EXPOSURE OF THE POPULATION OF MONROVIA TO HEAVY METALS THROUGH FISH CONSUMPTION

BY

Rafael Sarji Ngumbu, B.Sc. Chemistry (University of Liberia)

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DECLARATION

I hereby declare that this thesis is the result of my own work and that, to the best of my knowledge, it contains no material previously published by another person or material which has been accepted for the award of any other degree of the University or other institution, except where due acknowledgment has been made in the text.

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Student ……………………… …………………………..

Rafael Sarji Ngumbu Signature Date

PG8041412

Supervisor ……………………….. …………………………...

Dr. Ray Bright Voegborlo Signature Date

Supervisor ………………………….. ………………………...

Mr. E.E. Kwaansa-Ansah Signature Date

Head of Department …………………………. …………………………

Signature Date

DEDICATION

This work is dedicated to my parents Mr. and Mrs. Patrick K. Ngumbu, my daughter little Sawena Queenie Ngumbu and my late Grandmother Wendor Ngumbu.

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ABSTRACT

Heavy metal contaminants in fish are of particular global interest because of the potential risk to humans who consume them. While attention has focused on self-caught fish, most of the fish eaten by the populace come from commercial sources. In this study, concentrations of some heavy metals were determined in muscle tissue of sixty samples covering twenty nine (29) commercial fish species from eight markets in Monrovia, Liberia. A mixture of HNO_3, $HClO_4$ and H_2SO_4 was used for complete oxidation of organic tissue. Total mercury was determined by cold vapour atomic absorption spectrometry technique using an automatic mercury analyzer; while the levels of Pb, Cd, Cu, Fe and Zn were determined by flame atomic absorption spectrometry using an Atomic Absorption Spectrophotometer. The muscle concentrations of Hg, Cu, Pb, Cd, Fe and Zn ranged from 0.014-0.727, 0.101-2.990, 0.027-0.256, 0.002-0.347, 2.122-6.804 and 1.783-6.013 $\mu g\ g^{-1}$ wet weight respectively. Inter-metal correlations and relationships between metal concentrations and fish body size were discussed. Estimation of the dietary exposure of the consumers to these metals were determined based on data from the American Food Consumption Index and the associated risk was evaluated by comparing intakes with the Provisional Tolerable Weekly Intakes (PTWIs). Both the Hazard Quotient (HQ) and Hazard Index (HI) for Hg, Cu, Pb, Cd, Fe, and Zn in all the species were less than the USEPA guideline value of 1. This suggests that the exposure to the tested metals from the consumption of the studied fish species is not significant and is unlikely to pose any imminent health risk to the population of Monrovia.

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ABBREVIATIONS

EPA	Environmental Protection Agency
FAO	Food and Agriculture Organization
USEPA	United States Environmental Protection Agency
EU	European Union
WHO	World Health Organization
U.S. FDA	United State Food and Drug Administration
PTWI	Provisional tolerable weekly intake
FDA	Food and Drug Authority
ATSDR	Agency for Toxic Substances and Disease Registry
DHSS	Department of Health and Social Security
EFSA	European Food Safety Authority
MRL	Maximum Residue Limit
OEHHA	Office of Environmental Health Hazard Assessment
U.S. AF	United States Air Force
RAIS	Risk Assessment Information System
IPCS	International Programme on Chemical Safety

CHAPTER ONE

1. INTRODUCTION

1.1 BACKGROUND

The term heavy metal refers to a group of metals and metalloids with specific gravity greater than 4g/cm^3 or 5 times or more than that of water. Some metals such as Copper, Iron and Zinc are nutritionally essential for healthy life, but can be toxic at high concentrations (Duruibe *et al.*, 2007).

Depending upon their concentrations the trace elements may exert beneficial or harmful effects on plants, animals and human life (Forstner and Wittman, 1981). Some of these heavy metals such as Mercury, Lead and Cadmium are toxic to living organisms even at low concentrations, whereas others like Iron, Copper and Zinc are biologically essential and become toxic at relatively high concentrations. When ingested in large amounts, heavy metals combine with body's biomolecules like enzymes and proteins to form stable biotoxic compounds, thereby mutilating their structures and hindering the functions of these essential biomolecules (Duruibe *et al.*, 2007).

In the last decades, contamination of aquatic systems by heavy metals has become a global problem. Heavy metals may enter aquatic systems from different natural and anthropogenic sources, including industrial or domestic wastewater, application of pesticides and inorganic fertilizers, storm runoff, leaching from landfills, shipping and harbour activities, geological weathering of the earth crust and atmospheric deposition (Yilmaz, 2009). In natural aquatic ecosystems, metals occur in low concentrations. Since they cannot be degraded, they are deposited, assimilated or incorporated in water, sediment and aquatic organisms thereby causing heavy metal pollution in water bodies (Abdel-Baki *et al.*, 2011). Metals entering the aquatic ecosystems can be deposited in aquatic organisms through the effects of bioaccumulation via the food chain and can become potentially toxic when accumulation reaches a substantially high level (Huang, 2003).

Fishes are good bio-indicators of heavy metal contamination in aquatic systems occupying different tropic levels and are of different sizes and ages (Burger and Gochfeld, 2005). Substantial amounts of metals may accumulate in the soft and hard tissues of fish (Mansour and Sidky, 2002). Heavy metals enter fish through a number of routes: via skin, gills, food and non-food particles. Once absorbed, heavy metals are transported in the blood stream to either a storage point or to the liver for transformation and/or storage (Obasohan, 2008). Like in fish and other organisms, heavy metals are not destroyed by humans (Castro-Gonzeza and Méndez-Armentab, 2008). Instead, they tend to accumulate in the body tissues such as liver, muscles and bones and threaten the health of humans who consume them. Therefore, the heavy metals are amongst a class of pollutants which has captured the attention of many scientific researchers around the globe.

Over the last six decades, the world has witnessed numerous tragedies involving heavy metals pollution. An example of such problems occurred in 1952, around the Japanese fishing harbour of Minamata. Sewage containing mercury had previously been discharged into the Bay of Minamata from a polyvinyl plant operated by a company called Chisso. The mercury accumulated in seafood leading eventually to mercury poisoning in a population which consumed fish from the bay. The resulting disease called Minamata disease led to nearly 1000 deaths. Another example of heavy metals pollution occurred in 1955 in the vicinity of Toyama city, along the Jinzu River in Japan. A disease known by the locals as Itai-itai (It hurts! It hurts!) occurred in the population from the consumption of rice, fish and bivalves that were cadmium contaminated from wastewaters discharged by nearby mining plants (Chen and Chen, 2001;

Dural *et al.,* 2007). The 1986 Sandoz disaster along the upper Rhine and the 1998 contamination of the Coto de Donana nature reserve in southern Spain are few other examples of the numerous environmental disasters owed to heavy metals pollution (Chen and Chen, 2001).

The world's ever growing human population has increased the need for food supply. The demand for fish and shellfish products has increased greatly because they are very good and cheap protein sources. Worldwide, people obtain about a quarter of their animal protein from fish and shellfish (Bahnasawy *et al.,* 2009). In 2004, about three quarters (105.6 million tons) of the estimated world fish production was used for direct human consumption (FAO, 2007). The real importance of fish in human diet is not only in its content of cheap and high-quality protein, but also due to the two kinds of omega-3 polyunsaturated fatty acids (eicosapentenoic acid and docosahexenoic acid) present in fish. Omega-3 fatty acids are very important for normal growth as they have been known to reduce cholesterol levels and decrease the prevalence and incidence of heart diseases, stroke, and preterm delivery (Davisglus *et al*. 2002; Burger and Gochfeld, 2005; Al bader, 2008). Fish also contains vitamins and minerals which play essential role in supporting healthy living (Ikem and Egiebor, 2005). For most nonoccupationally exposed individuals, diet is the main route of exposure to environmental pollutants such as heavy metals (Llobet *et al.,* 2003). Since diet represents the main route of exposure to heavy metals, and fish represent a part of diet, it is likely that polluted fish could be a dangerous dietary source of certain toxic heavy metals (Bogut, 1997).

In the past few decades there has been a growing interest in assessing the levels of heavy metals in food including fish. Such interests were intended to ensure the safety of the food supply in order to minimize the potential hazardous effect on human health.

In Ghana, Voegborlo *et al*. (2004) determined mercury concentrations in 56 samples comprising twenty commercial fish species taken from the Gulf of Guinea, Ghana from November 2003 to February 2004. The results from the study showed that all the samples analyzed had Hg concentrations below WHO/FAO recommended limit suggesting that the mercury content of the fishes were unlikely to constitute any significant health hazard.

In Nigeria, Christopher *et al*. (2009) studied the Distribution of Pb, Zn, Cd, As and Hg in bones, gills, livers and muscles of Tilapia (*O. niloticus*) from Henshaw town beach market in Calabar. The results showed that the muscle of Tilapia contained the least concentrations of the heavy metals determined.

Alinnor and Obiji (2010) performed a study to examine heavy metals (Pb, Fe, Cd, Mn, Hg, Cu and Zn) composition in fish samples from Nworie River and in frozen fish samples purchased from Ekeonunwa. They pointed out that untreated waste products discharged into Nworie River contaminated the aquatic system with these elements. The report consequently warned against the consumption of fish obtained from the river. Also the study found that frozen fish samples purchased from Ekeonunwa market were contaminated with heavy metals.

In Libya, Khalifa *et al*. (2010) determined concentrations of Co, Cd, Pb, Fe and Cu in different tissues of six fish samples from the Mediterranean Sea. They found that the concentrations of Cd and Pb in all examined tissues were above the WHO recommended literature values (0.5 and 0.20 ppm respectively); suggesting that the consumption of fishes from this terrain could be of serious health consequence.

In India, Sivaperumal *et al*. (2007) evaluated concentrations of Cd, Pb, Hg, Cr, As, Zn, Cu, Co, Mn, Ni, and Se in commercially important species of fish, shellfish and fish products from markets in and around the Cochin area. Results from the study showed that different metals were present in the samples at different levels but within the maximum residual levels prescribed by the European Union (EU) and USFDA and the fish and shellfish from these areas were generally safe for human consumption.

In Jordan, Levels of Cd, Cu and Zn in three fish species, *Oreochromis aureus, Cyprinus carpio* and *Clarias lazera,* collected from the Northern Jordan Valley were investigated by Al-Weher, (2008). The study showed that levels of these heavy metals in muscles of the three fish species were within acceptable limits by FAO standards, except for the Zn concentration in muscles of *Oreochromis aureus* (70.76±31.21 µg/g dry wt.) which were attributed to the increase of agricultural and other anthropogenic activities in the area.

In Turkey, Yilmaz (2009) compared the concentrations of Cd, Cu, Mn, Pb, and Zn in tissues of three economically important fish (*Anguilla anguilla*, *M. cephalusnd* and *O. niloticus*) inhabiting Koycegiz Lake-Mugla. The highest concentration of trace metals in the tissues of *M.cephalus* in the lake was attributed to the trophic characteristics of this species. The study considered *M. cephalus* as the most suitable species for use as biomonitors of trace metals pollution in the Koycegiz Lake. Consequently, the report recommended the use of this species as a tool (biological indicator) for future monitoring programs, to evaluate the evolution of heavy metal pollution in that area. Results indicated that, concentrations of Pb and Zn for *O. niloticus*; Pb, Zn and Cd for *A. anguilla*; and Cd and Zn for *M. cephalus* were found to be higher than the Turkish Food Codex, European Units and WHO limits for human consumption and posed health risk to consumers.

In Argentina, Marcovecchio (2004) considered *M. furnieri* fish as good bioindicator of heavy metal pollution in the ecosystem. A marked relationship between metal contents of the studied species and their trophic and ecological habits was observed. The results indicated that levels of

Hg, Cd and Zn found in edible muscle tissue were lower than the international standards for human consumption.

In France, Shinn *et al*. (2009) assessed heavy metals contamination in River Lot between 1987 and 2007. The concentration of Cu, Zn, Cd and Pb were quantified in muscle and liver of fish species from the river as well as in water, sediment and moss. The results showed that the average concentrations of Cd in fish muscle were above the maximum safety levels for human consumption defined by the EC.

In USA, an investigation of Mn, Pb, As, Cd, Hg, and Se levels in commercial fish in New Jersey was performed by Burger and Gochfeld (2005). They reported that the levels of most metals were below those known to cause adverse effects in the fish themselves. However, the levels of As, Pb, Hg, and Se in some fish were in the range known to cause some sub-lethal effects in sensitive predatory birds and mammals and in some fish exceeded health-based standards set by FAO, USEPA, WHO, and USFDA.

1.2 PROBLEM STATEMENT

Most industries and companies in Monrovia including Cement, Paint, Brewery, Dye processing, Plastic and Shipping discharge their effluents into the Mesurado River which drains into the Atlantic Ocean, where most of the fish are obtained.

Also because of their relatively cheap prices, most residents of Monrovia tend to prefer imported frozen fish from different geographical regions around the world. These imported fish species often enter the country without monitoring contaminants and there is always a risk that the fish may contain contaminants, including heavy metals, above acceptable levels.

1.3 MAIN OBJECTIVE

The main objective of this study was to determine the exposure of the population of Monrovia to heavy metals through fish consumption.

1.4 SPECIFIC OBJECTIVES

The specific objectives were:

1. To determine the concentration of toxic elements (Pb, Hg, Cd) in fish collected from markets in Monrovia
2. To determine the concentrations of the essential elements (Zn, Cu, Fe) in fish collected from markets in Monrovia
3. To determine the relationship between the concentrations of the metals and some characteristics of the fish such as total length and fresh body weight
4. To determine the type of association between the essential and toxic metals in the fish samples
5. To evaluate the hazard ratios in order to estimate the potential risk of health hazards of heavy metals to the population from the consumption of fish, using daily intakes
6. To determine if consumption advisory will be required

1.5 JUSTIFICATION

Although many studies have been done on the levels of heavy metals in fish samples along the West African Sub-region (Voegborlo *et al*., 1999**;** Sodomou *et al*., 2005**;** Christopher *et al.*, 2009**;** Voegborlo and Adimado, 2010; Kwaansa-Ansah *et. al*., 2011), no such work has been conducted in Monrovia, Liberia.

Hg, Cd, and Pb are non essential metals and their toxic effect on human health is well documented (Telisman *et al*., 2000; Lee *et al*., 2003; Lidsky and Schneider, 2003; Murata *et al*., 2004; Singh, 2005). Cu, Fe and Zn are all essential metals and their toxic effect on human health begins when they are present beyond certain threshold levels (Fahmy, 2000; Momtaz, 2002).

Mercury is an environmental contaminant that is present in fish and seafood products largely as methylmercury (MeHg). Aquatic organisms possess a remarkable capacity to turn inorganic mercury into MeHg, thus rendering mercury more easily transferable throughout the aquatic food chain (Diez, 2008). Human health hazards from environmental mercury were tragically realized during the severe pollution incidents of Minamata and Niigata in Japan owing to consumption of fish contaminated by MeHg which was discharged from acetaldehyde manufacturing plants. After these tragic events, considerable efforts have been expended on monitoring mercury in the aquatic environment, and limits on mercury levels in seafood have been established in different countries. The Japanese Welfare Ministry has set an action level of 0.3 µg /g wet weight for concentration of MeHg in fish and shellfish. The Ministry of Health of the State of Minnesota (USA) has proposed a new standard of MeHg of 0.16 µg /g wet weight. The World Health Organization (WHO) in 1972 defined the first tolerable exposure levels for mercury base on data from the poisoning incidents in Minamata Bay, Japan, in the 1950s and 60s (Myers and Davidson, 2000). The safe intake level was defined at 3.3 µg /kg/week (0.47 µg/kg/day) for MeHg and 5 µg /kg/week (0.71 µg/kg/day) for total mercury (THg). These levels however may not sufficiently protect the developing foetus. Following data from two epidemiological studies that investigated the relationship between maternal exposure to mercury and impaired neurodevelopment in the Seychelles and Faroe Islands, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) re-evaluated the level for MeHg. The provisional tolerable weekly intake level (PTWI) is now set at 1.6 µg /kg/week (0.23 µg/kg/week) for MeHg, a level presumed to be safe also for the developing foetus. The tolerable level for THg still remains the same (JEFCA, 2011). Other public health agencies have, however, defined lower levels of tolerable exposure doses of total mercury. The U.S. Food and Drug Administration has defined a tolerable level of 3.5 µg /kg/week (0.5 µg /kg/day) for total mercury exposure, while the Agency for Toxic Substances and Disease registry has set a safe level of 2.1 µg /kg/week (0.3 µg /kg/day) for total mercury intake (Clarkson, 2002).

Cadmium (Cd) is a toxic heavy metal of great environmental concern. Cd levels in the environment vary widely and emissions to the environment are normally transported continually between the three main environmental compartments: air, water and soils. Cd in water can be accumulated in the body of marine organisms and can eventually enter the body of humans who consume these seafood products. Some effects associated with cadmium are renal (kidney) damage, anemia, hypertension and liver damage. In the late 1960s environmental cadmium contamination was established as the cause of an epidemic of bone disease (itai-itai disease) in Japan. Since that time, increasing scientific interest has been devoted to cadmium as an environmental contaminant. Awareness is now been disseminated in some countries concerning the small margin of safety between existing intake levels and levels that may cause adverse health effect to the population. The World Health Organization (WHO) in 1972 defined the first tolerable exposure levels for cadmium. The upper levels were set at a range of 6.7-8.3 µg /kg/week. In 1988, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) re-evaluated the levels and set a new limit of 7.0 µg/kg/week (1.0 µg/kg/day). Since then this tolerable level has been maintained as the upper level of cadmium intake (JECFA, 2011).

Lead (Pb) is a toxic metal that occurs naturally in the environment. However, most lead concentrations that are found in the environment are a result of human activities. Due to the application of lead in gasoline, an unnatural lead-cycle has consisted. In car engines lead is burned and lead salts are generated. These lead salts enter the environment through the exhausts of cars. The larger particles drop to the ground immediately and pollute soils or surface waters, while the smaller particles travel long distances through air and remain in the atmosphere to later fall as rain. This lead-cycle caused by human production is much more extended than the natural lead-cycle and has caused lead pollution to be an issue of worldwide concern. Lead, in water, accumulates in the body of fish and other marine organisms and it is eventually ingested by humans who consume these fish and seafood products (Oforka et *al*., 2012). The World Health Organization (WHO) in 1972 defined the first tentative tolerable exposure levels for lead. The PTWI limit for adults was set at 50 µg/kg/week; but this value did not apply to children. In 1986, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) re-evaluated the levels and set a new limit of 25 µg/kg/week for both adults and children (JECFA, 2011). Following data from several epidemiological studies on neurodevelopment in children (Lanphear *et al*., 2005) and systolic blood pressure in adults (Glenn *et al*., 2003; Vupputuri *et al.,* 2003; Nash *et al*., 2003; Glenn *et al*., 2006), JECFA concluded that the PTWI (25 µg/kg/week) could no longer be considered health protective, and it was withdrawn (JECFA, 2011). Despite these assertions, numerous studies still base their health risk assessment on the withdrawn values (Sun et *al*., 2009; Oforka et *al*., 2012; Kumar *et al*., 2013).

Zinc is essential for human health. Although humans can handle proportionally large concentrations of zinc, too much can cause health problems such as stomach cramps, skin irritations, vomiting, nausea and anemia. Very high levels of zinc can damage the pancreas and disturb protein metabolism in the human body (Kumar and Mukherjee, 2011). The Joint FAO/WHO Expert Committee on Food Additives (JECFA) has established a PTWI for Zinc of 7000 µg /kg/week which is equivalent to 1000 µg /kg/day. This value is significantly higher than the 4900 µg /kg/week (700 µg /kg/day) limit recommended for zinc in fish and seafood products by the European Food Safety Authority (FSA, 2006).

Iron (Fe) is as an essential element that helps in the production and release of energy in the human body. Although important, high levels of Fe intake can cause symptoms of acute toxicity. JEFCA has established a threshold value of 5600 µg /kg/week (800 µg /kg/day) for Fe intake from food (JEFCA, 2011).

Copper is present in all animals and plants as an essential nutrient. Although copper is an essential element, high levels of intake can cause symptoms of acute toxicity. The Joint FAO/WHO Expert Committee on Food Additives (JECFA) has established a PTWI for copper of 3500 µg /kg/week which is equivalent to 500 µg /kg/day. The Food Safety Authority (FSA) of European countries has established a lower safety guideline regarding weekly intake (WI) of copper from fish and shellfish. It recommends a PTWI value of 1120 µg /kg/week which is equivalent to 160 µg /kg/day (FSA, 2006).

The fish species in the current study may contain heavy metals above acceptable levels; so there is a need to monitor the heavy metal concentrations in the species consumed by the population of Monrovia. Determining the levels of such heavy metals and comparing the levels with guidelines will establish the potential health risk from the consumption of such fish species.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Sources of heavy metals

Apart from natural background geochemical sources, heavy metals are emitted from a variety of anthropogenic sources. Heavy metals emissions occur through a wide range of processes and pathways; including the air (via combustion, extraction and processing), the surface waters (via runoffs and releases from storage and transport) and the soil and ground waters through leaching. Of the three (air, water and soil), atmospheric emissions tend to be of greatest concern health-wise because of the quantities involved and the widespread dispersion and potential for exposure that often ensues.

The amounts of most heavy metals deposited to the earth surface from human activities are far greater than depositions from natural background sources. Possible sources include mining activities, disposal of metal-containing industrial effluents (Phuong *et al*., 1998), wastewater arising from informal settlements (Jackson *et al*., 2007), leachates from municipal and industrial landfill sites (Moodley *et al*., 2007), municipal wastewater, dry docking companies and petrol filling stations (Shriadah, 1998). Combustion processes are the main sources of heavy metals especially smelting, internal combustion engine, power generation and incineration (Nriagu, 1988).

2.2 Distribution pathways and fate of heavy metals in aquatic biomes

Once in the aquatic environment, metals are partitioned among the various aquatic environmental compartments (water, suspended solids, sediments and biota). The metals in the aquatic environment may occur either in dissolved, particulate or complex form. The main processes governing distribution and partition are dilution, dispersion, sedimentation and adsorption/desorption (Biney *et al.,* 1991). Nonetheless, some chemical processes could also occur depending on the physcio-chemical properties of the water (pH, dissolved ions and temperature). Adsorption could be the first step in the ultimate removal of metals from water. In the course of distribution, permanent or temporary storage of metals takes place in the sediments of both freshwater and marine environments. Microbial activity and redox processes may change the properties of sediments and affect the composition of interstitial water. As a result, Iron and Magnesium oxides may be converted to carbonates or sulphides, leading to a decrease in the absorption capacity of the sediments. Reworking of the sediments by aquatic organisms will bring sediments to the surface, where a significant fraction of the metal may be released (Kennish, 1992).

2.3 Biomagnifications and Bioaccumulations of heavy metals in fish

The easiest way to understand how bioaccumulation and biomagnification work is to use them in a food chain scenario. Bioaccumulation begins at the first level of a food chain where there is an increase in the concentration of a pollutant from the environment to the first consumer (i.e. pollutants to plankton to filter feeder). It can also refer to the amount of toxins in individual animals because as a top predator consumes multiple, contaminated food sources, it will "accumulate" more toxins. Biomagnification occurs when the concentration of a pollutant increases from one link in the food chain to another (i.e. polluted fish will contaminate the next consumer and continues up a tropic food web as each level consumes another) and results in the top predator containing the highest concentration levels. In order for biomagnification to occur, a pollutant must be long-lived, mobile, soluble in fats and biologically active. Examples of these types of pollutants include dichloro-diphenyl-trichloroethane (DDT), polychlorinated biphenyls (PCBs), heavy metals (Hg, Pb, Cd, etc.) and β-methylamino-L-alanine (BMAA). In high enough concentrations, these toxins can lead to serious health issues for marine fauna and humans (USEPA, 2003).

2.4 Selected heavy metals and their toxicity

2.4.1 Mercury

Mercury has very wide applications in science, agriculture, industry and dentistry and medical diagnostics. Common uses of mercury include thermometers and compact fluorescent light bulbs and control systems (ATSDR, 2007). The abundance of mercury in the earth's crust is about 0.08ppm. It occurs mainly as native mercury and as cinnabar (HgS). Natural mercury arises from the earth's crust through volcanic eruptions, coal burning, smelting, chlor-alkali production plants and evaporation from oceans. Approximately 10,000 tons of natural mercury originates from degassing of earth's crust; to this amount approximately 20,000 tons/year is added by anthropogenic activity (Hansen and Dasher, 1997). Mercury emissions from coal smoke are the main source of anthropogenic discharge and mercury pollution in atmosphere. It is estimated that the mercury emissions will increase at a rate of 5% a year (Zhang *et al*., 2002). According to Murray and Holmes (2004), the major contributors to Hg emission in the USA included coal-fired electric utilities (52.7%), municipal wastes combustion (5.6%), mercury-cell chlor-alkali plants and hazardous-waste incinerators (4% each), stationary internal combustion engines (ICEs) (3.5%), industrial, commercial and institutional (ICI) boilers (3.3%), lime manufacturing (3.0%) and medical waste incineration (1%). Informal gold mining has used mercury since antiquity. High contamination of Brazilian Amazon (Brazil is world's second largest producer of gold) is indicated by the strong presence of mercury in its biota (Grandjean *et al*., 1995).

2.4.1.2 Mercury in seafood

The emitted mercury both natural and anthropogenic is in an inorganic form, predominantly metallic vapour, which is carried off to great distances by winds and eventually falls in water bodies. In aquatic environments, inorganic mercury is microbiologically transformed into lipophilic organic compound, methyl mercury. This transformation makes mercury more prone to biomagnifications in food chains (Hansen and Dasher, 1997). Consequently, populations with traditionally high dietary intake of food originating from fresh or marine environment have highest dietary exposure to Hg. Extensive research done on locals across the globe have already established this for instance polar Eskimos. Persons who routinely consume fish or a particular species of fish are at an increased risk of methyl mercury poisoning (Hansen and Dasher, 1997). Since mercury intake is expressed on a per kilogram body weight basis, exposure of children under age 14 is two to three times high because of higher food intake per kilogram body weight. After measuring total mercury in the edible portions of 244 selected fish and shellfish purchased in Canada at the retail level, the Canadian advisee to children and women of child-bearing age is to limit their consumption of fresh and frozen tuna, swordfish and shark to not more than one meal per month (Dabeka *et al*., 2004).

2.4.1.3 Mercury Toxicity in Humans

Extensive evidence has shown that neural development extends from the embryonic period through adolescence and that different behavioral domains (e.g. sensory, motor and various cognitive functions) are sub served by different brain areas. Of prime concern, however, is the possibility that developmental exposure to neurotoxicants may result in an acceleration of age-related functional decline. This concern is compounded by the fact that developmental neurotoxicity that results in small effects can have a profound societal impact when amortized across the entire population and across the life span of humans (Rice and Barone, 2000). The difference in sensitivity between foetus and adult organism is between 2 and 5 with foetus being more susceptible to methyl mercury toxicity (Snyder, 1990). Maternal consumption during pregnancy of methyl mercury contaminated fish in Japan and of methyl mercury contaminated bread in Iraq caused psychomotor retardation in the offspring. Studies in Iraq suggested adverse fetal effects when maternal hair mercury concentrations were as low as 20 ppm. This raises a possibility that mothers consuming diet containing mercury could pass the toxicant to foetus **(**Murata *et al*., 2004) and to infants through breast milk (Grandjean et al., 1999).

Mercury toxicity is also potentially linked to autism (a disorder that can lead to lifelong disability) in children **(**Lee *et al*., 2003). Subtle neurological disorders in children due to mercury exposure have been documented **(**Johnson, 2004). Neuropathological examination of the brains of children prenatally exposed to organic mercury revealed dysplasia of cerebral and cerebellar cortexes, neuronal ectopia and several other developmental disturbances (Geelen and Dormans, 1990).

