% recovery (Greenberg *et al*. 1979).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Preparation of Glassware and Sample Containers

All glassware and sample containers used were soaked in detergent solution overnight; rinsed and soaked in 10% (v/v) HNO_3 overnight. They were rinsed with tap water followed by 0.5% (w/v) $KMnO_4$, tap water again and finally rinsed with distilled water. They were then dried before use.

3.2 Apparatus

The types of equipment used in this research are listed as follows:

- 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 for mercury determinations. The signals were obtained on a Yokogawa Model 3021 strip chart recorder.
- Unicam 929 Atomic Absorption Spectrometer.

3.3 Reagents and Solutions Prepared

All reagents used were of analytical reagent grade (BDH Chemicals Ltd, Poole, England) unless otherwise stated. Double distilled water was used for the preparation of all solutions.

1. Mercury stock standard solution (1000 mg/L) was prepared by dissolving 0.677 g of $HgCl_2$ in the acid mixture HNO_3-H_2SO_4-$HClO_4$ (2:10:2) in a 50 ml digestion flask with heating on a hot plate at a temperature between 250 ^{0}C ± 5 for 30 min and a clear solution was obtained. The solution was then diluted to 50 ml with distilled water after cooling.
2. Blank solutions were also prepared in the ratio of 1: 1: 1: 5 distilled water: HNO_3: $HClO_3$: H_2SO_4 bulked together for use as diluent.
3. Mercury standard working solutions were freshly prepared by diluting an appropriate aliquot of the stock solution through intermediate solutions using the blank solution.
4. Stannous chloride solution (10% v/v) was prepared by dissolving 10 g of the salt in 100 ml 1M HCl. The solution was aerated with nitrogen gas at 50 ml/min for 30 min to expel any elemental mercury from it.
5. Five molar (5M) NaOH was prepared by dissolving 20 g NaOH in 100 ml double distilled water.
6. $KMnO_4$ (0.5%) in 0.5M H_2SO_4 was prepared by dissolving 0.5 g $KMnO_4$ in 100 ml 0.5M H_2SO_4.
7. Cadmium Stock solution of 1000 ppm was prepared by dissolving 1g of pure cadmium metal in a 1000 ml mixture of distilled water: HCl (1:1).
8. Zinc Stock solution of 1000 ppm was prepared by dissolving 2.08 g of $ZnCl_2$ in a 1000 ml mixture of distilled water: HCl in the ratio of 1:1.

9. Cadmium and Zinc standard solutions were freshly prepared by diluting a calculated aliquot of the stock solutions through intermediate solutions using the blank solutions.

3.4 Sampling and Sample Preparation

Fish samples were obtained from local fishermen from five towns namely Dunkwa-on-Offin, Nkotumso, Dominase, Buabenso and Awisam along River Offin between February and July 2006. A hundred and forty eight (148) fish samples covering twelve (12) species were obtained. The samples were stored on ice in an ice chest and transported to the laboratory. They were then sorted out, identified and kept in a freezer at -20 ^{0}C prior to preparation for chemical analysis. Thereafter, the fish samples were thawed to room temperature, washed with distilled water, dried on tissue paper, the length and body weight of each was then taken in the laboratory. A portion of the edible muscle tissue was removed from the dorsal part of each fish using a stainless steel kitchen knife, homogenized and stored for analysis. Four sediments and a soil sample collected 200 m away from the river basin were taken using a plastic shovel from all the sampling location. The sediments and soils were placed in clean plastic bags and transported to the laboratory in an ice chest. The sediments and soils were air-dried in a dark room, homogenized and sieved prior to analysis.

3.5 Digestion Procedure

The fish samples were digested for total mercury determination by an open flask procedure as shown in scheme 3.0 below developed by Akagi and Nishimura (1991). In

this digestion method, 0.5 g of homogenized fish sample was weighed into 50 ml volumetric digestion flask and a mixture of 1 ml distilled water, 2 ml HNO_3-$HClO_3$ (1:1) and 5 ml H_2SO_4 were added. The mixture was then heated at a temperature of 250 ± 5 ^{0}C for 30 min until the solution became colourless. The sample solution was then cooled and diluted to 50 ml with double distilled water. The sediments and soils were also subjected to the same digestion procedure and the digest filtered with Whatman No 45 filter paper.

Scheme 3.0 Procedure for digestion of samples for total mercury in fish and sediments.

Sample (0.5 g in 50 mL digestion flask)

↓ H_2O, 1 mL

↓ HNO_3:$HClO_4$ (1:1), 2 mL

↓ H_2SO_4, 5 mL

↓ Heat at 200 ^{o}C ± 5 ^{o}C for 30 min

↓ Cool to room temperature

Digested Sample

↓ H_2O, make up to 50 mL

Sample solution, 5 mL

↓ 10% $SnCl_2$, 0.5 mL

Analysis for Hg using CVAAS – Automatic Mercury Analyzer Model HG 5000

3.6 Digestion of Blank and Standards

A blank and standard solution, 0.0, 25 and 50µl of 1µg/ml standard mercury solution were subjected to the same digestion treatment as the sample, to yield concentrations of 0, 25 and 50 ng/ml as standard solutions for the experimental analysis.

3.7 Determination of Mercury

Determination of mercury in all the digests were carried out by cold vapor atomic absorption spectrometry using an automatic Mercury Analyzer Model HG-5000 (Sanso Seisakusho Co., Ltd, Japan) developed at National Institute for Minamata Disease (NIMD) (Akagi and Nishimura, 1991).

3.7.1 Operation of Automatic Mercury Analyzer Model HG-5000

1. The instrument was switched on and left for 20 minutes to warm up
2. The start button was pressed to purge the system for 3 minutes
3. The reset button was pressed to stop purging
4. A 5 ml aliquot of the sample was introduced into the reaction vessel using a micropipette
5. Then 0.5 ml of the $SnCl_2.2H_2O$ was added from a dispenser
6. The start button was pressed immediately the stannous chloride was dispensed. After 30 seconds the 4 way valve rotated to allow the mercury vapour generated in the reaction vessel to flow into the absorption cell so as to generate a peak. Immediately the peak fell, a beep sounded.
7. Immediately after the beep, the tap was opened to expel the waste
8. The reset button was pressed to stop purging before the next sample was introduced

9. The tip of the micropipette was replaced with a new one

10. The process was repeated from step 4 for other samples, standard solutions and blank

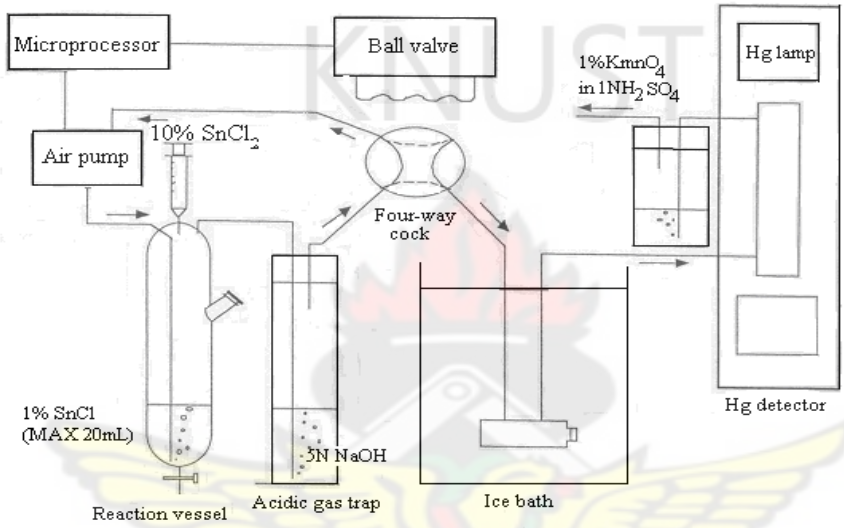

Fig. 3.0 Apparatus for mercury analysis by Cold Vapour Atomic Absorption Spectrometry (Akagi and Nishimura, 1991)

3.8 Determination of Cadmium and Zinc

The same digested sample in Section 3.5 was used for Cd and Zn determination. However, the digested sample after making it up to 50 ml was analysed for Cd and Zn using the Unicam 929 Atomic Absorption Spectrometer.

3.9 Determination of Recovery

Recovery of mercury was determined by adding increasing amounts of mercury to samples of two different fish species and two different sediments, which were taken through the digestion procedure. The resulting solutions were analysed for mercury. The results are reported in Table 4.1. Recovery for zinc and cadmium were also determined with the same samples and procedure. The results are shown in Table 4.2 and 4.3 respectively.

3.10 Determination of Mercury, Cadmium and Zinc in Certified Reference Material

The Certified Reference Material CRM-IAEA-407 fish tissue was subjected to the same digestion procedure as described in Section 3.5 and the results after analysis for Hg, Cd, and Zn is presented in Table 4.0

3.11 Statistical Analysis

The data obtained in this study were subjected to statistical analyses using Microsoft Excel. Linear regression and correlation analysis were conducted using the following variables: mercury concentration in fish, total fish length and fresh fish weight.

CHAPTER FOUR

4.0 Results and Discussion

The accuracy of the analytical technique used in this study was determined by carrying out recoveries and the analysis of Certified Reference Materials (CRM's) (CRM-IAEA-407 fish tissue). The results are presented in Table 4.0 to 4.3. Recoveries for Hg in fish ranged from 96.12 to 101.08%, that for Zn ranged from 95.00 to 99.00% and that of Cd ranged from 98.40 to 101.00%. Recoveries for Hg, Zn and Cd in sediments ranged from 96.00 to 101.80%, 97.50 to 103.75% and 99.33 to 103.33% respectively. The validity of the method have been proved by the agreement between the measured (0.219 to 0.220 mg/kg) and certified (0.216 to 0.228 mg/kg) for mercury and the measured (0.193 to 0.196 mg/kg) and certified (0.185 to 0.193 mg/kg) for cadmium. The results from the analysis were within the 95% confidence limit. There was however, small disagreement between the measured (67.1 to 68.2 mg/kg) and the certified (66.3 to 67.9 mg/kg) for zinc.

Table 4.0 Results for Hg, Cd and Zn in Certified Reference Material CRM-IAEA-407 Fish Tissue

Metal	Range(mg/kg)	IAEA Range(mg/kg)	Average (mg/kg)	IAEA Average (mg/kg)
Hg	0.219-0.220	0.216-0.228	0.220	0.222
Cd	0.193-0.196	0.185-0.193	0.195	0.189
Zn	67.1-68.2	66.3-67.9	67.7	67.1

Table 4.1 Recovery of mercury from fish and sediments

Sample	Hg added (ng/g)	Hg found (ng/g)	Hg recovered (ng/g)	% Recovery
Synodontis sp. (0.5g)	0	145.80	-	-
	25	169.83	24.03	96.12
	50	195.00	49.20	98.40
Tilapia zilli (0.5g)	0	158.33	-	-
	25	183.60	25.27	101.08
	50	208.24	49.91	99.82
Buabenso Sediment (BUA S4) (0.2g)	0	290.00	-	-
	25	314.00	24.00	96.00
	50	339.30	49.30	98.60
Dunkwa Sediment (DUN S1) (0.2g)	0	286.45	-	-
	25	311.90	25.45	101.80
	50	335.49	49.04	98.08

Table 4.2 Recovery of Zinc from fish and sediments

Sample	Zn added (mg/kg)	Zn found (mg/kg)	Zn recovered (mg/kg)	% Recovery
Synodontis sp. (0.5g)	0	18.06	-	-
	0.8	18.82	0.76	95.00
	1.0	19.03	0.97	97.00
Tilapia zilli (0.5g)	0	22.22	-	-
	0.8	23.01	0.79	98.75
	1.0	23.21	0.99	99.00
Buabenso Sediment (BUA S4) (0.2g)	0	80.24	-	-
	0.8	81.07	0.83	103.75
	1.0	81.25	1.01	101.00
Dunkwa Sediment (DUN S1) (0.2g)	0	66.58	-	-
	0.8	67.36	0.78	97.50
	1.0	67.56	0.98	98.00

Table 4.3 Recovery of Cadmium from fish and sediments

Sample	Cd added (mg/kg)	Cd found (mg/kg)	Cd recovered (mg/kg)	% Recovery
Synodontis sp. (0.5g)	0	25.40	-	-
	3.0	28.39	2.99	99.67
	5.0	30.37	4.97	99.40
Tilapia zilli (0.5g)	0	10.22	-	-
	3.0	13.25	3.03	101.00
	5.0	15.14	4.92	98.40
Buabenso Sediment (BUA S4) (0.2g)	0	47.86	-	-
	3.0	50.96	3.10	103.33
	5.0	52.88	5.02	100.40
Dunkwa Sediment (DUN S1) (0.2g)	0	53.47	-	-
	3.0	56.45	2.98	99.33
	5.0	58.57	5.10	102.00

4.1 Total Mercury Concentrations in Different Fish Species and Sediments

Thirty (30) fish samples representing five (5) fish species namely *Tilapia zilli* (Tedea; Apatrɛ; Apataa), *Chrysichthys nigrodigitatus* (Nkontro), *Oreochromis niloticus* (Apatrɛ; Apataa; Mpatoa), *Heterobranchus sp.* (Adwene) and *Sarotherodon melanotheron* (Apatrɛ; Apataa; Mpatoa) were obtained from Dominase. Four sediment samples were taken from the river bed and a soil sample which serves as a control was taken 200 m away from the river bank. Total mercury (Hg) concentration for *Tilapia zilli* (n=13) yielded a mean muscle tissue mercury concentration of 222.18±85.99 ng/g wet weight and mercury concentration range from 96.33 to 403.05 ng/g wet weight. Mercury concentration in ng/g wet weight in *Chrysichthys nigrodigitatus* ranged from 182.75 to 409.49 (mean=311.35±83.07, n=5), from 90.79 to 228.87 (mean=165.31±69.69, n=3) for *Oreochromis niloticus*, from 34.77 to 38.28 (mean=35.79±1.42, n=5) for *Heterobranchus sp.* and from 82.72 to 316.42 (mean=146.33±113.59, n=4) for *Sarotherodon melanotheron*. All the fish samples from Dominase showed mercury concentrations below the World Health Organisation (WHO) limit of 500 ng/g wet weight. Trophic level defines the feeding position of an organism in a food chain as primary producer, herbivore, primary carnivore, etc. Beckvar *et al*. (1996) reported that diet has a significant role in the overall body burden of mercury, both between and within species. Differences in total mercury concentrations between species reflect diet differences due to trophic position; within-species differences are related to dietary requirements of various developmental stages. The levels of mercury obtained conform to the observations made by Beckvar *et al*. (1996). For instance, *Chrysichthys nigrodigitatus* at trophic level 2.6 had a higher mean Hg concentration (ng/g wet weight) of 311.35±83.07

than 146.33±113.59 for *Sarotherodon melanotheron* (trophic level 2.5) which is at a trophic level just 0.1 below that of *Chrysichthys nigrodigitatus.* Several researchers have documented a positive relationship between Hg concentrations and fish length, weight and/or age (Beckvar *et al*., 1996; Bidone *et al*., 1997; Lacerda *et al*., 2000; Lange *et al*., 1994; Ward and Neumann, 1999; Wiener and Spry, 1996). A good correlation was observed between muscle tissue Hg concentration and fresh weight of fish for *Chrysichthys nigrodigitatus* (r^2 = 0.6526), *Oreochromis niloticus* (r^2 = 0.9131) and *Heterobranchus sp.* (r^2 = 0.6203) whereas a poor correlation was observed for *Tilapia zilli* (r^2 = 0.0835) and *Sarotherodon melanotheron* (r^2 = 0.3181). A poor correlation between muscle tissue Hg concentration and total fish length was however observed for all the species; *Tilapia zilli* (r^2 = 0.0845), *Chrysichthys nigrodigitatus* (r^2 = 0.3237), *Oreochromis niloticus* (r^2 = 0.0722), *Heterobranchus sp.* (r^2 = 0.0709), and *Sarotherodon melanotheron* (r^2 = 0.3174). Though the average mercury level of 144.55±38.21 ng/g recorded in sediment from Dominase was higher than the 97.45 ng/g recorded for control, it was below the WHO/FAO maximum permissible limit in sediments of 1000 ng/g.

Oreochromis niloticus (Apatrɛ; Apataa; Mpatoa), *Tilapia zilli* (Tedea; Apatrɛ; Apataa), *Heterobranchus sp.* (Adwene) and *Labeo coubie* (Apempemabo) obtained from Nkotumso recorded total Hg concentrations in their muscle tissue well below the WHO limit. The Hg concentration in ng/g wet weight recorded in the muscle tissue of *Oreochromis niloticus* ranged from 59.79 to 247.51 (mean=132.13±53.51, n=14), from 57.16 to 97.60 (mean=78.97±19.71, n=6) for *Tilapia zilli*, from 1.02 to 168.44 (mean=88.69±79.58, n=4) for *Heterobranchus sp.* and from 100.83 to 190.76

(mean=121.35±34.33, n=6) for *Labeo coubie*. A poor correlation was observed between muscle tissue Hg concentration and fresh weight for *Oreochromis niloticus* (r^2=0.1755), *Tilapia zilli* (r^2=0.0053) and *Labeo coubie* (r^2 =0.2012). There were also no significant correlation between muscle tissue Hg concentration and total length for *Oreochromis niloticus* (r^2=0.1425), *Tilapia zilli* (r^2=0.0662) and *Labeo coubie* (r^2 =0.1252). However, a significant correlation was observed between muscle tissue Hg concentration, fresh weight (r^2=0.9216) and total length (r^2=0.8098) for *Heterobranchus sp.* High correlation between muscle tissue mercury concentration and total length and fresh weight of fish are normally observed among piscivorous species whereas poor correlations between these parameters are observed among herbivorous species (Lange *et al*., 1994). A similar observation was made in this study. *Heterobranchus sp.* a piscivorous fish with trophic level usually above 3.0 exhibited a significant correlation between mercury concentration and total length and fresh weight whereas *Oreochromis niloticus*, *Tilapia zilli* and *Labeo coubie* herbivorous species all of trophic level 2.0 showed no significant correlation.

Boszke *et al.* (2003) reported that the inter-species differences in mercury concentrations in crustaceans can be related to different feeding habits of the species. For example, the benthic crustacean *Crangon crangon* is mainly exposed to mercury contained in the bottom sediment, while *Palaemon adspersus* is specie living among aquatic plants. Regression analysis gave a negative relationship ($p<0.05$) between total mercury concentration and body length/weight only for *Palaemon adspersus*. An elevated level of mercury with a mean of 1010.08±102.89 ng/g was recorded in sediment relative to 137.80 ng/g of the control but sediment levels do not correlate to levels in fish. An elevated level of mercury in the sediment which does not correlate to levels in fish might

be due to high concentrations of organic substances and reduced sulfur that complexes free Hg (II) ions in sediments thus reducing the availability of mercury to biota (Rubinstein et al., 1983). Many investigators have also reported no correlation between sediment and tissue concentrations of mercury for higher-trophic-level species (Duckerschein et al., 1992; Lindqvist, 1991) such as *Heterobranchus sp.*.

Among the eight fish species obtained from Dunkwa-on-Offin, a muscle tissue Hg concentration in ng/g wet weight ranging from 63.92 to 259.76 (mean=145.39±68.61, n=10) was recorded for *Oreochromis niloticus* (Apatrɛ; Apataa; Mpatoa), from 264.39 to 756.83 (mean=473.24±213.27, n=5) for *Chrysichthys nigrodigitatus* (Nkontro), from 120.75 to 157.90 (mean=143.77±16.49, n=5) for *Labeo coubie* (Apempemabo), from 97.90 to 173.52 (mean=141.58±39.16, n=3) for *Brycinus sp.*(Atɛsoɔ) and from 379.50 to 794.59 (mean=587.04±293.52, n=2) for *Hepsetus odoe* (Odom). Specie each of *Mormyrus sp.* (Deasera), *Papyrocranus afer* (Supako) and *Heterobranchus sp.*(Adwene) also yielded muscle concentration of 46.81, 53.29 and 65.72 ng/g wet weight respectively. The highest muscle tissue mercury concentration of 794.59 ng/g wet weight was recorded in *Hepsetus odoe* whereas the lowest of 46.81 ng/g wet weight was recorded in *Mormyrus sp.*. With the exception of a specie of *Hepsetus odoe* which recorded the highest Hg concentration (794.59 ng/g) and two species of *Chrysichthys nigrodigitatus* (756.83 ng/g and 630.38 ng/g) all the fish samples studied showed muscle tissue mercury concentrations below the World Health Organisation (WHO) limit of 500 ng/g wet weight. An increase in muscle tissue Hg concentration with trophic level was observed. *Hepsetus odoe* at trophic level 4.5 recorded mean muscle tissue Hg concentration of 587.04±293.52 ng/g wet weight, *Chrysichthys nigrodigitatus* at trophic

level 2.6 recorded mean muscle tissue Hg concentration of 473.24±213.27 ng/g wet weight whereas *Oreochromis niloticus* at trophic level 2.0 recorded mean muscle tissue Hg concentration of 145.39±68.61 ng/g weight wet. Thus muscle tissue Hg concentrations increased with trophic levels. However, the increase in Hg concentrations with trophic levels observed in this study was larger between *Oreochromis niloticus* (trophic level 2.0) and *Chrysichthys nigrodigitatus* (trophic level 2.6) than between *Chrysichthys nigrodigitatus* (trophic level 2.6) and *Hepsetus odoe* (trophic level 4.5). The levels of mercury obtained also indicated that fish of the same species from Dunkwa-on-Offin had different concentrations of mercury.