In another survey of fish eating population with low hair Hg levels <10 ppm, it was found that neurological symptoms particularly sensory disturbances such as glove and stocking type occurred at a very high rate (Harada *et al*., 1994). The adult population of Amazonian ecosystem with hair mercury below 50µg/g demonstrated near visual contrast sensitivity, decreased manual dexterity, tendency for increased muscular fatigue, decreased muscular strength among women significantly in a dose dependent manner (Label *et al.,* 1998). Similarly disruption of attention, fine motor function and verbal memory was also found in adults of fish eating populations on exposure to low mercury levels (Yokoo *et al*., 2003).

2.4.2 Lead

Lead is found in small amounts in the earth's crust. It can be found in all parts of our environment and it is emitted from human activities like mining, manufacturing and the burning of fossil fuels. Airborne lead can be deposited on soil and water, thus reaching humans via the food chain.

The principal source of Pb in the marine environment appears to be the exhaust of vehicles run with leaded fuels that reaches the sea water by way of run-off and wind-blown dust (Castro and Huber, 1997). Lead is found at high concentration in muscles and organs of fish. When accumulated in the human body, it replaces calcium in bones. Lead exposure has been mainly related to retardation of neurobehavioral development (Lidsky and Schneider**,** 2003; Castoldi *et al.*, 2003). The EU maximum residue limits permitted in fish is 0.3 µg/g for Pb (Herreros *et al.*, 2008).

2.4.2.1 Lead Toxicity in humans

In human, the toxic effects of Pb have been demonstrated at very low levels, and some studies have even suggested that there may be no level of exposure below which Pb is harmless. Lead toxicity involves several organs and can result to a variety of biochemical defects (WHO, 1995).

Lead is particularly toxic to the brain, kidneys, lungs, heart and reproductive system. Exposures can cause impairments in intellectual functioning, kidney damage, miscarriage, increased blood pressure and hypertension (Silbergeld, 1996). Data from European Food Safety Authority (EFSA) have related exposure to Pb to effects like neurotoxicity, nephrotoxicity, carcinogenicity and endocrine and reproductive failures in adults **(**Herreros *et al*., 2008). Moderate exposure to Pb can also significantly reduce human semen quality and is related to damage to DNA in children and impairment of the reproductive function in adults (Telisman *et al*., 2000).

Several studies have shown that Pb exposures can significantly reduce the Intelligent Quotient (IQ) of school- aged children; some estimates suggest that every 10-microgram-per deciliter increase in Pb levels in the blood is associated with a 1-to-5-point decrease in the Intelligent Quotient (IQ) of exposed children (Goyer, 1996). Lead exposures have also been associated with aggressive behavior, delinquency and attention disorders in boys between the ages of 7 and 11 (Needleman *et al*., 1996).

The Joint FAO/ WHO Expert Committee on Food Additives provisionally recommend that the weekly intake of Pb should not exceed 25 μg/kg or 0.025 mg/kg body weight for infants, children and adults (FAO/WHO, 1993).

2.4.3 Cadmium

Cadmium is a natural element in the earth's crust and it is usually found as a mineral with other elements. All soils and rocks, including coal and mineral fertilizer, have some levels of cadmium in them. In industry and consumer products, it is used for batteries (Ni-Cd batteries of mobile phones), pigments, metal coatings and plastics. It also forms alloys with some other metals. Cadmium enters air from mining, industry, and burning of coal and household wastes. Its particles can travel long distance in air before falling to the ground or in water (Singh, 2005).

Cadmium is widely distributed at low levels in the environment and is not an essential element for humans, animals and plants. The WHO/FAO has determined a maximum tolerable weekly intake of 7µg/kg body weight for human (USFDA, 1993). The EU maximum residue limit (MRL) permitted in fish is 0.1-0.3 µg/g (Herreros *et al*., 2008).

2.4.3.1 Cadmium Toxicity in Humans

Over the last century, the human body burden of Cd has increased dramatically due to increasing environmental, industrial and anthropogenic activities (Thrush, 2000). Humans normally absorb

Cd into the body either by ingestion or inhalation (Lauwerys, 1979). Cadmium is more efficiently absorbed from the lungs than from the gastrointestinal tract (ATSDR, 2005). The latter usually reflects the toxic action of a high body burden on the kidney and possibly the skeleton. The absorption efficiency is a function of solubility of the specific cadmium compound as well as its exposure, concentration and route. According to an IPCS report (1992), about 2-6% of the Cd ingested is actually taken up into the human body.

Cadmium retention in body tissues is related to the formation of Cd-metallothionein, a Cd protein complex of low molecular weight. Cadmium accumulates in the human body; particularly in the liver and kidney cortex (IPCS, 1992, Jarup *et al*., 1998). It has an elimination half life of 10-30 years (Jarup *et al*., 1998).

The effects of Cd on the kidney take the form of renal dysfunction and subsequent pathological changes. The former is reflected by failure to reabsorb substances normally, and often results in aminoaciduria, proteinuria, glucosuria and decrease renal tubular absorption of phosphate. Cadmium excretion and low molecular weight proteinuria are early symptoms of renal tubular Cd damage (WHO, 1995). Other toxicity symptoms induced by cadmium include gastrointestinal disorders and hypertension. It is also reported that intoxication with Cd in pregnant women has been related to reduced pregnancy length and newborn weight and, recently, to disorders of the endocrine and/or immune system in children (Schoeters *et al*., 2006).

People with severe Cd nephropathy may exhibit excessive urinary loss of calcium. With chronic Cd exposure, urinary calcium may eventually decline to become less than normal. Associated skeletal changes probably related to calcium loss to Cd exposure include osteoporosis (Staesson *et. al*., 1999; Alfven *et al*., 2000; Nordberg *et al*., 2002) and osteomalacia (bone changes or disorders associated to intense skeletal pains). These metabolic disorders were common features of a Cd poisoning syndrome nicknamed ‘itai-itai” observed in Japan around the end of the Second World War. Current estimate suggest that more than 200 million people worldwide have osteoporosis and that the prevalence of this disease is escalating (Reginster and Burlet, 2006). Inhalation of Cd causes acute inflammatory reaction of the lungs. Long term exposure produces chronic bronchitis and increased susceptibility to infections like bronchiectasis and emphysema. Other pulmonary irritants, particularly cigarette smoke, a significant source of Cd, may exacerbate its toxic effects (WHO, 1995). U.S. EPA (2005) and OEHHA (2005) have determined that there is sufficient evidence that Cd is carcinogenic to humans. OEHHA derived an inhalation potency factor based on inhalation studies in humans, but no oral studies in humans or animals were identified that were judged suitable for developing oral cancer potency for Cd. The most significant measure of excessive Cd exposure is increased Cd excretion in urine. Increased urinary Cd reflects recent exposure, increased body burden and elevation of renal Cd. Urinary Cd measurement thus provides a good index of excessive Cd exposure.

2.4.4 Copper

Copper is widely used for wire production and in the electrical industry. Its main alloys are brass (with zinc) and bronze (with tin). Other applications are kitchenware, water delivery systems, and copper fertilizers (Bradi, 2005). Copper is considered as an essential constituent of metalloenzymes of living organisms and is required in hemoglobin synthesis and in catalysis of metabolic reactions (Dural *et al*., 2007). It plays a crucial role in many biological enzyme systems that catalyze redox reactions. However, if present at relatively high concentrations in the environment, toxicity to aquatic organisms may occur. Copper in the ionic forms Cu^{2+}, Cu_2OH^+ and $CuOH^+$ is toxic to fish (Moore, 1991).

2.4.4.1 Copper Toxicity in Humans

Acute copper toxicity in humans is very rare and often results from contamination of foodstuffs by copper containers or from accidental or deliberate ingestion or large quantities of copper salts (IPCS, 1998) Following acute ingestion of copper salts in amounts that exceed approximately 1.0 g, systemic effects are generally observed. The effects include gastrointestinal mucosal ulcerations and bleeding, acute hemolysis and hemoglobinuria, hepatic necrosis with jaundice , nephropathy with azotemia and oliguria, cardiotoxicity with hypotension, tachyeardia and tachypnea, and central-nervous-system(CNS) manifestation, including dizziness, convulsion, headache, stupor, headache and coma (U.S. AF, 1990). Acute hemolytic anemia and kidney effects, indicative of renal tubular damage, were observed in a child 2 days after drinking a solution containing approximately 3 g copper sulfate (RAIS, 1992).

Although the chronic toxicity from long-term exposure to copper has not been extensively investigated, studies of patients with Wilson's disease, a genetic defect that results in accumulation of copper in tissues, provide information on the chronic toxicity of Cu. Wilson's disease may affect many organs and systems and is characterized by hepatic cirrhosis, brain damage, kidney damage, demyelination and hemolytic anaemia. Patients may also suffer from poor coordination, psychological impairment, trmors, disturbed gait, rigidity and eye opacities (ATSDR, 1990; Goyer, 1991). An increased dietary intake of Cu may be partially responsible for a disease known as Indian childhood cirrhosis, which usually occurs in children, aged 6 months to 5 years. The disease is characterized by high levels of Cu in the liver, interlobular fibrosis and widespread hepatic necrosis with poor hepatic regeneration (U.S. AF, 1990). A prospective population study of men residing in eastern Finland, an area with high levels of Cu in drinking water, established a positive correlation between serum Cu levels and risk of acute myocardial infarction (Salonen *et al*., 1991). It has also been shown that high copper levels can lead to an increase in the rate of free radical formation (Gwozdzinski, 1995), teratogenicity (Stouthart *et al*., 1996) and chromosomal aberrations (Fahmy, 2000).

2.4.5 Iron

The major source of atmospheric contamination is from the iron and steel industry, electric arc furnaces, welding, incineration and the burning of fossil fuels (Ayres and Hellier, 1998). Iron and its alloys are used mainly in the transportation, construction, machine and energy industries.

Iron is essential for healthy growth of all living things. It is needed for a variety of biochemical reactions, DNA synthesis, formation of hemoglobin, oxygen transport, electron transfer and catalytic effects. In the human body, there are 3-4 g of iron, most of which is involved in the formation of red blood cells. Most of the remaining iron is stored in the liver and spleen as ferritin and hemosiderin. Iron in excess is potentially toxic to all forms of life and by all routes of exposure: toxic to plants at concentrations of 200 $mgFeL^{-1}$ and toxic to human at concentrations of 200 mgFe day^{-1}. Iron dust, usually in the form of the oxides can cause conjunctivitis, choroiditis, retinitis and siderosis of tissues, pulmonary fibrosis and increased risk of lung cancer (Sunderman, 1993).

2.4.5.1 Iron Toxicity in Humans

Iron is regulated primarily by absorption since humans have no physiological mechanism by which excess iron is excreted. Excess body iron can be highly toxic. This toxicity involves many organs leading to a variety of serious diseases such as liver disease, heart disease, diabetes mellitus, hormonal abnormalities, dysfunctional immune system, etc. The tissue damage associated with iron overload is believed to result primarily from free radical reactions mediated by iron (Fraga and Oteiza, 2002).

The body normally absorbs less iron if its stores are full, but some individuals are poorly defended against iron toxicity. Once considered rare, iron overload has emerged as an important disorder of iron metabolism. Iron overload is known as hemochromatosis and is usually caused by a gene that enhances iron absorption (Dural *et al*., 2007). Other causes of iron overload include repeated blood transfusions, massive doses of dietary iron, and rare metabolic disorders. Additionally, long term over consumption of iron may cause hemosiderosis, a condition characterized by large deposits of the iron storage protein hemosiderin in the liver and other tissues. Iron overload is most often diagnosed when tissue damage occurs, especially in iron-storing organs, such as the liver. Infections are likely to develop because bacteria thrive on iron rich blood. Ironically, some of the signs of iron overload are analogous to those of iron deficiency: fatigue, headache, irritability, and lowered work performance (Bury *et al*., 2003; Dural *et al*., 2007). Other common symptoms of iron overload include enlarged liver, skin pigmentation, lethargy, joint diseases, loss of body hair, amenorrhea, and impotence. Untreated hemochromatosis aggravates the risks of diabetes, liver cancer, heart disease and arthritis (Franchini, 2006).

2.4.6 Zinc

Zinc is used in many industries as manufacture of dry cell batteries, production of alloys such as brass or bronze, producing a galvanized coating (Momtaz, 2002). The main sources of Zn pollution in the environment are zinc fertilizers, sewage sludge, and mining (Bradi, 2005). It is an essential element for the life of animal and human beings (Momtaz, 2002) and is present in many enzymes involved in important physiological functions like protein synthesis. It is also essential for male reproductive activity (Aprill and Sims, 1990; Sunderman, 1993).

2.4.6.1 Zinc Toxicity in Humans

A number of reports outline the effect of acute exposure to Zn in humans. However, most of these reports are poorly documented with inadequate characterization of the actual exposure levels; although some estimates of exposure have been made. For instance, high concentrations of Zn in drinks (up to 2500 mg/L) have been linked with effects severe abdominal cramping, diarrhea, tenesmus, bloody stools, nausea, and vomiting in 300 people, and symptoms of nausea, vomiting and diarrhea in more than 40 people (Brown *et al*., 1964; Fosu-Amankwah, 2010). The amount of Zn ingested was estimated to be approximately 325-650 mg.

Lethargy, along with drowsiness, unsteady gait, and increase serum lipase and amylase levels, was seen in an individual who had ingested 12 g of elemental Zn, equivalent to 150 mg/kg body weight, resulting in increase in blood Zn concentrations (Murphy, 1970).

Excess Zn levels in a small number of children were associated with severe chronic chloestatic liver disease progressing to end-stage biliary cirrhosis in these subjects. An adverse lymphocytic response was reported in 11 healthy men who ingested 150 mg of elemental Zn twice a day for 6 weeks (Phillips *et al*., 1996).

Zinc has been reported to cause the same signs of illness as does Pb and can easily be mistakenly diagnosed as Pb poisoning. Excess amount of Zn can cause system dysfunctions, impairment of growth and reproductive defects. Other clinical signs of Zn toxicity have been reported as vomiting, diarrhea, bloody urine, icterus (yellow mucus membrane), liver failure, kidney failure and anemia (Duruibe *et al*., 2007).

There are inherent difficulties in estimating Zn requirements for humans, with a number of physiological, dietary and environmental factors affecting various populations. However the WHO has set a guideline value of 15 mg/day as maximum daily intake for adults (WHO, 1995).

2.5.1 Brief highlights of selected fish species

2.5.1.1 *Pseudotolithus senegalensis* (Cassava croaker)

Known in Liberian setting as Cassava fish, this species has an evenly arched head and nape, with eye diameter less than the interorbital width. It is silvery grey or yellowish on the back and sides with a characteristics whitish ventral region. The back has a number of darker diagonal stripes placed close together. The fins are all more or less yellowish, and are without definite markings.

It is a demersal tropical climate species and is found in brackish and marine environments; usually at depths up to 70 meters. It inhabits muddy, sandy, and rocky bottoms in coastal waters. Smaller individuals are found in shallow waters, but rarely enter estuaries. It primarily feeds on fish, shrimp, prawns and crabs. It is called croaker for the repetitive croaking sounds it makes (Chao and Trewavas, 1990).

2.5.1.2 *Pomadasys rogerii* (Pigsnout grunt)

The Pigsnout grunt is a benthopelagic tropical climate species that is found in brackish and marine environments; usually at depths of 25 to 90 meters. It is silvery in colour, with a bluish grey back, and with series of small black spots on the back which follow the oblique rows of scales. There is a characteristic large black spot on the hinder part of the gill-cover. There is usually a series of round blackish spots at the base of the dorsal fin between the rays, sometimes with a second series higher up. The species has an oblong and compressed body with a silvery ventral portion. It has characteristics dark brown spots irregularly spread on the back and side but not extending to the upper back anterior. It inhabits sandy and muddy bottoms of coastal waters and estuaries, and feeds on fish, worms, mollusks and benthic crustaceans (Eschmeyer *et al.*, 1983). It is known locally (in Liberia) as grunter.

2.5.1.3 *Seriola carpenteri* (Guinean amberjack)

The Guinean amberjack, known by Liberians as Wakie, Judusloyah or Cullehey, is a marine dwelling species with elongated, shallow and slightly compressed body. Juveniles of this species have five black vertical bands on the sides and a dark nuchal bar extending from the eye to dorsal-fin origin. Large adults have characteristics “old rose” colour. Members of the species are generally confined only in coastal waters over continental shelf, from the surface to at least 200m. They are well confined to areas where surface temperature exceed 25°C, with a distribution perhaps influenced by seasonal movements of the 18-27°C water mass along the African coast (Smith-Vaniz,1986).

2.5.1.4 *Galeoides decadactylus* (Lesser African Threadfin)

Known locally as butter nose, the Lesser African threadfin or Guinean threadfin occurs over sandy (Schneider, 1990) and muddy bottoms in shallow waters, frequently in brackish habitats. It is greenish grey above, with some more or less distinct darker yellowish stripes running along the series of scales, silvery white on the flanks and beneath. There is a round dark spot on the side above the pectoral fin and a black marking on the lower side of the tip of the gristly and semi-transparent snout. The pectoral fins are dark and the species is said to occur in lagoons as well as on the coast and in fresh water. They are mostly found along the eastern Atlantic Ocean. Members of this species feed on benthic invertebrates (Daget and Njock, 1986).

2.5.1.5 *Stromateus fiatola* (Blue butterfish)

Known in Liberia as Marry fish, the blue butterfish is a pelagic, subtropical climate species that is found in marine environments; usually at depths of 10 to 70 meters. It inhabits waters over continental shelves and feeds primarily on zooplankton, small fishes, and sometimes medusa. Members of this species are blue to brownish in color with darker spots dorsally, silver to whitish ventrally and juveniles have vertical bars on body and small black pelvic fins. The body is covered with tiny scales. The pelvic fins are present in the young fish, but disappear with age (Haedrich**,** 1986).

2.5.1.6 *Trachinotus goreensis* (Longfin Pompano)

Known in Liberia as small corvally, the Longfin Pompano is a marine species that frequently occurs in brackish terrains. Members of this species are pelagic-neritic, often operating within depth range of about 0-100m. It inhabits coastal waters and estuaries (Schneider, 1990**)** and is very common in the eastern Atlantic Ocean. The fish has a silvery skin, with the scales small and scarcely apparent, and the colour is grayish blue above and paler beneath (Uyeno *et al*., 1983).

2.5.1.7 *Arius latiscutatus* (Rough-head sea catfish)

The rough-head sea catfish (known locally as catfish) is a demersal tropical climate species that is found in marine and brackish environments; usually at depths of 30 to 70 meters. It is frequently found in brackish estuaries and will sometimes enter freshwater. It primarily feeds on fish, benthic invertebrates, zooplanktons, and detritus. The general coloration is steely blue above and white beneath. The pectoral and dorsal fins are armed with saw-edged spines which the fish uses for defense against attackers (Schneider, 1990).

2.5.1.8 *Pagrus caeruleostictus* (Bluespotted seabream)

The bluespotted seabream (known locally as snapper) is a pelagic marine species with a depth range of 30-50 meters. It is generally found in hard bottoms (mainly in rocky terrains); the older individuals in the deeper part of the range, the young in inshore areas. The colour is reddish, with iridescent hues. The head is a vivid gold colour, especially in the region between the eyes and the mouth. There are some sky-blue spots scattered along the back and upper parts of the flanks. The fins are reddish, and the tail has a narrow black margin. It feeds mainly on bivalves and also on crustaceans and fish (Uyeno *et. al*., 1983).

2.5.1.9 *Selene setapinnis* (Atlantic moonfish)

The Atlantic Moonfish (locally called bighead Porjoe) is a benthopelagic marine dwelling fish species that is very common in brackish terrains. Adults are usually found near the bottom from inshore waters to at least 54 m depth, but may form schools near the surface. Juveniles are found on muddy bottoms brackish estuaries and in coastal marine waters. Adults feed on small fishes and crustaceans (Uyeno *et. al*., 1983).

2.5.2.0 *Trichiurus lepturus* (Atlantic cutlassfish or Largehead hairtail)

Known locally as Silver fish, the Largehead hairtail is a benthopelagic species found mainly in coastal waters, over muddy bottom, and occasionally at the surface at night. The body is covered with a delicate silvery skin, and the silvery coating seems to come off when handled. The lateral line starts near the upper edge of the gill-cover, bends downwards, and then runs along the lower part of the body and parallel with it to the tail. The lower jaw protrudes beyond the upper. The strongest teeth are at the front of the upper jaw. Young and immature ones feed on crustaceans and small fishes while the adults are more piscivorous (Uyeno *et. al*., 1983).

2.5.2.1 *Pseudotolithus elongates* (Bobo croaker)

The Bobo croaker (known locally as white boy) is a demersal tropical climate species that is found in brackish and marine environments; usually at depths of 50 to 100 meters. It inhabits muddy bottoms and also enters estuaries and coastal lagoons, where it feeds on smaller fishes and shrimps (Schneider, 1990).

2.5.2.2 *Epinephelus goreensis* (Dungat grouper)

The dungat grouper (locally called black groper) is a demersal, tropical climate species that is found in marine environments; usually at depths of 80 to 300 meters. Adults of this species can be founder in deeper waters. It inhabits rocky, sandy, and muddy bottoms and feeds primarily on crustaceans and fish (Chao and Trewavas, 1990).

2.5.2.3 *Sardinella aurita* (Spanish sardine)

The Spanish sardine or round sadinella (locally called sardine fish) is a coastal, pelagic species that prefers clear saline water. It ranges from inshore and near surface to the edge of shelf down to 350 m. Juveniles stay in nursery areas (often in warmer terrains) but upon maturity rejoin adult stocks in the colder offshore waters. It has a distinct black spot on the hind edge of its gill cover but no black spot at the dorsal fin. It is distinguished from other sardines by the larger and more sharply pointed head, the less flattened body, which is not so sharp along the belly, and by the larger opercular bones supporting the gill-cover. The coloration is bluish grey above, and rainbow silvery on the sides. The dorsal fin is yellowish, and the deeply forked tail dark. This species feeds mainly on zooplankton, especially copepods, with phytoplanktons being eaten by juveniles (Uyeno *et. al*., 1983).

2.5.2.4 *Elops senegalensis* (Senegalese ladyfish)

Locally known as Morla or Tenpound, the Senegalese ladyfish is a coastal pelagic species occurring inshore and some way up the tidal rivers to the edge of the shelf. It can be found in tropical and brackish terrains. It is often mistaken for the Atlantic Ladyfish but is distinguished by the number of gill rakers on the lower part of the first gill arc and the number of scales on the lateral line. The lower jaw does not project beyond the upper, and the whole of the front part of the band of teeth in the upper jaw is exposed when the mouth is closed. Members of this species feed on fish and shrimps (Schneider, 1990).

2.5.2.5 *Sardinella maderensis* (Madeiran sardine)

The Madeiran Sardinella (known locally as Bonny fish) is a pelagic, coastal zone, subtropical climate species that is found in brackish and marine environments; usually at depths of 0 to 80-meters. It has an elongated but moderately compressed body that is variable in depth. The dorsal portion of the fish is blue-green while the lower flanks are silvery with faint gold mid-lateral line. The dorsal fin is yellow with dusky margin. It inhabits coastal waters and primarily feeds on small planktonic invertebrates, fish larvae, and phytoplanktons (Uyeno *et. al*., 1983).

2.5.2.6 *Albula vulpes* (Bonouk/Bonefish)

The Bonouk (locally called Morlay) is a fish species that is found in brackish or marine environment; usually at depths of 0 to 84 m (Uyeno *et. al*., 1983). It is amphidromous (can migrate from fresh waters to the seas or vice versa). It is a silvery fish with a prominent snout and a somewhat pig-like mouth. The teeth in the jaws are minute, but there is a large patch of blunt teeth on the tongue, which bites against another patch on the roof of the mouth. It uses these teeth for crushing shellfish. It is khaki gray on the back and silvery white on the sides and belly. It is more or less pelagic but feeds on benthic worms, crustaceans, and mollusks and the young form feed on planktons (Eschmeyer *et al.*, 1983). It tolerates oxygen poor water by inhaling air into a lung-like air bladder (Lieske and Myers, 1994).

2.5.2.7 *Thussus obesus* (Bigeye tuna)

Found in warm temperate waters of the Atlantic, Pacific and Indian Oceans, this schooling, pelagic, seasonally migratory species is suspected of making rather extensive migrations. It is locally known as Tuna fish. The coloration is bluish above, becoming silvery beneath, with purplish blue shades on the sides of the head. The soft dorsal and anal fins are blackish towards their margins and the finlets are distinctly yellow. The large forked tail is gray. Its diet includes squid, crustaceans, mullet, sardines, small mackerels and some deep water species like threadfins, sea breams and jack (Froese *et al*., 2011).

2.5.2.8 *Priacanthus arenatus* (Atlantic bigeye)

The Atlantic bigeye (locally known as Chicken soup fish or Wajay) is a benthic dwelling fish species found around depths of 15-75m. Juveniles of this species are mostly pelagic and found in upper layers of the ocean. The fish has a deep body which is ovate and laterally compressed. It is bright red in color but may change to silvery white with pattern of broad reddish bars on head and body. The fins are all pale brownish and the eyes are very large. The mouth is large and oblique; with a projecting lower jaw and a maxilla nearly reaching to vertical level from anterior border of the eye. It feeds on small fishes, crustaceans and polychaetes (Froese *et al*., 2011).

2.5.2.9 *Euthynnus alletteratus* (Little Tunny)

Little Tunny (known locally as Blood fish or Spotted Kanmu) is a pelagic species that is found mostly in coastal waters especially in the temperate and tropical zones of the Atlantic Ocean. It is smaller in size and less migratory than other tunas. It has a robust and fusiform body. The colour is steel blue above, becoming paler and more silvery on the flanks and belly. There may be some obliquely placed wavy stripes on the sides above the lateral line. The upper fins are all dusky while the lower ones are pale. The Little Tunny's habitat tends to be near-shore waters, much closer to shore than most other tunas. They live in and around inlets, points, jetties, and sandbars. All of these places are where bait fish like sardine and menhaden, both favorites of the Little Tunny, form large schools, which are very helpful to the Little Tunny's feeding style (Bahou *et al*., 2006).

2.5.3.0 *Lutjanus campechanus* (Red snapper)

The red snapper is a light red-colored fish found in schools living in the great Atlantic coast. Gregarious, these fish are found in schools close to the ocean floor on rocky outcrops, ledges, artificial reefs and oil drilling platforms, usually at depths between 30-200 feet (Smith, 1997). Adults are found over rocky bottoms. Juveniles inhabit shallow waters, common over sand or muddy bottoms. They feed mainly on fishes, shrimps, crabs, worms, cephalopods, and some planktonic items including urochordates and gastropods (Allman *et al*., 2002).

2.5.3.1 *Scomberomorus tritor* (West African mackerel)

The West African Spanish mackerel (locally known as mackerel) is a pelagic, tropical climate species that is found in brackish and marine environments; usually at depths of 20 to 25 meters. The fish is slightly blue, darker blue on the back, paler on the flanks, and whitish on the belly. It has a series of short vertical greenish gray stripes on the sides. The spinous part of the dorsal fin is black while the soft part is greenish black. The anal fin and the finlets behind both dorsal and anal fins are grayish. The pectoral fins are dark gray and the caudal fin greenish black. It is found in warm waters and forms schools close to shore. It enters coastal lagoons to feed and eats primarily clupeids, particularly Shad (Froese *et al*., 2011).

2.5.3.2 *Scomber colias* (Atlantic chub mackerel)

The Atlantic chub mackerel (known locally as Sea mackerel) is a coastal pelagic marine species that inhabits temperate and sun-tropical waters worldwide at depths ranging from near the surface down to about 300m. It has an elongated, fusiform and slightly compressed body in the form of a spindle with a sharp pointed snout and large mouth opening. It feeds mostly on small crustaceans, eggs and small schooling fish (Froese *et al*., 2011).