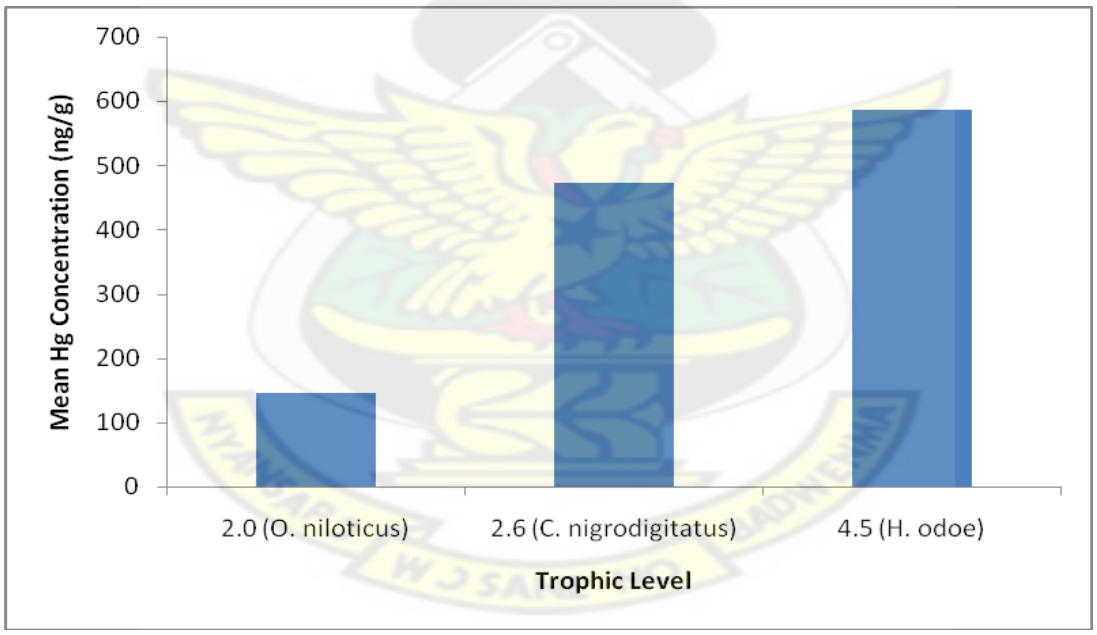

Fig. 4.18 Relationship between Mean Hg Concentration in fish and Trophic Level.

A significant correlation was observed between muscle tissue Hg concentration and fresh weight of fish for *Labeo coubie* (r^2 = 0.7260) but that obtained for *Oreochromis niloticus* (r^2 = 0.1605), *Chrysichthys nigrodigitatus* (r^2 = 0.4094) and *Brycinus sp.* (r^2 = 0.1594)

were insignificant. Again, a good correlation was obtained between muscle tissue Hg concentration and total length of fish for *Labeo coubie* (r^2 = 0.9638) but poor correlation was obtained for *Oreochromis niloticus* (r^2 = 0.4948), *Chrysichthys nigrodigitatus* (r^2 = 0.4518) and *Brycinus sp.* (r^2 = 0.1153). Correlation values were not determined for *Hepsetus odoe* (n=2), *Mormyrus sp.* (n=1), *Papyrocranus afer* (n=1) and *Heterobranchus sp.* (n=1) because at least three values or samples are required for regression analysis to determine correlation. Though the average mercury levels in sediment from Dunkwa-on-Offin 186.15±77.18 ng/g was higher than the control 44.61 ng/g, it was below the WHO/FAO maximum permissible limit in sediment of 1000 ng/g. There was no correlation between mercury levels in sediment and fish. A similar finding was reported by Rose *et al.*, 1999.

Fishes obtained from Buabenso gave a muscle tissue Hg concentration in ng/g wet weight range from 115.46 to 649.40 (mean=257.14±132.71, n=23) for *Synodontis sp.* (Kokochichi; Obochichi), from 211.06 to 411.16 (mean=299.40±102.08, n=3) for *Chrysichthys nigrodigitatus* (Nkontro), from 153.63 to 179.29 (mean=166.46±18.15, n=2) for *Tilapia zilli* (Tedea; Apatrɛ; Apataa), and from 105.32 to 112.73 (mean=109.02±5.24, n=2) for *Schilbe mystus* (Abadeɛ). A *Synodontis sp.* had muscle tissue Hg concentration of 649.40 ng/g wet weight which was above the WHO limit but the rest were below this limit. Correlation between muscle tissue Hg concentration and fresh weight (r^2=0.0749), and total length (r^2=0.0469) was found for *Synodontis sp.* There were, however, a good correlation between muscle tissue Hg concentration and fresh weight (r^2=0.9835), and total length (r^2=0.9817) for *Chrysichthys nigrodigitatus.* Though

Schilbe mystus is at trophic level 3.3 and *Tilapia zilli* is at trophic level 2.0 (lowest trophic level specie among Buabenso fish), *Schilbe mystus* recorded the lowest tissue Hg concentration of 105.32 ng/g wet weight contrary to observation made by Becker and Bigham (1995), and Beckvar *et al*. (1996) that high trophic level fish tend to have a higher Hg concentration than low trophic level fish in an aquatic food chain. An average mercury concentration of 424.30±260.12 ng/g was recorded for sediment and 72.60 ng/g for control. This was below the WHO/FAO Hg limit in sediments. Correlation was poor between Hg concentration in fish and the sediments. This conforms to observation made by other researchers (Rose *et al*., 1999).

The thirty fish samples obtained from Awisam consisted of only *Synodontis sp.*(Kokochichi; Obochichi) which gave muscle tissue Hg concentration range from 140.86 to 795.94 ng/g wet weight with a mean of 289.76±125.60 ng/g wet weight. Varied mercury concentrations in muscle were observed among the thirty *Synodontis sp.* and this might be due to different *Synodontis* species that were found within the family Mochokidae as well as different feeding patterns among the same *Synodontis sp.*. With exception of a specie which had an elevated Hg concentration of 795.94 ng/g wet weight, all the species had Hg concentration falling below the WHO limit of 500 ng/g wet weight. A poor correlation was observed between muscle tissue Hg concentration and fresh weight (r^2 = 0.4042) and total length (r^2 = 0.0149). An average mercury concentration in sediment was found to be 96.11±30.07 ng/g whereas that of the control was 61.55 ng/g. Sediment level was below the WHO/FAO limit of 1000 ng/g. Correlation between Hg in fish and sediment was poor and this is in agreement with the observation

made by Rose *et al*. (1999) who reported that mercury concentrations in bed sediments are not necessarily correlated with concentration in fish tissue.

Generally, a regression analysis carried between the mean average of Hg in fish and mean of Hg in sediment from all the five sampling areas gave negative correlation (r^2= -0.638).

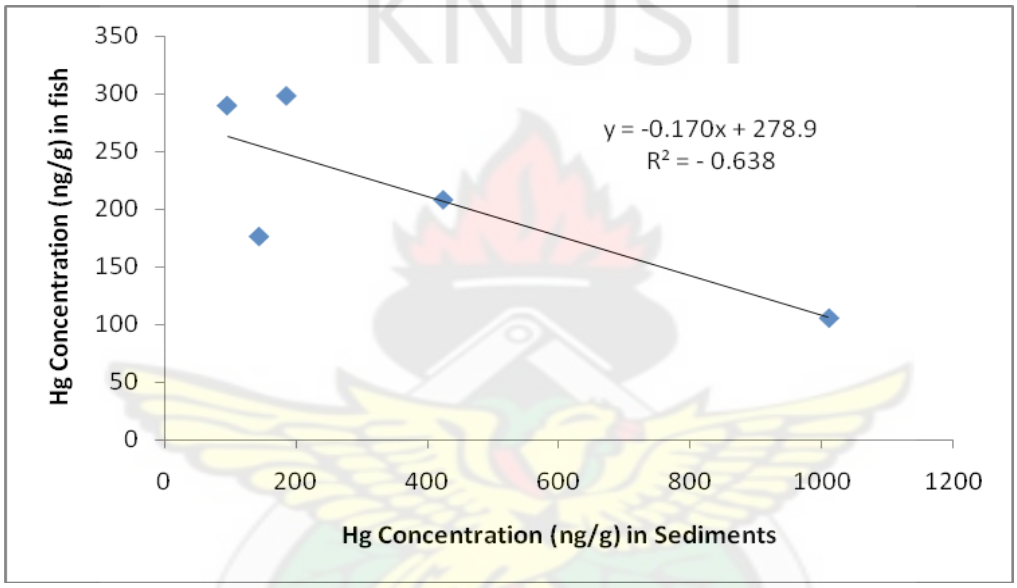

Fig. 4.33 Correlation between Hg concentration in Fish and Sediments

This implies that as Hg concentration in the sediment increases, there will be low concentrations in the water column thus translating to low Hg concentration in fish with increasing Hg in sediments as long as the fish is not feeding on sediment particles. Factors that control methylation such as microbial activity and mercury in sediment (upper layer), dissolved organic content (humic content), salinity, pH, and redox potential (WHO, 1990) may not favour methylation process in the Offin basin. Again, mercury

distribution in both fish and sediment showed an irregular trend as the river flows towards River Pra at Awisam.

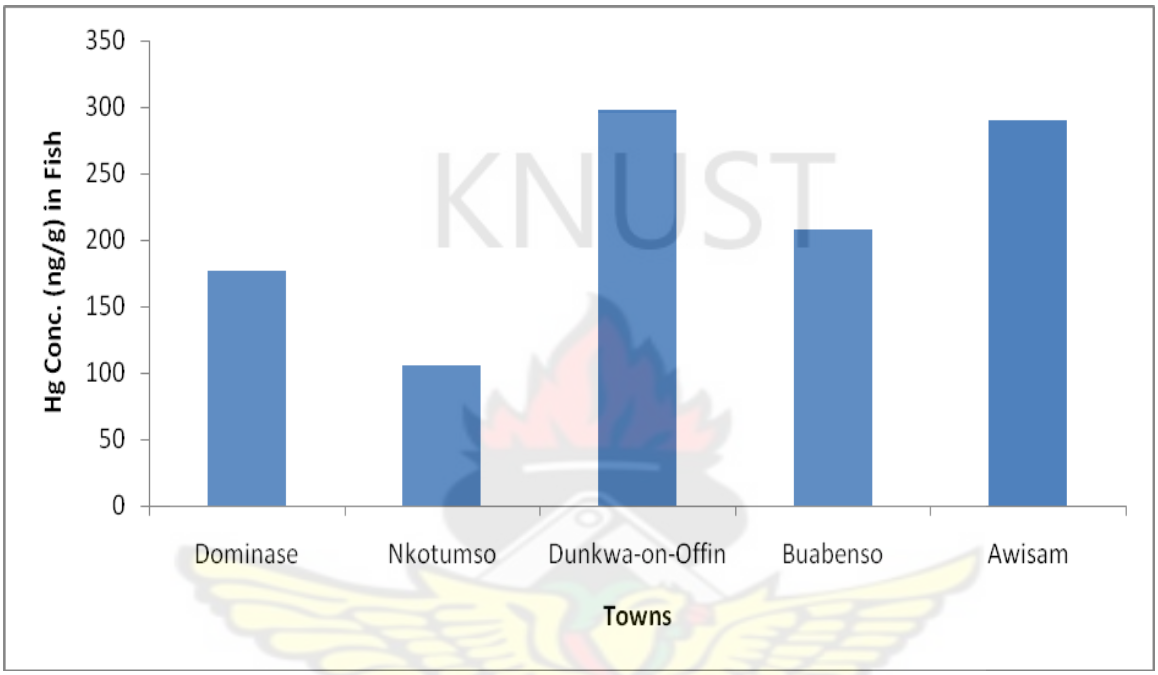

Fig. 4.34 Mercury distribution in fish in all sampling areas

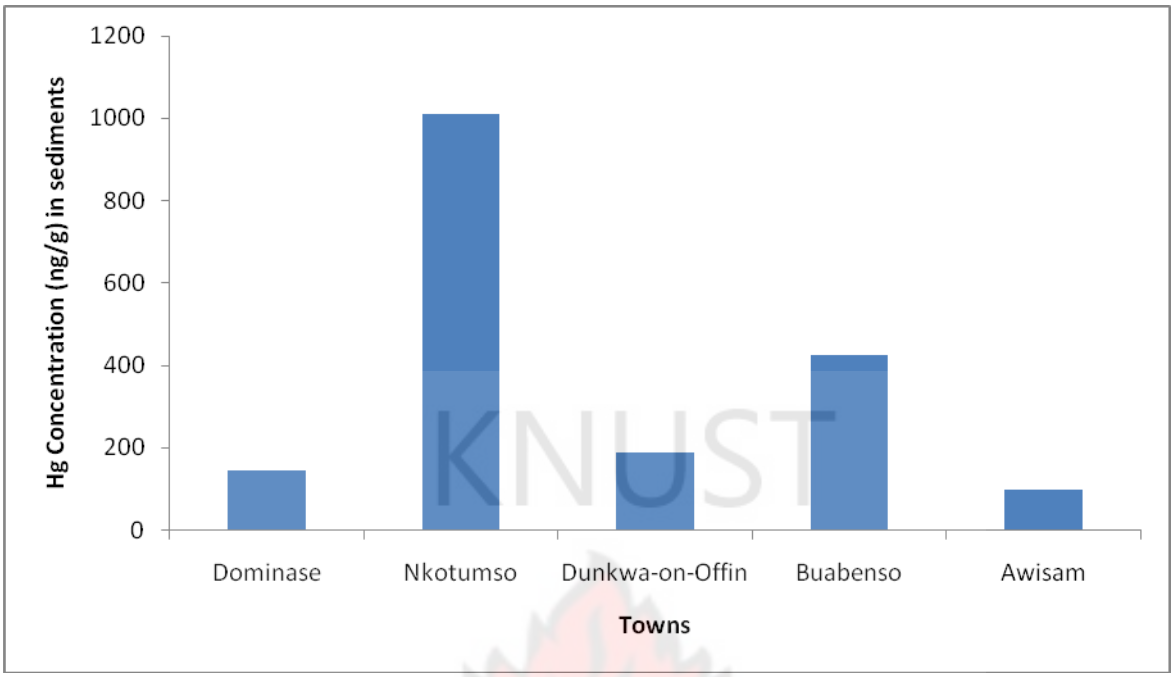

Fig. 4.35 Mercury distribution in sediments in all sampling areas

Table 4.4 Total Hg, Zn and Cd Concentrations in fish muscle samples from Dominase, Nkotumso, Dunkwa-on-Offin, Buabenso and Awisam

Specie Name (local name in Akan)	Sample size(n)	Trophic level*	Mean Total Length (range, cm)	Mean Fresh Weight (range, g)	Mean Hg Concentration (range, ng/g)	Mean Zn Concentration (range, mg/kg)	Mean Cd Concentration (range, mg/kg)
Dominase							
Tilapia zilli (Tedea; Apatrɛ; Apataa)	13	2.0	19.11±2.50 (15.70 - 25.00)	168.31±73.53 (85.51 - 368.31)	222.18±85.99 (96.33 - 403.05)	8.21±1.88 (ND – 11.05)	0.10 (ND – 0.10)
Chrysichthys nigrodigitatus (Nkontro)	5	2.6	25.02±1.60 (23.30 - 26.70)	205.10±39.22 (171.20 - 265.75)	311.35±83.07 (182.75 - 409.49)	10.45±3.37 (4.47 – 12.52)	0.10 (ND – 0.10)
Oreochromis niloticus (Apatrɛ; Apataa; Mpatoa)	3	2.0	22.47±0.25 (22.20 - 22.70)	261.15±22.25 (246.40 - 286.75)	165.31±69.69 (90.79 - 228.87)	4.03±2.05 (ND – 5.48)	ND
Heterobranchus sp. (Adwene)	5	3.2-3.7	32.42±1.92 (30.10 - 35.00)	292.60±30.72 (261.22 - 335.85)	35.79±1.42 (34.77 - 38.28)	4.21±1.58 (2.58 – 6.67)	0.10 (ND – 0.10)
Sarotherodon melanotheron (Apatrɛ; Apataa; Mpatoa)	4	2.5	22.40±2.89 (19.80 - 25.00)	235.88±100.25 (145.81 - 324.10)	146.33±113.59 (82.72 - 316.42)	ND	0.10 (ND – 0.10)
Nkotumso							
Oreochromis niloticus (Apatrɛ; Apataa; Mpatoa)	14	2.0	17.92±2.28 (14.00 - 21.50)	150.31±54.72 (56.14 - 262.42)	132.13±53.51 (59.79 - 247.51)	5.41±1.99 (1.29 – 8.07)	0.10 (ND – 0.10)
Tilapia zilli (Tedea; Apatrɛ; Apataa)	6	2.0	14.28±1.71 (11.30 - 15.80)	66.18±16.17 (41.12 - 82.70)	78.97±19.71 (57.16 - 97.60)	7.26±2.62 (5.12 – 12.38)	ND
Heterobranchus sp. (Adwene)	4	3.2-3.7	33.80±15.31 (15.80 - 47.50)	383.33±312.25 (85.50 - 663.01)	88.69±79.58 (1.02-168.44)	5.29±2.88 (2.17 – 8.32)	ND

Table 4.4 Continued

Specie Name (local name in Akan)	Sample size(n)	Trophic level*	Mean Total Length (range, cm)	Mean Fresh Weight (range, g)	Mean Hg Concentration (range, ng/g)	Mean Zn Concentration (range, mg/kg)	Mean Cd Concentration (range, mg/kg)
Labeo coubie (Apempemabo)	6	2.0	20.77±1.07 (19.10 - 21.70)	183.98±31.81 (133.22 - 207.01)	121.35±34.33 (100.83 - 190.76)	1.83±1.24 (ND – 3.17)	ND
Dunkwa-on-Offin							
Oreochromis niloticus (Apatrɛ; Apataa; Mpatoa)	10	2.0	17.17±0.91 (15.50 - 18.60)	117.01±17.61 (85.90 - 139.75)	145.39±68.61 (63.92 - 259.76)	5.67±0.98 (4.13 – 7.37)	0.10 (ND – 0.10)
Chrysichthys nigrodigitatus (Nkontro)	5	2.6	20.14±2.29 (17.40 - 23.00)	112.96±36.85 (79.44 - 171.41)	473.24±213.27 (264.39 - 756.83)	8.03±2.28 (5.66 – 11.45)	ND
Labeo coubie (Apempemabo)	5	2.0	19.10±1.44 (16.70 - 20.30)	159.25±37.90 (105.09 - 191.16)	143.77±16.49 (120.75 - 157.90)	8.01±1.28 (7.02 – 10.02)	0.10 (ND – 0.10)
Brycinus sp. (Atɛsoɔ)	3	2.2-3.3	20.77±3.59 (18.40 - 24.90)	173.03±101.91 (99.82 - 289.42)	141.58±39.16 (97.90 - 173.52)	7.57±1.84 (5.58 – 9.21)	0.10 (ND – 0.10)
Hepsetus odoe (Odom)	2	4.5	24.30±0.85 (23.70 - 24.90)	117.51 (117.51)	587.04±293.52 (379.50 - 794.59)	10.40±0.88 (9.78 – 11.02)	ND
Buabenso							
Synodontis sp. (Kokochichi; Obochichi)	23	2.7-3.4	19.93±5.04 (13.50 - 32.00)	86.42±65.63 (24.32 - 278.40)	257.14±132.71 (115.46 - 649.40)	3.22±1.03 (ND – 5.38)	0.10 (ND – 0.10)
Chrysichthys nigrodigitatus (Nkontro)	3	2.6	23.17±0.45 (22.70 - 23.60)	118.64±22.71 (92.91 - 135.90)	299.40±102.08 (211.06 - 411.16)	ND	ND

Table 4.4 Continued

Specie Name (local name in Akan)	Sample size(n)	Trophic level*	Mean Total Length (range, cm)	Mean Fresh Weight (range, g)	Mean Hg Concentration (range, ng/g)	Mean Zn Concentration (range, mg/kg)	Mean Cd Concentration (range, mg/kg)
Tilapia zilli (Tedea; Apatrɛ; Apataa)	2	2.0	17.60±1.13 (16.80 - 18.40)	103.13±26.61 (84.31 - 121.94)	166.46±18.15 (153.63 - 179.29)	ND	ND
Schilbe mystus (Abadeɛ)	2	3.3	14.80±0.99 (14.10 - 15.50)	30.01±7.76 (24.53 - 35.50)	109.02±5.24 (105.32 - 112.73)	ND	ND
Awisam							
Synodontis sp. (Kokochichi; Obochichi)	30	2.7-3.4	19.58±2.79 (15.00 - 24.80)	86.63±30.68 (40.48 - 171.60)	289.76±125.60 (140.86 - 795.94)	6.47±2.83 (2.87 – 18.16)	0.09 (ND – 0.10)

***sp.* = specie** ***adapted from: Fishbase.org (2003)** **ND = Not Detected**

4.2 Total Zinc Concentrations in Different Fish Species and Sediments

The total zinc (Zn) concentration in fish muscle from the five experimental locations in the Offin River is presented in Table 4.4. The total Zn concentration in mg/kg wet weight in the edible muscle tissue of fish from Dominase ranged from below detection to 11.05 (mean=8.21±1.88, n=13) for *Tilapia zilli*, from 4.47 to 12.52 (mean=10.45±3.37, n=5) for *Chrysichthys nigrodigitatus*, from below detection to 5.48 (mean=4.03±2.05, n=3) for *Oreochromis niloticus* and from 2.58 to 6.67 (mean=4.21±1.58, n=5) for *Heterobranchus sp.*. However, the level of zinc in the muscle tissue was below the instrumental detection limit for the four samples of *Sarotherodon melanotheron* (Apatrɛ; Apataa; Mpatoa). This might be due to the low ability of *Sarotherodon melanotheron* (Apatrɛ; Apataa; Mpatoa) to accumulate Zn or good ability to excrete it from the body compared to the other species. A similar finding has been made by Amoo *et al.* (2003). Zinc concentrations in all fish analysed were below the WHO maximum permissible limit of 1000 mg/kg and the general guideline limit for zinc in food of 50 mg/kg (Zienab, 2006). The soil sample (control) recorded higher Zn concentration (35.57 mg/kg) than the sediment which recorded a mean concentration of 23.54±6.34 mg/kg. The sediment Zn concentration recorded is higher than 16 mg/kg, the mean Zn recorded in sediment from Wiwi River (Biney and Beeko, 1991). However, the mean Zn levels in sediment obtained at Dominase is lower than the mean of 82.5 mg/kg reported for sediments from Africa inland waters (Committee for Inland Fisheries of Africa, 1992), 95 mg/kg been the level reported for unpolluted sediments (GESAMP, 1982; Salomons and Forstner, 1984) as well as the widely used Canadian sediment guidelines for the protection of aquatic life of 124 mg/kg (CCME, 1999).

Oreochromis niloticus (n=14), *Tilapia zilli* (n=6), *Heterobranchus sp.* (n=4) and *Labeo coubie* (n=6) obtained from Nkotumso recorded total Zn concentration in muscle tissue range in mg/kg wet weight in their muscle tissue from 1.29 to 8.07 (mean=5.41±1.99), from 5.12 to 12.38 (mean=7.26±2.62), from 2.17 to 8.32 (mean=5.29±2.88) and from below detection to 3.17 (mean=1.83±1.24) respectively. The general range for Zn concentration in fish muscle tissue is from below detection to 12.38 mg/kg. Though levels of Zn in fish were lower than WHO limit and general guideline limit for food, it was slightly higher than the range (3.0 to 11.8 mg/kg) reported for fish in Africa inland waters by Committee for Inland Fisheries of Africa (1992). The mean average of all the fishes from Nkotumso 4.95±2.27 mg/kg was however lower than the 6.65±0.45 mg/kg reported by *Oze et al*. (2006) for fish in Qua-Iboe river in Nigeria. The sediments yielded an average of 20.44±4.78 mg/kg whereas the control recorded 25.50 mg/kg. Higher Zn concentration in soil (control) than sediment suggest that levels in sediment might be due to erosion of soil or water runoffs from mine fields carrying zinc into the Offin River following rain event. Bioavailability of Zn in the aquatic environment was not favoured as indicated by low fish Zn levels relative to that of the sediments. Zn sediment levels were below the level reported for unpolluted sediments (GESAMP, 1982; Salomons and Forstner, 1984) as well as Canadian sediment guidelines for the protection of aquatic life (CCME, 1999).

The levels of Zn in mg/kg wet weight found in the muscle tissues of fish from Dunkwa-on-Offin falls within the following ranges: from 4.13 to 7.37 (mean=5.67±0.98, n=10) for *Oreochromis niloticus*, from 5.66 to 11.45 (mean=8.03±2.28, n=5) for *Chrysichthys nigrodigitatus*, from 7.02 to 10.02 (mean=8.01±1.28, n=5) for *Labeo coubie*, from 5.58-

9.21 (mean=7.57±1.84, n=3) for *Brycinus sp.*, from 9.78 to 11.02 (mean=10.40±0.88, n=2) for *Hepsetus odoe*. Zn concentration in muscle tissues of specie each of *Mormyrus sp.*, *Papyrocranus afer* and *Heterobranchus sp.* were 10.02, 11.63 and 12.85 mg/kg respectively. Zinc levels in muscle tissue of all the fish were below the WHO maximum permissible limit of 1000 mg/kg and the general guideline limit for zinc in food of 50 mg/kg (Zienab, 2006). Levels of Zn recorded in all the fish from Dunkwa-on-Offin ranged from 4.13 to 12.85 mg/kg with a mean average of 9.27±2.37 mg/kg. These levels observed were higher than those reported by other researchers in Africa. Biney and Beeko (1991) reported 3.0 mg/kg of zinc in fish from Wiwi River, Ghana and Committee for Inland Fisheries of Africa (1992) also reported Zn range in fish in Africa inland waters from 3.0 to 11.8 mg/kg. The elevated levels observed might be due to the extensive mining activities in the Offin River. An average of 25.81±6.55 mg/kg was measured in four river sediments relative to a higher value of 81.49 mg/kg for the soil (control). The Zn concentration in sediments were below 95 mg/kg, the level reported for unpolluted sediments (GESAMP, 1982; Salomons and Forstner, 1984) as well as the Canadian sediment guidelines for the protection of aquatic life of 124 mg/kg (CCME, 1999). Sediment Zn levels were higher than those recorded for fish suggesting that bioavailability is not favoured by factors such as pH, hardness, alkalinity, dissolved oxygen, temperature, complexing ligands and zinc concentration (EPA, 2003; Weatherley *et al.*, 1980).

With exception of *Synodontis sp*. (n=23) which recorded muscle tissue Zn concentration range from below detection limit to 5.38 mg/kg wet weight (mean 3.22±1.03 mg/kg) which was below the WHO limit, all the fish species from Buabenso namely,

Chrysichthys nigrodigitatus (n=3), *Tilapia zilli* (n=2), and *Schilbe mystus* (n=2) had levels of zinc below the detection level of the instrument. The mean Zn concentration recorded for the sediment was 34.93±14.71 mg/kg whereas 8.45 mg/kg was observed for the control. This was contrary to the observation made in the other four sampling areas. Mean levels of Zn was about 11 times higher in sediment than in fish suggesting that bioavailability is not favoured by factors such as pH, hardness, alkalinity, dissolved oxygen, temperature, complexing ligands and zinc concentration (EPA, 2003; Weatherley *et al.*, 1980) and that the sediment is acting as a depository for zinc in the Offin River at Buabenso. However, the Zn concentration in sediments were below 95 mg/kg, the level reported for unpolluted sediments (GESAMP, 1982; Salomons and Forstner, 1984) as well as the widely used Canadian sediment guidelines for the protection of aquatic life of 124 mg/kg (CCME, 1999).

Thirty *Synodontis sp*. from Awisam recorded a range from 2.87 to 18.16 mg Zn/kg wet weight in muscle tissues with a mean of 6.47±2.83 mg Zn/kg. In all the fish samples analysed, the maximum zinc concentration (18.16 mg/kg wet weight) determined was in *Synodontis sp*. from Awisam. Though Zn levels were below the WHO limit and the general guideline limit for Zn in food, it was however, higher than the range (3.0-5.6 µg/g) reported by Biney *et al*. (1994) for fish from West African inland waters and a range from 1.32 to 5.08 mg/kg in fish species from river Nile at Hawamdia and Kafer-El-Zayat (Khallaf *et al.*, 1994). The mean Zn concentration of 6.47±2.83 mg Zn/kg was lower than the 6.65 ± 0.45 mg/kg reported by Oze *et al*. (2006) for fish in Qua-Iboe River in Nigeria. Levels of 57.46 mg Zn/kg and 21.58±6.40 mg Zn/kg were recorded for soil (control) and mean sediment respectively. Levels of zinc in sediments was higher than

those determined in fish indicating that the sediment is acting as a depository for zinc as have been observed by Besada *et al.* (2002) and Eja *et al.* (2003). Zn sediment levels were below the 95 mg/kg level reported for unpolluted sediments (GESAMP, 1982; Salomons and Forstner, 1984) as well as 124 mg/kg Canadian sediment guidelines for the protection of aquatic life (CCME, 1999).

Generally, there was poor correlation between zinc levels in fish and sediments. An irregular distribution of zinc in fish and sediments was observed as the river flows downstream towards river Pra.

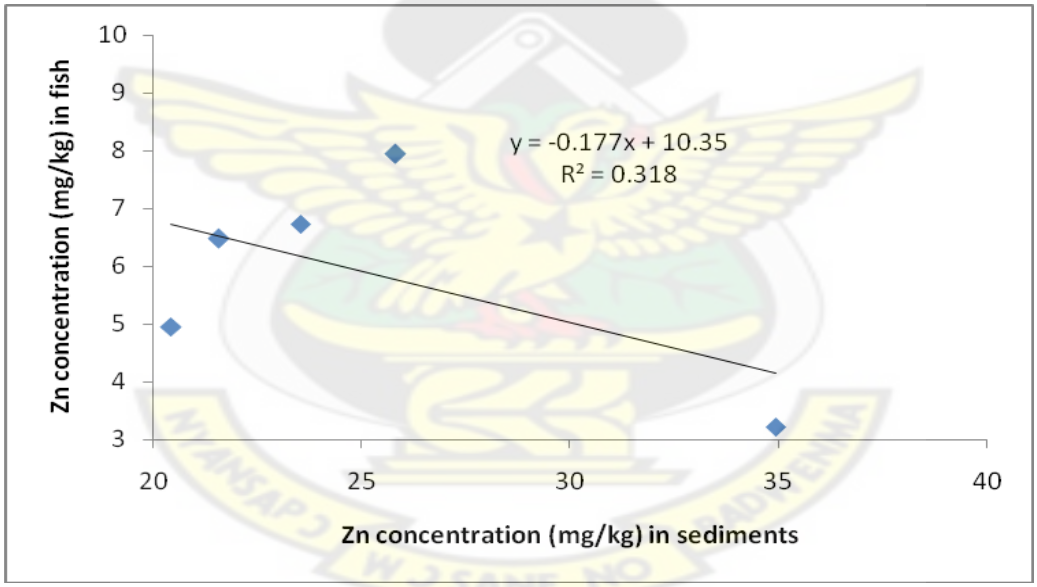

Fig. 4.36 Correlation between Zn Concentration in Fish and Sediments

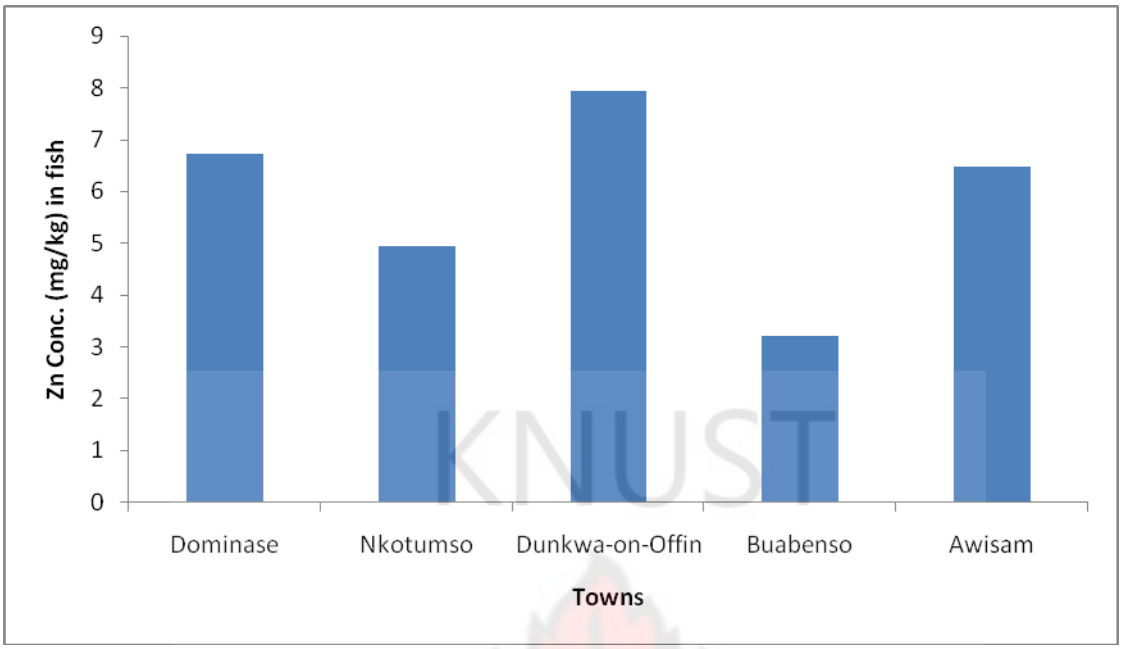

Fig. 4.37 Distribution of Zinc in fish in all sampling areas

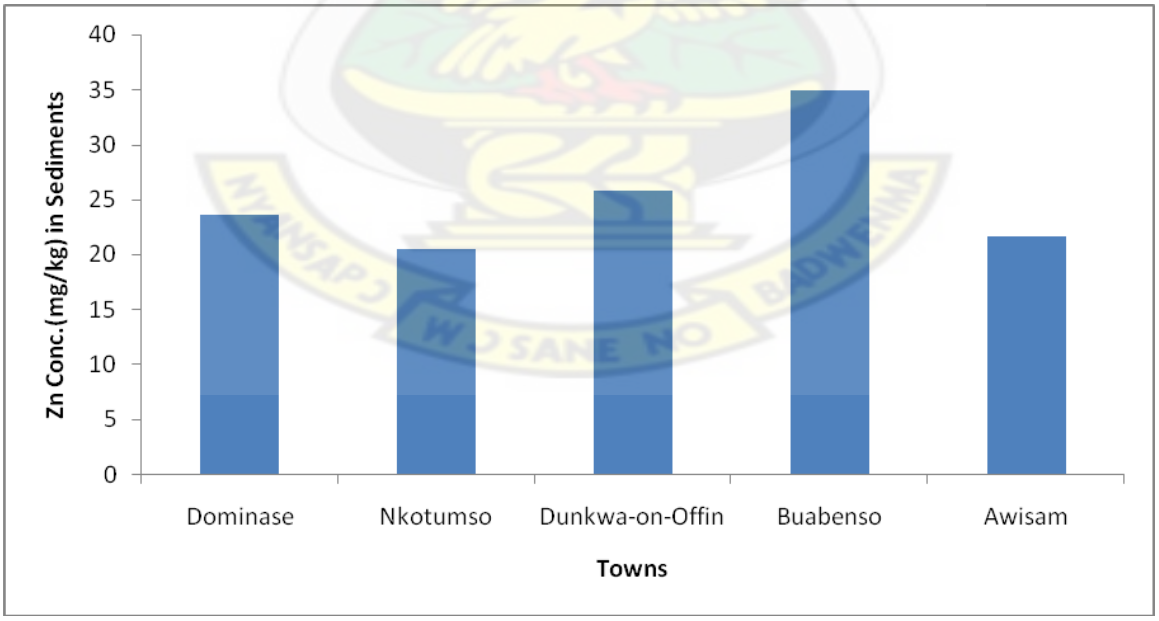

Fig. 4.38 Distribution of Zinc in sediments in all sampling areas

4.3 Total Cadmium Concentrations in Different Fish Species and Sediments

Cadmium concentrations in fish muscle from the five experimental locations along the Offin River are presented in Table 4.4. The total Cd concentration in mg/kg wet weight in the edible muscle tissue of fish from Dominase ranged from below detection to 0.10 (mean=0.10, n=13) for *Tilapia zilli*, from below detection to 0.10 (mean=0.10, n=5) for *Chrysichthys nigrodigitatus*, from below detection to 0.10 (mean=0.10, n=5) for *Heterobranchus sp.* and from below detection to 0.10 (mean=0.10, n=4) for *Sarotherodon melanotheron*. Three individual samples of *Oreochromis niloticus* had Cd levels below the instrument's detection limit. Cd levels recorded in fish were below the WHO/FAO standard of 1.0 mg/kg wet weight for fish (JECFA, 2002). Though low, Cd levels were consistent with values reported by Obasohan *et al.*(2006) who investigated the monthly variations of heavy metals in *Malapterurus electricus* and *Chrysichthys nigrodigitatus* from Ogba River in Benin City, Nigeria and reported an annual mean Cd range in mg/kg wet weight from 0.03 to 0.12 and 0.04 to 0.13 respectively.

With the exception of *Oreochromis niloticus* (n=14) which recorded Cd concentration range from below detection to 0.10 mg/kg fresh weight (mean=0.10 mg/kg) in edible muscle tissue which was below the WHO/FAO limit, all other species from Nkotumso namely *Tilapia zilli* (n=6), *Heterobranchus sp*. (n=4) and *Labeo coubie* (n=6) recorded Cd concentrations below the instrument's detection limit. However, Cd levels measured are comparable to the range from 0.05 to 0.13 mg/kg in fish spices from river Nile at Hawamdia and Kafer-El-Zayat (Khallaf *et al*., 1994). It is lower than 0.38 ± 0.06 mg/kg reported for fish in Qua-Iboe River, Nigeria (Oze *et al.,* 2006).

Oreochromis niloticus (n=10), *Labeo coubie* (n=5) and *Brycinus sp.* (n=3) were the only species obtained from Dunkwa-on-Offin which recorded cadmium (Cd) concentration in mg/kg wet weight in their muscle tissues in the range from below detection to 0.10 (mean=0.10), below detection to 0.10 (mean=0.10) and below detection to 0.10 (mean=0.10) respectively. *Chrysichthys nigrodigitatus* (n=5), *Hepsetus odoe* (n=2), *Mormyrus sp.* (n=1), *Papyrocranus afer* (n=1) and *Heterobranchus sp.* (n=1) had Cd concentration below the detection limit of the instrument. Cd levels recorded in fish were below the WHO/FAO standard of 1.0 mg/kg wet weight for fish (JECFA, 2002). However, it was well within the range reported for fish from Africa inland waters from 0.004 to 0.19 mg/kg wet weight (Committee for Inland Fisheries of Africa, 1992) and below the mean value of 0.19 mg/kg wet weight reported for fish from Wiwi River, Ghana (Biney and Beeko, 1991).

Twenty three samples of *Synodontis sp.* from Buabenso recorded from below detection to 0.10 mg Cd/kg wet weight (mean=0.10mg Cd/kg). Cd concentration range in muscle tissue in *Chrysichthys nigrodigitatus* (n=3), *Tilapia zilli* (n=2), and *Schilbe mystus* (n=2) were below the detection limit of the instrument. The Cd concentrations determined were well below the WHO/FAO maximum permissible limit of 1.0 mg/kg fresh weight of fish; however, results are consistent with those obtained by other researchers in Africa. Biney *et al* (1994) reported a Cd concentration range in fish from West African inland waters of 0.03-0.19 mg/kg wet weight and Amoo *et al*. (2005) reported 0.03-0.21 mg/kg wet weight for fish in Lake Kainji, Nigeria.

Synodontis sp. (n=30) from Awisam had Cd concentration range in muscle tissue from below detection to 0.10 mg/kg wet weight and a mean concentration of 0.09 mg/kg. However, the Cd concentration was below the 1.0 mg/kg WHO/FAO standard and was within the range (0.004 to 0.19 mg/kg wet weight) predicted for fish in Africa inland waters (Committee for Inland Fisheries of Africa, 1992).