2.5.3.3 *Trachinotus maxillosus* (Guinean pompano)

The Guinean pompano is a pelagic-neritic marine species that often lives in brackish and tropical terrains. Adults are found in shallow coastal areas and estuaries (Schneider, 1990). The species is said to be exclusively benthotrophic, feeding mainly on gastropods and nematodes (Ajah *et al*., 2006).

2.5.3.4 *Tylosurus crocodilus crocodilus* (Hound needlefish)

The Hound needlefish (locally called Gar fish, Susuah or Penten) is an oceanodromous (Riede, 2004) marine species which operates around depth range of about 0-13m (Mundy, 2005). It is a highly reflective, silvery fish with a thin elongated body and long, narrow pointed jaws and a forked tail. The upper and lower jaws are nearly equal in length. It may have a darkish bar, or bars on the gill cover. Members of this species have a long, slender body, covered with small scales. Both jaws are prolonged into a slender beak, and are armed with sharp, unequal, needle-like teeth. The fins are all supported by soft rays. The dorsal and anal portions are more or less opposite to one another and placed on the hinder part of the body. The pectoral fins are high up on the sides of the body and the pelvics are well back. They are found near the coasts in all warm seas, and generally swim near the surface. Some species enter rivers and a few are found permanently in fresh water. It is widely distributed along the Eastern and Northern Atlantic: Fernando Po, Cameroon, Liberia, and Ascension Island (Collette and Parin, 1990); from Senegal and Guinea and Cape Verde (Mundy, 2005).

2.5.3.5 *Cephalopholis taeniops* (Bluespotted seabass)

The Bluespotted seabass (locally known as Rock fish) is a demersal marine dwelling fish species that operates within depth range of 20-200 m. It has a reddish orange colour and the head, body and median-fins are covered with distinct small blue spots with dark edges. Juveniles are brown or olive. Members of this species mainly occupy sandy and rocky bottoms and feed on crustaceans and fish. They are protogynous hermaphrodites, i.e. they mature first as females and later change sex (Page and Burr, 1991).

2.5.3.6 *Lepomis gibbosus* (Pumpkinseed sunfish)

The Pumpkinseed sunfish (locally known as Pumpkin fish) is a fresh water-dwelling benthopelagic fish species. Adults inhabit vegetated lakes and ponds, as well as vegetated pools of creeks and small rivers; and can as well be found in shallow weedy waters, often in the sunniest openings and large streams. The species is dark, olive-green on its back, with mottled sides. Base color of the sides is yellowish, spotted with orange, red and blue. Its belly is yellow to bright orange. Cheeks and gill covers are marked with alternate worm-shaped bands of blue-green and yellow. Bluish-black gill cover flaps are edged with white, yellow, orange or blue, with a small half moon spot of red. It feeds on Insects, small mollusks, small fishes and crustaceans, as well as fish eggs (Page and Burr, 1991).

2.5.3.7 *Elops lacerta* (Atlantic ladyfish)

The Atlantic ladyfish (locally called Shinny lady) is a pelagic species that lives in shallow coastal waters with sandy-muddy substrates. Member of this species are capable of surviving in fresh water habitats quite far inland. It has a slim silver body with a blue-green back and small scales. The head is small and pointed and the tail has a deep fork. The lower jaw projects beyond the upper and covers the front part of the band of teeth in the upper jaw when the mouth is closed. It feeds primarily on small fishes, mainly clupeids, crustaceans and mollusks (Moelents, 2010).

2.5.3.8 *Harengula jaguana* (Scaled sardine)

Known locally as Zipper fish, the Scaled sardines are marine (especially coastal) and estuarine schooling pelagic and demersal fish commonly found over sand and mud bottoms and on and around sea grass meadows (Sogard *et al*., 1989; Carpenter, 2002).They are euryhaline species and can be encountered in habitats ranging from coastal marine areas to mesohaline estuaries to hypersaline lagoons (Carpenter, 2002). It has a fusiform and laterally compressed body that is relatively deep. The abdomen is markedly more curved than the dorsum and has 28-31 scutes that form the distinct keel that is a defining characteristic of members of the sardine family (Clupeidae). The lower limb of the first gill arch is lined with 30-40 fine gill rakers (Robbins *et al*., 1986, Carpenter, 2002). The top and upper sides are blue-black with faint lateral streaks. The lower sides and abdomen are lighter in color and silvery. A dark 'shoulder' spot just posterior to the gill cover is present, although it may be faint in some individuals. Adult scaled sardines are planktivores, feeding on a variety of prey items including copepods, mysids, amphipods, isopods, ostracods, insect larvae, and small mollusks (Carpenter, 2002).

2.5.3.9 *Chloroscombrus chrysurus* (Atlantic bumper)

The Atlantic bumper (known locally as Porjoe) is a pelagic, coastal zone, tropical species that is found in brackish and marine environments; usually at depths of 0 to 55 meters. It has a very deep and compressed body with ventral side more complex than the dorsal portion. The mouth is small and oblique, with an upper jaw extending nearly below the anterior eye margin. Its head and body are dark above and members of the species have silvery sides and bellies. There is a characteristic black spot on the upper part of the tail, near the body. It inhabits soft bottoms, but sometimes forms schools near the surface. Juveniles are often found in more oceanic waters. It primarily feeds on fish, cephalopods, and zooplankton (Smith-Vaniz *et al*., 1986).

2.6 Analytical methods for the determination of heavy metals in fish tissues

2.6.1 Analytical methods for mercury determination in fish tissues

Numerous studies have applied different methods for the determination of mercury in environmental and biological samples. Most researchers have used atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS) or neutron activation analysis (NAA). In addition, methods based on mass spectrometry (MS) and anodic stripping voltammetry (ASV) have also been tested. Of the available methods, cold vapor (CV) AAS appears to be the most widely used.

All the previously mentioned analytical techniques represent a considerable improvement on the original "dithizone" method. The dithizone method was widely used up to the initiation 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 fish tissues and other foodstuffs are in the range of 85-99% and the reproducibility can yield a coefficient of variation of as low as 2% (WHO, 1976; EPA, 1994).

The neutron activation analysis (NAA) is another method used to determine total mercury in fish tissues. 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. With a detection limit of 0.1-0.3 ng of mercury, the NAA 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) 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% (Magos, 1971). Some studies have also employed gas chromatography (GC) for the direct determination of methylmercury in fish tissues (EPA, 1994).

Of the available methods, Cold Vapour-AAS is the method of choice (Munaf *et al.*, 1991) and the method recommended by EPA (Beckert *et al.*, 1990; EPA, 1994). The CVAAS was used for analyzing total mercury in fish muscle tissues in this study. The technique and procedure is discussed below.

2.6.2 The Cold Vapour (CV) Atomic Absorption Technique

The traditional methods for the determination of Hg include flameless AAS, AFS and ICP-AES, 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 (EPA, 1994). Two reducing agents usually employed for CV analysis are tin (II) chloride ($SnCl_2$) and sodium borohydride ($NaBH_4$).

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

2.6.3 Analytical methods for Pb, Cd, Cu, Fe and Zn Analysis in fish tissues

Numerous methods have been used to determine levels of heavy metals such as Pb, Cd, Zn, Cu, and Fe in fish tissues. Some commonly used analytical methods include inductively-coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (F-AAS, GF-AAS), ICP-mass spectrometry (ICP-MS) and X-ray fluorescence (XRF). Electroanalytical techniques such as polarography or stripping voltammetry and neutron activation analysis (NAA) have also been tested (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/L. This technique offers adequate sensitivity for heavy metals in environmental and biological samples. The multi-element capability offered by ICP-AES is a considerable advantage over AAS methods (AOAC, 1998; EPA, 1994).

Neutron activation analysis (NAA) is a useful technique for the non-destructive analysis of solid samples, and requires a minimum of sample preparation (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 (IPCS, 2001).

ICP mass spectrometry (ICP-MS) offers excellent sensitivity. The technique is ideally suited to environmental and biological samples; the greater sensitivity means that any difficulties due to a high content of solids are overcome by dilution. Detection limits have been reported to be as low as 0.017 µg/L, with recoveries ranging from 99 to 117% (APHA, 1998).

X-ray fluorescence (XRF) is a relatively new procedure based on polarized X-rays. Another technique, energy dispersive x-ray fluorescence (EDXRF,) has been used to detect trace metals in dried food samples with better precision (e.g., detection limit, 0.8 ppm) than AAS methods (Nielson *et al*. 1991).

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. Of the available methods, the AAS techniques appear to be the most widely used and most sensitive with recoveries ranging from 94 to 109% (Muys, 1984). It was therefore used for the determination of Cd, Pb, Cu, Fe and Zn in the fish samples in this study. The technique involves the absorption of light of a specific wavelength by atomic species of the element as it is excited in a flame or other thermal device. The amount of light absorbed by the atomic species is proportional to the concentration of the element present in the ground state. Thus if the element can be atomized without excitation a high sensitivity can be achieved.

CHAPTER THREE

3. Materials and Methods

3.1 Apparatus

All plastic and glassware used were first soaked in detergent solution overnight; rinsed with distilled water and soaked in 10% (v/v) HNO_3 overnight. They were later rinsed with distilled water followed by 0.5% (w/v) $KMnO_4$ and again rinsed with distilled water. All washed plastic and glassware were allowed to air-dry prior to use.

For total mercury, cold vapor atomic absorption spectrometric measurements were performed using semi-automated Mercury Analyzer HG 5000 (Sanso Seisakusho Co., Ltd., Japan), equipped with mercury lamp operated at a wavelength of 253.7 nm.

For the determination of Cd, Pb, Cu and Zn and Fe, flame atomic absorption spectrometric measurements were performed using a Flame Atomic Absorption Spectrophotometer PG 990 (PG Instruments Ltd., China). For the determination of each metal, a lamp whose cathode consists of the element of interest was employed as a source. The analyses were carried out using an acetylene-air flame.

For sample digestion, solid aluminum top hotplate HP1-2 with the dimensions (w x d x h) 457 x 305 x 160 mm (Clifton, UK) was employed. Aluminum heating block with the dimensions (w x d x h) 95 x 75 x 50 mm with six round holes was used. Each hole is 28 x 47mm and the digestion tubes were inserted into the holes of the heating block which was then placed on the surface of the hotplate to be heated. The hotplate could accommodate 12 heating blocks allowing for the digestion of a maximum of 72 samples. Pyrex 50 ml graduated stoppered test tubes (26 x 200 mm) were employed as the digestion vessels.

3.2 Reagents and standard solutions

Perchloric acid ($HClO_4$), Sulphuric acid (H_2SO_4), Hydrochloric acid (HCl), Sodium hydroxide (NaOH), Tin (II) chloride ($SnCl_2$), Mercuric chloride ($HgCl_2$), Potassium permanganate ($KMNO_4$) and Nitric acid (HNO_3) were the chemicals employed in this research. All reagents used were of analytical reagent grade (BDH Chemicals Ltd, Poole, England) unless otherwise stated. Double distilled water was used for all dilutions.

3.3 Preparation of reagents

3.3.1 Preparation of Mercuric standard solution

Mercury stock standard solution (1000 mgL^{-1}) was prepared by dissolving 0.0677 g of $HgCl_2$ in the acid mixture HNO_3:H_2SO_4:$HClO_4$ (1:5:1) in a 50 ml volumetric digestion flask with heating on a hotplate at a temperature of 210 ^oC for about 30 minutes when a colorless solution was obtained. The solution was then diluted to the 50 ml mark with distilled water. Mercury standard working standard solution (1 mgL^{-1}) was then prepared by diluting the stock solution 1000 times. Blank solutions were also prepared alongside and bulked together for use as a diluent. The calibration solutions were freshly prepared by diluting an appropriate aliquot of the working standard solution using blank solution. Stannous chloride solution (10% w/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^{-1} for 30 min to expel any elemental mercury from it.

3.3.2 Preparation of Cd, Pb, Cu, Fe and Zn standard solutions

Stock standard solutions of Cd, Pb, Cu, Fe and Zn were prepared from a standard stock mixture (1000 mgL^{-1}). The amount of the stock solution required to prepare a working standard solution for each metal was computed. The working solutions were freshly prepared by diluting an appropriate aliquot of the stock solution through intermediate solutions.

3.3.3 Preparation of Analytical blank solution

Approximately 1 ml of distilled water was measured into a digestion flask. Exactly 2 ml of a mixture of nitric and perchloric acid (HNO_3:$HClO_4$) in the ratio 1:1 was added followed by addition of 5 ml sulfuric acid and swirled to mix. The solution was then heated on an electronic hotplate at 210^oC for 30 minutes and cooled to room temperature before being diluted with distilled water to the 50 ml mark. A number of this blank solution was prepared and bulked together in a 2.5 L bottle.

3.3.4 Reagents for the Mercury Analyzer

The 5.0 M NaOH solution required for the Mercury Analyzer was prepared by dissolving 20 g of sodium hydroxide with distilled water in a 100 ml conical flask. Potassium permanganate ($KMnO_4$) in 0.5% v/v H_2SO_4 was prepared by dissolving 0.5 g of $KMnO_4$ in 100 ml 0.5% v/v H_2SO_4 solution.

3.4 Sampling and sample preparation

3.4.1 Sampling

A total of 60 samples covering twenty nine fish species were purchased from eight markets in and around Monrovia from June 1, 2013 to August 14, 2013. The species selected for analysis were based on their popularity among local consumers and availability at the time of sampling. Species obtained were reflective of what was meant for human consumption. All samples were randomly obtained fresh on different occasions from the markets. The markets were Poultry market located in Paynesville, Rally Town market located on UN Drive, Duala market located on the Bushrod Island, West point market located in West point, Popoe Beach on the Bushrod Island, Junkpen Town market in Sinkor, Redlight market kitchen in Paynesville and Kineja Beach in ELWA. The samples were kept on ice and transported to the Bureau of National Fisheries, Monrovia for identification. The fish species used in the study are presented in Table 3.1.

Table 3.1: A list of fish species used in this study

No	**Scientific Name**	**FAO English Name**	**Local Name(s)**
1	*Albula vulpes*	Bonouk	Morlay
2	*Arius latiscutatus*	Rough-head sea fish	Catfish
3	*Cephalopholis taeniops*	Bluespotted seabass	Rock fish
4	*Chloroscombrus chrysurus*	Atlantic bumper	Porjoe
5	*Elops lacerta*	Atlantic ladyfish	Shinny lady
6	*Elops senegalensis*	Senegalese ladyfish	Tenpound, Morla
7	*Epinephelus goreensis*	Dungat grouper	Black grouper
8	*Euthynnus alletteratus*	Little tunny	Blood fish, Spotted Kanmu
9	*Galeoides decadactylus*	Lesser African threadfin	Butter Nose
10	*Harengula jaguana*	Scaled sardine	Zipper fish
11	*Lepomis gibbosus*	Pumpkinseed sunfish	Pumpkin fish
12	*Lutjanus campechanus*	Red Snapper	Red Snapper
13	*Pagrus caeruleostictus*	Bluespotted seabream	Snapper
14	*Pomadasys rogerii*	Pigsnout grunt	Grunter
15	*Priacanthus arenatus*	Atlantic bigeye	Wajay, Chicken soup fish
16	*Pseudotolithus elongatus*	Bobo croaker	White boy
17	*Pseudotolithus senegalensis*	Cassava croaker	Cassava fish (S/N)
18	*Sardinella aurita*	Spanish Sardine	Sardine fish
19	*Sardinella maderensis*	Madeiran sardine	Bonny
20	*Scomber colias*	Atlantic Chub mackerel	Sea Mackerel
21	*Scomberomorus tritor*	Spanish mackerel	Mackerel fish
22	*Selene setapinnis*	Atlantic moonfish	Big head Porjoe
23	*Seriola carpenteri*	Guinean amberjack	Judusloyah, Cullehey, Wakie
24	*Stromateus fiatola*	Blue butter fish	Marry fish
25	*Thunnus obesus*	Bigeye Tuna	Tuna fish
26	*Trachinotus goreensis*	Long fin pompano	Small Corvally
27	*Trachinotus maxillosus*	Guinean Pompano	Pompano
28	*Trichiurus lepturus*	Atlantic cutlassfish	Silver fish
29	*Tylosurus crocodilus crocodilus*	Hound needlefish	Penten, Susuah, Gar fish

The samples were washed with distilled water and dried on tissue paper and weighed. Following the measurement of total length (TL, cm) and total weight (TW, g), a portion of dorsal muscle tissue from each sample was removed using a stainless steel scissors and stored in a clean plastic bag. The samples were then coded for easy identification and kept in a freezer until they were ready for transportation to Ghana. The frozen samples were placed into zip poly ethylene bags, stored on ice in an ice chest and transported from Monrovia to Kumasi for analysis. Prior to digestion the samples were allowed to thaw and they were placed in clean glass vials and a pair of surgical scissors was used to cut the tissues of each sample into very small pieces to achieve homogeneity. The homogenized samples were kept in a freezer until analysis.

3.4.2 Digestion

The muscle tissues were digested by an open flask procedure (Akagi and Nishimura, 1991). The accuracy of this procedure has been verified at the National Institute for Minamata Disease in Japan through interlaboratory comparison exercises (Malm *et al.*, 1995) and by participating in the analyses of certified reference materials (CRMs; e.g. IAEA 085, 086, 142 and 407) supplied by the International Atomic Energy Agency (IAEA). Though specific for mercury determination, this method of digestion has also proven to be effective for other heavy metals (Burger and Gochfeld, 2005).

In the digestion procedure, 1.0 g of homogenized tissue was weighed into a 50-ml Pyrex glass stoppered test tube (26 mm x 47mm) and 2 ml H_2O, 4 ml HNO_3-$HClO_4$ (1:1) and 10 ml H_2SO_4 was added in turns. The mixture was then heated at a temperature of 210^{o}C for about 30 minutes when a colorless solution was obtained. The digest was allowed to cool to room temperature and later diluted with distilled water to the 50 ml mark. The solution was then shaken thoroughly and finally transferred into a stoppered glass bottle and kept in a fridge until analysis.

3.5 Determination of Mercury in fish

The determination of total mercury in all the digested samples was carried out using Cold Vapor Atomic Absorption Spectroscopic (CVAAS) technique employing a semi-automated Mercury Analyzer HG 5000 (Sanso Seisakusho Co., Ltd., Japan), developed at the National Institute of Minamata Disease (NIMD). The instrument was designed specifically for the determination of mercury using the CVAAS technique. A schematic diagram of the instrument is shown in Figure 3.1. The analyzer consists of an air circulation pump, a reaction vessel, tin (II) chloride dispenser, acid gas trap and a four way stop-cock with tygon tubes to which is attached a ball valve; and the operation of this ball valve and the air circulation pump are controlled by a microprocessor.

During the determination, a known volume of the sample solution (5 ml) was introduced into the reaction vessel using a micropipette with disposable tips. The reaction vessel was immediately closed tightly. After 30 seconds, the four way stop-cock rotated 90^{o} and the mercury vapor was swept into the absorption cell and the response was recorded. The peak heights obtained were used for the computation of the concentration of total mercury in the sample using the formula:

$$\mathrm{THg}\ (\mu g/g) = \frac{\mathrm{Cstd}(\mu g)}{(\mathrm{Pstd}-\mathrm{Pbl})} \times \frac{(\mathrm{Ps}-\mathrm{Pbl})}{\text{sample weight}(g)}$$

Where THg is total mercury; Cstd is concentration of a known standard solution; and Pstd, Ps and Pbl are peak heights of the known standard, the sample and the blank respectively. Standard solutions of 0.4, 0.8, 1.0 and 1.2 µg/ml were used for the calibration of the analyzer.

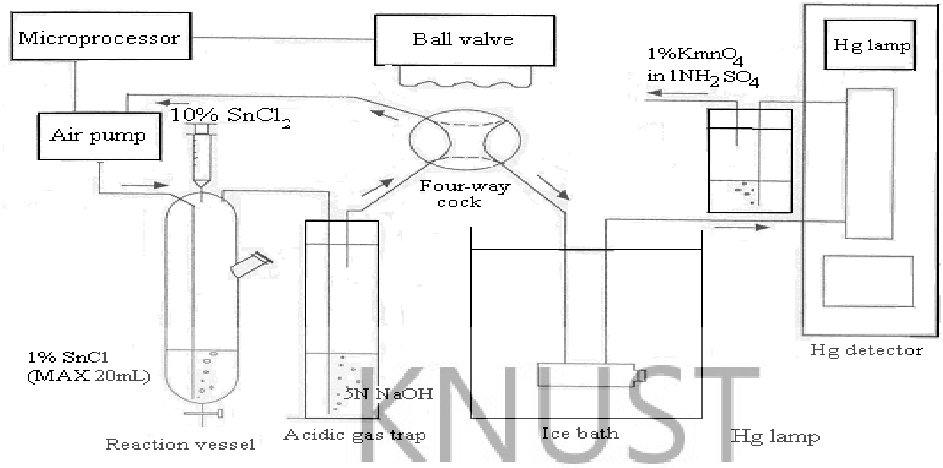


Figure 3.1: Schematic Diagram of Mercury Analyzer (Akagi and Nishimura, 1991)

3.6 Determination of Cd, Pb, Cu, Fe and Zn in fish

Flame Atomic Absorption Spectrophotomer PG 990 (PG Instruments Ltd., China) was used for determining the concentrations of Cd, Pb, Fe, Cu and Zn. The absorption wavelengths for the metals were 228.8 nm for Cd, 217.0 nm for Pb, 248.3 nm for Fe, 324.7 nm for Cu and 213.9 nm for Zn.

Calibration was done to establish the instrument’s response to the known set of standards. The working standards (for the calibration) were prepared in varying concentrations; each from a stock solution of the analyte of interest. A calibration curve (for each analyte) was obtained by measuring the signals for a series of working solutions of known concentrations. Then by presenting the digests to the instrument, signals were obtained. The calibration curve was then used to determine the concentration of the element of interest in the digest. The final concentration of each metal in µg/g was calculated using the formula:

$$C\ (\mu g/g) = \frac{R(\mu g/ml)\ \mathbf{x}\ DF \times 50ml}{\text{sample wt (g)}}$$

Where: R is the concentration in µg/ml obtained from the calibration curve and DF is the Dilution Factor.

3.7 Quality Assurance

Recovery studies were performed in order to establish the accuracy of the method. Recovery of the metals was determined by spiking one sample with increasing amounts of metal standard solution. The spiked samples were then taken through the same digestion procedure (as all other samples) and analyzed for heavy metal concentrations. To assess the precision of the overall procedure, the samples were divided in batch of eight and for each batch; three replicate analyses of one of the samples were conducted. Analyses of all sample digests were performed in duplicate by the instrument. Certified Reference Material (CRM), Fish Homogenate IAEA-407 from International Atomic Energy Agency, Vienna was also included in quintuplicate.

3.8 Statistical Analysis

Statistical tools in Microsoft Excel (2003) were used in this study for computation of descriptive parameters such as average, range, standard error values and standard deviation. Microsoft Excel (2003) was also used to plot graphs.

CHAPTER FOUR

4. Results and discussion

A total of sixty samples comprising twenty nine fish species were analyzed for total Mercury (THg), Cadmium (Cd), Lead (Pb), Copper (Cu), Iron (Fe) and Zinc (Zn). Precision and accuracy of the analytical procedure were evaluated by repeated analyses of samples and certified reference material (IAEA-407 fish homogenate) from the International Atomic Energy Agency in Vienna, Austria. The validity of the method has been proved by agreement between the measured and the certified concentrations in the fish homogenate. The results from the analysis (Table 4.1) were all within the 95% percent confidence limit.

Table 4.1: Analytical results (in µg g^{-1}) of certified reference material IAEA-407 (fish homogenate), showing local laboratory values and recommended values

Metal	Measured value (Mean±SD)	n	Certified value (Mean±SD)
Hg	0.212 ±0.0092	5	0.222 ±0.024
Cd	0.191 ±0.0074	5	0.189 ±0.019
Pb	0.15 ±0.01	5	0.12 ±0.06
Cu	3.27 ±0.20	5	3.28 ±0.40
Fe	141.0±4.0	5	146.0 ±14.0
Zn	65.8±1.2	5	67.1 ±3.8

To further determine the degree of accuracy of the overall procedure, three replicates of one sample were spiked with increasing concentrations of the metal of interest. The sample was taken through the same digestion procedure as all other samples and then analyzed for the metals. The recoveries are presented in Table 4.2. Recoveries between 85-105% for spiked samples demonstrate the accuracy of the methods used.

Table 4.2: Recovery of heavy metals from fish samples

Sample	Hg added (ng)	Hg found (ng)	Hg recovered (ng)	% Recovery
Epinephelus goreensis (1.0g)	0	39	----	----
	20	60	21	105
	40	77	38	95
	50	85	46	92
Sample	Pb added (ng)	Pb found (ng)	Pb recovered	% Recovery
Harengula jaguana (1.0g)	0	67	----	----
	20	86	19	95
	40	109	42	105
	50	118	51	102
Sample	Cd added (ng)	Cd found (ng)	Cd recovered	% Recovery
Pseudotolithus elongatus (1.0g)	0	2	---	---
	20	20	18	90
	40	41	39	97.5
	50	53	51	102
Sample	Cu added (ng)	Cu found (ng)	Cu recovered	% Recovery
Elops senegalensis (1.0g)	0	212	----	----
	20	229	17	85
	40	247	35	87.5
	50	259	47	94
Sample	Fe added (ng)	Fe found (ng)	Fe recovered	% Recovery
Trichiurus lepturus (1.0g)	0	2417	----	----
	20	2436	19	95
	40	2454	37	92.5
	50	2468	51	102
Sample	Zn added (ng)	Zn found (ng)	Zn recovered	% Recovery
Chloroscombrus chrysurus (1.0g)	0	2093	----	----
	20	2111	18	90
	40	2135	42	105
	50	2142	49	98

4.1 Mercury

All the fish species analyzed in this study are consumed by humans. Results of total mercury (THg) levels in muscle of fish (µg g^{-1} on wet weight basis) from markets in Monrovia, Liberia are presented in Table 4.3. Mean mercury concentration ranged from 0.014 to 0.727 µg g^{-1} wet weight. *Albula vulpes* (Bonefish) recorded the highest mean concentration of THg (0.727 µg g^{-1} wet weight) followed by *Euthynnus alletteratus* (0.434 µg g^{-1} wet weight). Mercury concentrations in all the other fish samples were less than 0.3 µg g^{-1} wet weight, which is below the 0.5 µg g^{-1} wet weight limit recommended by FAO/WHO (1972) and adopted by many countries (CIFA, 1992). One sample each of *Lutjanus campechanus*, *Priacanthus arenatus* and *Seriola carpenteri* recorded concentrations of 0.440, 0.428 and 0.352 µg g^{-1} wet weight respectively; which are below the recommended limit. *Sardinella maderensis* recorded the lowest mean THg concentration (0.014 µg g^{-1} wet weight). Very little information on mercury concentration in *Albula vulpes* was found perhaps because the fish is mostly considered for recreational fishery rather than for commercial consumption purposes in other parts of the world (Crabtree *et al.*, 1996). In Florida, for example, the commercial sale of bonefish is prohibited, and regulations on recreational fishery include a limit of one bag of fish per angler per day (Crabtree *et al*., 1997). The high concentration of mercury in bonefish could be attributed to its feeding habits. Feeding habits of bonefish have been studied by Warmke and Erdman (1963) in Puerto Rico and Colton and Alevision (1983) in the Bahamas. Both studies confirmed the bonefish as a predator of benthic and epibenthic prey including crustaceans, gulf toadfish, gastropods, bivalves and shrimps. Dewailly *et al.* (2008) determined THg levels in locally consumed fish species in Bermuda. In their study, *Abula vulpes* recorded THg concentration of 0.5 µg g^{-1} wet weight; a value lower than that (0.727 µg g^{-1} wet weight) reported in this study. The THg concentration in *Euthynnus alletteratus* found in this study *was* notably lower than that found by Yan Cai (2005), who reported a level of 1.08 µg g^{-1} wet weight in *Euthynnus alletteratus* from the Gulf of Mexico, Mexico.

Table 4.3 Total mercury concentration (µg g^{-1} wet weight) in muscle of commercial fish samples from markets in Monrovia, Liberia (2013)

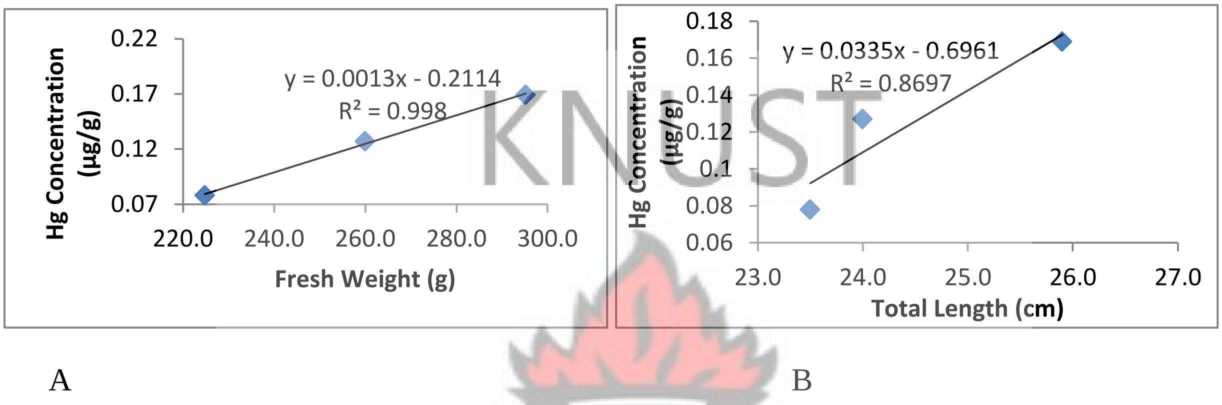
Species	Sample size (n)	Total length Range (cm)	Fresh weight Range (g)	THg Conc. Range µg g^{-1}	THg Conc. Mean µg g^{-1}
Albula vulpes	1	28.7	399.5	0.727	0.727
Arius latiscutatus	3	22.5-28.2	148.8-312.7	0.061-0.238	0.167
Cephalopholis taeniops	2	14.5-16.5	81.5-83.7	0.091-0.099	0.095
Chloroscombrus chrysurus	2	15.4-16.5	49.4-61.4	0.043-0.091	0.067
Elops lacerta	2	27.5-30.4	303.3-383.2	0.063-0.200	0.132
Elops senegalensis	2	27.5-33.3	271.5-507.2	0.065-0.175	0.120
Epinephelus goreensis	1	27.4	561.9	0.039	0.039
Euthynnus alletteratus	1	46.5	1340.5	0.434	0.434
Galeoides decadactylus	3	18.5-24.2	160.0-268.6	0.055-0.117	0.096
Harengula jaguana	2	23.6-24.2	194.8-211.6	0.073-0.085	0.079
Lepomis gibbosus	2	14.5-15.5	152.3-170.8	0.141-0.201	0.171
Lutjanus campechanus	3	13.5-15.8	76.4-108.3	0.025-0.440	0.173
Pagrus caeruleostictus	3	19.5-21.5	154.7-188.3	0.094-0.240	0.170
Pomadasys rogerii	3	23.5-25.9	224.8-295.2	0.078-0.169	0.125
Priacanthus arenatus	3	11.5-20.1	37.3-100.5	0.023-0.428	0.206
Pseudotolithus elongatus	1	23.4	210.0	0.122	0.122
Pseudotolithus senegalensis	2	31.3-31.5	430.1-435.2	0.028-0.285	0.157
Sardinella aurita	3	16.4-18.2	55.1-85.8	0.006-0.021	0.070
Sardinella maderensis	3	20.5-21.6	118.4-129.5	0.015-0.176	0.014
Scomber colias	1	50.2	799.1	0.132	0.132
Scomberomorus tritor	2	26.2-26.4	243.0-253.9	0.090-0.095	0.093
Selene setapinnis	2	27.6-31.7	417.2-612.3	0.053-0.168	0.035
Seriola carpenteri	2	33.9-37.2	577.4-806.3	0.097-0.352	0.225
Stromateus fiatola	2	26.1-26.5	374.6-428.4	0.033-0.076	0.055
Thunnus obesus	3	21.5-24.3	128.3-159.9	0.166-0.266	0.226
Trachinotus goreensis	1	24.9	479.3	0.124	0.124
Trachinotus maxillosus	1	24.9	276.5	0.043	0.043
Trichiurus lepturus	2	57.2-72.5	295.3-378.3	0.042-0.065	0.054
Tylosurus crocodilus crocodilus	2	35.5-39.5	230.8-431.2	0.083-0.259	0.171

Voegborlo *et al.* (2006) determined the levels of THg in muscle tissues of different commercial fish species from the Gulf of Guinea, Ghana. In *Chloroscombrus chrysurus* (Atlantic bumper), the mean THg concentration was 0.112 µg g^{-1} wet weight, whereas in *Pseudotolithus senegalensis* (Cassava croaker) it was 0.047 µg g^{-1} wet weight, which were higher than those reported in the current study. These investigators (Voegborlo *et al.*, 2006) also reported mean THg levels in *Galeoides* *decadactylus, Sardinella aurita, Pseudotolithus senegalensis* and *Stromateus fiatola* as 0.048, 0.016, 0.031 and 0.003 µg g^{-1} wet weight respectively; which were lower than those found in the current study. In another survey, Mol *et al*. (2001) determined the levels of THg in commercial fish species from Suriname. The author reported mean THg concentrations of 0.29 and 0.16 µg g^{-1} wet weight for *Selene setapinnis* and *Trichiurus lepturus* respectively. These values were lower than those reported in the current study. The concentrations of mercury in the fish samples obtained in this study were not high when compared to some other areas of the world and can be said to reflect background mercury concentrations that are even much lower than most published mercury concentrations in fish from non-polluted areas of the world. For example mercury in the edible portion of various fish species purchased from supermarkets and specialty fish markets in New Jersey in 2004 were in the range 0.01-0.65 µg g^{-1} wet weight, with which our values agree (Burger and Gochfeld, 2005). In another study, mercury concentrations in different commercial fish species landed on the Castellan Coast of Spain in 1989 were in the range 0.16-0.84 µg g^{-1} wet weight, within which our values fall (Hernades *et al*., 1990). Mercury concentrations reported in this study were lower when compared to values reported for other tropical, less industrialized areas like Mozambique, Reunion Islands, Thailand and Papua New Guinea (CIFA, 1992; Kojadinovic *et al*., 2008). This confirms the assertion that geographical location in addition to other factors like metabolic differences appears to be important with regards to the mercury content of fish; and this is further illustrated by the analysis of fish from different locations. Samples of wahoo fish obtained from a heavily contaminated part of the Gulf of Mexico had values up to 3.31 µg g^{-1} wet weight; wahoo caught in the area of Bermuda had values of 0.06-1.0 µg g^{-1} wet weight whereas Fijian wahoo had mean mercury concentration of 0.17 µg g^{-1} wet weight. In a study of swordfish from six areas extending from Caribbean Sea to Grand banks, significant variations from one area to another were observed in mean mercury levels (WHO, 1976).

Mercury can accumulate in some fish species more than others. Level of mercury in fish depends on their species, size, and mercury levels in the environment and food sources. Therefore, larger, longer-living fish and predatory fish contain higher levels of mercury. In addition, mercury levels in fish may be increased due to mercury pollutions present in the environment where the fish lived (Yan Cai, 2005). The level of mercury found in a fish is related to the level of mercury in its aquatic environment and its place in the food chain (Monteiro and Lopes, 1990). Apart from that mercury also biomagnifies through the food chain; so large predatory fish species tend to have higher levels than non-predatory fish or species at lower levels in the food chain. It is methylmercury that is of particular concern, as this is the form that is easily absorbed in living tissues and is known to bioaccumulate and biomagnify in animals and humans. Nearly all mercury that bioaccumulates in fish is methylmercury (USEPA, 2000).

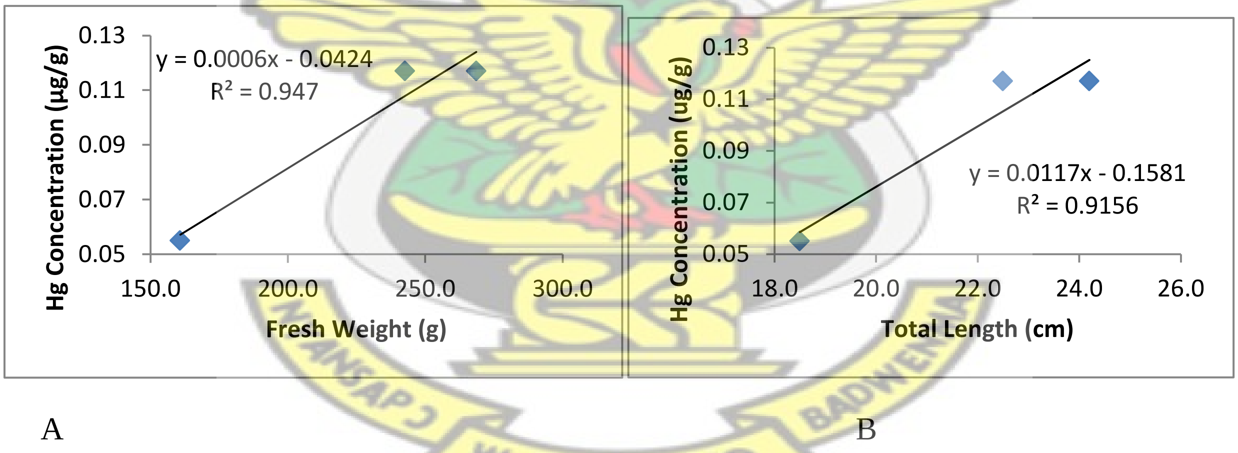
Mercury levels have been reported to be related to the age/size of fish (Yan Cai, 2005; Voegborlo *et al*., 2006). Positive relationship between fish mercury concentration, weight and length within an individual water body has been documented (Storelli *et al*., 2002). Good correlation ($R^2 \geq 0.5$) normally existed among carnivorous species while herbivorous species normally showed poor correlation. This observation was reported for tuna which is a carnivore (Voegborlo *et al*., 2006). Positive correlations between mercury concentration and size have been previously found in sharks (Storelli *et al*., 2002) and freshwater eels (Redmayene *et al*., 2000). Similarly, a positive correlation was found in giant perch from Lake Murray in Papua New Guinea (Kyle and Ghani, 1982) but it is noted that this is an enclosed water system. The fish samples in this study were purchased from several different locations around Monrovia and it is thus difficult to trace their origin. Examining interspecific differences in fish obtained from markets is often challenging because the fish come from different geographic sources. For example, Bonouk (Bonefish) and Cassava croaker are usually locally caught; Red snapper and Bigeye tuna may come from North pacific waters or the Indian Ocean, while Guinean amberjack and Bobo croaker may have come from a wide range of tropical waters. We were unable to obtain information from markets about the sources of their fish. While sampling by purchasing fish in markets makes it difficult to compare among types and interpret levels because the geographical sources of the fish are unknown. It is the mix that consumers are exposed to when they purchase fish. In this study, linear regressions were used to describe correlations between THg concentration and fresh body weight and total length of the samples. Only species with a sample size of three (n=3) or more were considered. A total of nine species were subjected to regression studies. There was significant correlation between THg and fresh body weight and total length in all nine species namely *Pomadasys rogerii, Galeoides decadactylus, Arius latiscutatus, Pagrus caeruleostictus, Sardinella maderensis, Sardinella aurita, Thunnus obesus, Priacanthus arenatus* and *Lutjanus campechanus*. A significantly positive correlation was noted between THg and fresh body weight and total length in all the species considered except *Sardinella maderensis,* where significantly negative correlation was obtained. The correlations are indicated as regression lines in Figure 4.1 - 4.9. Out of the nine species in this category, only two (*Sardinella maderensis* and *Sardinella aurita)* are herbivores. The rest are carnivores and significant positive relationship between THg concentration and age/size has been well documented especially amongst carnivorous species (Yan Cai, 2005; Voegborlo *et al*., 2006). Positive correlation in *Sardinella aurita* (Figure 4.8) could be attributed to the fact that some fish were old even though they stopped growing. Size (total length and body weight) appears to be the major determining factor of fish age, but this may not always be true for all individuals. Low food supply, for example, can result into poor growth even for aging fish.

An interesting trend was observed in *Sardinella maderensis* (Figure 4.5). In this case, the regression was significantly correlated with a negative slope, indicating a decrease in THg level with increasing total length and fresh body weight. *Sardinella maderensis* is a herbivore and as such may not experience biomagnification. The sampling information for this species showed that all three samples were purchased from the same market but on different dates, indicating that the samples may have been collected from different water bodies; hence that regression trend.



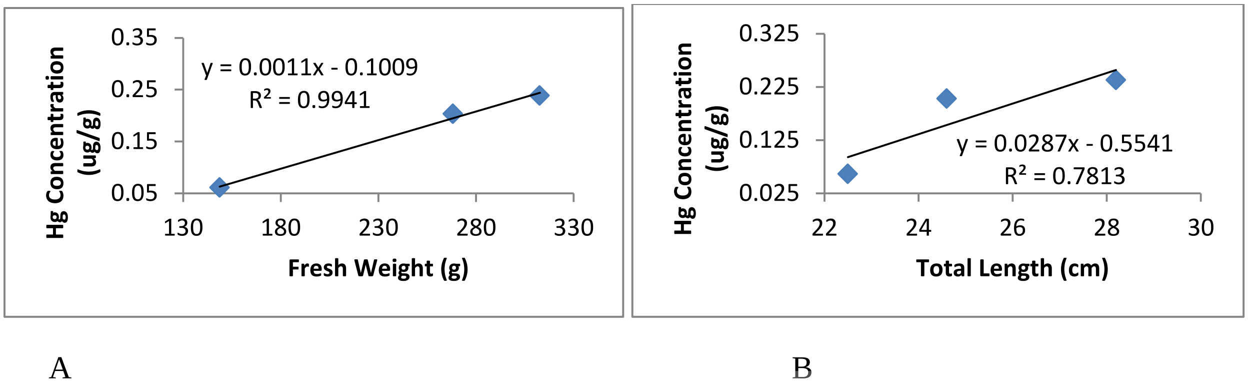
A B

Figure 4.1: Relationship between mercury concentration and body weight (A) and total length (B) for *Pomadasys rogerii*



A B

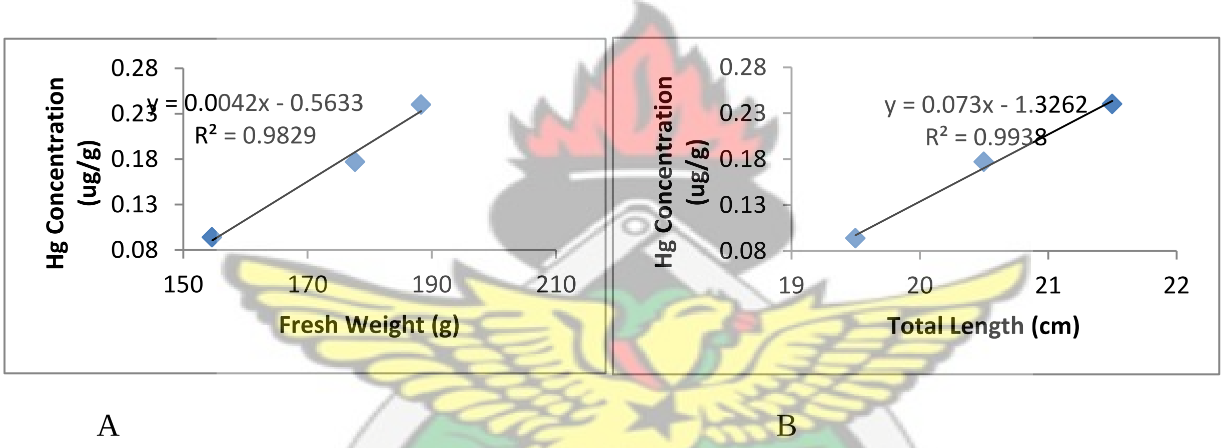
Figure 4.2: relationship between mercury concentration and body weight (A) and total length (B) for *Galeoides decadactylus*



A

B

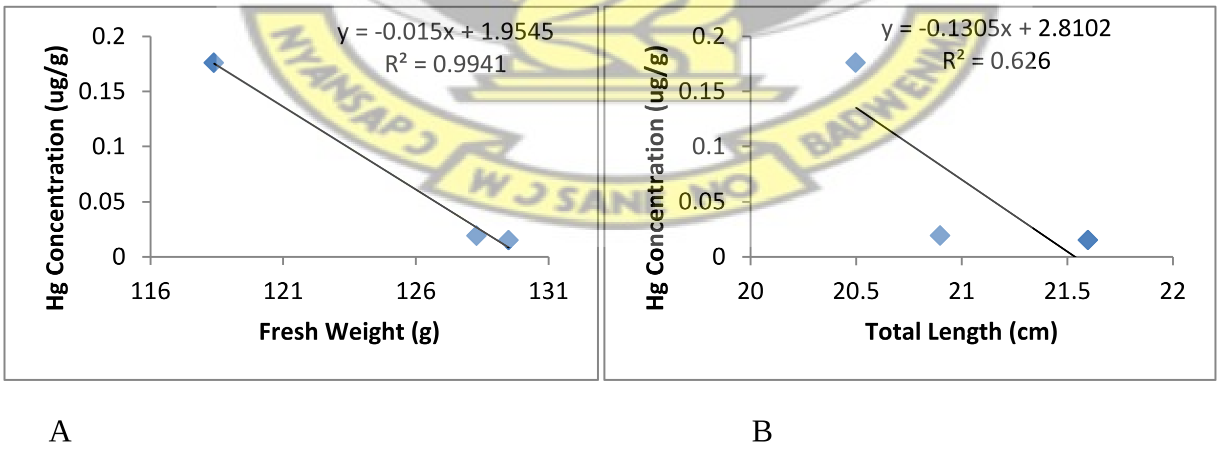
Figure 4.3: Relationship between mercury concentration and body weight (A) and total length (B) for *Arius latiscutatus*



A

B

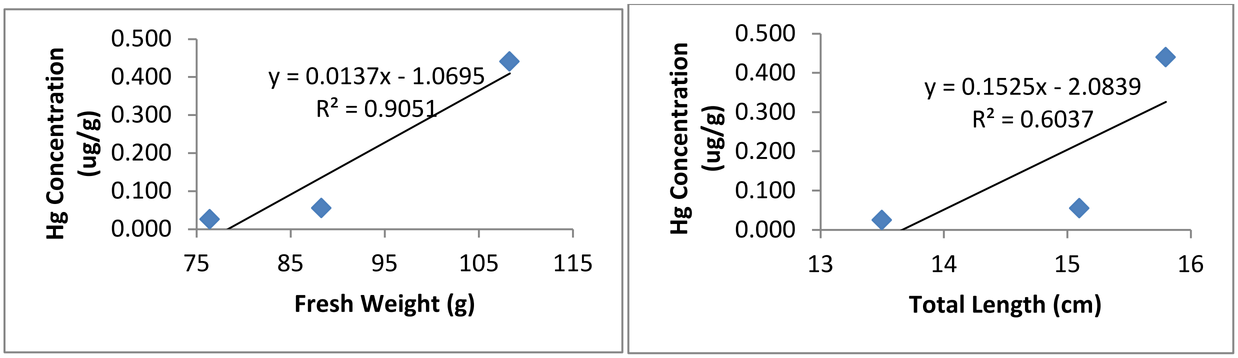
Figure 4.4: Relationship between mercury concentration and body weight (A) and total length (B) for *Pagrus caeruleostictus*



A

B

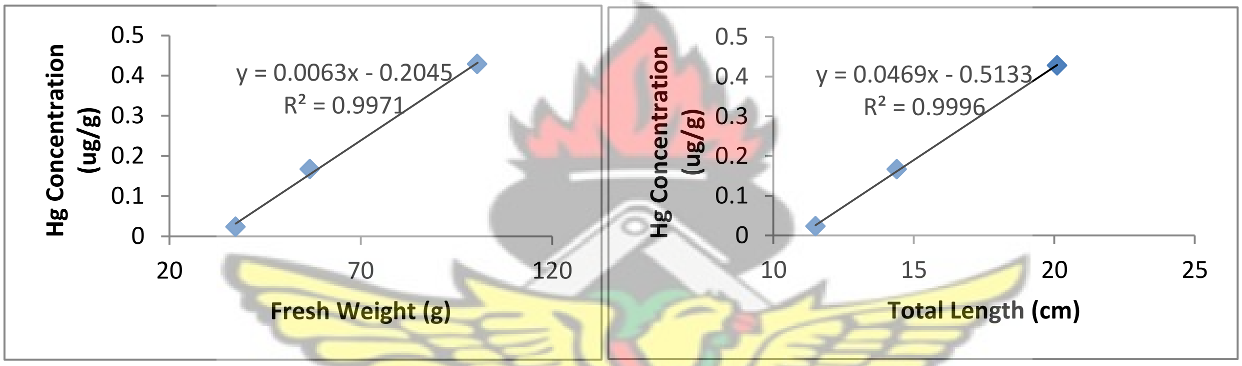
Figure 4.5: Relationship between mercury concentration and body weight (A) and total length (B) for *Sadinella maderensis*



A

B

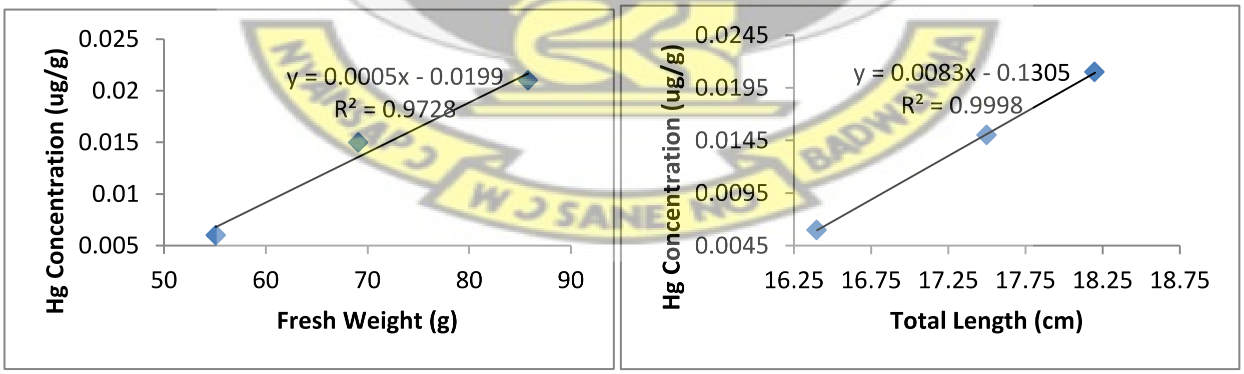
Figure 4.6: Relationship between mercury concentration and body weight (A) and total length (B) for *Lutjanus campechanus*



A

B

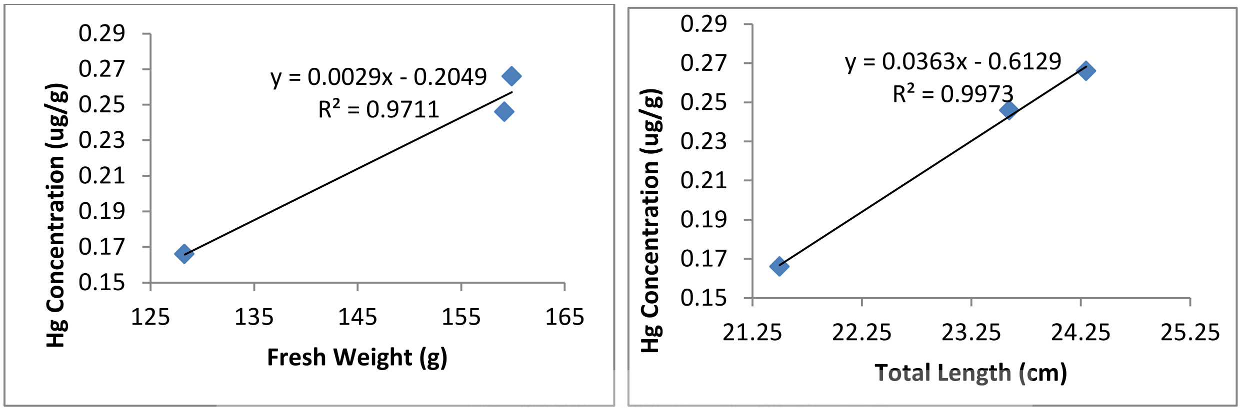
Figure 4.7: Relationship between mercury concentration and body weight (A) and total length (B) for *Priacanthus arenatus*



A

B

Figure 4.8: Relationship between mercury concentration and body weight (A) and total length (B) for *Sardinella aurita*



A

B

Figure 4.9: Relationship between mercury concentration and body weight (A) and total length (B) for *Thunnus obesus*

In this study, risks to health from heavy metal contaminantion of fish were assessed by comparing estimates of dietary exposure with the Provisional Tolerable Weekly Intakes (PTWIs) recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). For total mercury, the PTWI guideline of 5.0 µg/kg body wt/wk was used in this study (JECFA, 2003). The potential hazards of metals transferred to humans are probably dependent on the amount of fish consumed by an individual. Data on the amount of fish consumed by an average Liberian adult per day or week is not available; thus data from American food consumption index were employed in the current study. According to recent surveys, the average American consumes about 32.57 grams of fish and shellfish per day or 228 g/week (USEPA, 2012), and this consumption rate was used in the health-risk assessment. Human health risk in terms of hazard quotient (HQ) was calculated by comparing the estimated weekly intake of the each metal with the PTWI. For the purpose of calculating HQ, the PTWI is defined as the amount of weekly exposure to a toxic compound that does not show the symptoms of toxic effects from the exposed organism; while HQ is known as the magnitude of quantifiable potential for developing non-carcinogenic health effects after averaged exposure period (USEPA, 2012). Hazard Index (HI), was derived by summing the HQ values of metals. It has been suggested that if HQ is equal to or less than one (≤1), no appreciable health risk is expected. Hazard index or ΣHQs value of less than one (<1) suggests no risks either from any metal alone or in combination with others. The following equations were used for estimating WI, HQ and HI:

$$\text{WI } (\mu g/\ kg/\ week) = (Cs \times CR) / BW$$

$$\text{Hazard Quotient (HQ)} = WI / PTWI$$

$$\text{Hazard Index (HI)} = HQ_{Hg} + HQ_{Pb} + HQ_{Cd} + HQ_{Fe} + HQ_{Zn} + HQ_{Cu}$$

Where, Cs is the measured metal concentration in fish muscle tissue (µg g^{-1} wet weight), CR is the fish consumption rate (32.57 g/day or 228 g/wk), BW is the average body weight for an adult (70 kg) and PTWI is the guideline value of the individual metal (µg/ kg body wt/ wk).

The average THg intakes from all the fish species in this study were much lower than the recommended value as shown in Table 4.4. The HQ for THg in each fish species was less than one, indicating no potential health risk to the consumers. The low hazard values of the different fish species indicate low exposure to THg from fish consumption. The HQ for the fish species (0.009-0.474) was in agreement with the 0.31-0.41 range reported for the average consumer in Hong Kong (CFS, 2008). The fish with the highest reported mean concentration of THg was *Albula vulpes.* To exceed the PTWI, an adult would have to consume more than 490 g of *Albula vulpes* per week; a scenario which is quite unlikely. Thus the THg levels in the tested fish species may not pose any known risk to health for the population of Monrovia.