Generally, the distribution of cadmium in fish muscle tissue showed an irregular pattern as the river flows downstream towards river Pra. Both sediment and soil (control) from all the five sampling locations had Cd levels below the instrument's detection limit. However, for unpolluted sediment from freshwaters, GESAMP (1982) and Salomons and Forstner (1984) report Cd levels of 0.11 mg/kg. Canadian sediment guidelines for the protection of aquatic life is 0.6 mg/kg for cadmium in freshwater sediments (CCME, 1999). Thus the lower cadmium levels observed in fish could be due to the fact that Cd was the least available metal in water and sediment in Offin River. A similar conclusion was also made in Ogba River, Nigeria (Obasohan *et al.*, 2006).

The mercury concentrations determined in fish had a mean range from 35.79 to 587.04 ng/g compared to the mean 424.00 ng/g obtained by Cheetham (2000) in Offin River. Five fishes exceeded the WHO safety limit of 500 ng/g but none of the fishes determined by Cheetham (200) exceeded WHO safety limit. A mean Hg sediment range from 96.11 to 1010.08 ng/g was observed in this study compared to the mean 545.00 ng/g reported by Cheetham. Thus sediment mercury concentration in Offin River has doubled at some sites. The zinc levels in fish were between 35.8 to 251.9 times more than that determined by Cheetham (2000). A mean range from 1.826 to 12.849 mg/kg was recorded in fish relative to 0.051 mg/kg by Cheetham. Again, zinc levels in sediment were between 219.8 to 375.5 times higher than that recorded by Cheetham (2000). A mean range from 20.442 to 34.932 mg/kg was measured in sediment as compared to 0.093 mg/kg by Cheetham (2000).

This increase in levels of mercury and zinc in fish and sediment may be attributed to the extensive mining in the Offin River by artisanal miners (*galamsey*). The pumping of water that gets into open pit back into the river and the washing of mining fields into the river whenever it flooded might also add to the causes of the increment in levels of Hg and Zn. Though the levels of mercury and zinc might have increased in the aquatic environment since the year 2000, it remains fairly below the WHO threshold.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

This study analysed total Hg, Cd, and Zn concentrations in edible fish muscle tissue, sediment and soil from five sampling areas along the Offin River. From the outcome of this research it could be concluded that:

- The cadmium and zinc concentrations in fish tissue were generally below the WHO maximum permissible limit, however, five (5) out of one hundred and forty eight (148) fish samples analysed representing 3.4% had tissue mercury concentrations above this limit.

- The total muscle tissue mercury concentrations in ng/g wet weight of fish sampled ranged from 34.77 to 409.49 at Dominase, 1.02 to 247.51 at Nkotumso, 46.81 to 794.59 at Dunkwa-on-Offin, 105.32 to 649.40 at Buabenso and 140.86 to 795.94 at Awisam. Sediments sampled recorded mean values of 144.55±38.21, 1010.08±102.89, 186.15±77.18, 424.30±260.12 and 96.11±30.07 ng/g at Dominase, Nkotumso, Dunkwa-on-Offin, Buabenso and Awisam respectively. About 37.5% and 18.8% fish species showed positive correlation between muscle tissue mercury concentration and fresh weight and total length of fish respectively. *Synodontis sp.* (an omnivorous fish) concentrated the highest muscle tissue mercury among all the species analyzed.

- The total zinc levels in mg/kg wet weight recorded in muscle tissue of all the fish sampled ranged from below detection to 12.52 at Dominase, below detection to 12.38 at Nkotumso, 4.13 to 12.85 at Dunkwa-on-Offin, below detection to 5.38 at Buabenso and 2.87 to 18.16 at Awisam. Mean zinc levels in mg/kg recorded in sediments sampled were 23.54±6.34 at Dominase, 20.44±4.78 at Nkotumso, 25.81±6.55 at Dunkwa-on-Offin, 34.93±14.71 at Buabenso and 21.58±6.40 at Awisam. Again, *Synodontis sp.* had the highest muscle tissue zinc concentration among the species analyzed.

- Total cadmium levels in mg/kg wet weight measured in muscle tissue of fish sampled ranged from below detection to 0.10 at Dominase, below detection to 0.10 at Nkotumso, below detection to 0.10 at Dunkwa-on-Offin, below detection to 0.10 at Buabenso and below detection to 0.10 at Awisam. However, cadmium levels in sediments were below the detection level of the instrument. Though cadmium levels were generally low, *Synodontis sp.* was among the fish species that recorded maximum tissue cadmium of 0.10 mg/kg wet weight. Generally, there was an irregular distribution of these metals in fish as the river flows downstream towards river Pra.

- With only 3.4% of fish analysed were found to be contaminated with mercury, this study has shown that consumption of fish from Offin River is unlikely to constitute health risks so far as the Hg, Cd and Zn concentrations are concerned. However, continuous mining along the banks of Offin River coupled with long term bioaccumulation of heavy metals through food chain is of major concern.

The study has also revealed that *Synodontis sp.* (an omnivorous fish) has a good Hg, Cd and Zn accumulation potential and may serve as a biomarker for toxicological studies for these metals in the Offin River.

5.2 RECOMMENDATIONS

The following recommendations are made based on the outcome of the research:

- This study showed elevated levels of mercury and zinc compared to those observed in the year 2000. It also showed escalating *galamsey* activities along the banks of Offin River. It is therefore recommended that a longer and more regular monitoring should be undertaken by researchers to ensure human health safety.

- Some inhabitants particularly those living near the river use the water for domestic purposes such as washing of cooking utensils and cloths, and bathing. Analysis of the water should be carried out to regularly ascertain whether the water is of good quality for use by inhabitants (Picture 12, Appendix III).

- Further work should be done to determine the levels of metals in fish to ascertain seasonal variations. The levels of metals in different organs of the fish must also be determined to ascertain any trends.

- Heavy metal concentrations in fish in other inland waters in Ghana particularly those close to industrial establishment should be determined to ascertain if levels in fish is safe for consumption.

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APPENDIX I

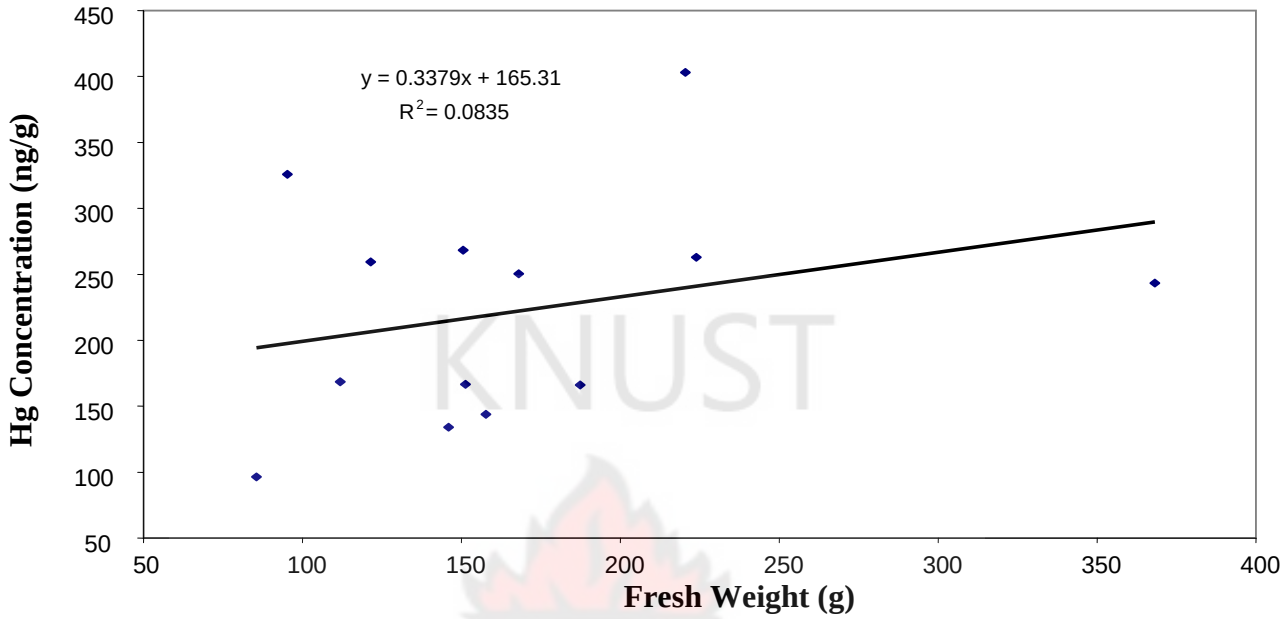


Fig. 4.0 Relationship between Hg concentration on wet basis and fresh weight for *Tilapia zilli* from Dominase.

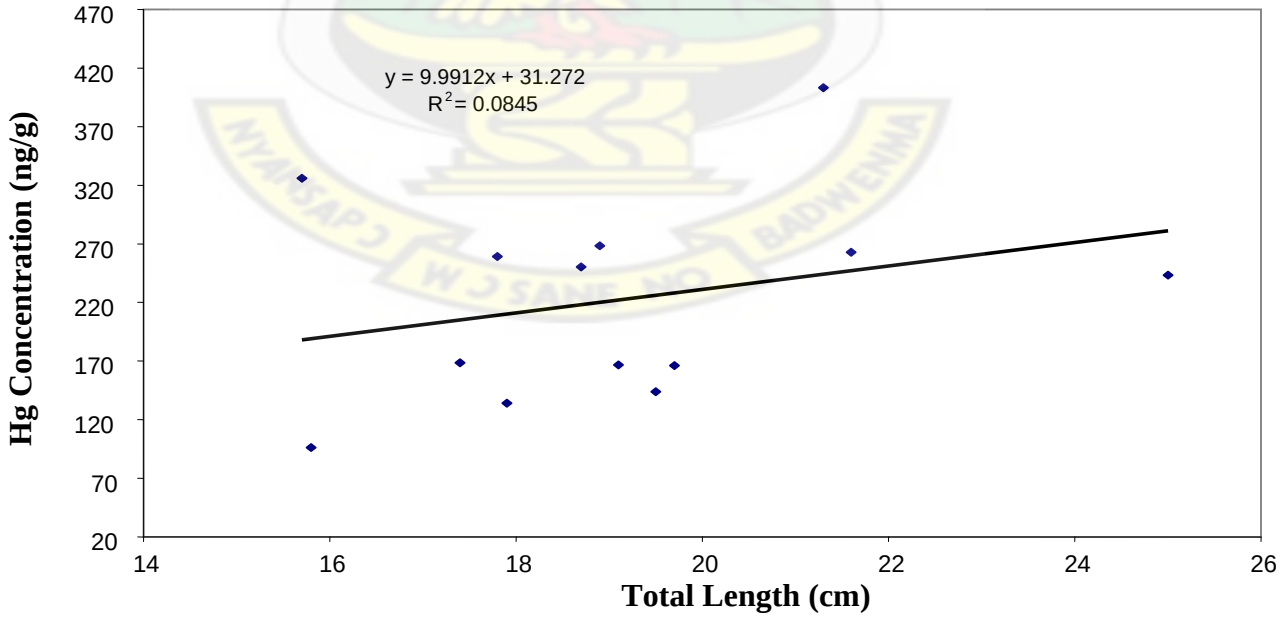


Fig. 4.1 Relationship between Hg concentration on wet weight basis and total length for *Tilapia zilli* from Dominase.

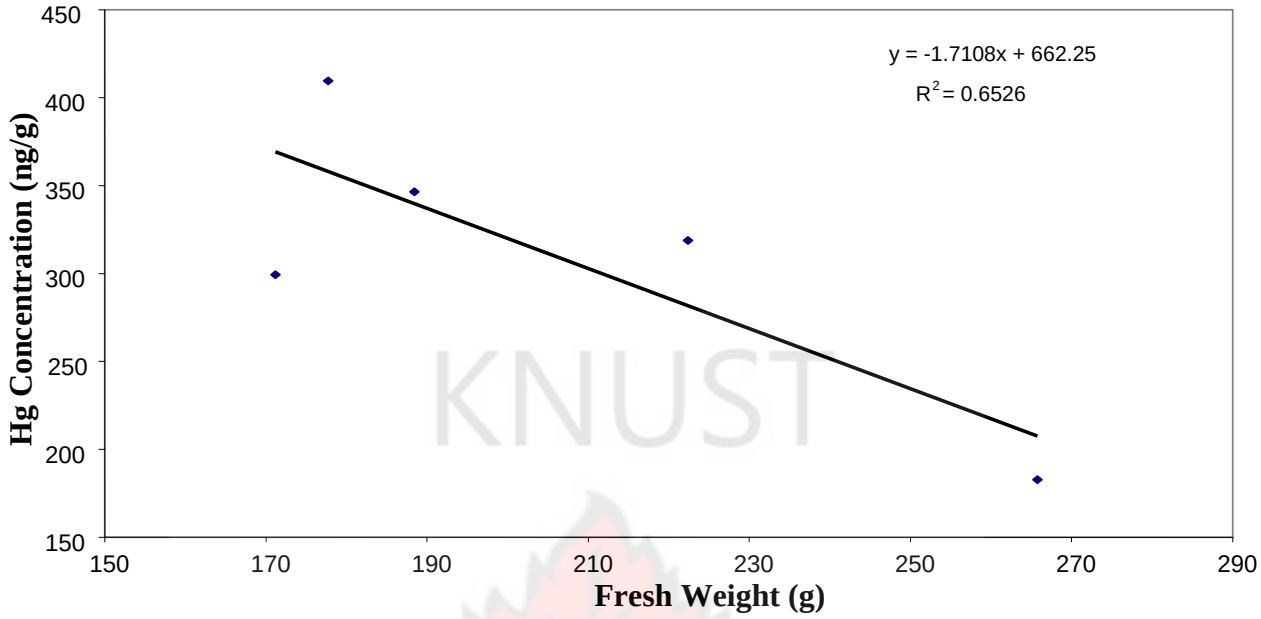


Fig. 4.2 Relationship between Hg concentration on wet basis and fresh weight for *Chrysichthys nigrodigitatus* from Dominase.

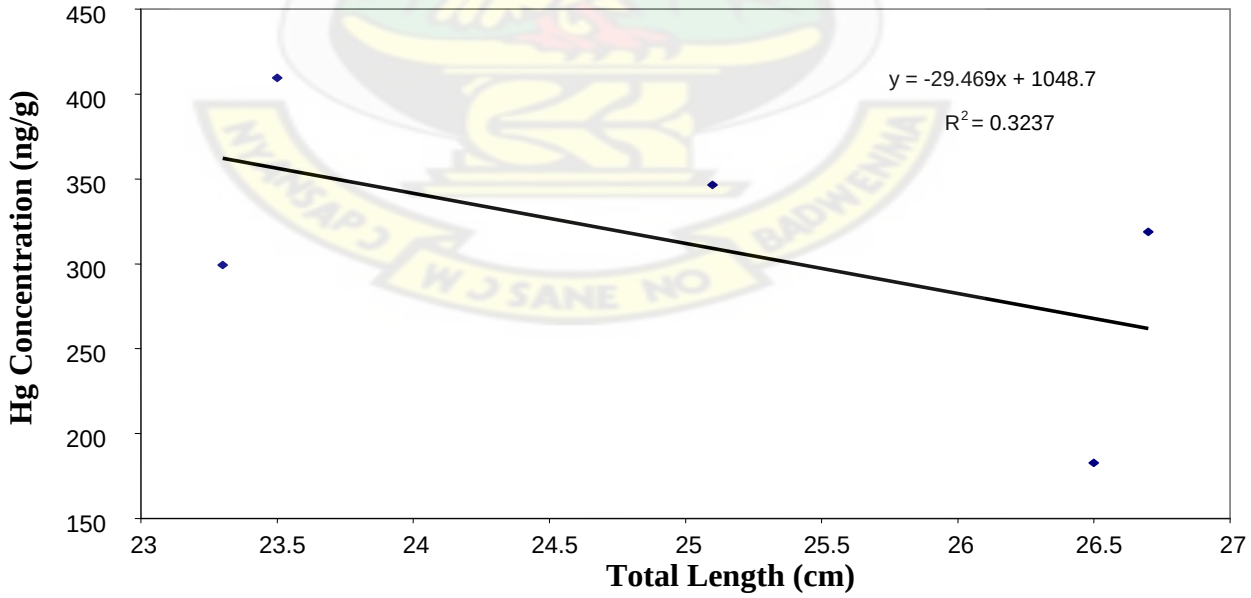


Fig. 4.3 Relationship between Hg concentration on wet weight basis and total length for *Chrysichthys nigrodigitatus* from Dominase.

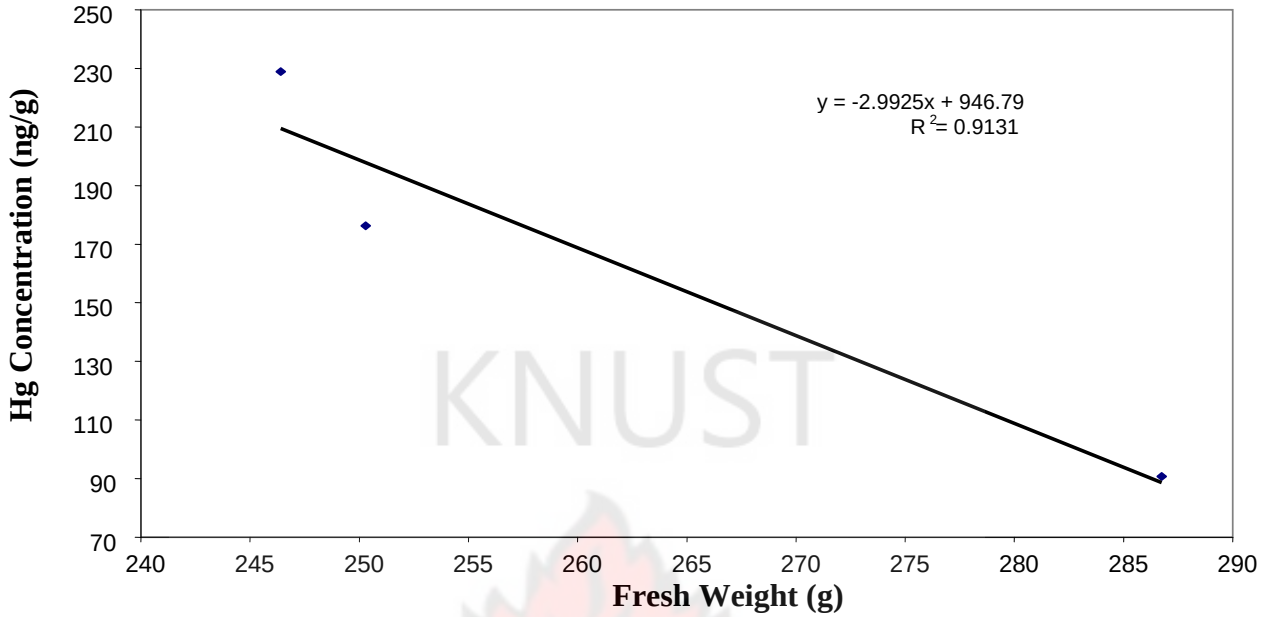


Fig. 4.4 Relationship between Hg concentration on wet basis and fresh weight for *Oreochromis niloticus* from Dominase.

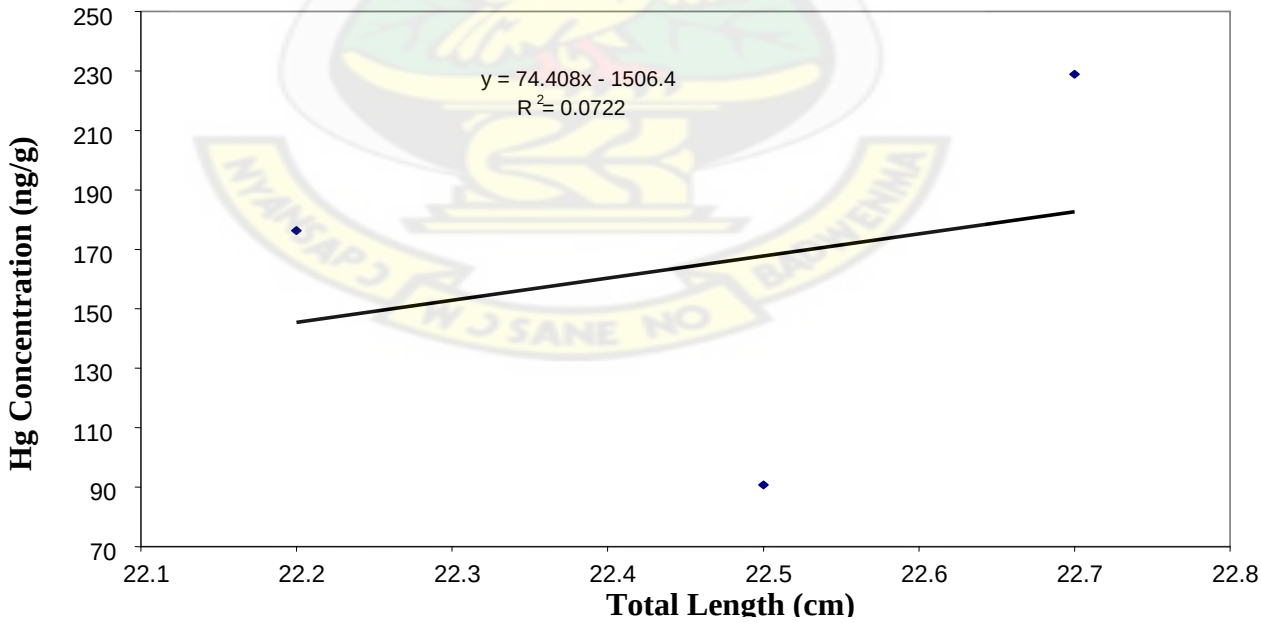


Fig. 4.5 Relationship between Hg concentration on wet weight basis and total length for *Oreochromis niloticus* from Dominase.