Table 4.4: Mean dietary intake of total mercury

	Species	Hg Conc. (µg/g)	WCR (g/person/ wk)	Weekly Intake (WI) (µg/kg body weight/wk)	Hazard Quotient (HQ)
1	*A. vulpes*	0.727	228	2.368	0.474
2	*A. latiscutatus*	0.167	“	0.544	0.109
3	*C. taeniops*	0.095	“	0.309	0.062
4	*C. chrysurus*	0.067	“	0.218	0.044
5	*E. lacerta*	0.132	“	0.430	0.086
6	*E. senegalensis*	0.120	“	0.391	0.078
7	*E. goreensis*	0.039	“	0.127	0.025
8	*E. alletteratus*	0.434	“	1.414	0.283
9	*G. decadactylus*	0.096	“	0.313	0.063
10	*H. jaguana*	0.079	“	0.257	0.051
11	*L. gibbosus*	0.171	“	0.557	0.111
12	*L. campechanus*	0.173	“	0.563	0.113
13	*P. caeruleostictus*	0.170	“	0.554	0.111
14	*P. rogerii*	0.125	“	0.407	0.081
15	*P. arenatus*	0.206	“	0.671	0.134
16	*P. elongatus*	0.122	“	0.397	0.079
17	*P. senegalensis*	0.157	“	0.511	0.102
18	*S. aurita*	0.070	“	0.228	0.046
19	*S. maderensis*	0.014	“	0.046	0.009
20	*S. colias*	0.132	“	0.430	0.086
21	*S. tritor*	0.093	“	0.303	0.061
22	*S. setapinnis*	0.035	“	0.114	0.023
23	*S. carpenteri*	0.225	“	0.733	0.147
24	*S. fiatola*	0.055	“	0.179	0.036
25	*T. obesus*	0.226	“	0.736	0.147
26	*T. goreensis*	0.124	“	0.404	0.081
27	*T. maxillosus*	0.043	“	0.140	0.028
28	*T. lepturus*	0.054	“	0.176	0.035
29	*T.C. crocodilus*	0.171	“	0.557	0.111

Note: PTWI (µg/kg body weight/wk) = 5.0
WCR = weekly consumption rate

4.2 Copper

Copper is present in all animals and plants as an essential nutrient. Although copper is an essential element, high levels of intake can cause symptoms of acute toxicity. The accumulation of copper in liver leads to cirrhosis; in brain can lead to death of neurons with neurological symptoms; and in kidney leads to renal tubular damage (Forstner and Wittmann, 1983).

Results of copper (Cu) levels in muscle of fish (µg g^{-1} on wet weight basis) from markets in Monrovia, Liberia are presented in Table 4.5. Copper concentration ranged from 0.101 to 3.230 µg g^{-1} wet weight. *Sardinella aurita* recorded the highest mean concentration (2.990 µg g^{-1} wet weight) followed by *Sardinella maderensis* (2.598 µg g^{-1} wet weight). Mean copper concentrations in all the other fish samples were less than 2.0 µg g^{-1} wet weight, which is far below the 30 µg g^{-1} limit recommended by FAO (1983). *Trachinotus goreensis* recorded the lowest mean copper concentration (0.101 µg g^{-1} wet weight).

The concentrations of copper in the fish samples obtained in this study were not high when compared to some other areas of the world and can be said to reflect background copper concentrations that are even much lower than most published copper concentrations in fish from non-polluted areas of the world. For example, Yilmaz (2003) determined the levels of some heavy metals in fish samples from Iskenderun bay, Turkey. The author reported copper concentrations ranging from 0.7 to 2.0 µg g^{-1}. This range is in agreement with those reported in the current study (0.101-3.230 µg g^{-1}) and the values are far below the FAO guideline limit of 30 µg g^{-1}.

Table 4.5 Copper concentration (μg g^{-1} wet weight) in muscle of commercial fish samples from markets in Monrovia, Liberia (2013)

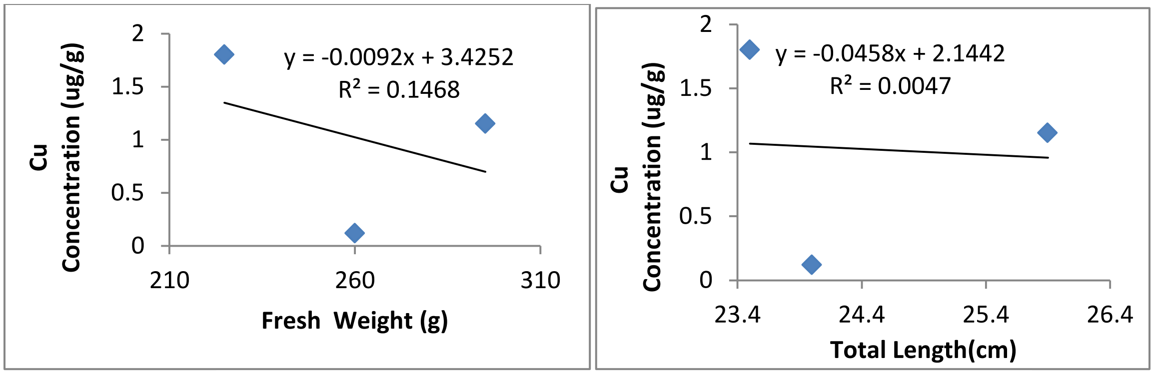
Species	Sample size (n)	Total length Range (cm)	Fresh weight Range (g)	Cu Conc. Range μg g^{-1}	Cu Conc. Mean μg g^{-1}
Albula vulpes	1	28.7	399.5	0.211	0.211
Arius latiscutatus	3	22.5-28.2	148.8-312.7	0.280-2.017	0.937
Cephalopholis taeniops	2	14.5-16.5	81.5-83.7	0.179-0.198	0.189
Chloroscombrus chrysurus	2	15.4-16.5	49.4-61.4	0.124-1.019	0.572
Elops lacerta	2	27.5-30.4	303.3-383.2	0.204-0.861	0.533
Elops senegalensis	2	27.5-33.3	271.5-507.2	0.113-0.311	0.212
Epinephelus goreensis	1	27.4	561.9	1.813	1.813
Euthynnus alletteratus	1	46.5	1340.5	0.613	0.613
Galeoides decadactylus	3	18.5-24.2	160.0-268.6	0.112-0.181	0.152
Harengula jaguana	2	23.6-24.2	194.8-211.6	0.277-0.419	0.348
Lepomis gibbosus	2	14.5-15.5	152.3-170.8	0.112-0.143	0.128
Lutjanus campechanus	3	13.5-15.8	76.4-108.3	0.351-1.101	0.821
Pagrus caeruleostictus	3	19.5-21.5	154.7-188.3	0.168-0.400	0.257
Pomadasys rogerii	3	23.5-25.9	224.8-295.2	0.120-1.802	1.025
Priacanthus arenatus	3	11.5-20.1	37.3-100.5	0.101-0.563	0.379
Pseudotolithus elongatus	1	23.4	210.0	0.105	0.105
Pseudotolithus senegalensis	2	31.3-31.5	430.1-435.2	0.135-0.784	0.460
Sardinella aurita	3	16.4-18.2	55.1-85.8	2.811-3.230	2.990
Sardinella maderensis	3	20.5-21.6	118.4-129.5	1.823-3.011	2.598
Scomber colias	1	50.2	799.1	0.423	0.423
Scomberomorus tritor	2	26.2-26.4	243.0-253.9	0.113-0.322	0.218
Selene setapinnis	2	27.6-31.7	417.2-612.3	0.981-1.680	1.331
Seriola carpenteri	2	33.9-37.2	577.4-806.3	0.103-0.181	0.142
Stromateus fiatola	2	26.1-26.5	374.6-428.4	0.303-1.081	0.692
Thunnus obesus	3	21.5-24.3	128.3-159.9	0.211-0.813	0.542
Trachinotus goreensis	1	24.9	479.3	0.101	0.101
Trachinotus maxillosus	1	24.9	276.5	0.281	0.281
Trichiurus lepturus	2	57.2-72.5	295.3-378.3	0.674-1.072	0.873
Tylosurus crocodilus crocodilus	2	35.5-39.5	230.8-431.2	0.211-0.324	0.268

Anim *et al*. (2011) studied the accumulation profile of heavy metals in fish samples collected from Nsawam, along the Densu River in Ghana. The copper levels reported in their study ranged from 45.6±0.74 to 110.56±0.86 μg g^{-1} wet weight (mean= 75.62 μg g^{-1} wet weight). These values were far higher than those reported in this study. The values reported by these authors are even far higher than the FAO guideline limit of 30 μg g^{-1} (FAO, 1983). In a survey of fish samples from North-East India, Kumar *et al*. (2012) reported mean copper levels of 3.9 ±0.7 μg g^{-1}. This value is in agreement with those found in the current study and is well below the acceptable limits. In another study, Ahmed and Naim (2008) determined levels of some heavy metals in fish samples from the Gulf of Aquaba. The authors reported copper concentrations in the range 0.9-1.3 μg g^{-1}, with which our values agree. Other authors reported the copper levels in the range of 0.38-3.16 μg g^{-1} in fish from Lake Macquarie, New South Wales, Australia (Roach *et al*., 2008), 7.12±3.3 μg g^{-1} in fish from sewage fed lake of Karnataka, India (Puttaiah and Kiran, 2008), 0.06-0.35 μg g^{-1} in market fish from South China (Cheung *et al*., 2008), 0.13-0.57 μg g^{-1} in freshwater fish from Lithuania (Staniskiene *et al*., 2009), 2.09±0.40 μg g^{-1} in fish muscles from Taiwan (Lin, 2009), 0.02-0.17 μg g^{-1} in freshwater fish from West Pomerania, Poland (Magdalena *et al*., 2009), 0.10- 2.78 μg g^{-1} in fish from Euphrates, Turkey (Mol *et al*., 2010), 7.59 μg g^{-1} in fish collected from Pennar estuary, India (Ravanaiah and Murthy, 2010), 0.40-0.59 μg g^{-1} in fish from freshwater lake of Bhopal, India (Malik *et al*., 2010) and 0.3-2.6 μg g^{-1} in fish samples from Malaysia (Mazlin *et al*., 2009). According to Mason (2000), accumulation of metals is generally species specific and may be related to the feeding habits of the fish. However, the efficiency of metal uptake from contaminated water and food may differ in relation to ecological needs, metabolism, and the contamination gradients of water, food, and sediment, as well as salinity and temperature.

There appears to be contrasting views on the pattern of correlation between fish size (total length and body weight) and the concentrations of essential heavy metals such as copper, zinc and iron. For example, Oguzie (2003) reported a significantly positive correlation between copper content and the body weight of *channa obscura* (a predatory fish) collected from the lower Ikpba River in Benin city, Nigeria. Luczynska and Tonska (2006) investigated the effect of fish size on the contents of Cu, Zn, Fe and Mn in Perch and Pike fish from four lakes (Lanskie, Pluszne, Dluzek and Maroz) located in the

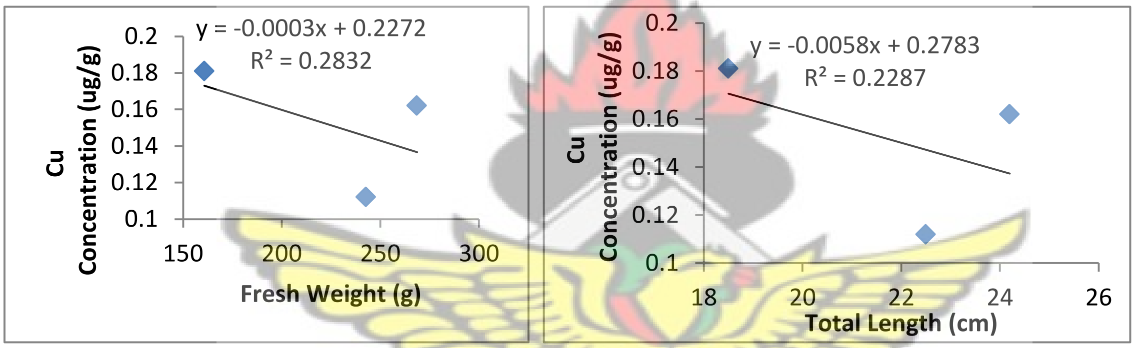
Olsztyn Lake District (northeastern Poland) from 1999-2000. The authors noted negative correlations between copper content and body weight and total length of Perch at all sites except Lake Pluszne. The concentrations of copper in the muscles of Pike from lakes Lanskie and Maroz were positively correlated with body weight and total length, whereas with Pike from lakes Pluszne and Dluzek, negative correlation was observed between copper content and the body weight and total length. According to De Wet *et al*. (1994), an inverse correlation occurred between the body mass and copper content in *Pseudocrenilabrus philander* from a mine- polluted impoundment. The youngest fish showed the highest concentrations of copper. Negative relationships between fish length and copper concentrations were also reported by Canli and Atli (2003).

A total of nine species were subjected to regression studies. The results are shown in Figures 4.10-4.18. Out of the nine species considered, only two namely *Lutjanus campechanus* (Figure 4.15) and *Thunnus Obesus* (4.16) showed significant negative correlations between fresh body weight and total length and copper concentrations . The rest of the species showed no significant correlation between body size (weight and length) and copper content. This result appears to confirm earlier assertions that copper does not undergo biomagnification. Apparently body concentrations of copper is regulated and maintained at a certain level (Widianarko *et al*., 2000). The existing theory on the influence of body size on the accumulation of heavy metals in animals as exemplified by several bioaccumulation studies on different aquatic and terrestrial species (Janssen and Bedaux, 1989; Van Hattum *et al*., 1991; Mersch *et al*., 1996) does not appear to hold for copper.



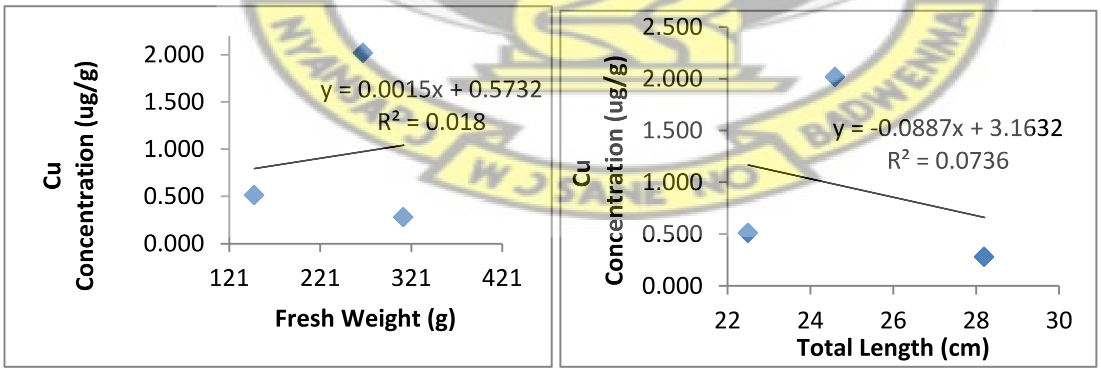
(A) (B)

Figure 4.10: Relationship between copper concentration and body weight (A) and total length (B) for *Pomadasys rogerii*



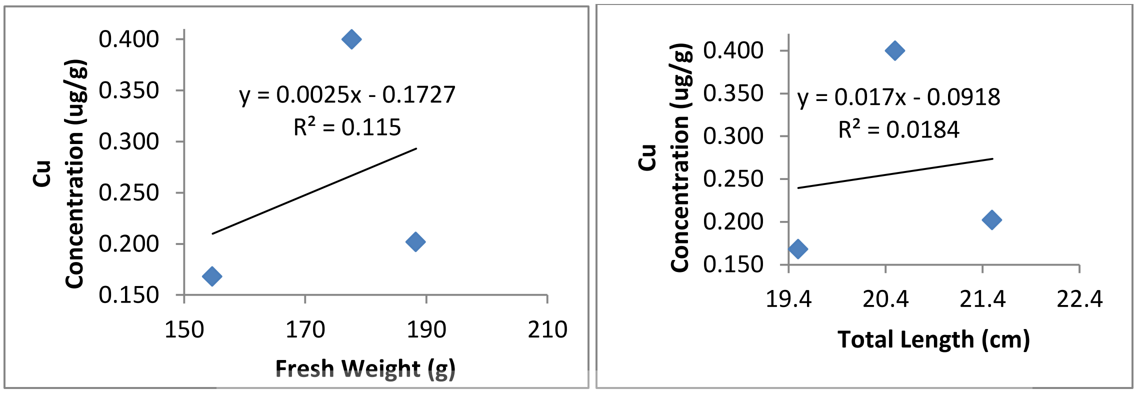
(A) (B)

Figure 4.11: Relationship between copper concentration and body weight (A) and total length (B) for *Galeoides decadactylus*



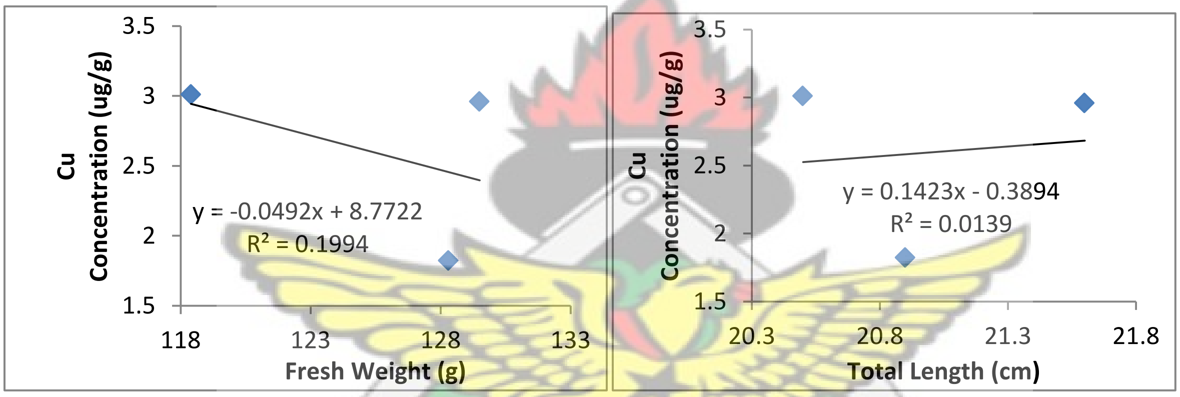
(A) (B)

Figure 4.12: Relationship between copper concentration and body weight (A) and total length (B) for *Arius latiscutatus*



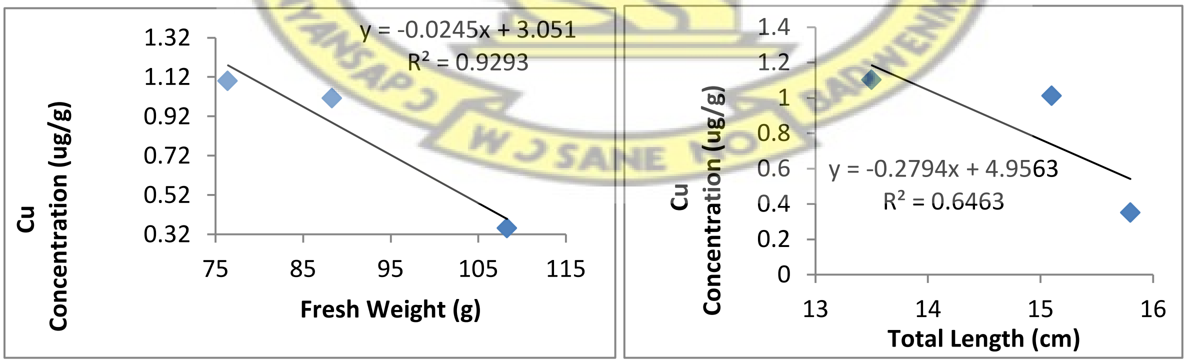
(A) (B)

Figure 4.13: Relationship between copper concentration and body weight (A) and total length (B) for *Pagrus caeruleostictus*



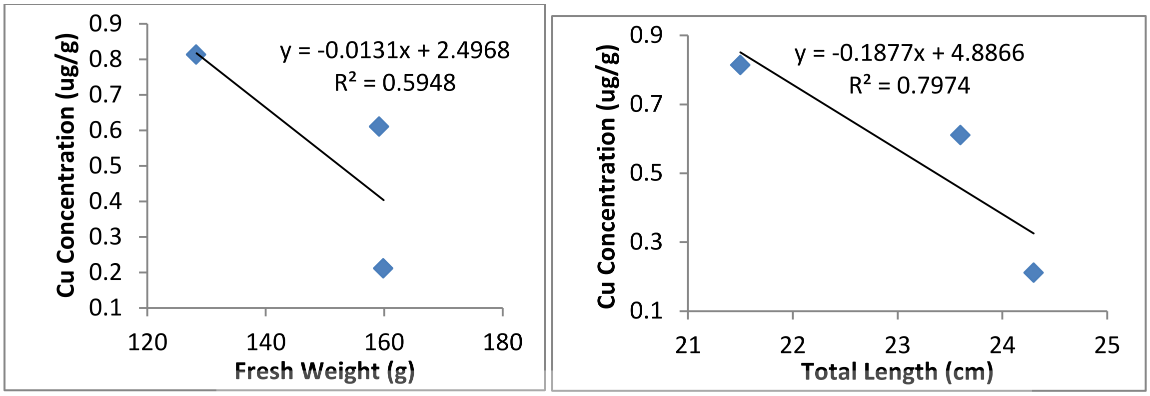
(A) (B)

Figure 4.14: Relationship between copper concentration and body weight (A) and total length (B) for *Sardinella maderensis*



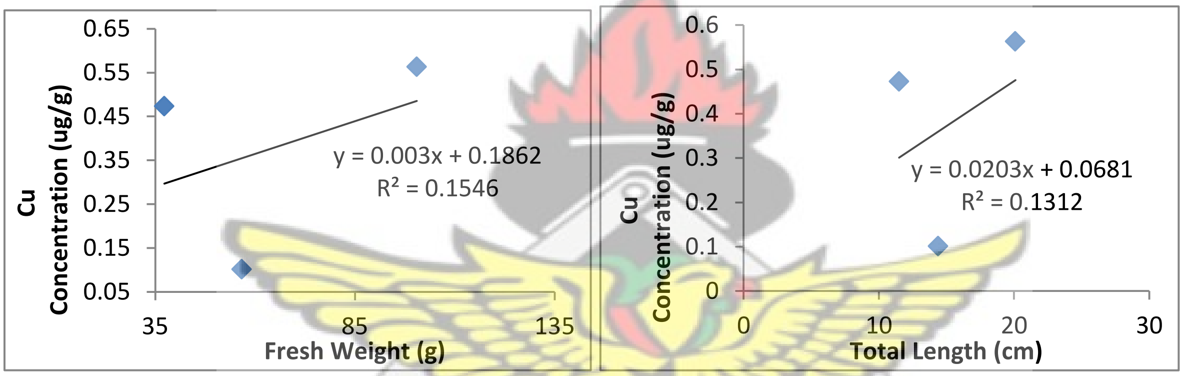
(A) (B)

Figure 4.15: Relationship between copper concentration and body weight (A) and total length (B) for *Lutjanus campechanus*



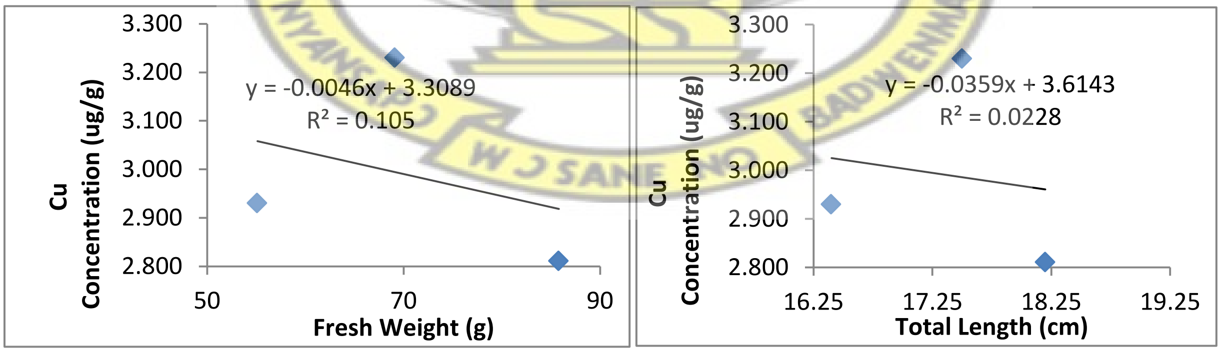
(A) (B)

Figure 4.16: Relationship between copper concentration and body weight (A) and total length (B) for *Thunnus Obesus*



(A) (B)

Figure 4.17: Relationship between copper concentration and body weight (A) and total length (B) for *Priacanthus arenatus*



(A) (B)

Figure 4.18: Relationship between copper concentration and body weight (A) and total length (B) for *Sardinella aurita*

Copper is an essential micronutrient involved in certain physiological processes and metabolic activities in organisms. Although important, studies have shown that elevated levels of copper can be dangerous to human health (Goyer, 1991; Salonen *et al*., 1991; Gwozdzinski, 1995). In view of this, risks to human health from copper contamination of fish were assessed by comparing estimates of dietary exposure with the Provisional Tolerable Weekly Intake (PTWI) recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). For copper, the PTWI guideline of 3500 µg/kg body weight/week which is equivalent to 500 µg/kg body weight/day (PTDI) was used in this study (JECFA, 2003). The daily consumption rate of 32.57 grams of fish or 228 g/week (USEPA, 2012) was adopted from the American food consumption index and used in the health-risk assessment. The average copper intakes from all the fish species in this study were much lower than the recommended value as shown in Table 4.6. The Hazard Quotient (HQ) in the studied species ranged from 0.0001 to 0.0028; which is extremely low when compared to the hazard values of other studies in Literature (Llobet *et al*., 2003; Ling *et al*., 2009; Mansilla-Rivera and Rodríguez-Sierra, 2011). The species with the highest reported mean concentration of copper was *Sardinella aurita* (2.990 µg/g). If an adult consumes 32.57g/day of *Sardinella aurita*, he would take in approximately 97.38 µg/day (681.69 µg/week) of copper. This amounts to a weekly intake (WI) of 9.738 µg/kg body weight/week for a 70 kg person; which is far below the JEFCA (2003) recommended Provisional Tolerable Weekly Intake (PTWI) of 3500 µg/kg body weight/week. To exceed the PTWI, an adult would have to consume about 81.9 Kg of *Sardinella aurita* weekly; which is very unlikely.

The dietary intake of fish estimated from the present study is well below FAO/WHO guideline limit. Thus the copper levels in the tested fish species may not pose any known health risk to the population of Monrovia.