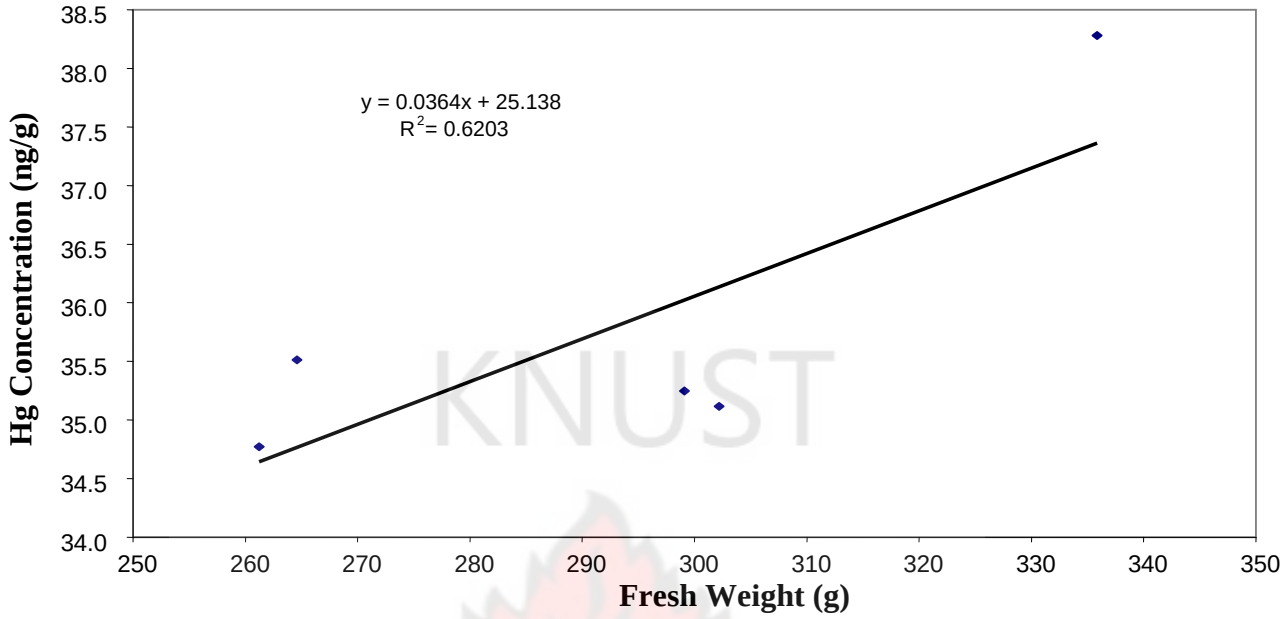


Fig. 4.6 Relationship between Hg concentration on wet basis and fresh weight for *Heterobranchus sp.* from Dominase.

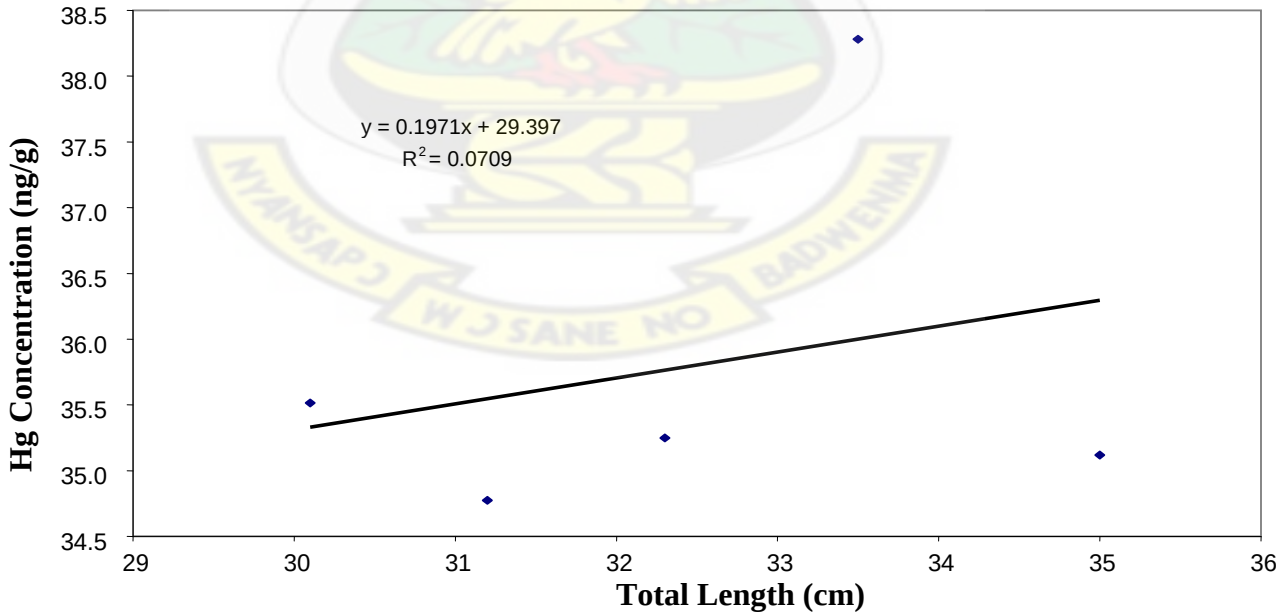


Fig. 4.7 Relationship between Hg concentration on wet weight basis and total length for *Heterobranchus sp.* from Dominase.

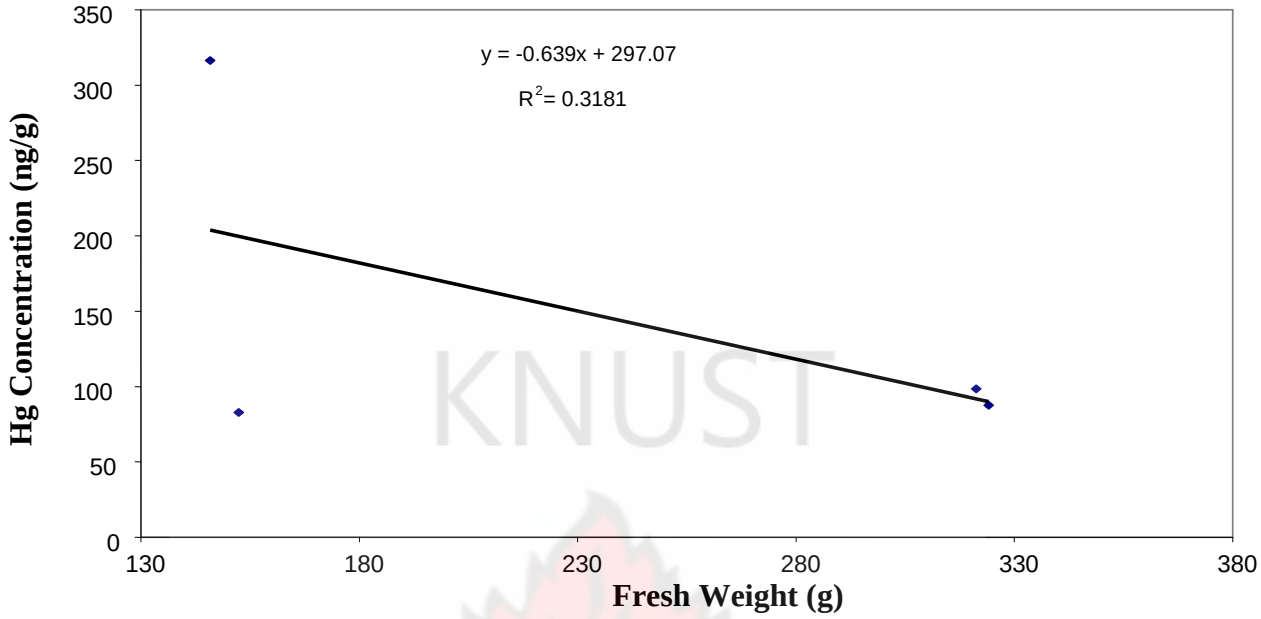


Fig. 4.8 Relationship between Hg concentration on wet basis and fresh weight for *Sarotherodon melanotheron* from Dominase.

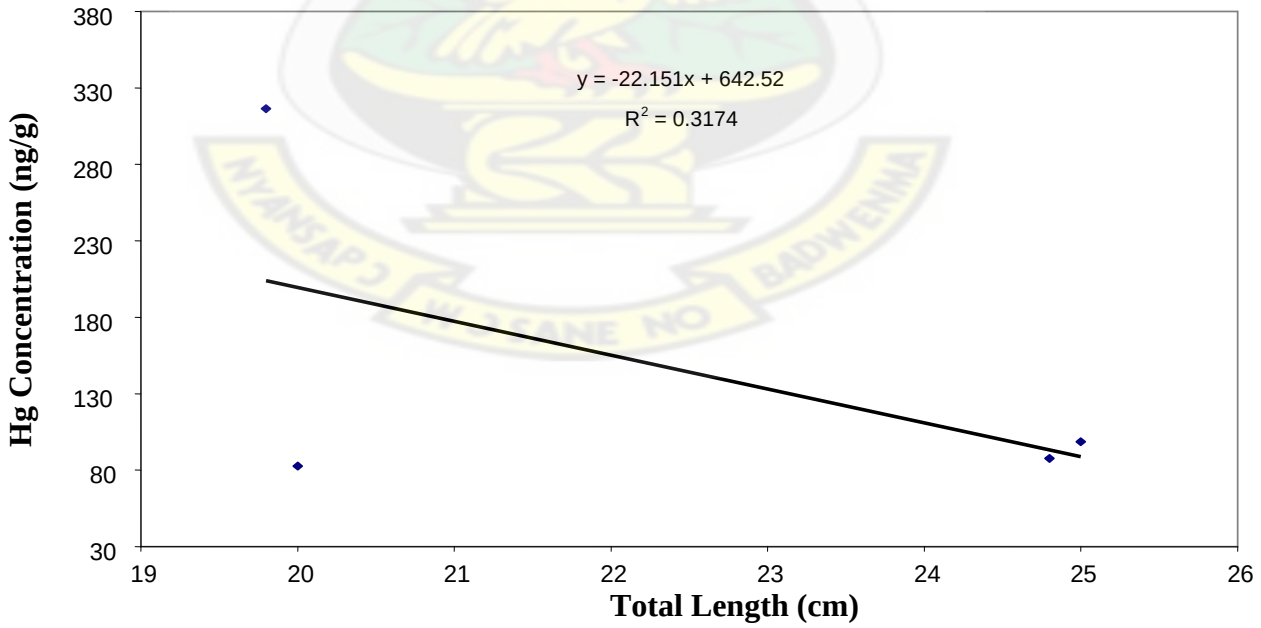


Fig. 4.9 Relationship between Hg concentration on wet weight basis and total length for *Sarotherodon melanotheron* from Dominase.

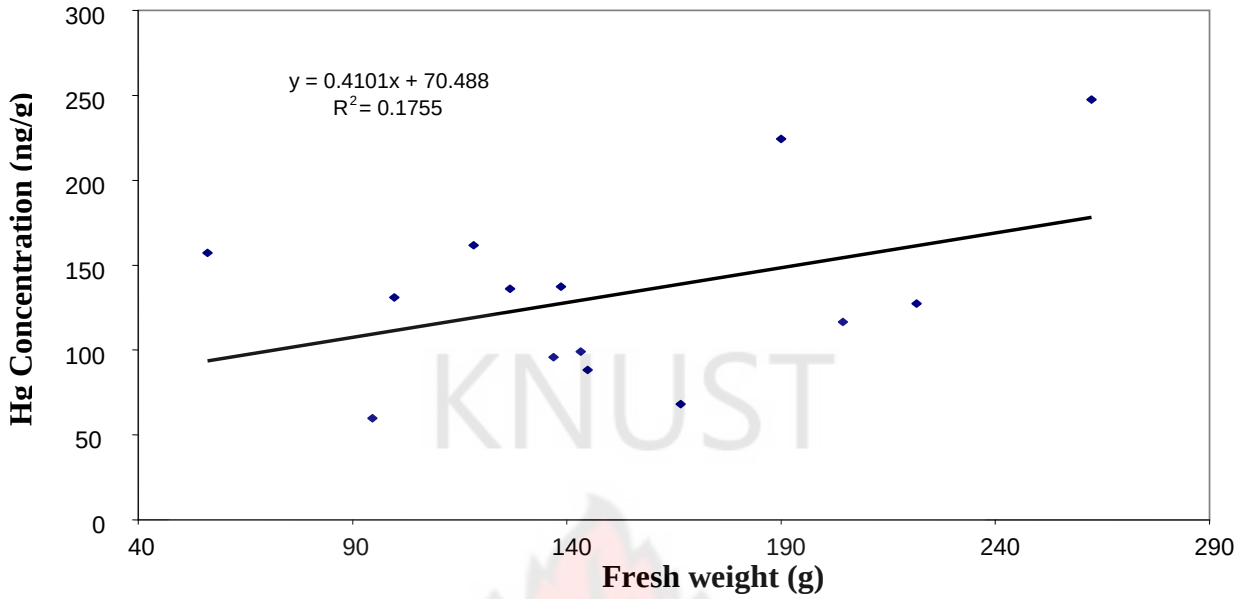


Fig. 4.10 Relationship between Hg concentration on wet basis and fresh weight for *Oreochromis niloticus* from Nkotumso.

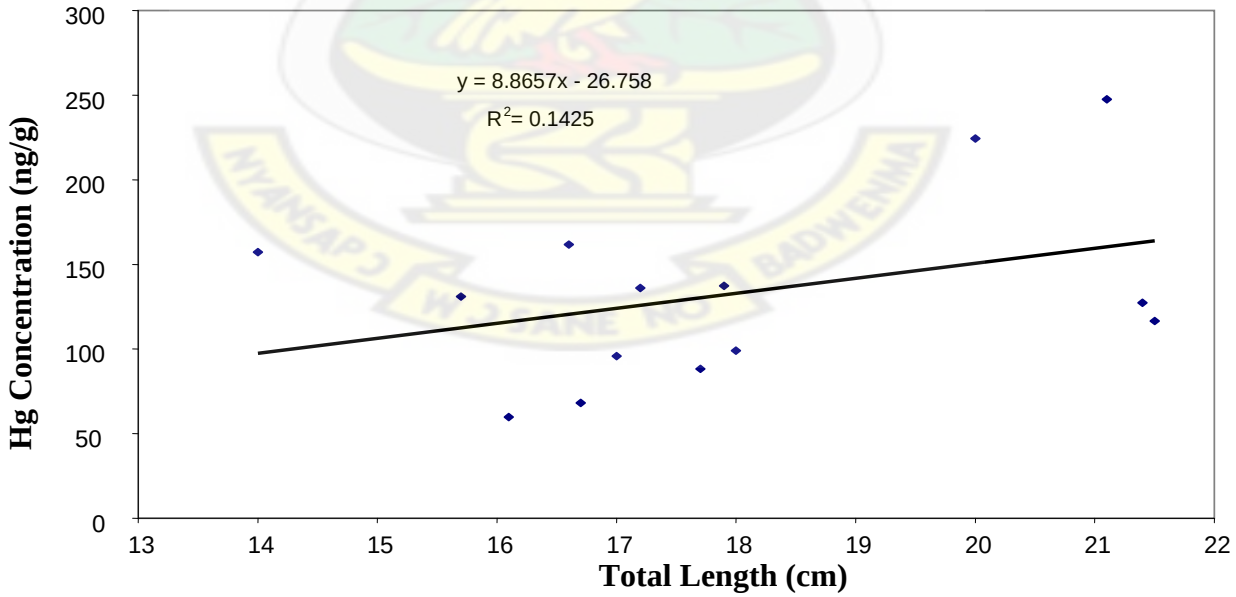


Fig. 4.11 Relationship between Hg concentration on wet weight basis and total length for *Oreochromis niloticus* from Nkotumso.

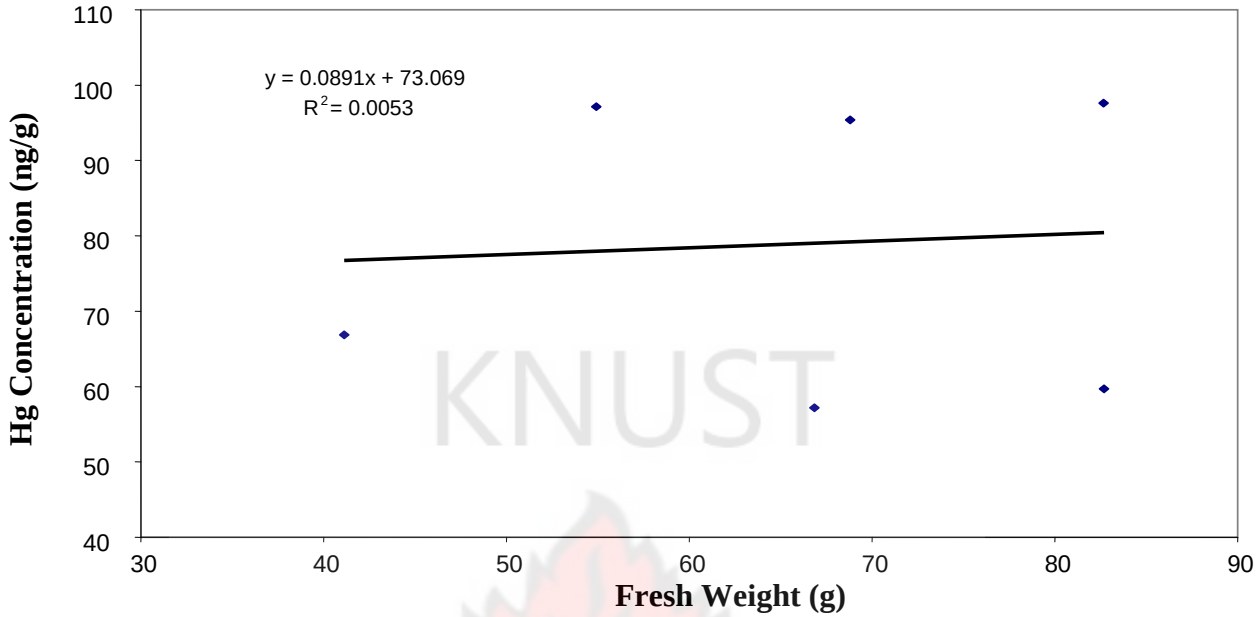


Fig. 4.12 Relationship between Hg concentration on wet basis and fresh weight for *Tilapia zilli* from Nkotumso.

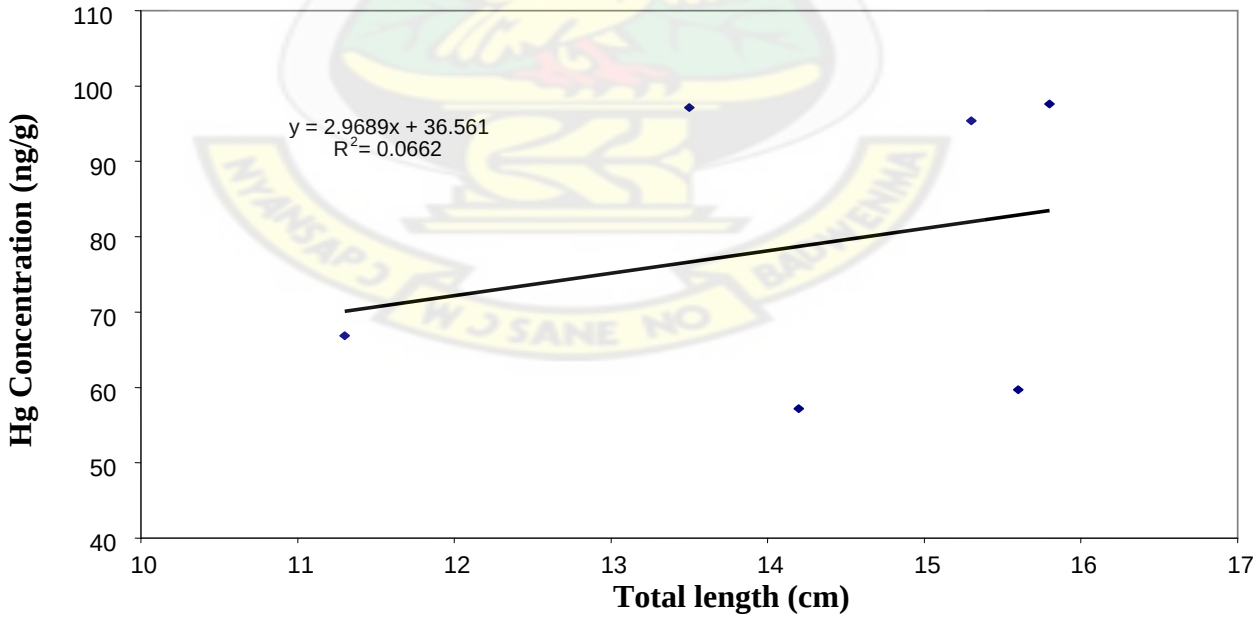


Fig. 4.13 Relationship between Hg concentration on wet weight basis and total length for *Tilapia zilli* from Nkotumso.

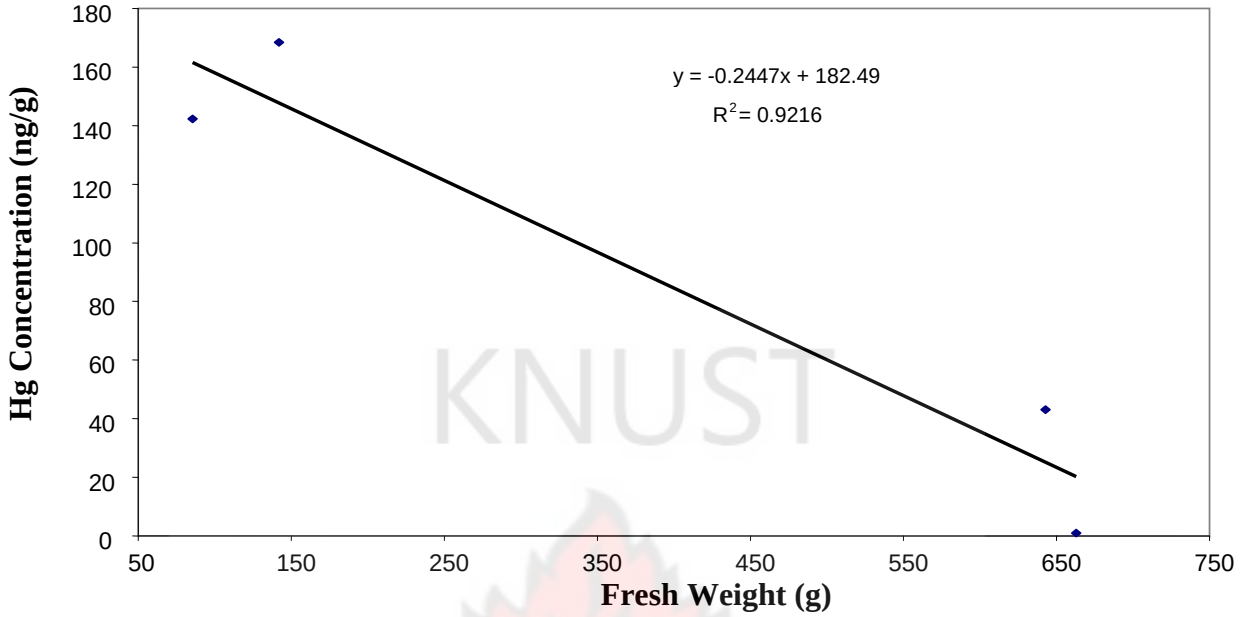


Fig. 4.14 Relationship between Hg concentration on wet basis and fresh weight for *Heterobranchus sp.* from Nkotumso.

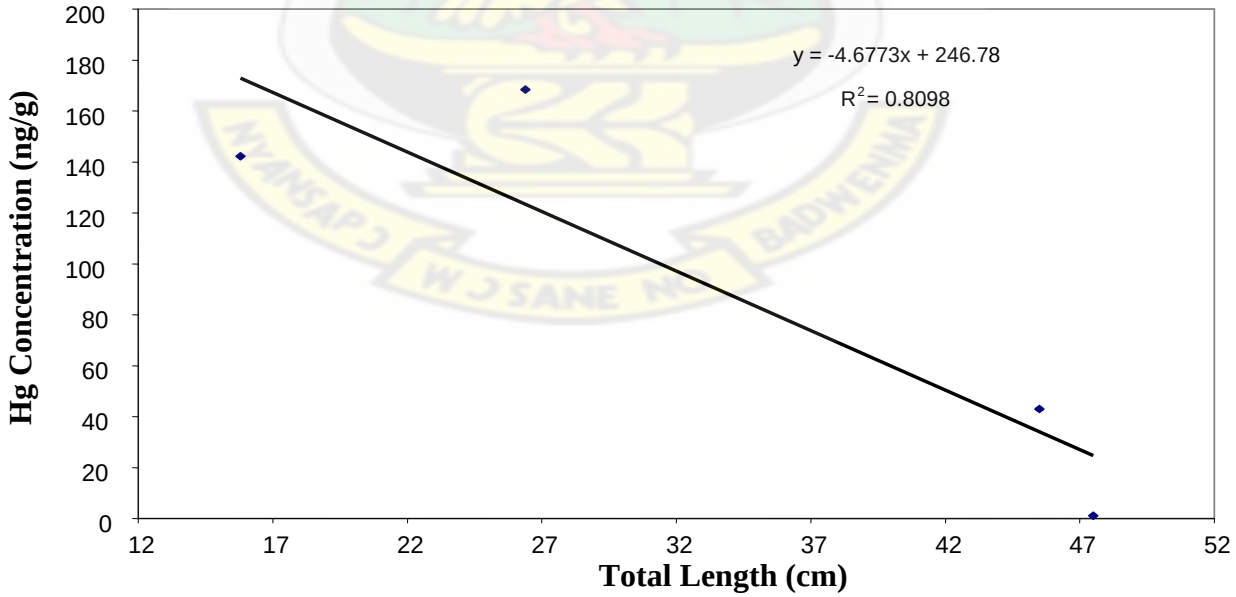


Fig. 4.15 Relationship between Hg concentration on wet weight basis and total length for *Heterobranchus sp.* from Nkotumso.

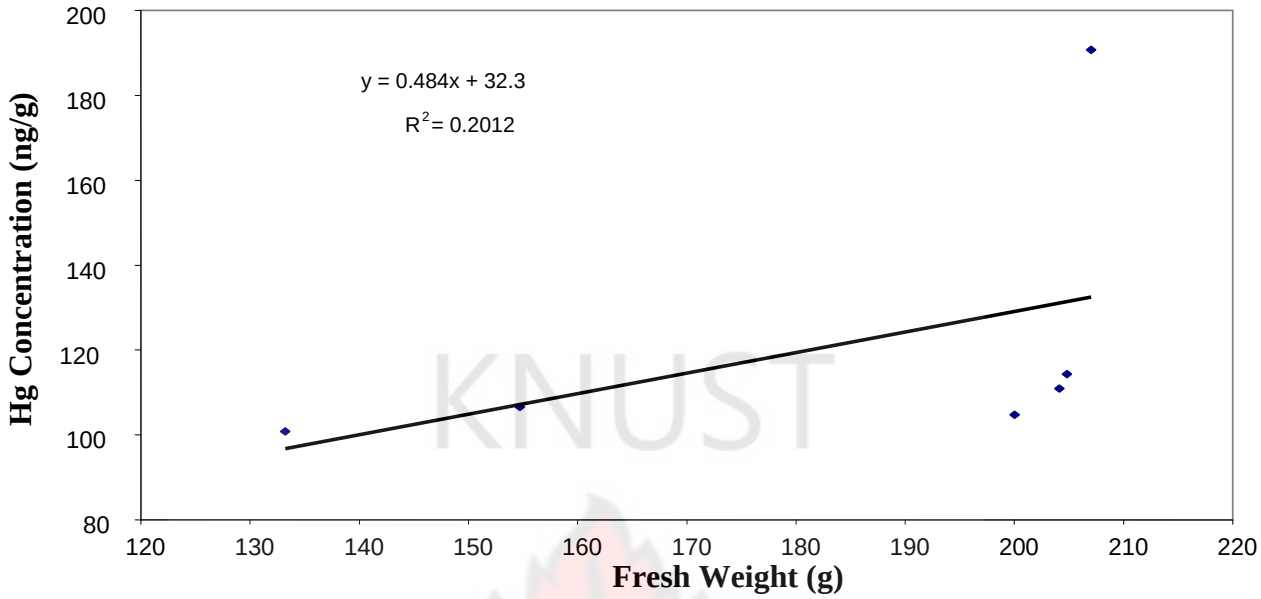


Fig. 4.16 Relationship between Hg concentration on wet basis and fresh weight for *Labeo coubie* from Nkotumso.

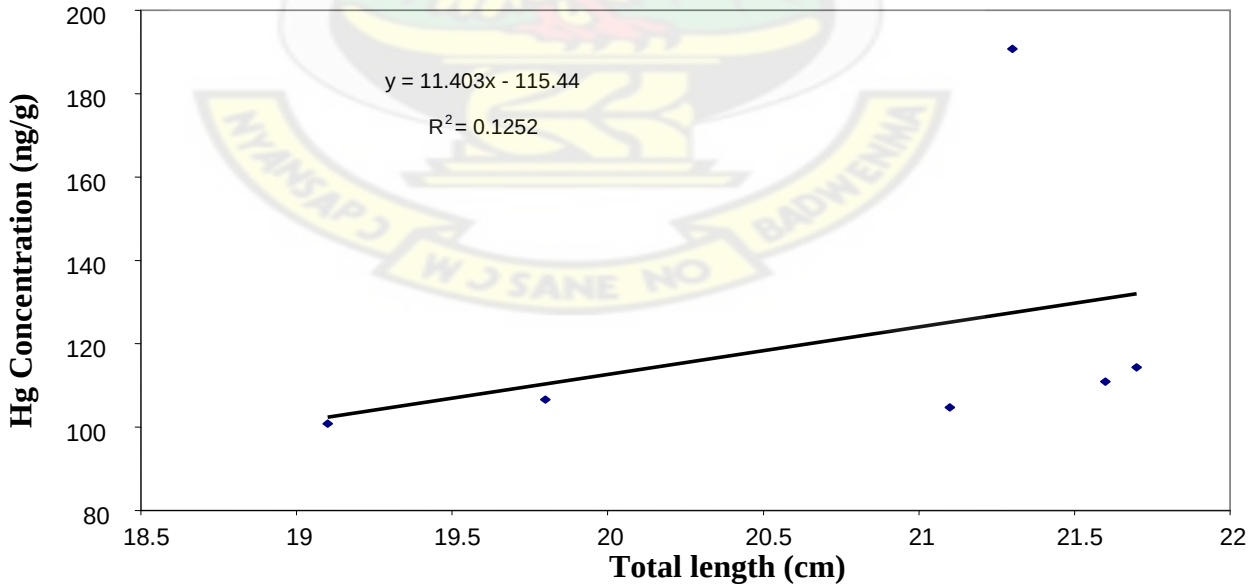


Fig. 4.17 Relationship between Hg concentration on wet weight basis and total length for *Labeo coubie* from Nkotumso.

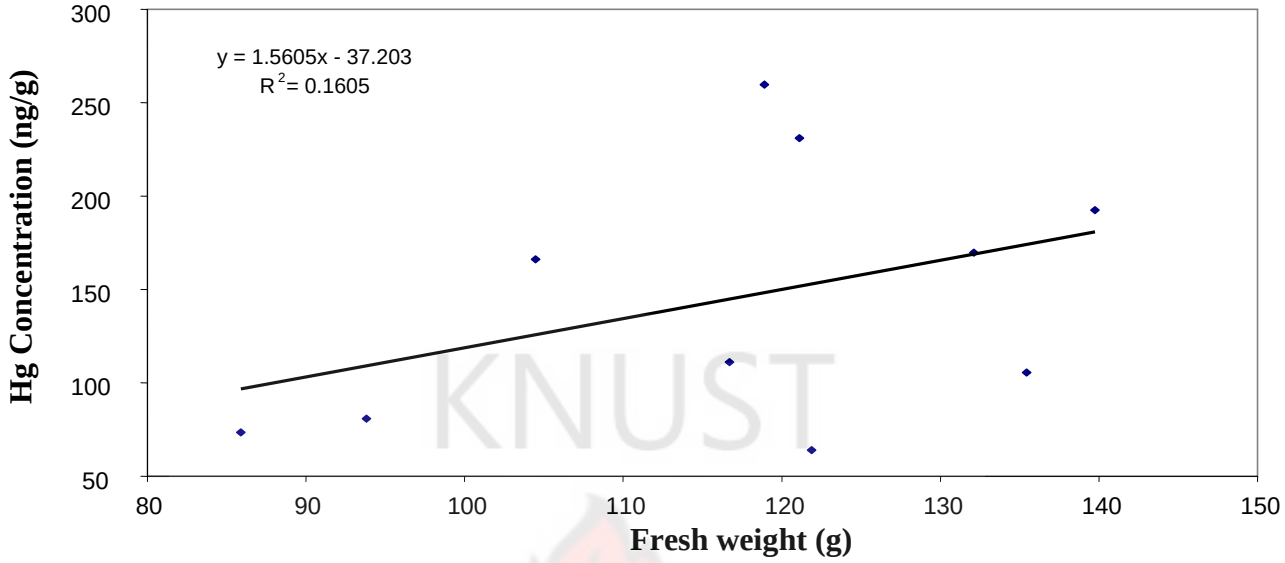


Fig. 4.19 Relationship between Hg concentration on wet basis and fresh weight for *Oreochromis niloticus* from Dunkwa-on-Offin.

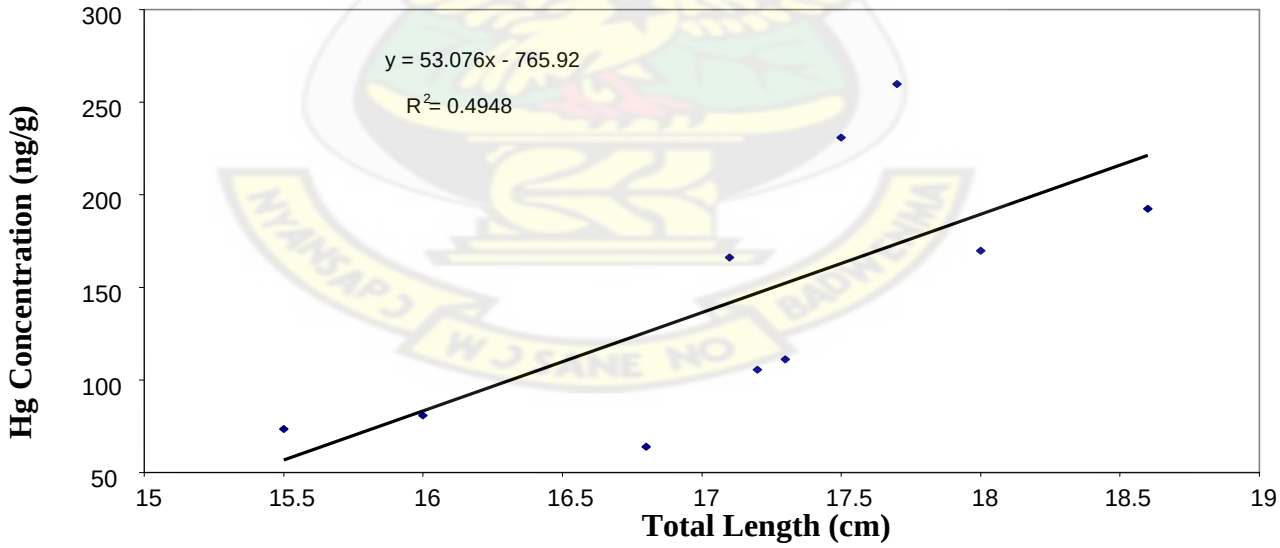


Fig. 4.20 Relationship between Hg concentration on wet weight basis and total length for *Oreochromis niloticus* from Dunkwa-on-Offin.

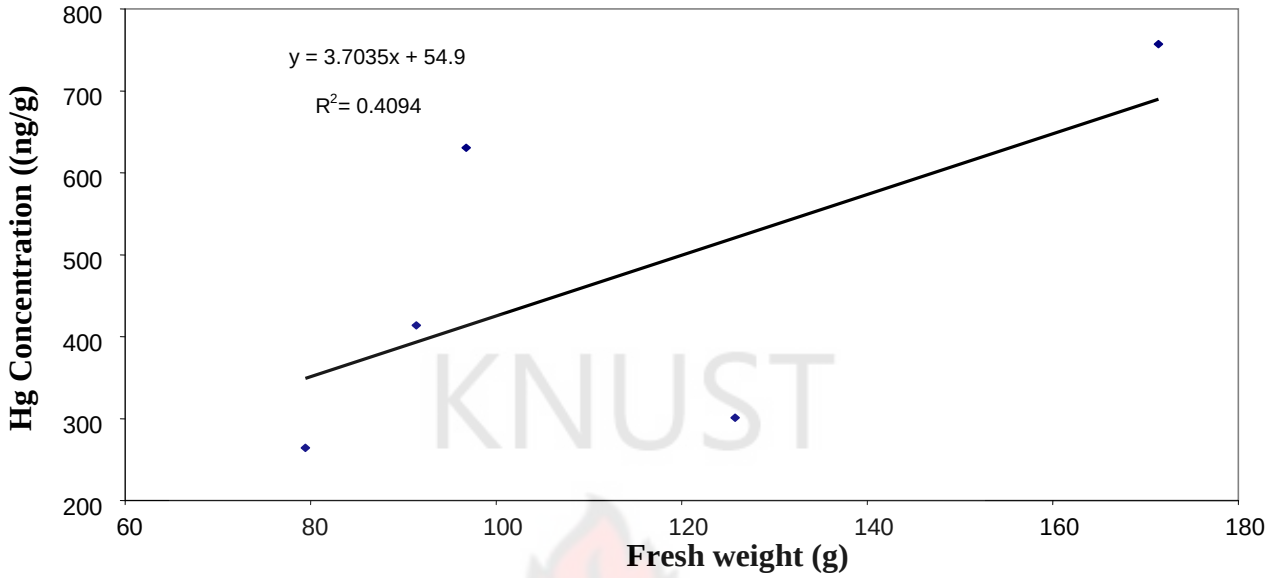


Fig. 4.21 Relationship between Hg concentration on wet basis and fresh weight for *Chrysichthys nigrodigitatus* from Dunkwa-on-Offin.

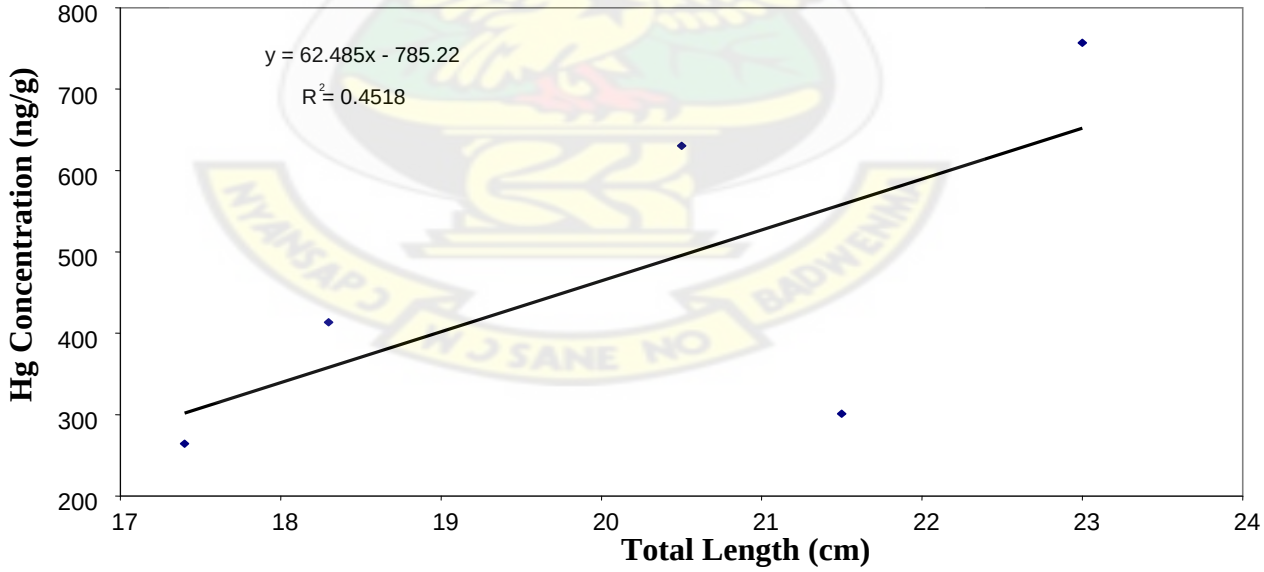


Fig. 4.22 Relationship between Hg concentration on wet weight basis and total length for *Chrysichthys nigrodigitatus* from Dunkwa-on-Offin.