Table 4.6: Mean dietary intake of copper

	Species	Cu Conc. (μg/g)	WCR (g/person/wk)	Weekly Intake (WI) (μg/kg body weight/wk)	Hazard Quotient (HQ)
1	*A. vulpes*	0.211	228	0.687	0.0002
2	*A. latiscutatus*	0.937	“	3.052	0.0009
3	*C. taeniops*	0.189	“	0.616	0.0002
4	*C. chrysurus*	0.572	“	1.863	0.0005
5	*E. lacerta*	0.533	“	1.736	0.0005
6	*E. senegalensis*	0.212	“	0.690	0.0002
7	*E. goreensis*	1.813	“	5.905	0.0017
8	*E. alletteratus*	0.613	“	1.997	0.0006
9	*G. decadactylus*	0.152	“	0.495	0.0001
10	*H. jaguana*	0.348	“	1.133	0.0003
11	*L. gibbosus*	0.128	“	0.417	0.0001
12	*L. campechanus*	0.821	“	2.674	0.0008
13	*P. caeruleostictus*	0.257	“	0.837	0.0002
14	*P. rogerii*	1.025	“	3.338	0.0010
15	*P. arenatus*	0.379	“	1.234	0.0004
16	*P. elongatus*	0.105	“	0.342	0.0001
17	*P. senegalensis*	0.460	“	1.498	0.0004
18	*S. aurita*	2.990	“	9.738	0.0028
19	*S. maderensis*	2.598	“	8.462	0.0024
20	*S. colias*	0.423	“	1.378	0.0004
21	*S. tritor*	0.218	“	0.710	0.0002
22	*S. setapinnis*	1.331	“	4.335	0.0012
23	*S. carpenteri*	0.142	“	0.462	0.0001
24	*S. fiatola*	0.692	“	2.254	0.0006
25	*T. obesus*	0.542	“	1.765	0.0005
26	*T. goreensis*	0.101	“	0.329	0.0001
27	*T. maxillosus*	0.281	“	0.915	0.0003
28	*T. lepturus*	0.873	“	2.843	0.0008
29	*T.C. crocodilus*	0.268	“	0.873	0.0002

Note: PTWI (μg/kg body weight/wk) = 3500
WCR = weekly consumption rate

4.3 Lead

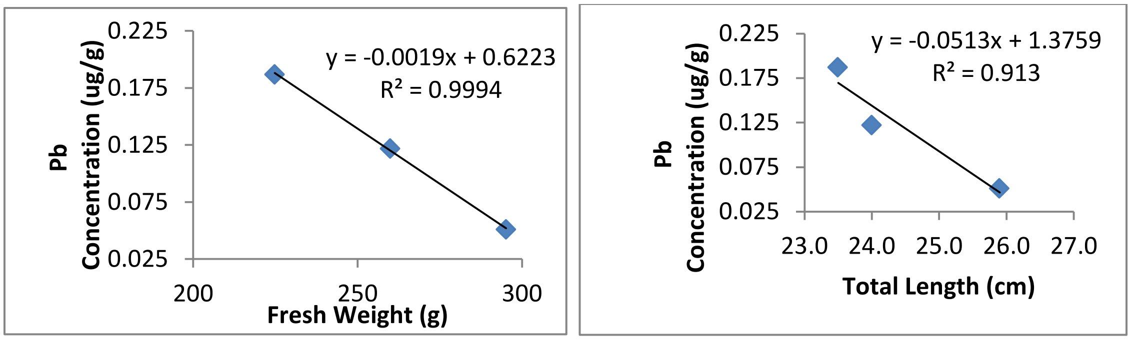
Lead has no biological role in the human body and can be toxic even at very minute concentrations (Doherty *et al.,* 2010). Results of Lead (Pb) levels in muscle of fish (µg g^{-1} on wet weight basis) from markets in Monrovia, Liberia are presented in Table 4.7. Mean Pb concentration ranged from 0.027 to 0.256 µg g^{-1} wet weight. *Trichiurus lepturus* recorded the highest mean concentration of 0.256 µg g^{-1} wet weight followed by *Tylosurus crocodilus crocodilus* (0.231 µg g^{-1} wet weight). Mean Pb concentrations in all the other fish samples were less than 0.190 µg g^{-1} wet weight, which is below the 2.0 µg g^{-1} wet weight limit recommended by FAO (1983) and the Codex Alimentarius (2002) standard of 0.2 µg g^{-1} wet weight. In all the 29 species analyzed in this study, only *Trichiurus lepturus* (0.256 µg g^{-1} wet weight) and *Tylosurus crocodilus crocodilus* (0.231 µg g^{-1} wet weight) had mean Pb levels above the Codex Alimentarius (2002) specific level for lead in fish (0.2 µg g^{-1}). *Sardinella maderensis* recorded the lowest mean Pb concentration of 0.027 µg g^{-1} wet weight.

Mean Pb levels obtained in this study are either in agreement or much lower than most published Pb concentrations in fish from non-polluted regions of the world. For example Pb concentrations in the edible portions of various fish species purchased from supermarkets in New Jersey in 2004 are in the range 0.02-0.24 µg g^{-1} wet weight (Burger and Gochfeld, 2005), with which our values agree. In another study, Pb concentrations in various commercial fish species sampled from Nitra River (Slovakia) in 2003 were in the range 0.20-5.81 µg g^{-1} wet weight, with a mean concentration of 0.80 ± 0.02 µg g^{-1} wet weight (Andreji *et al*., 2005), below which our values fall. In a survey of different fish species from Black, Marmara, Aegean and Mediterranean Seas in Turkey, Turkmen *et al*. (2008) reported Pb levels in fish muscle ranging from 0.04 to 1.31 µg g^{-1} wet weight, below which our values fall. In general, Pb concentrations reported in this study are much lower when compared to some values reported for other tropical countries like Nigeria and Malaysia (Doherty *et al.,* 2010; Oronsaye *et al*., 2010; Kamaruzzaman *et al.,* 2010). Lead levels have also been reported by other authors for some fish species included in this study. For example, Igwemmar *et al*. (2013) reported heavy metals levels in the muscle tissues of some locally consumed fish species sold in Gwagwalada market, Abuja, Nigeria. In their study, *Sardinella maderensis* recorded mean Pb concentration of 0.01 µg g^{-1} wet weight; a value lower than the 0.027 µg g^{-1} wet weight reported for the same species. In another study, Burger and Gochfeld (2005), reported heavy metals levels in different commercial fish species sold in supermarkets and specialty fish markets in New Jersey. The authors reported mean Pb levels in Red snapper (*Lutjanus campechanus*) and Croaker (*Pseudotolithus sp*.) as 0.12±0.01 and 0.09±0.01 µg g^{-1} wet weight respectively; which are values that are in agreement with those reported for the same species in this study.

Table 4.7: Lead concentration (µg g^{-1} wet weight) in muscle of commercial fish samples from markets in Monrovia, Liberia (2013)

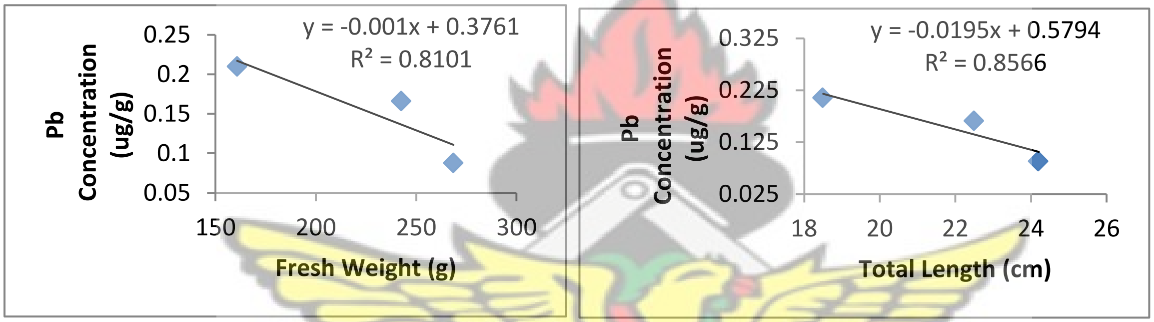
Species	Sample size (n)	Total length Range (cm)	Fresh weight Range (g)	Pb Conc. Range µg g^{-1}	Pb Conc. Mean µg g^{-1}
Albula vulpes	1	28.7	399.5	0.079	0.079
Arius latiscutatus	3	22.5-28.2	148.8-312.7	0.097-0.186	0.134
Cephalopholis taeniops	2	14.5-16.5	81.5-83.7	0.022-0.056	0.039
Chloroscombrus chrysurus	2	15.4-16.5	49.4-61.4	0.010-0.176	0.093
Elops lacerta	2	27.5-30.4	303.3-383.2	0.156-0.200	0.178
Elops senegalensis	2	27.5-33.3	271.5-507.2	0.113-0.131	0.112
Epinephelus goreensis	1	27.4	561.9	0.045	0.045
Euthynnus alletteratus	1	46.5	1340.5	0.051	0.051
Galeoides decadactylus	3	18.5-24.2	160.0-268.6	0.088-0.210	0.155
Harengula jaguana	2	23.6-24.2	194.8-211.6	0.050-0.084	0.067
Lepomis gibbosus	2	14.5-15.5	152.3-170.8	0.010-0.050	0.030
Lutjanus campechanus	3	13.5-15.8	76.4-108.3	0.068-0.150	0.103
Pagrus caeruleostictus	3	19.5-21.5	154.7-188.3	0.032-0.121	0.070
Pomadasys rogerii	3	23.5-25.9	224.8-295.2	0.051-0.187	0.120
Priacanthus arenatus	3	11.5-20.1	37.3-100.5	0.102-0.191	0.149
Pseudotolithus elongatus	1	23.4	210.0	0.041	0.041
Pseudotolithus senegalensis	2	31.3-31.5	430.1-435.2	0.052-0.104	0.078
Sardinella aurita	3	16.4-18.2	55.1-85.8	0.061-0.197	0.120
Sardinella maderensis	3	20.5-21.6	118.4-129.5	0.013-0.028	0.027
Scomber colias	1	50.2	799.1	0.081	0.081
Scomberomorus tritor	2	26.2-26.4	243.0-253.9	0.014-0.050	0.032
Selene setapinnis	2	27.6-31.7	417.2-612.3	0.061-0.095	0.078
Seriola carpenteri	2	33.9-37.2	577.4-806.3	0.080-0.160	0.120
Stromateus fiatola	2	26.1-26.5	374.6-428.4	0.020-0.062	0.041
Thunnus obesus	3	21.5-24.3	128.3-159.9	0.132-0.226	0.179
Trachinotus goreensis	1	24.9	479.3	0.030	0.034
Trachinotus maxillosus	1	24.9	276.5	0.082	0.082
Trichiurus lepturus	2	57.2-72.5	295.3-378.3	0.201-0.311	0.256
Tylosurus crocodilus crocodilus	2	35.5-39.5	230.8-431.2	0.161-0.301	0.231

Various species of fish from the same water body may accumulate different amounts of metals. Interspecies differences in metal accumulation may be related to living and feeding habits. Ney and Van Hassel (1983), found that lead and zinc concentrations were higher in benthic fish. According to Jezierska and Witeska (2001), the concentrations of most metals (except for mercury) are usually inversely related to the age and size. Measurements of bioaccumulation of Pb by *Pseudocrenilabrus* *philander* from a mine-polluted impoundment revealed that there was an inverse relationship between metal concentrations and body mass of fish (De Wet *et al*. 1994). According to Allen-Gill and Martynov (1995), an inverse correlation occurred between the age/size and Pb content in *Coregonus clupeaformis*, and a similar relationship was found between accumulation of Pb and age/size of *Catostomus commersoni* (Ney and Van Hassel, 1983). Negative relationships between fish length and metal concentrations (for Cr, Pb, and Cu) were also reported by Canli and Atli (2003). A significant declining trend of Pb concentrations with increasing fish size was also observed by Smock (1983). In contrast, positive correlations between fish size/age and Pb contents have been reported by some other authors (Farkas *et al*., 2003; Imanpour Namin *et al*., 2011). A total of nine species were subjected to regression studies. The results are shown in Figures 4.19- 4.27. Out of the nine species considered, three species namely *Sardinella maderensis, Arius latiscutatus* and *Pagrus caeruleostictus* showed no significant correlations between fresh body weight and total length and lead concentrations. The rest of the species showed significant negative correlations between body size (weight and length) and Pb contents. This result appears to concur with earlier assertions that Pb concentrations were inversely proportional to the body weight and total length of fish (De Wet *et al*. 1994; Allen-Gill and Martynov, 1995; Canli and Atli, 2003). None of the samples recorded increasing Pb levels with increasing body mass as reported by Farkas *et al*. (2003) and Imanpour Namin *et al*. (2011). Lead levels in fish could therefore be related to a number of intricate factors other than diet.



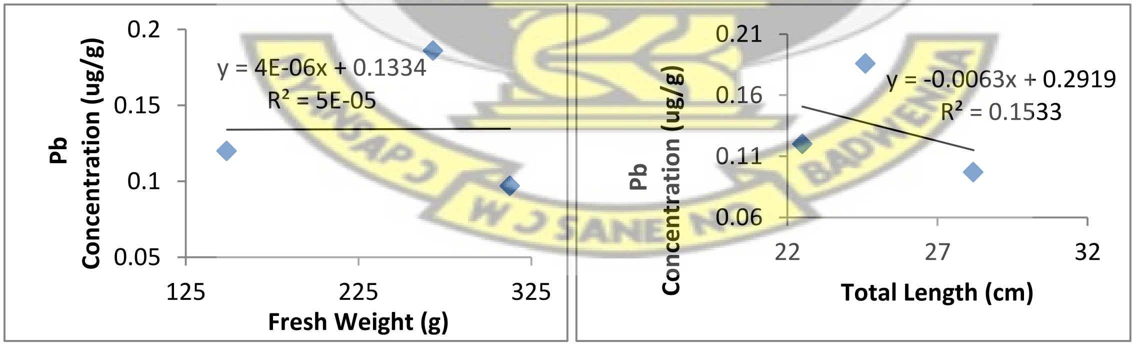
(A) (B)

Figure 4.19: Relationship between lead concentration and body weight (A) and total length (B) for *Pomadasys rogerii*



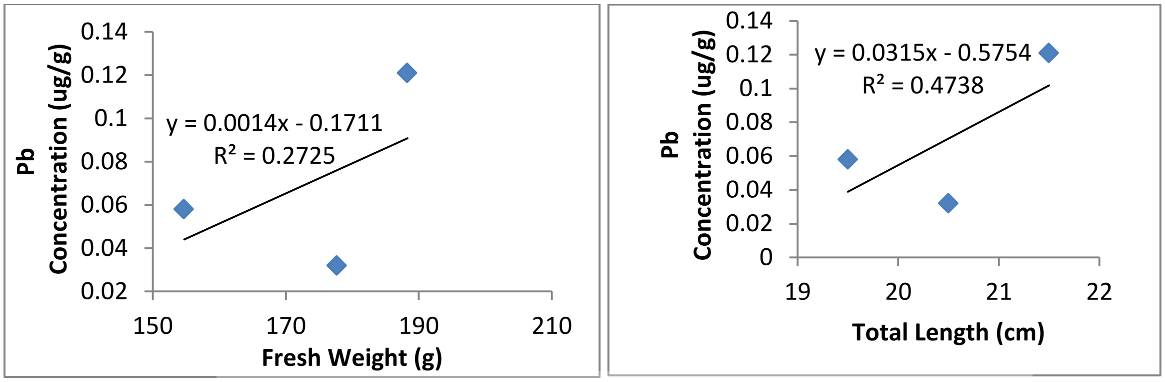
(A) (B)

Figure 4.20: Relationship between lead concentration and body weight (A) and total length (B) for *Galeoides decadactylus*



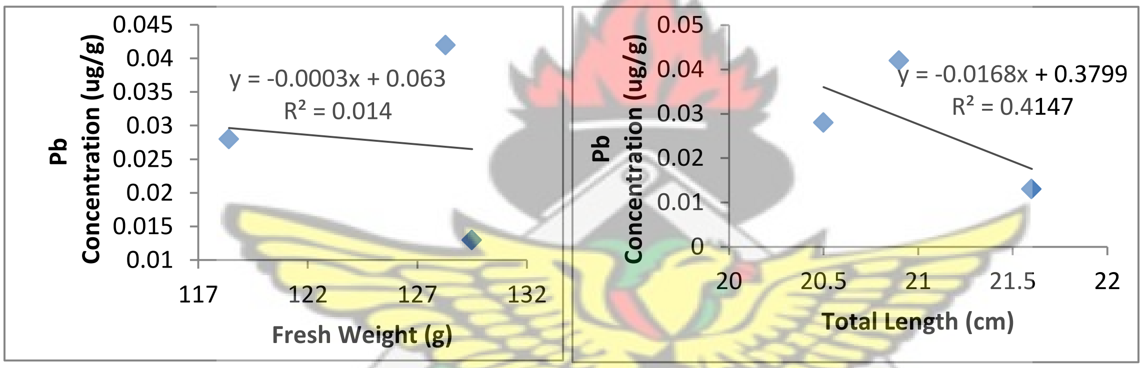
(A) (B)

Figure 4.21: Relationship between lead concentration and body weight (A) and total length (B) for *Arius Latiscutatus*



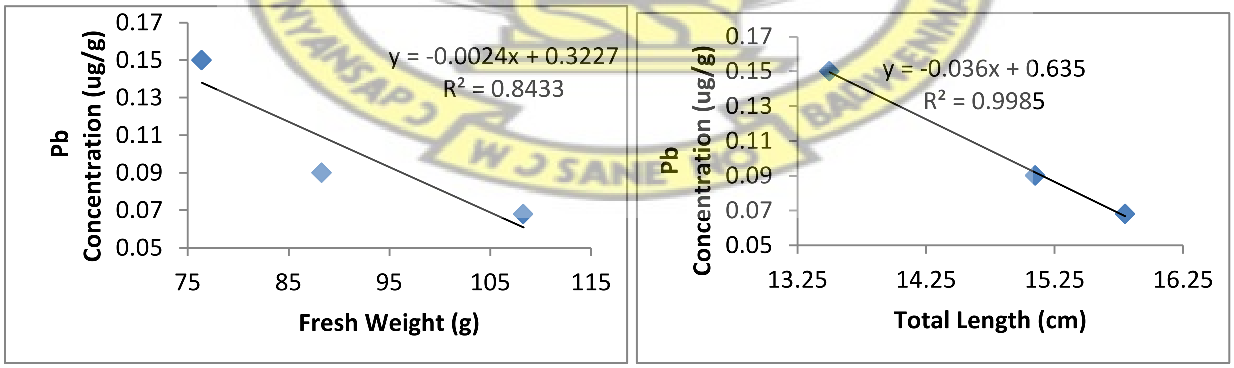
(A) (B)

Figure 4.22: Relationship between lead concentration and body weight (A) and total length (B) for *pagrus caeruleostictus*



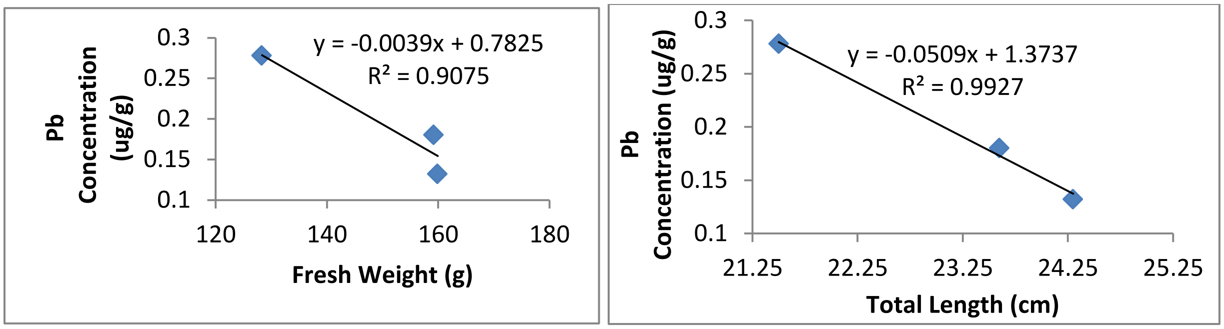
(A) (B)

Figure 4.23: Relationship between lead concentration and body weight (A) and total length (B) for *Sardinella Maderensis*



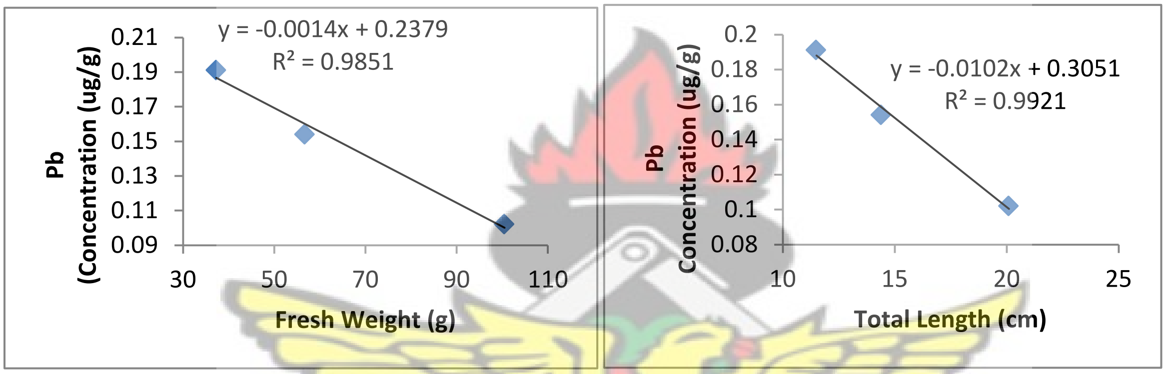
(A) (B)

Figure 4.24: Relationship between lead concentration and body weight (A) and total length (B) for *Lutjanus campechanus*



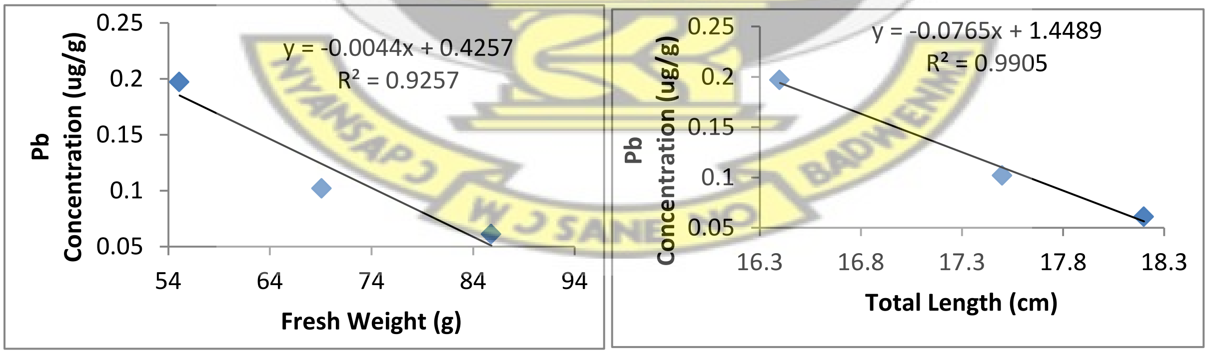
(A) (B)

Figure 4.25: Relationship between lead concentration and body weight (A) and total length (B) for *Thunnus obesus*



(A) (B)

Figure 4.26: Relationship between lead concentration and body weight (A) and total length (B) for *Priacanthus arenatus*



(A) (B)

Figure 4.27: Relationship between lead concentration and body weight (A) and total length (B) for *Sardinella aurita*

Lead is a neurotoxin that causes behavioral deficits in vertebrates (Weber and Dingel, 1997), and can cause decreases in survival, growth rates and learning (Eisler, 1988). Levels of 50 ppm in the diet can cause reproductive effects in some predators, and dietary levels as low as 0.1–0.5 ppm are associated with learning deficits in some vertebrates (Eisler, 1988). In this study, risks to human health from Pb contamination of fish were assessed by comparing estimates of dietary exposure with the Provisional Tolerable Weekly Intakes (PTWIs) recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). There is currently no evidence of a threshold of critical lead induced-effects. The last PTWI value of 25 µg/kg/week was withdrawn following data from several epidemiological studies on neurodevelopment in children (Lanphear *et al*., 2005) and systolic blood pressure in adults (Glenn *et al*., 2003; Vupputuri *et al*., 2003; Nash *et al*., 2003; Glenn *et al*., 2006). However this withdrawn value (25 µg/kg/week) is still been used by many authors for health risk assessments (Sun et *al*., 2009; Oforka et *al*., 2012; Kumar *et al*., 2013); hence the value was used in the current study. The average Pb intakes from all the fish species in this study were much lower than the recommended value as shown in Table 4.8.

Table 4.8: Mean dietary intake of lead

	Species	Pb Conc. (µg/g)	WCR (g/person/ wk)	Weekly Intake (WI) (µg/kg body weight/wk)	Hazard Quotient (HQ)
1	*A. vulpes*	0.079	228	0.257	0.010
2	*A. latiscutatus*	0.134	“	0.436	0.017
3	*C. taeniops*	0.039	“	0.127	0.005
4	*C. chrysurus*	0.093	“	0.303	0.012
5	*E. lacerta*	0.178	“	0.580	0.023
6	*E. senegalensis*	0.112	“	0.365	0.015
7	*E. goreensis*	0.045	“	0.147	0.006
8	*E. alletteratus*	0.051	“	0.166	0.007
9	*G. decadactylus*	0.155	“	0.505	0.020
10	*H. jaguana*	0.067	“	0.218	0.009
11	*L. gibbosus*	0.030	“	0.098	0.004
12	*L. campechanus*	0.103	“	0.335	0.013
13	*P. caeruleostictus*	0.070	“	0.228	0.009
14	*P. rogerii*	0.120	“	0.391	0.016
15	*P. arenatus*	0.149	“	0.485	0.019
16	*P. elongatus*	0.041	“	0.134	0.005
17	*P. senegalensis*	0.078	“	0.254	0.010
18	*S. aurita*	0.120	“	0.391	0.016
19	*S. maderensis*	0.027	“	0.088	0.004
20	*S. colias*	0.081	“	0.264	0.011
21	*S. tritor*	0.032	“	0.104	0.004
22	*S. setapinnis*	0.078	“	0.254	0.010
23	*S. carpenteri*	0.120	“	0.391	0.016
24	*S. fiatola*	0.041	“	0.134	0.005
25	*T. obesus*	0.179	“	0.583	0.023
26	*T. goreensis*	0.034	“	0.111	0.004
27	*T. maxillosus*	0.082	“	0.267	0.011
28	*T. lepturus*	0.256	“	0.834	0.033
29	*T.C. crocodilus*	0.231	“	0.752	0.030

Note: PTWI (µg/kg body weight/wk) = 25
WCR = weekly consumption rate

The Hazard Quotient (HQ) in the studied species ranged from 0.004 to 0.033; which is lower when compared to the hazard values of other studies in Literature (Ysart *et al*., 2000; Leblanc *et al*., 2000; Blanusa and Juresa, 2001). The HQ for the fish species in this study are far lower than the 0.06-0.40 reported for Croatian population (Blanusa and Juresa, 2001). The species with the highest reported mean concentration of Pb was *Trichiurus lepturus* (0.256 µg/g wet weight). If an adult consumes

32.57g/day of *Trichiurus lepturus*, he would take in approximately 8.34 µg/day (58.37 µg/week) of lead. This amounts to a weekly intake (WI) of 0.834 µg/kg body weight/week for a 70 kg person; which is below the JEFCA (2003) recommended Provisional Tolerable Weekly Intake (PTWI) of 25 µg/kg body weight/week. To exceed the PTWI, an adult would have to consume about 7 Kg of *Trichiurus lepturus* per week; which is very unlikely.

The dietary intake of fish estimated from the present study is well below FAO/WHO guideline limit. Thus the tested fish species may not pose any known risk to health for the local population considering Pb.

4.4 Cadmium

Cadmium (Cd) is a non-biolgically essential metal which can be potentially toxic to human even at minute concentrations (Andreji *et al*., 2005). Results of cadmium (Cd) levels in muscle of fish (µg g^{-1} on wet weight basis) from markets in Monrovia, Liberia are presented in Table 4.9. Cadmium concentrations ranged from 0.002 to 0.347 µg g^{-1} wet weight. *Elops lacerta* recorded the highest concentration of Cd (0.347 µg g^{-1} wet weight) followed by *Seriola carpenteri* (0.245 µg g^{-1} wet weight), *Euthynnus alletteratus* (0.231 µg g^{-1} wet weight) and *Lepomis gibbosus* (0.230 µg g^{-1} wet weight). Cadmium concentrations in all the other fish samples were less than 0.200 µg g^{-1} wet weight, which is below the 1.0 µg g^{-1} wet weight limit recommended by FAO/WHO (JECFA, 2003). *Pseudotolithus elongatus* recorded the lowest mean cadmium concentration (0.002 µg g^{-1} wet weight).