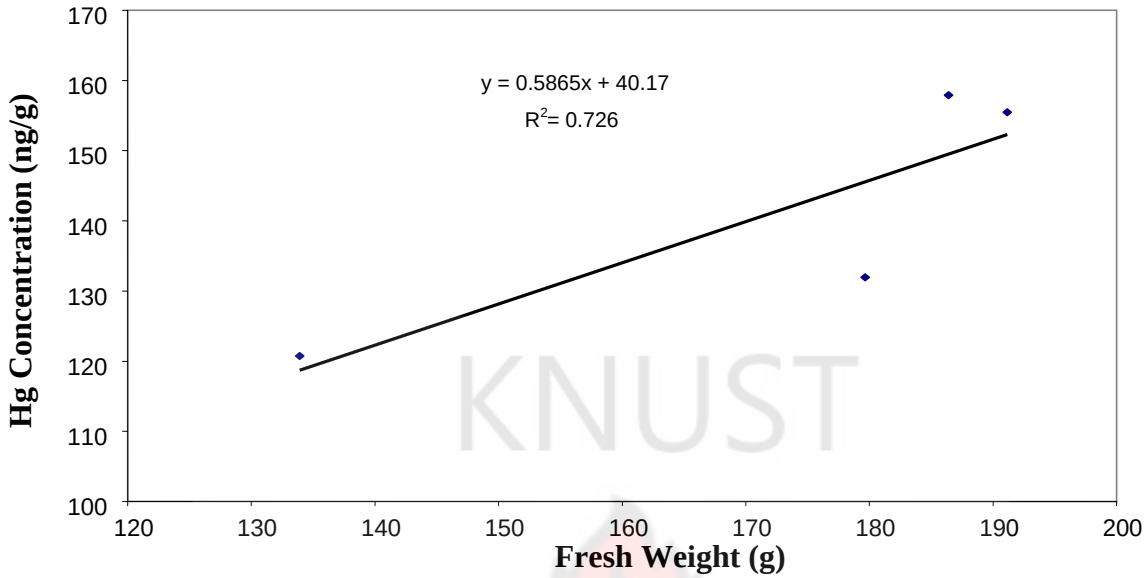


Fig. 4.23 Relationship between Hg concentration on wet basis and fresh weight for *Labeo coubie* from Dunkwa-on-Offin.

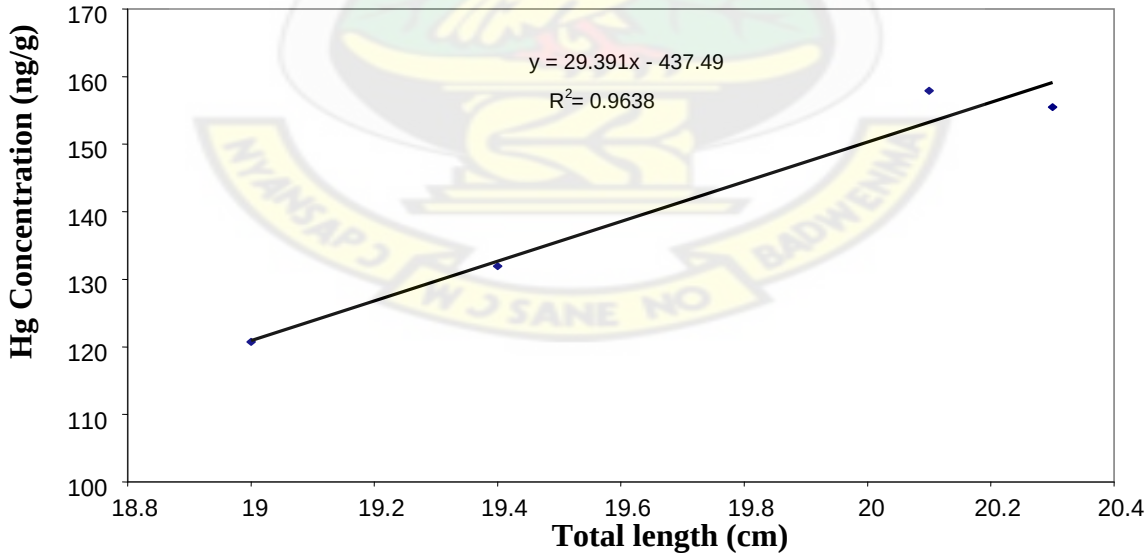


Fig. 4.24 Relationship between Hg concentration on wet weight basis and total length for *Labeo coubie* from Dunkwa-on-Offin.

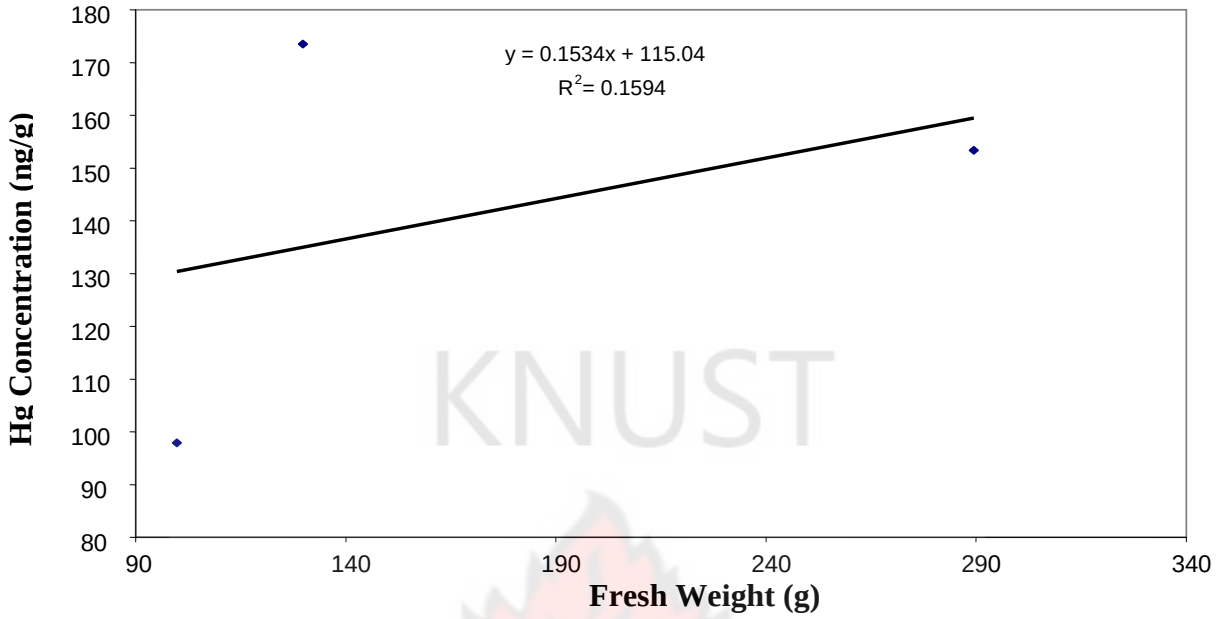


Fig. 4.25 Relationship between Hg concentration on wet basis and fresh weight for *Brycinus sp.* from Dunkwa-on-Offin.

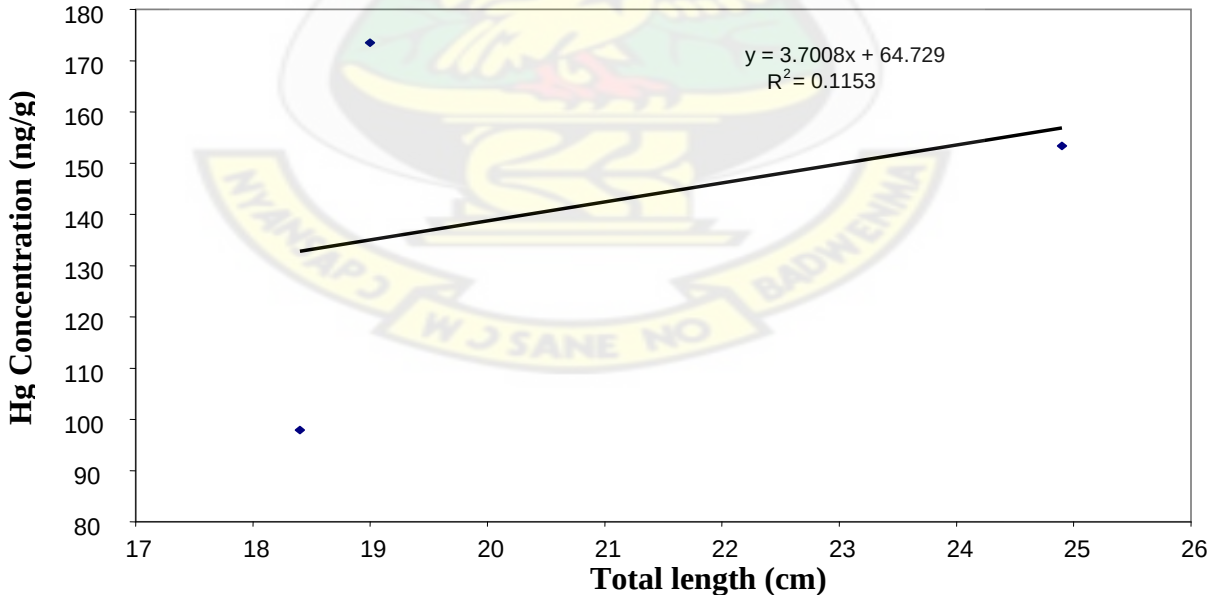


Fig. 4.26 Relationship between Hg concentration on wet weight basis and total length for *Brycinus sp.* from Dunkwa-on-Offin.

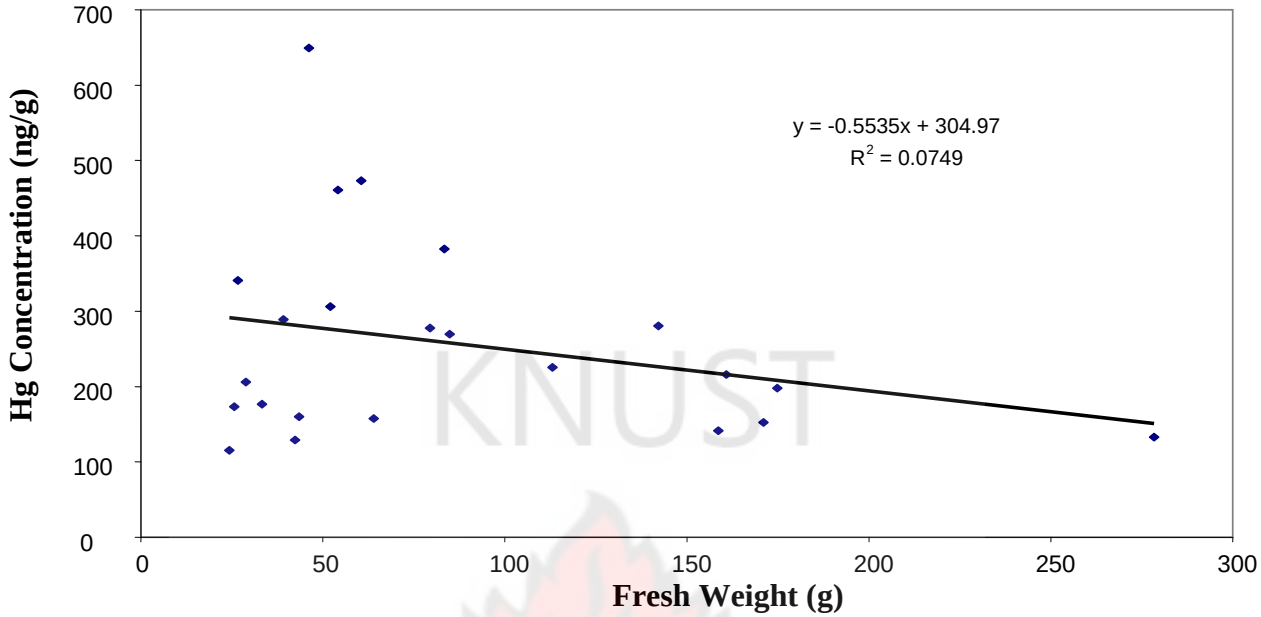


Fig. 4.27 Relationship between Hg concentration on wet basis and fresh weight for *Synodontis sp.* from Buabenso.

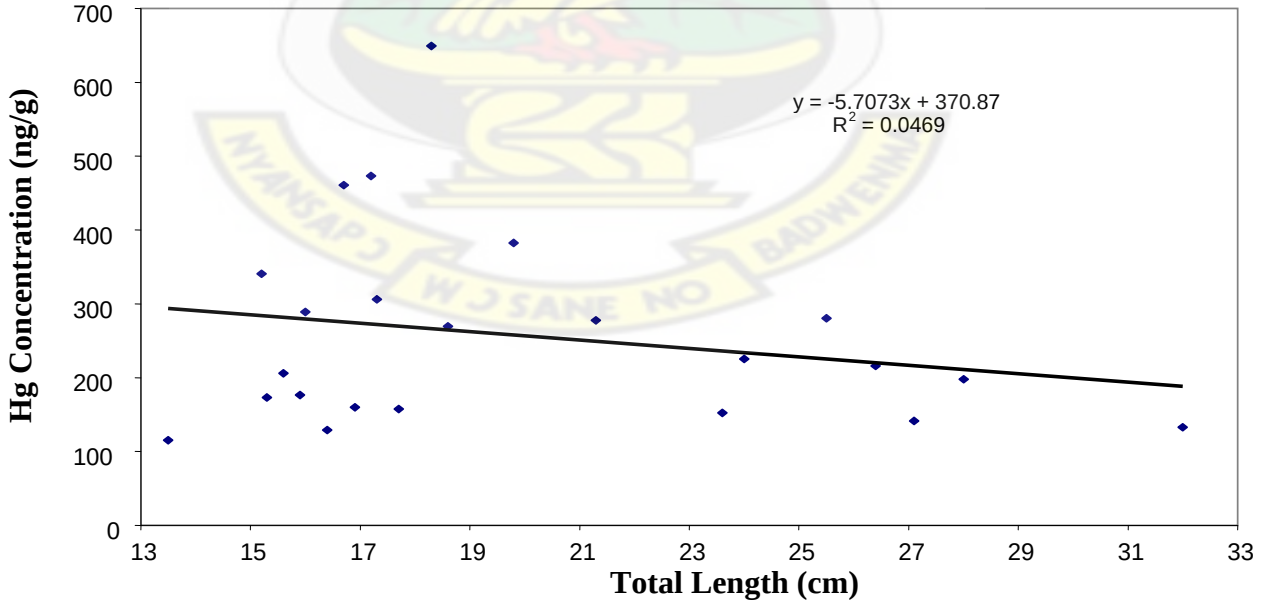


Fig. 4.28 Relationship between Hg concentration on wet weight basis and total length for *Synodontis sp.* from Buabenso.

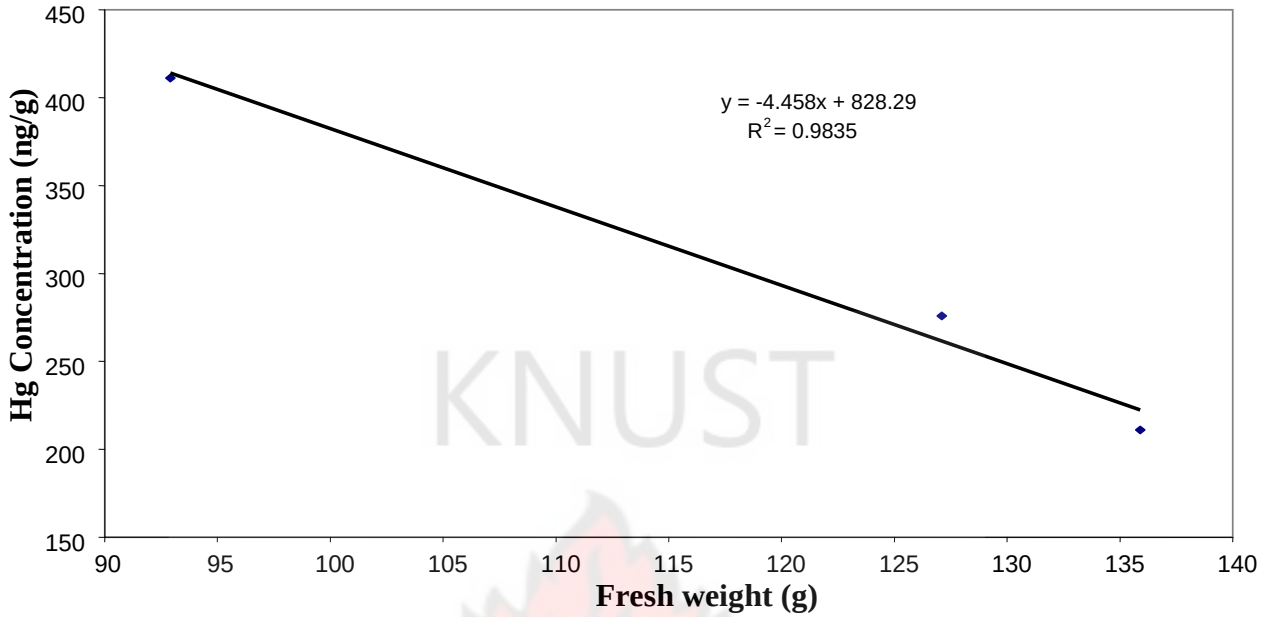


Fig. 4.29 Relationship between Hg concentration on wet basis and fresh weight for *Chrysichthys nigrodigitatus* from Buabenso.

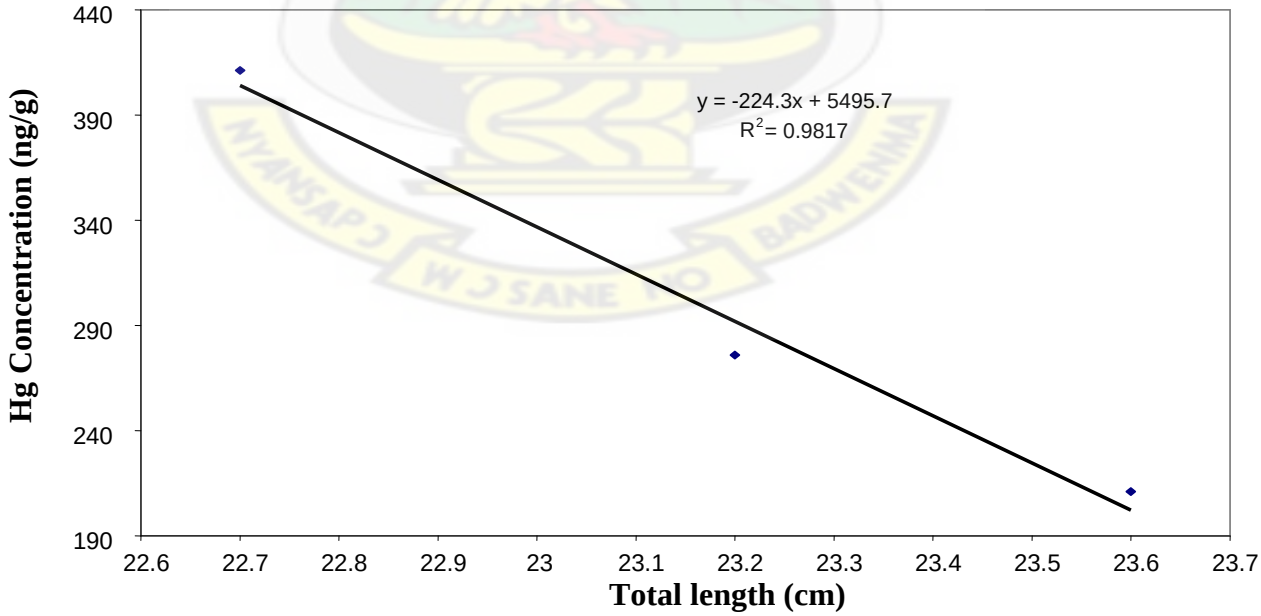


Fig. 4.30 Relationship between Hg concentration on wet weight basis and total length for *Chrysichthys nigrodigitatus* from Buabenso.