Generally, cadmium concentrations in this study are moderate when compared to Cd levels in fish species from other parts of the world. For example, Cd contents in the muscle of several fish species from Beysehir Lake, Turkey were in the range 2.17-4.00 µg g^{-1} wet weight (Ozparlak *et al*., 2012), below which our values fell. In a survey of heavy metals in different commercial fish species from the Nitra River (Slovakia), Andreji *et al*. (2005) reported Cd concentrations in fish muscle in the range 0.06-0.58 µg g^{-1} wet weight (mean=0.23 ± 0.13 µg g^{-1} wet weight); within which our values fall. In another study, Turkemen *et al*. (2008) surveyed heavy metal contents in several fish species from the Black, Marmara, Aegean and Mediterranean Seas, Turkey. The authors reported Cd levels in the studied species in the range 0.02-0.30 µg g^{-1} wet weight; with which our values agree. Cadmium levels in the fish species in this study are generally lower when compared with results from Turkey (Erdogrul and Ates, 2006) and Pakistan (Tariq *et al*., 1993).

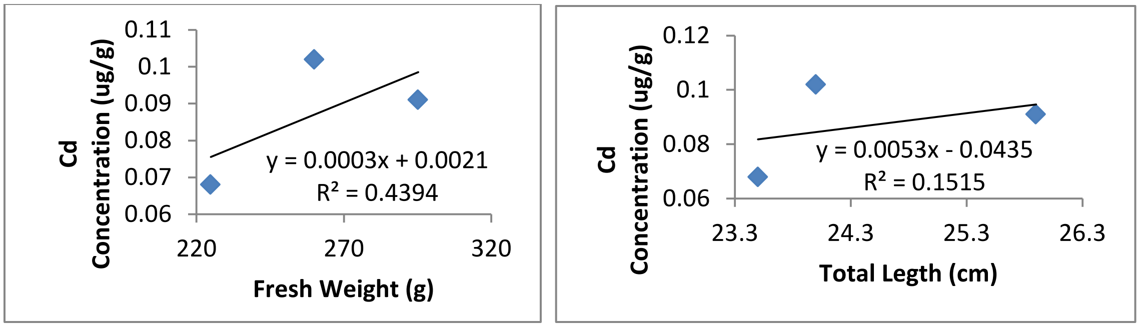
Table 4.9 Cadmium concentration (µg g^{-1} wet weight) in muscle of commercial fish samples from markets in Monrovia, Liberia (2013)

Species	Sample size (n)	Total length Range (cm)	Fresh weight Range (g)	Cd Conc. Range µg g^{-1}	Cd Conc. Mean µg g^{-1}
Albula vulpes	1	28.7	399.5	0.117	0.117
Arius latiscutatus	3	22.5-28.2	148.8-312.7	0.021-0.100	0.064
Cephalopholis taeniops	2	14.5-16.5	81.5-83.7	0.003-0.005	0.004
Chloroscombrus chrysurus	2	15.4-16.5	49.4-61.4	0.100-0.161	0.131
Elops lacerta	2	27.5-30.4	303.3-383.2	0.301-0.393	0.347
Elops senegalensis	2	27.5-33.3	271.5-507.2	0.127-0.132	0.130
Epinephelus goreensis	1	27.4	561.9	0.009	0.009
Euthynnus alletteratus	1	46.5	1340.5	0.231	0.231
Galeoides decadactylus	3	18.5-24.2	160.0-268.6	0.006-0.122	0.070
Harengula jaguana	2	23.6-24.2	194.8-211.6	0.053-0.211	0.132
Lepomis gibbosus	2	14.5-15.5	152.3-170.8	0.211-0.248	0.230
Lutjanus campechanus	3	13.5-15.8	76.4-108.3	0.002-0.010	0.006
Pagrus caeruleostictus	3	19.5-21.5	154.7-188.3	0.002-0.121	0.072
Pomadasys rogerii	3	23.5-25.9	224.8-295.2	0.068-0.102	0.087
Priacanthus arenatus	3	11.5-20.1	37.3-100.5	0.002-0.211	0.113
Pseudotolithus elongatus	1	23.4	210.0	0.002	0.002
Pseudotolithus senegalensis	2	31.3-31.5	430.1-435.2	0.013-0.067	0.008
Sardinella aurita	3	16.4-18.2	55.1-85.8	0.002-0.100	0.061
Sardinella maderensis	3	20.5-21.6	118.4-129.5	0.009-0.082	0.047
Scomber colias	1	50.2	799.1	0.193	0.193
Scomberomorus tritor	2	26.2-26.4	243.0-253.9	0.009-0.101	0.055
Selene setapinnis	2	27.6-31.7	417.2-612.3	0.091-0.177	0.134
Seriola carpenteri	2	33.9-37.2	577.4-806.3	0.201-0.288	0.245
Stromateus fiatola	2	26.1-26.5	374.6-428.4	0.098-0.132	0.115
Thunnus obesus	3	21.5-24.3	128.3-159.9	0.081-0.102	0.092
Trachinotus goreensis	1	24.9	479.3	0.186	0.186
Trachinotus maxillosus	1	24.9	276.5	0.072	0.072
Trichiurus lepturus	2	57.2-72.5	295.3-378.3	0.127-0.193	0.160
Tylosurus crocodilus crocodilus	2	35.5-39.5	230.8-431.2	0.012-0.211	0.112

Cadmium levels have also been reported for some fish species included in this study. For example, Sarsah *et al*. (2011) investigated the levels of toxic elements in marine organisms (fish and mollusk) along the coast of Ghana. In their study, *Sardinella maderensis* recorded mean Cd concentration of 0.03±0.004 µg g^{-1} wet weight; a value in agreement with the 0.027 µg g^{-1} wet weight reported for the same species in this study. In another study, Burger and Gochfeld (2005) reported heavy metals levels in different commercial fish species sold in supermarkets and specialty fish markets in New Jersey.

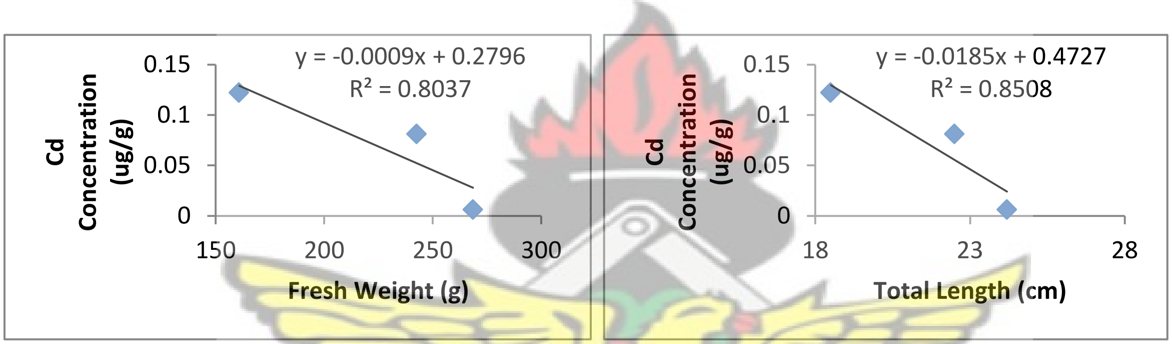
The authors reported mean Cd levels in Red snapper (*Lutjanus campechanus*) and Croaker (*Pseudotolithus sp*.) as 0.002±0.001 and 0.001±0.0004 µg g^{-1} wet weight respectively; which are values in agreement with those reported for the same species in this study.

The ATSDR review of the literature (2005) indicates that Cd may bioaccumulate at all levels of aquatic and terrestrial food chains. It accumulates largely in the liver and kidneys of vertebrates and not in muscle tissue. Intestinal absorption of Cd is low and biomagnification through the food chain may not be significant (Sprague, 1986). A total of nine species were subjected to regression studies. The results are shown in Figures 4.28 - 4.36. Out of the nine species considered, two species namely *Galeoides decadactylus* and *Priacanthus arenatus* showed significant negative correlations between Cd content and size. Three species (*Lutjanus campechanus*, *Thunnus obesus* and *Pagrus caeruleostictus*) showed significant positive correlation between Cd content and fish body weight and total length. In *Sardinella maderensis* (Figure 4.32), the Cd content was negatively correlated with the fish body weight but there was no significant correlation between the total length and Cd level in the fish. In *Arius latiscutatus* (Figure 4.30), the Cd content was negatively correlated with the fish total length but there was no significant trend noted between Cd level and fresh body weight of the fish. In the case of *Sardinella aurita* and *Pomadasys rogerii*, there were no significant correlation between Cd content and fish size.



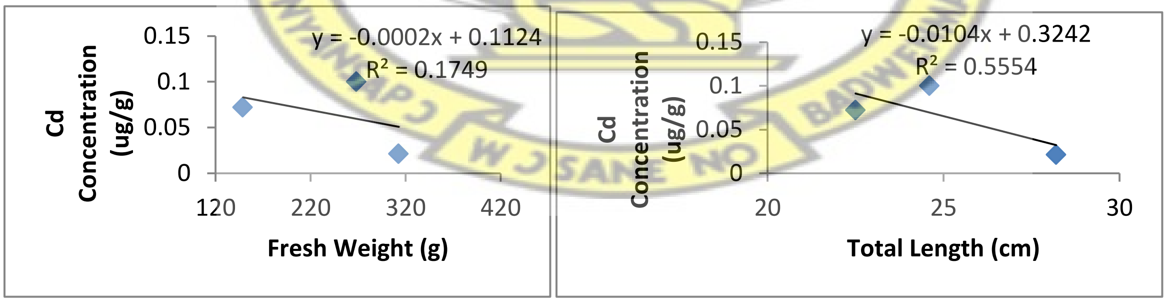
(A) (B)

Figure 4.28: Relationship between cadmium concentration and body weight (A) and total length (B) for *Pomadasys rogerii*



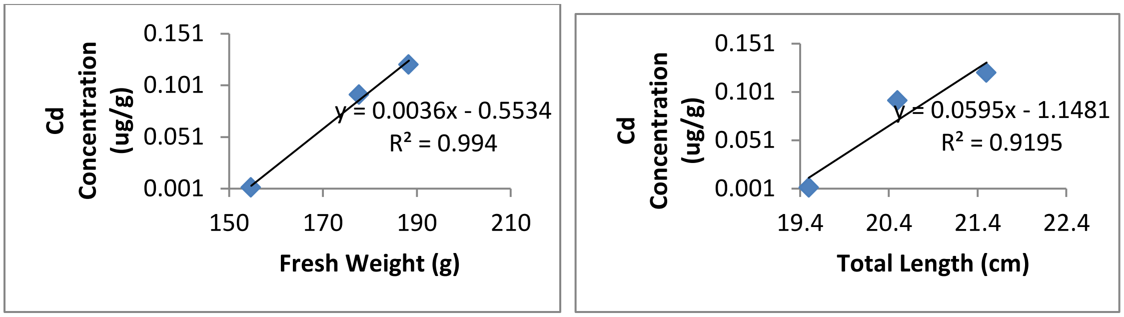
(A) (B)

Figure 4.29: Relationship between cadmium concentration and body weight (A) and total length (B) for *Galeoides decadactylus*



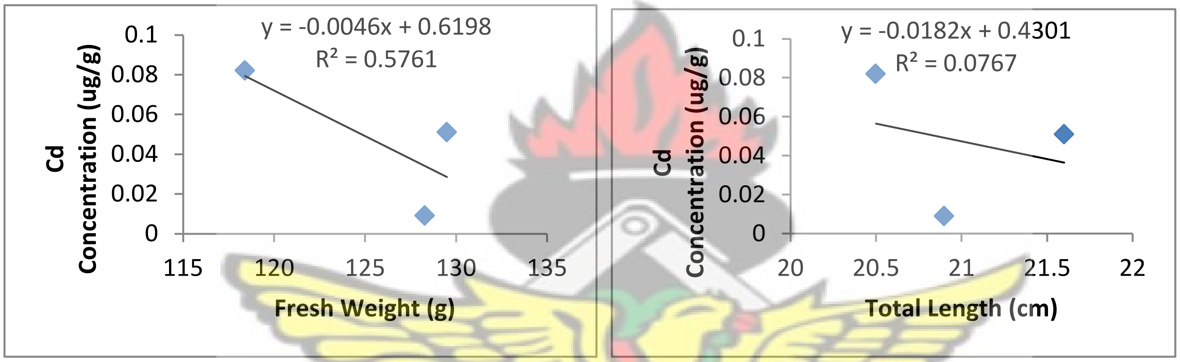
(A) (B)

Figure 4.30: Relationship between cadmium concentration and body weight (A) and total length (B) for *Arius latiscutatus*



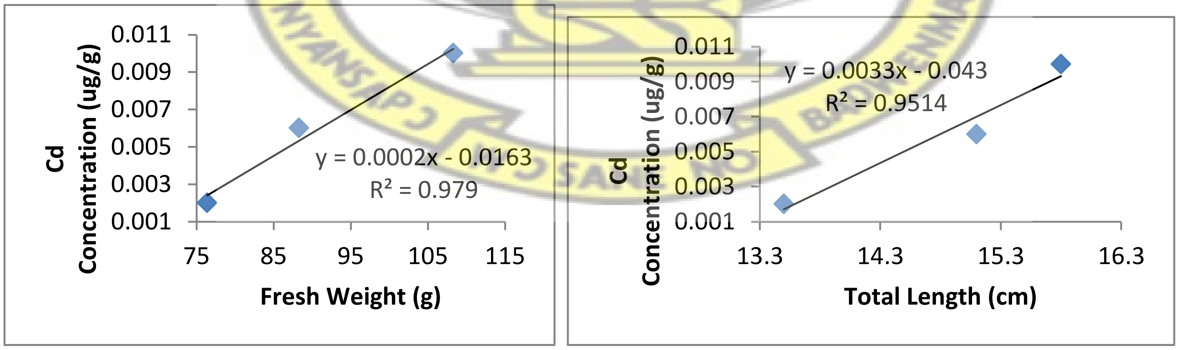
(A) (B)

Figure 4.31: Relationship between cadmium concentration and body weight (A) and total length (B) for *Pagrus caeruleostictus*



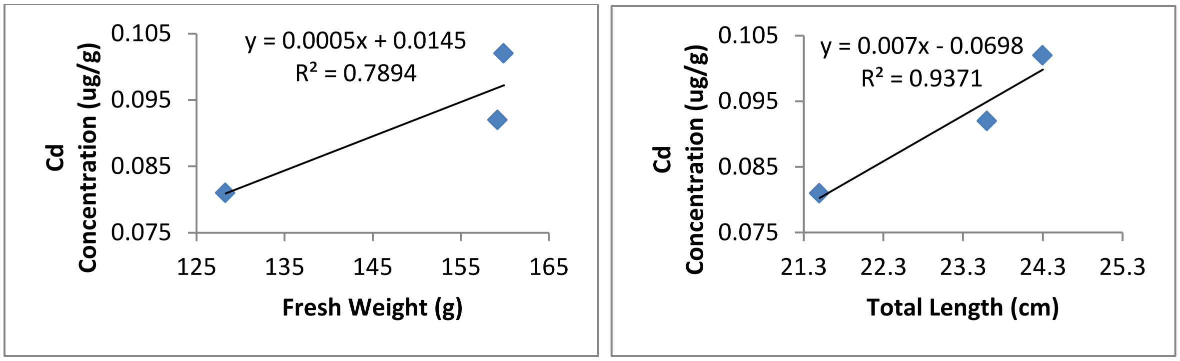
(A) (B)

Figure 4.32: Relationship between cadmium concentration and body weight (A) and total length (B) for *Sardinella maderensis*



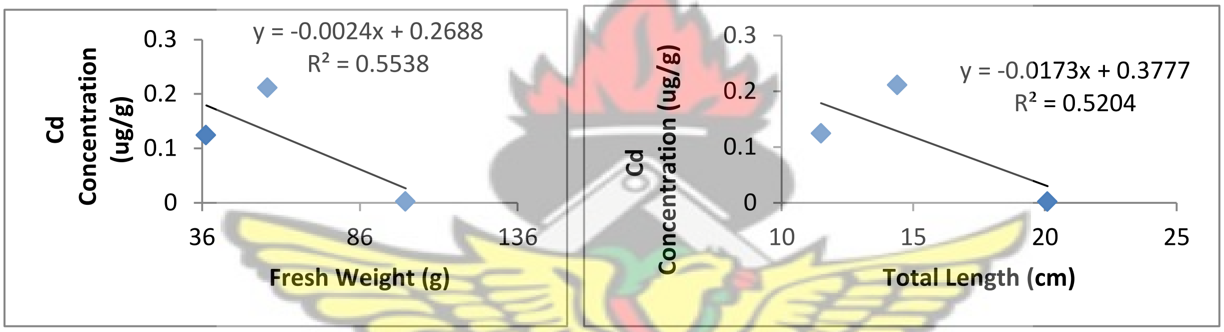
(A) (B)

Figure 4.33: Relationship between cadmium concentration and body weight (A) and total length (B) for *Lutjanus campechanus*



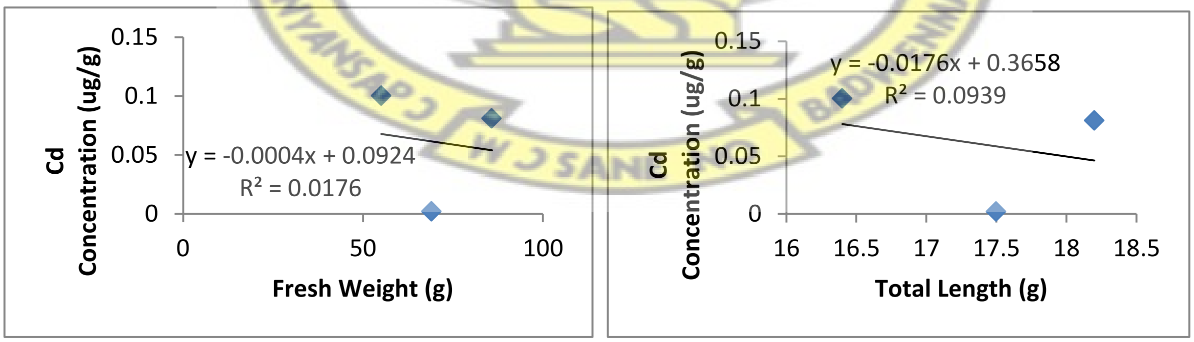
(A) (B)

Figure 4.34: Relationship between cadmium concentration and body weight (A) and total length (B) for *Thunnus obesus*



(A) (B)

Figure 4.35: Relationship between cadmium concentration and body weight (A) and total length (B) for *Priacanthus arenatus*



(A) (B)

Figure 4.36: Relationship between cadmium concentration and body weight (A) and total length (B) for *Sardinella aurita*

Cadmium is a non-essential heavy metal which mediates its toxic activities by various mechanisms. It has the potential to interact with extracellular and intracellular protein, rendering them not only potentially allergenic, but also predisposed to oxidative stress. In human, cadmium has the potential to displace essential elements from their protein carriers; resulting in deficiency disorders (Theron *et al*., 2012). In this study, risks to human health from Cd contamination of fish were assessed by comparing estimates of dietary exposure with the Provisional Tolerable Weekly Intake (PTWI) recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). For cadmium, the PTWI guideline of 7 μg/kg body weight/week was used in this study (JECFA, 2003). The daily consumption rate of 32.57 grams of fish or 228 g/week (USEPA, 2012) was adopted from the American food consumption index and used in the health-risk assessment. The average cadmium intakes from all the fish species in this study were much lower than the recommended value as shown in Table 4.10.

Table 4.10: Mean dietary intake of cadmium

	Species	Cd Conc. (µg/g)	WCR (g/person/wk)	Weekly Intake (WI) (µg/kg body weight/wk)	Hazard Quotient (HQ)
1	*A. vulpes*	0.117	228	0.381	0.054
2	*A. latiscutatus*	0.064	“	0.208	0.030
3	*C. taeniops*	0.004	“	0.013	0.002
4	*C. chrysurus*	0.131	“	0.427	0.061
5	*E. lacerta*	0.347	“	1.130	0.161
6	*E. senegalensis*	0.130	“	0.423	0.060
7	*E. goreensis*	0.009	“	0.029	0.004
8	*E. alletteratus*	0.231	“	0.752	0.107
9	*G. decadactylus*	0.070	“	0.228	0.033
10	*H. jaguana*	0.132	“	0.430	0.061
11	*L. gibbosus*	0.230	“	0.749	0.107
12	*L. campechanus*	0.006	“	0.020	0.003
13	*P. caeruleostictus*	0.072	“	0.235	0.034
14	*P. rogerii*	0.087	“	0.283	0.040
15	*P. arenatus*	0.113	“	0.368	0.053
16	*P. elongatus*	0.002	“	0.007	0.001
17	*P. senegalensis*	0.008	“	0.026	0.004
18	*S. aurita*	0.061	“	0.199	0.028
19	*S. maderensis*	0.047	“	0.153	0.022
20	*S. colias*	0.193	“	0.629	0.090
21	*S. tritor*	0.055	“	0.179	0.026
22	*S. setapinnis*	0.134	“	0.436	0.062
23	*S. carpenteri*	0.245	“	0.798	0.114
24	*S. fiatola*	0.115	“	0.375	0.054
25	*T. obesus*	0.092	“	0.300	0.043
26	*T. goreensis*	0.186	“	0.606	0.087
27	*T. maxillosus*	0.072	“	0.235	0.034
28	*T. lepturus*	0.160	“	0.521	0.074
29	*T.C. crocodilus*	0.112	“	0.365	0.052

Note: PTWI (µg/kg body weight/wk) = 7.0
WCR = weekly consumption rate

The Hazard Quotient (HQ) in the studied species ranged from 0.001 to 0.161; which is in agreement with the 0.114 reported for cadmium in fish from Bac Ninh Province, Vietnam (Hagberg, 2009). The species with the highest reported mean concentration of cadmium was *Elops Lacerta* (0.347 µg/g wet weight). If an adult consumes 32.57g/day of *Elops Lacerta,* he would take in approximately 11.302 µg/day (79.113 µg/week) of cadmium. This amounts to a weekly intake (WI) of 1.130 µg/kg body weight/week for a 70 kg person; which is below the JEFCA (2003) recommended Provisional Tolerable Weekly Intake (PTWI) of 7 µg/kg body weight/week. To exceed the PTWI, an adult would have to consume more than 1.5 Kg of *Elops Lacerta* per week; which is quite unlikely.

The dietary intake of fish estimated from the present study is far below FAO/WHO guideline limit. Thus the tested fish species may not pose any known risk to health for the local population considering cadmium.

4.5 Iron

Iron is present in all animals and plants as an essential nutrient. Although iron is an essential element, high levels of intake can cause symptoms of acute toxicity (Islam *et al*., 2010). Results of iron (Fe) levels in muscle of fish (µg g^{-1} on wet weight basis) from markets in Monrovia, Liberia are presented in Table 4.11. Mean Fe concentration ranged from 2.122 to 6.804 µg g^{-1} on wet weight basis. *Sardinella maderensis* recorded the highest mean concentration of Fe (6.804 µg g^{-1} wet weight) followed by *Sardinella aurita* (6.538 µg g^{-1} wet weight) and *Epinephelus goreensis* (5.711 µg g^{-1} wet weight). Mean Fe concentration in all the other fish samples were less than 4.500 µg g^{-1} wet weight, which is far below the 100 µg g^{-1} wet weight maximum permissible limit in fish recommended by FAO/WHO (1989). *Arius latiscutatus* recorded the lowest mean Fe concentration (2.122 µg g^{-1} wet weight).

The concentration of Fe in the fish samples obtained in this study are relatively low when compared to some other areas of the world and can be said to reflect background Fe concentrations. They are either in agreement or much lower than most published Fe concentrations in fish from non-polluted areas of the world. For example, Chen and Chen (2001) determined heavy metals levels in nine commercial fish species from the Ann-Ping coastal waters, Taiwan. The authors reported Fe concentrations in the range of 2.35 - 7.72 µg g^{-1} wet weight; which is almost similar to the findings in this study (2.122 - 6.804 µg g^{-1}). Igwemmar *et al*. (2013), determined heavy metals contents in different commercial fish species from the Gwagwadala market, Abuja. The authors reported Fe levels in *Sardinella Maderensis* as 3.99 µg g^{-1} wet weight; which is below the 6.804 µg g^{-1} wet weight reported for the same species in this study. In a survey of heavy metals in four common Slovak fish species from the Nitra River

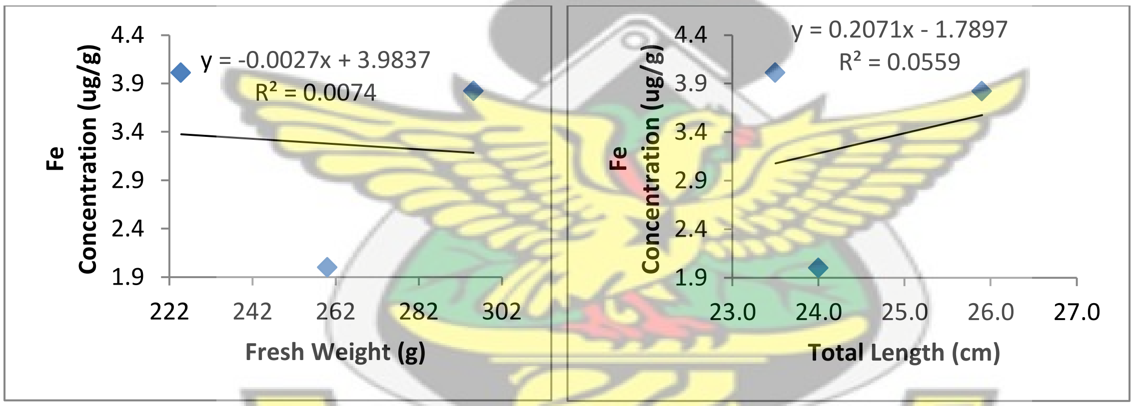
(Slovakia), Andreji *et al*. (2005) reported Fe concentrations in the range 3.41-15.14 µg g^{-1} wet weight; most of which are above those reported in the current study.