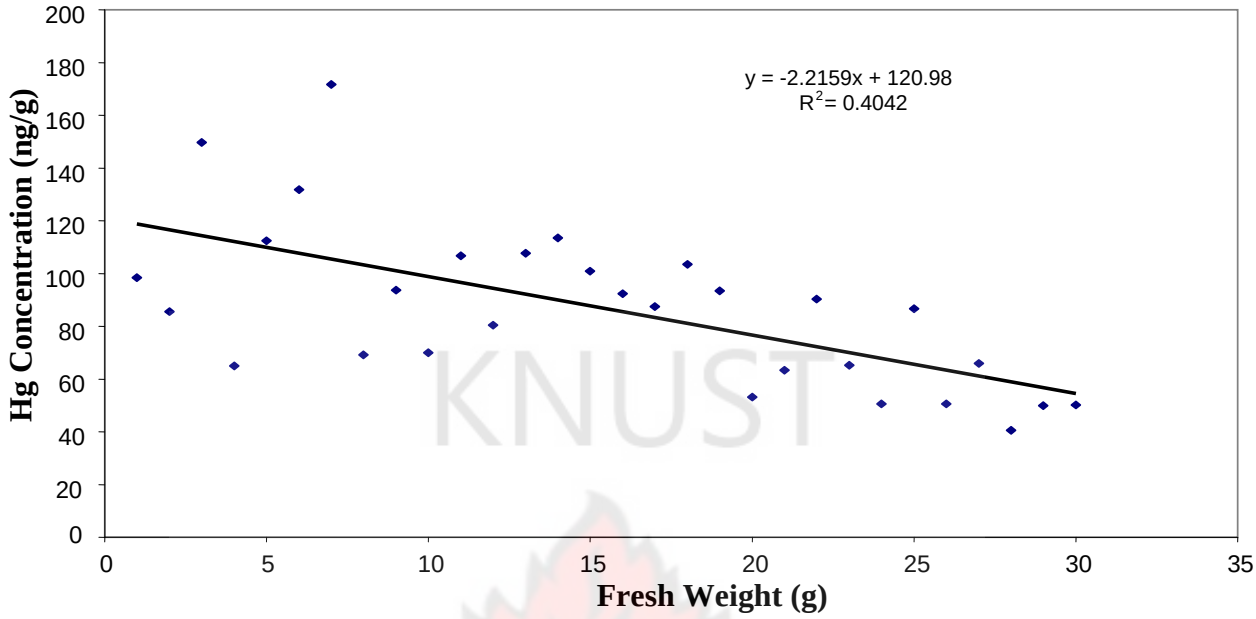


Fig. 4.31 Relationship between Hg concentration on wet basis and fresh weight for *Synodontis sp.* from Awisam.

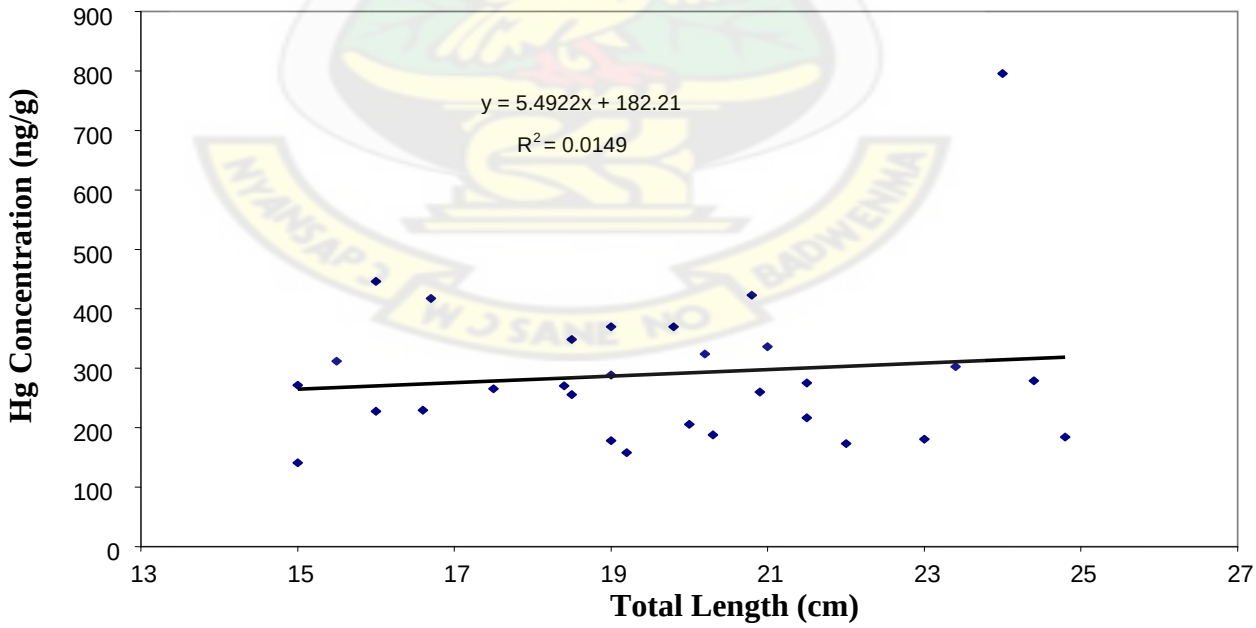


Fig. 4.32 Relationship between Hg concentration on wet weight basis and total length for *Synodontis sp.* from Awisam.

APPENDIX II

RESULTS

DOMINASE

Table 4.5 Results for *Tilapia zilli*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
DOM A1	150.62	18.90	11.05	ND	268.41
DOM A2	146.00	17.90	5.90	ND	134.02
DOM A3	168.11	18.70	6.46	ND	250.28
DOM A4	95.32	15.70	7.75	ND	325.88
DOM A5	157.70	19.50	8.94	ND	143.80
DOM A6	111.90	17.40	8.27	ND	168.44
DOM A7	121.54	17.80	9.73	ND	259.25
DOM A8	223.90	21.60	9.71	ND	262.79
DOM A9	151.32	19.10	ND	ND	166.71
DOM A10	368.13	25.00	5.20	0.10	243.30
DOM A11	220.53	21.30	ND	ND	403.05
DOM A12	187.40	19.70	9.14	ND	166.08
DOM A13	85.51	15.80	ND	ND	96.33

Table 4.6 Results for *Chrysichthys nigrodigitatus*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
DOM B1	177.73	23.50	11.38	ND	409.49
DOM B2	222.40	26.70	11.97	ND	318.91
DOM B3	265.75	26.50	12.52	0.10	182.75
DOM B4	171.20	23.30	4.47	ND	299.24
DOM B5	188.43	25.10	11.93	ND	346.38

Table 4.7 Results for *Oreochromis niloticus*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
DOM D1	286.75	22.50	5.48	ND	90.79
DOM D2	246.40	22.70	ND	ND	228.87
DOM D3	250.30	22.20	2.58	ND	176.26

Table 4.8 Results for *Heterobranchus sp.*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
DOM F1	264.60	30.10	4.13	ND	35.51
DOM F2	261.22	31.20	2.58	ND	34.77
DOM F3	335.85	33.50	4.52	0.10	38.28
DOM F4	302.20	35.00	6.67	ND	35.12
DOM F5	299.10	32.30	3.16	ND	35.25

Table 4.9 Results for *Sarotherodon melanotheron*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
DOM G1	324.10	24.80	ND	0.10	87.61
DOM G2	152.40	20.00	ND	ND	82.72
DOM G3	145.81	19.80	ND	ND	316.42
DOM G4	321.22	25.00	ND	0.10	98.58

NKOTUMSO

Table 4.10 Results for *Oreochromis niloticus*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
NKT A1	136.91	17.00	7.12	ND	95.76
NKT A2	189.98	20.00	3.88	ND	224.43
NKT A3	204.44	21.50	4.46	ND	116.59
NKT A4	138.66	17.90	6.46	ND	137.32
NKT A5	99.71	15.70	4.96	ND	130.91
NKT A6	143.30	18.00	2.94	ND	99.05
NKT A7	144.91	17.70	5.08	ND	88.31
NKT A8	166.56	16.70	6.30	0.10	68.04
NKT A9	94.61	16.10	7.50	ND	59.79
NKT A10	56.14	14.00	7.43	ND	157.19
NKT A11	126.80	17.20	3.64	ND	135.97
NKT A12	221.63	21.40	8.07	ND	127.33
NKT A13	118.28	16.60	6.65	ND	161.59
NKT A14	262.42	21.10	1.29	ND	247.51

Table 4.11 Results for *Tilapia zilli*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
NKT D1	82.67	15.80	5.62	ND	97.60
NKT D2	68.81	15.30	5.12	ND	95.38
NKT D3	66.85	14.20	6.73	ND	57.16
NKT D4	54.92	13.50	6.54	ND	97.15
NKT D5	41.12	11.30	7.17	ND	66.84
NKT D6	82.70	15.60	12.38	ND	59.67

Table 4.12 Results for *Heterobranchus sp.*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
NKT E1	642.81	45.50	7.06	ND	43.04
NKT E2	663.01	47.50	8.32	ND	1.02
NKT E3	85.50	15.80	3.60	ND	142.27
NKT E4	142.00	26.40	2.17	ND	168.44

Table 4.13 Results for *Labeo coubie*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
NKT F1	154.71	19.80	2.29	ND	106.58
NKT F2	207.01	21.30	0.89	ND	190.76
NKT F3	204.81	21.70	3.17	ND	114.32
NKT F4	200.01	21.10	2.59	ND	104.74
NKT F5	133.22	19.10	ND	ND	100.83
NKT F6	204.11	21.60	0.20	ND	110.90

DUNKWA-ON-OFFIN

Table 4.14 Results for *Oreochromis niloticus*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
DUN A1	118.90	17.70	4.13	ND	259.76
DUN A2	85.90	15.50	5.55	0.10	73.49
DUN A3	93.82	16.00	5.39	ND	80.88
DUN A4	135.45	17.20	5.22	ND	105.53
DUN A5	116.71	17.30	5.59	ND	111.12
DUN A6	121.10	17.50	5.80	ND	230.93
DUN A7	139.75	18.60	7.37	ND	192.41
DUN A8	121.88	16.80	6.20	ND	63.92
DUN A9	104.48	17.10	4.55	0.10	166.05
DUN A10	132.10	18.00	6.90	ND	169.79

Table 4.15 Results for *Chrysichthys nigrodigitatus*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
DUN B1	171.41	23.00	5.66	ND	756.83
DUN B2	125.77	21.50	6.30	ND	301.03
DUN B3	96.77	20.50	8.09	ND	630.35
DUN B4	79.44	17.40	8.65	ND	264.39
DUN B5	91.40	18.30	11.45	ND	413.58

Table 4.16 Results for *Labeo coubie*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
DUN C1	179.67	19.40	10.02	ND	131.93
DUN C2	133.92	19.00	8.56	0.10	120.75
DUN C3	191.16	20.30	7.14	ND	155.46
DUN C4	186.40	20.10	7.31	ND	157.90
DUN C5	105.09	16.70	7.02	ND	152.81

Table 4.17 Results for *Brycinus specie*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
DUN DI	289.42	24.90	5.58	0.10	153.33
DUN D2	129.86	19.00	7.92	0.10	173.52
DUN D3	99.82	18.40	9.21	ND	97.90

Table 4.18 Results for *Hepsetus odoe*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
DUN E1	117.51	23.70	9.78	ND	794.59
DUN E2	117.51	24.90	11.02	ND	379.50

Table 4.19 Results for *Mormyrus sp.*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
DUN F	66.81	22.50	10.02	ND	48.61

Table 4.20 Results for *Papyrocranus afer*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
DUN G	131.93	10.10	11.63	ND	53.29

Table 4.21 Results for *Heterobranchus sp.*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
MUDFISH	288.50	32.50	12.85	ND	65.72

BUABENSO

Table 4.22 Results for *Synodontis sp.*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
BUA A1	160.81	26.40	3.46	ND	215.97
BUA A2	278.40	32.00	3.47	0.10	132.69
BUA A3	158.66	27.10	3.63	ND	141.50
BUA A4	113.15	24.00	4.43	ND	225.26
BUA A5	142.20	25.50	5.38	ND	280.43
BUA A6	174.82	28.00	2.75	ND	198.10
BUA A7	171.10	23.60	2.86	ND	152.50
BUA A8	79.41	21.30	2.20	ND	277.80
BUA A9	84.90	18.60	4.16	ND	269.47
BUA A10	83.40	19.80	1.90	ND	382.74
BUA A11	63.92	17.70	1.77	ND	157.67
BUA A12	60.51	17.20	3.19	ND	473.28
BUA A13	54.20	16.70	2.70	ND	460.93
BUA A14	46.21	18.30	ND	ND	649.40
BUA A15	52.10	17.30	ND	ND	306.22
BUA A16	39.21	16.00	ND	ND	289.14
BUA A17	42.32	16.40	ND	ND	128.87
BUA A18	33.32	15.90	ND	ND	176.56
BUA A19	28.84	15.60	ND	ND	206.19
BUA A20	25.61	15.30	ND	ND	173.16
BUA A21	26.60	15.20	ND	ND	340.94
BUA A22	24.32	13.50	ND	0.10	115.46
BUA A23	43.53	16.90	ND	ND	160.01

Table 4.23 Results for *Chrysichthys nigrodigitatus*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
BUA B1	127.10	23.20	ND	ND	276.00
BUA B2	135.90	23.60	ND	ND	211.06
BUA B3	92.91	22.70	ND	ND	411.16

Table 4.24 Results for *Tilapia zilli*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
BUA T1	84.31	16.80	ND	ND	153.63
BUA T2	121.94	18.40	ND	ND	179.29

Table 4.25 Results for *Schilbe mystus*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
BUA S1	24.53	15.50	ND	ND	105.32
BUA S2	35.50	14.10	ND	ND	112.73

AWISAM

Table 4.26 Results for *Synodontis sp.*

SAMPLE LABEL	WEIGHT(g)	LENGTH(cm)	Zn Concentration (mg/kg)	Cd Concentration (mg/kg)	Hg Concentration (ng/g)
AW A1	98.41	19.00	5.05	0.09	288.81
AW A2	85.51	19.20	4.08	ND	157.82
AW A3	149.74	20.8	4.64	ND	422.66
AW A4	64.90	15.00	5.27	ND	271.79
AW A5	112.42	21.00	5.37	ND	336.39
AW A6	131.82	24.40	4.63	ND	278.68
AW A7	171.60	24.80	6.39	ND	184.36
AW A8	69.21	20.90	5.39	ND	259.97
AW A9	93.63	20.30	18.16	ND	188.19
AW A10	69.90	17.50	8.15	ND	265.33
AW A11	106.65	24.00	7.35	ND	795.94
AW A12	80.41	18.50	8.45	ND	348.37
AW A13	107.60	23.00	7.84	ND	180.80
AW A14	113.51	23.40	9.16	ND	302.53
AW A15	100.90	20.20	3.61	ND	324.18

AW A16	92.30	22.00	3.68	ND	173.12
AW A17	87.44	21.50	5.45	0.09	275.04
AW A18	103.42	19.80	5.26	ND	369.77
AW A19	93.41	21.50	5.99	0.10	216.72
AW A20	53.21	16.70	5.84	ND	417.48
AW A21	63.32	19.00	6.37	ND	177.89
AW A22	90.32	20.00	5.80	ND	205.58
AW A23	65.20	19.00	7.43	ND	369.50
AW A24	50.51	16.60	8.25	ND	229.55
AW A25	86.66	18.50	7.80	ND	255.67
AW A26	50.53	18.40	9.31	ND	270.49
AW A27	65.88	16.00	2.87	ND	446.19
AW A28	40.48	15.50	3.85	ND	311.72
AW A29	49.92	15.00	4.46	ND	140.86
AW A30	50.11	16.00	8.15	ND	227.50

Table 4.27 Results for Sediments and Soil (Control)

SAMPLE	LOCATION	Mean Zn concentration (mg/kg)	Mean Cd concentration (mg/kg)	Mean Hg concentration (ng/g)
Sediments	Dominase	23.54	ND	144.55
Soil	Dominase	35.57	ND	97.45
Sediments	Nkotumso	20.44	ND	1010.08
Soil	Nkotumso	25.50	ND	137.80
Sediments	Dunkwa-on-Offin	25.81	ND	186.15
Soil	Dunkwa-on-Offin	81.49	ND	44.61
Sediments	Buabenso	34.93	ND	424.30
Soil	Buabenso	8.45	ND	72.60
Sediments	Awisam	21.58	ND	96.11
Soil	Awisam	57.46	ND	61.55

APPENDIX III

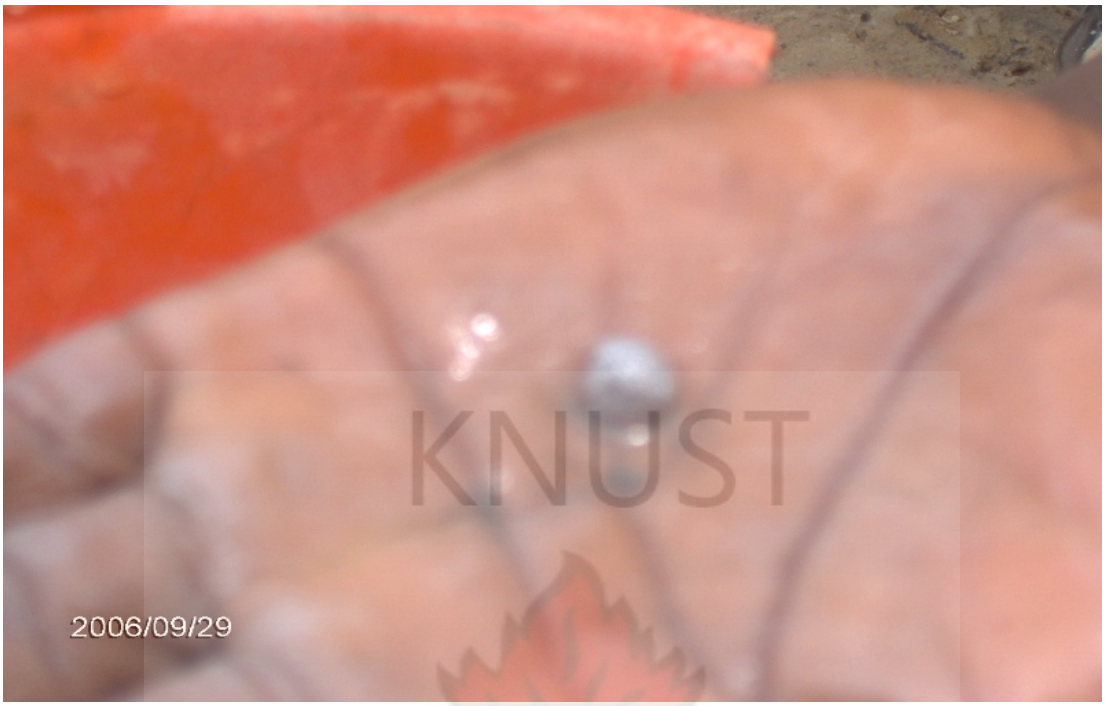
PICTURES

Picture 1. Front View of Dunkwa Continental Goldfields Dredge in Offin River

Picture 2. Front View of Dunkwa Continental Goldfields Dredge showing Dredging buckets.

Picture 3. Side View of Dunkwa Continental Goldfields Dredge

Picture 4. Removal of alluvial gold from the jute sacks after which the gold bearing ore is concentrated in a flat pan.



Picture 5. Mercury-Gold amalgam is formed by bringing mercury into contact with concentrated ore.

Picture 6. Burning of mercury-gold amalgam to expel mercury and recover gold

Picture 7. Alluvial gold obtained after burning mercury-gold amalgam.

Picture 8. An Excavator removing the top soil to expose the gold bearing ore.

Picture 9. Blocks from buildings that have been pulled down to make land available for mining.

Picture 10. Dug mine pit at the river bank that has been filled by Offin River after been left overnight.

Picture 11. River water been pumped out of the mine pit back into the Offin River which is just behind the Excavator.

Picture 12. A lady fetching river water for use.

Picture 13. Pictures of various species of fish

Oreochromis niloticus

Sarotherodon melanotheron

Mormyrus sp.

Hepsetus odoe

Tilapia zilli

Brycinus sp.

Heterobranchus sp.

Papyrocranus afer

Chrysichthys nigrodigitatus

Labeo coubie

Synodontis sp.

Schilbe mystus