Table 4.11 Iron concentration (µg g^{-1} wet weight) in muscle of commercial fish samples from markets in Monrovia, Liberia (2013)

Species	Sample size	Total length Range (cm)	Fresh weight Range (g)	Fe Conc. Range µg g^{-1}	Fe Conc. Mean µg g^{-1}
Albula vulpes	1	28.7	399.5	2.128	2.128
Arius latiscutatus	3	22.5-28.2	148.8-312.7	1.374-2.866	2.122
Cephalopholis taeniops	2	14.5-16.5	81.5-83.7	2.531-3.115	2.823
Chloroscombrus chrysurus	2	15.4-16.5	49.4-61.4	3.861-4.739	4.300
Elops lacerta	2	27.5-30.4	303.3-383.2	3.263-3.081	3.172
Elops senegalensis	2	27.5-33.3	271.5-507.2	3.866-4.138	4.002
Epinephelus goreensis	1	27.4	561.9	5.711	5.711
Euthynnus alletteratus	1	46.5	1340.5	4.241	4.241
Galeoides decadactylus	3	18.5-24.2	160.0-268.6	1.006-3.113	2.349
Harengula jaguana	2	23.6-24.2	194.8-211.6	1.921-3.011	2.466
Lepomis gibbosus	2	14.5-15.5	152.3-170.8	2.112-4.431	3.272
Lutjanus campechanus	3	13.5-15.8	76.4-108.3	1.800-3.921	2.814
Pagrus caeruleostictus	3	19.5-21.5	154.7-188.3	1.902-3.611	2.704
Pomadasys rogerii	3	23.5-25.9	224.8-295.2	2.002-4.012	3.278
Priacanthus arenatus	3	11.5-20.1	37.3-100.5	1.792-3.721	2.841
Pseudotolithus elongatus	1	23.4	210.0	3.210	3.210
Pseudotolithus senegalensis	2	31.3-31.5	430.1-435.2	2.006-4.210	3.108
Sardinella aurita	3	16.4-18.2	55.1-85.8	5.981-7.011	6.538
Sardinella maderensis	3	20.5-21.6	118.4-129.5	5.992-7.621	6.804
Scomber colias	1	50.2	799.1	2.503	2.503
Scomberomorus tritor	2	26.2-26.4	243.0-253.9	3.002-3.672	3.337
Selene setapinnis	2	27.6-31.7	417.2-612.3	2.090-3.652	2.871
Seriola carpenteri	2	33.9-37.2	577.4-806.3	3.112-5.010	4.061
Stromateus fiatola	2	26.1-26.5	374.6-428.4	3.126-4.800	3.963
Thunnus obesus	3	21.5-24.3	128.3-159.9	1.790-3.912	2.734
Trachinotus goreensis	1	24.9	479.3	2.391	2.391
Trachinotus maxillosus	1	24.9	276.5	2.200	2.200
Trichiurus lepturus	2	57.2-72.5	295.3-378.3	2.021-2.832	2.427
Tylosurus crocodilus crocodilus	2	35.5-39.5	230.8-431.2	1.982-3.011	2.497

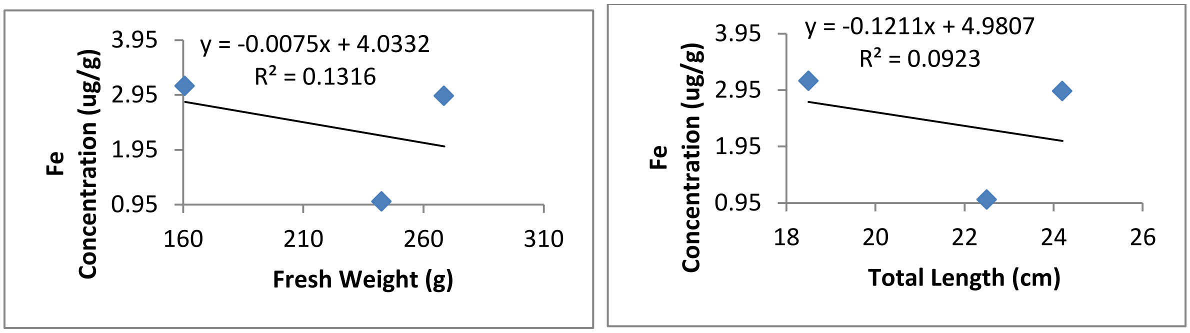
In Ghana, Anim *et al*. (2011) studied heavy metals accumulation in fish samples from Nsawam, along the Densu River. In their study, the concentration of Fe ranged from 5.96±0.16 to 10.8±0.43 µg g^{-1} wet weight; below which most of our values fall. The observed values in this study are lower than Fe concentrations reported for commercial fish species from Nigeria (Nwani *et al*., 2010) and Korea (Islam *et al*., 2010).

The bioaccumulation of heavy metals in different fish tissues depends on various factors including ecological needs, metabolism, and the contamination gradients of water, food, and sediment, as well as salinity and temperature (Mason, 2000). Studies have proven that the muscle tissue of fish accumulate lower amounts of iron than do other organs (Berninger and Pennanen, 1995; Pourang, 1995). Many authors have focused their attention on the relationship between metal content in fish muscle and size (weight and length) of fish (De Wet *et al*., 1994; Oguzie, 2003; Luczynska and Tonska, 2006). Luczynska and Tonska (2006) investigated the effect of fish size on the contents of Cu, Zn, Fe and Mn in Perch and Pike from four lakes (Lanskie, Pluszne, Dluzek and Maroz) located in the Olsztyn Lake District (Northeastern Poland) from 1999-2000. The authors noted no significant positive correlation between iron content and body weight and total length of Perch at all sites except Lake Lanskie, where the correlation was significantly negative. However, a significantly positive correlation was noted in Pike from Lake Pluszne. The iron levels in Pike from the remaining lakes decreased with increasing body weight. Negative relationships between fish length and iron concentrations were also reported by Canli and Atli (2003). A total of nine species were subjected to regression studies. The results are shown in Figures 4.37 - 4.45. Out of the nine species considered, only *Thunnus Obesus* showed significant negative correlations between both fresh body weight and total length and Fe concentration. *Arius latiscutatus*, *Pagrus caeruleostictus* and *Sardinella maderensis* each showed significant negative correlation between Fe content and fish body weight but there were no significant trends noted between the total length and Fe content of the fish. In *Sardinella aurita* and *Lutjanus campechanus,* there were significant negative correlations between Fe content and fish length but no notable trends were recorded between body weight and Fe content of the fish. The rest of the species showed no significant correlation between body size (weight and length) and Fe content. This result appears to confirm earlier assertions that Fe concentrations were not dependent on fish body weight or length (Widianarko *et al*., 2000). There were no significant positive correlations recorded for any of the nine species considered. This appears to confirm earlier assertions that other organs accumulate great amounts of iron than the muscle tissues (Berningen and Pennanen; Pourang, 1995).



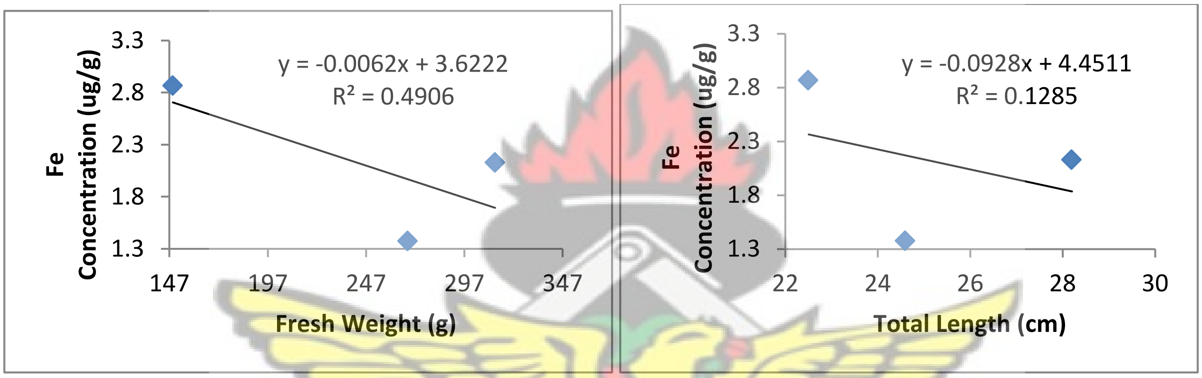
(A) (B)

Figure 4.37: Relationship between iron concentration and body weight (A) and total length (B) for *Pomadasys rogerii*



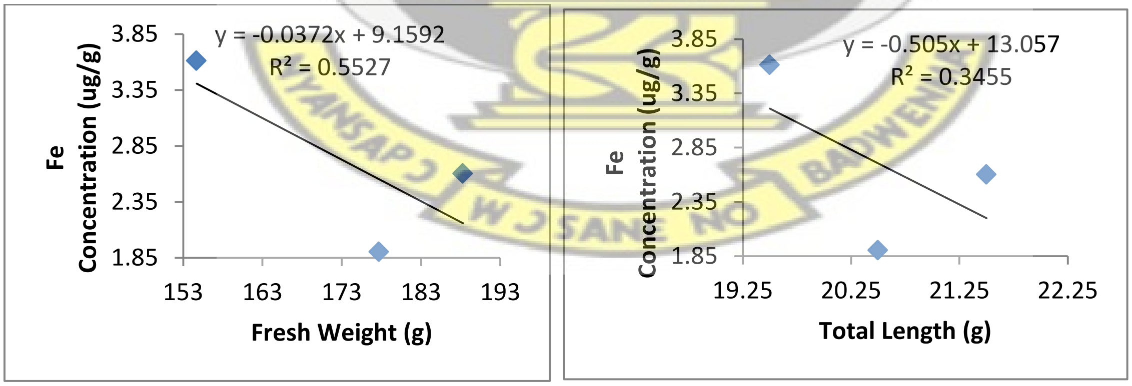
(A) (B)

Figure 4.38: Relationship between iron concentration and body weight (A) and total length (B) for *Galeoides decadactylus*



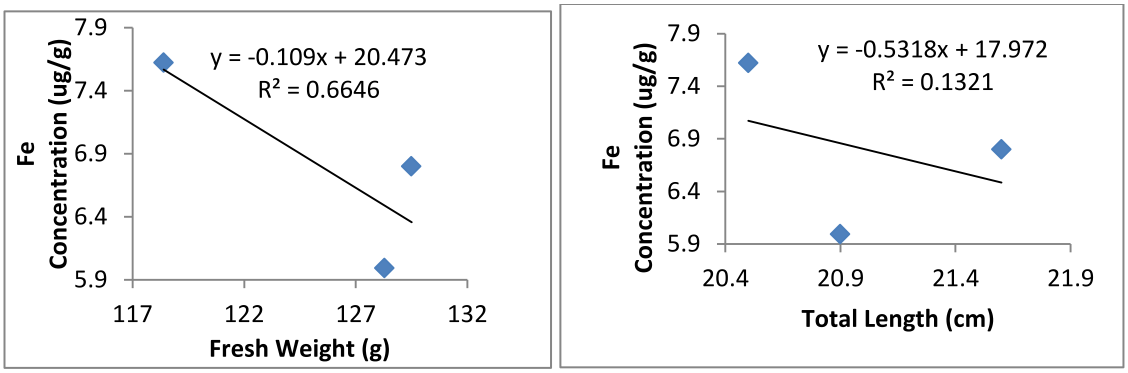
(A) (B)

Figure 4.39: Relationship between iron concentration and body weight (A) and total length (B) for *Arius latiscutatus*



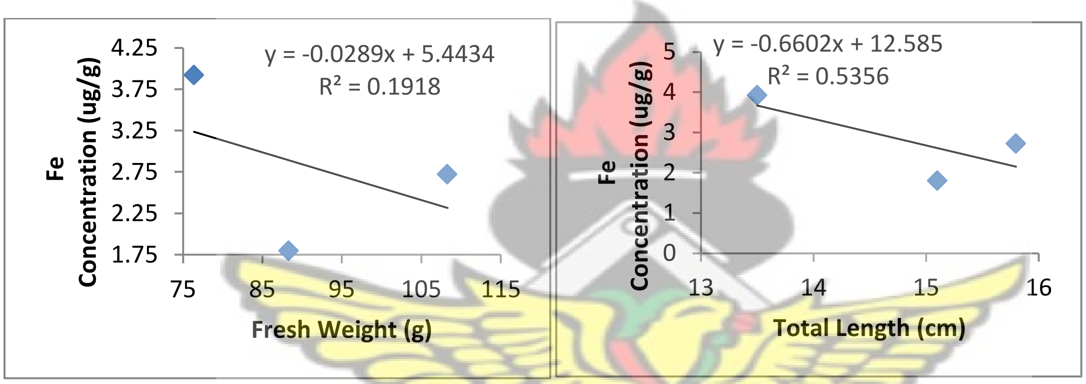
(A) (B)

Figure 4.40: Relationship between iron concentration and body weight (A) and total length (B) for *Pagrus caeruleostictus*



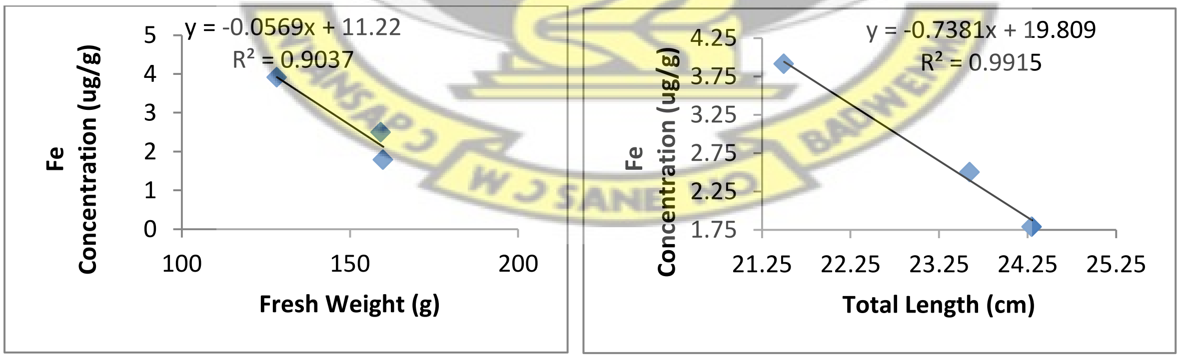
(A) (B)

Figure 4.41: Relationship between iron concentration and body weight (A) and total length (B) for *Sardinella maderensis*



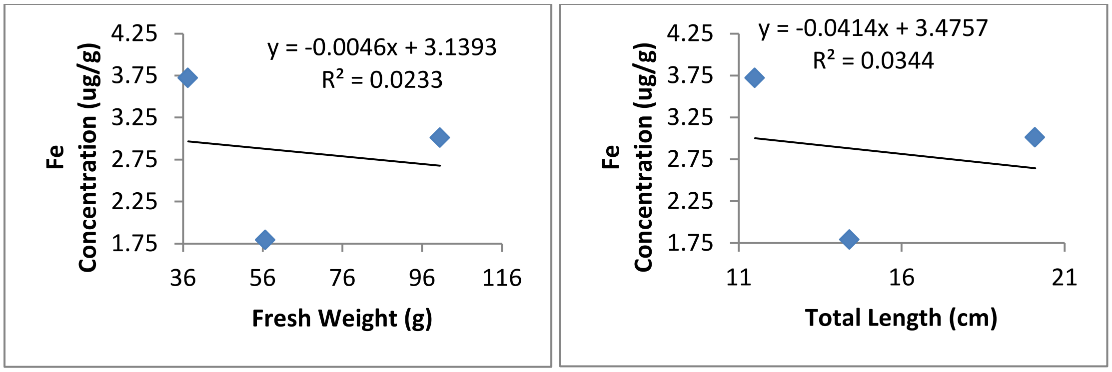
(A) (B)

Figure 4.42: Relationship between iron concentration and body weight (A) and total length (B) for *Lutjanus campechanus*



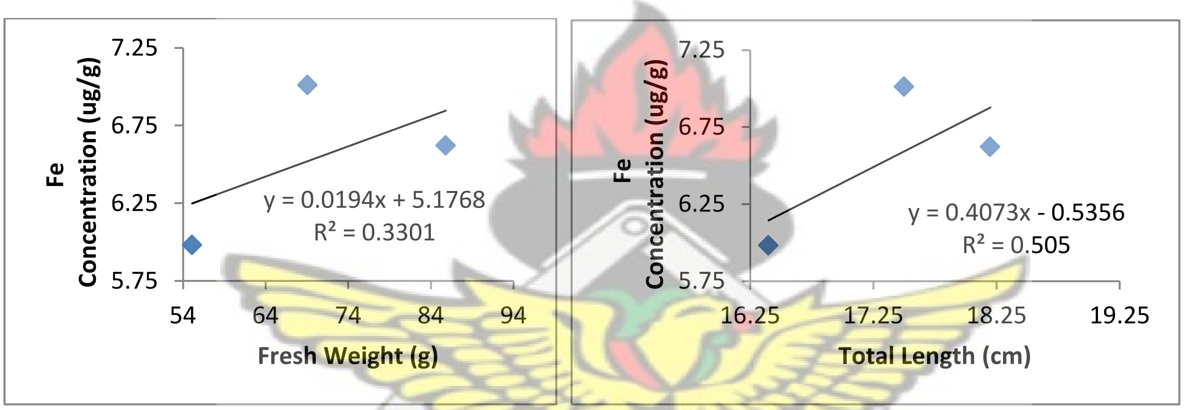
(A) (B)

Figure 4.43: Relationship between iron concentration and body weight (A) and total length (B) for *Thunnus Obesus*



(A) (B)

Figure 4.44: Relationship between iron concentration and body weight (A) and total length (B) for *Priacanthus arenatus*



(A) (B)

Figure 4.45: Relationship between iron concentration and body weight (A) and total length (B) for *Sardinella aurita*

Iron is an essential element in human diet. It forms part of haemoglobin, which allows oxygen to be carried from the lungs to the tissues. Severe Fe deficiency causes anaemia in humans (Igwemmar *et al*. 2013), while excess Fe intake can lead to symptoms of acute toxicity (Fraga and Oteiza, 2002). In this study, risks to human health from iron contamination of fish were assessed by comparing estimates of dietary exposure with the Provisional Tolerable Weekly Intake (PTWI) recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). For iron, the PTWI guideline of 5600 μg/kg body weight/week which is equivalent to

800 μg/kg body weight/day (PTDI) was used in this study (JECFA, 2011). The daily consumption rate of 32.57 grams of fish or 228 g/week (USEPA, 2012) was adopted from the American food consumption index and used in the health-risk assessment. The average iron intake from all the fish species in this study was much lower than the recommended value as presented in Table 4.12.

The Hazard Quotient (HQ) in the studied species ranged from 0.001 to 0.004; which is extremely low when compared to the hazard values for other studies in Literature (Singh *et al.*, 2012; Al Sayegh *et al.*, 2012; Fathi *et al.*, 2013). The HQ for iron obtained in this study is comparable with reports from China (Zhuang *et al.*, 2013). The species with the highest reported mean concentration of Fe was *Sardinella maderensis* (6.804 μg/g). If an adult consumes 32.57g/day of *Sardinella aurita*, he would take in approximately 221.61 μg/day (1551.31 μg/week) of iron. This amounts to a weekly intake (WI) of 22.162 μg/kg body weight/week for a 70 kg person; which is far below the JEFCA (2003) recommended Provisional Tolerable Weekly Intake (PTWI) of 5600 μg/kg body weight/week. To exceed the PTWI, an adult would have to consume about 57.6 Kg of *Sardinella maderensis* per week; which is very much unlikely.

The dietary intake of fish estimated from the present study is well below FAO/WHO guideline limit. Thus the tested fish species may not pose any known risk to health for the population of Monrovia considering iron.

Table 4.12: Mean dietary intake of iron

	Species	Fe Conc. (µg/g)	WCR (g/person/wk)	Weekly Intake (WI) (µg/kg body weight/wk)	Hazard Quotient (HQ)
1	*A. vulpes*	2.128	228	6.931	0.001
2	*A. latiscutatus*	2.122	“	6.912	0.001
3	*C. taeniops*	2.823	“	9.195	0.002
4	*C. chrysurus*	4.300	“	14.006	0.003
5	*E. lacerta*	3.172	“	10.332	0.002
6	*E. senegalensis*	4.002	“	13.035	0.002
7	*E. goreensis*	5.711	“	18.602	0.003
8	*E. alletteratus*	4.241	“	13.814	0.002
9	*G. decadactylus*	2.349	“	7.651	0.001
10	*H. jaguana*	2.466	“	8.032	0.001
11	*L. gibbosus*	3.272	“	10.657	0.002
12	*L. campechanus*	2.814	“	9.166	0.002
13	*P. caeruleostictus*	2.704	“	8.807	0.002
14	*P. rogerii*	3.278	“	10.677	0.002
15	*P. arenatus*	2.841	“	9.254	0.002
16	*P. elongatus*	3.210	“	10.455	0.002
17	*P. senegalensis*	3.108	“	10.123	0.002
18	*S. aurita*	6.538	“	21.295	0.004
19	*S. maderensis*	6.804	“	22.162	0.004
20	*S. colias*	2.503	“	8.153	0.001
21	*S. tritor*	3.337	“	10.869	0.002
22	*S. setapinnis*	2.871	“	9.351	0.002
23	*S. carpenteri*	4.061	“	13.227	0.002
24	*S. fiatola*	3.963	“	12.908	0.002
25	*T. obesus*	2.734	“	8.905	0.002
26	*T. goreensis*	2.391	“	7.788	0.001
27	*T. maxillosus*	2.200	“	7.166	0.001
28	*T. lepturus*	2.427	“	7.905	0.001
29	*T.C. crocodilus*	2.497	“	8.133	0.001

Note: PTWI (µg/kg body weight/wk) = 5600
WCR = weekly consumption rate

4.6 Zinc

Zinc (Zn) is an essential trace metal for both plants and animals. Although Zn is an essential micronutrient, excess intake may be toxic to human (Sivapermal *et al*., 2007). Results of zinc concentration in muscle of fish (µg g^{-1} on wet weight basis) from markets in Monrovia, Liberia are presented in Table 4.13. Zinc concentration ranged from 1.783 to 6.013 µg g^{-1} wet weight. *Scomberomorus tritor* recorded the highest mean concentration of Zn (6.013 µg g^{-1} wet weight) followed by *Trachinotus maxillosus* (5.922 µg g^{-1} wet weight) and *Stromateus fiatola* (5.721 µg g^{-1} wet weight). Mean zinc concentration in all the other fish samples were less than 5.700 µg g^{-1} wet weight, which is below the 50 µg g^{-1} wet weight limit recommended by FAO/WHO (1983). *Cephalopholis taeniops* recorded the lowest mean zinc concentration (1.783 µg g^{-1} wet weight).

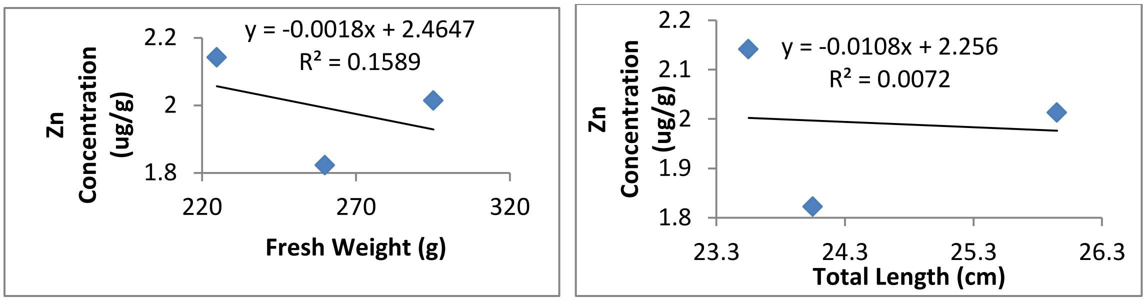
Zinc concentrations in this study are comparable with other published Zn concentrations in fish species from other areas of the world. For example, the concentration of zinc in the literature have been reported in the range of 2.67-19.1µg g^{-1} in market fish from South China (Cheung *et al*., 2008), 37.68±11.91µg g^{-1} in fish from sewage fed lake of Karnataka, India (Puttaiah and Kiran, 2008), 14.0-75.4 µg g^{-1} in fish from Lake Macquarie, New South Wales, Australia (Roach *et al*., 2008), 37.98±6.49 µg g^{-1} in fish muscle from Taiwan (Lin, 2009), 10.03-22.0 µg g^{-1} in freshwater fish from Lithuania (Staniskiene *et al*., 2009), 2.8-6.8 µg g^{-1} in fish from West Pomerania, Poland (Magdalena *et al*., 2009), 10.27-19.74 µg g^{-1} in fish from Euphrates, Turkey (Mol *et al*., 2010), 0.48-1.88 µg g^{-1} in fish muscle from freshwater lake of Bhopal, India (Malik *et al*., 2010), mean of 10.49 µg g^{-1} in fish collected from Pennar estuary, India (Ravanaiah and Murthy, 2010), 2.19-5.86 µg g^{-1} in fish from Cape Fear River watershed, North Carolina, USA (Michael *et al*., 2011) and 18.92-30.04 µg g^{-1} in fish samples from Densu River, Ghana (Anim *et al*., 2011).

Table 4.13 Zinc concentration (µg g^{-1} wet weight) in muscle of commercial fish samples from markets in Monrovia, Liberia (2013)

Species	Sample size	Total length Range(cm)	Fresh weight Range (g)	Zn Conc. Range (µg/g)	Zn Conc. Mean (µg/g)
Albula vulpes	1	28.7	399.5	3.811	3.811
Arius latiscutatus	3	22.5-28.2	148.8-312.7	2.100-3.511	2.591
Cephalopholis taeniops	2	14.5-16.5	81.5-83.7	1.646-1.920	1.783
Chloroscombrus chrysurus	2	15.4-16.5	49.4-61.4	1.972-2.214	2.093
Elops lacerta	2	27.5-30.4	303.3-383.2	2.611-2.859	2.735
Elops senegalensis	2	27.5-33.3	271.5-507.2	2.980-3.504	3.242
Epinephelus goreensis	1	27.4	561.9	4.972	4.972
Euthynnus alletteratus	1	46.5	1340.5	4.113	4.113
Galeoides decadactylus	3	18.5-24.2	160.0-268.6	2.116-2.602	3.466
Harengula jaguana	2	23.6-24.2	194.8-211.6	2.611-2.933	2.772
Lepomis gibbosus	2	14.5-15.5	152.3-170.8	2.932-4.911	3.922
Lutjanus campechanus	3	13.5-15.8	76.4-108.3	1.810-2.502	2.144
Pagrus caeruleostictus	3	19.5-21.5	154.7-188.3	2.102-3.251	2.251
Pomadasys rogerii	3	23.5-25.9	224.8-295.2	1.822-2.141	1.992
Priacanthus arenatus	3	11.5-20.1	37.3-100.5	2.102-3.251	2.757
Pseudotolithus elongatus	1	23.4	210.0	4.621	4.621
Pseudotolithus senegalensis	2	31.3-31.5	430.1-435.2	3.428-5.113	4.271
Sardinella aurita	3	16.4-18.2	55.1-85.8	3.412-4.611	3.840
Sardinella maderensis	3	20.5-21.6	118.4-129.5	3.012-4.218	4.015
Scomber colias	1	50.2	799.1	5.021	5.021
Scomberomorus tritor	2	26.2-26.4	243.0-253.9	5.900-6.126	6.013
Selene setapinnis	2	27.6-31.7	417.2-612.3	2.931-3.552	3.242
Seriola carpenteri	2	33.9-37.2	577.4-806.3	4.860-5.112	4.986
Stromateus fiatola	2	26.1-26.5	374.6-428.4	5.630-5.812	5.721
Thunnus obesus	3	21.5-24.3	128.3-159.9	1.621-2.502	2.578
Trachinotus goreensis	1	24.9	479.3	4.902	4.902
Trachinotus maxillosus	1	24.9	276.5	5.922	5.922
Trichiurus lepturus	2	57.2-72.5	295.3-378.3	1.781-3.011	2.396
Tylosurus crocodilus crocodilus	2	35.5-39.5	230.8-431.2	1.923-2.612	2.268

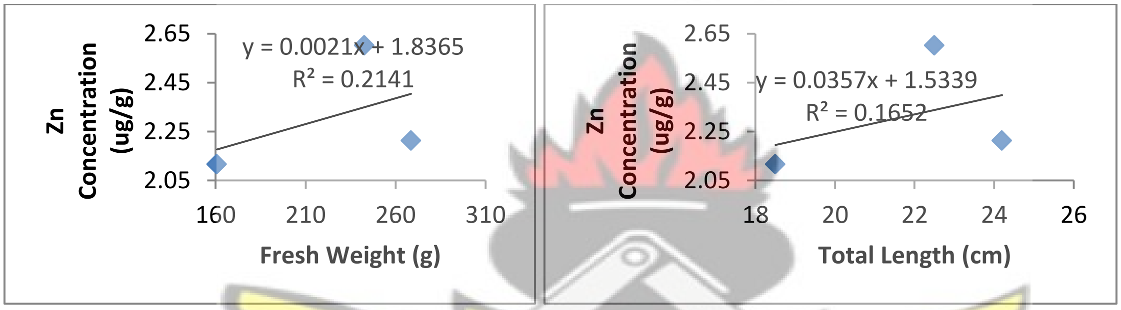
Like iron, the bioaccumulation of zinc in different fish tissues depends on factors like ecological needs, metabolism, and the contamination gradients of water, food, and sediment, as well as salinity and temperature (Mason, 2000). Protasowicki *et al*. (1983) reported that feeding strategy influenced the content of Zn in fish. Luczynska and Tonska (2006) investigated the effect of fish size on the contents of Zn, Cu, Fe and Mn in Perch and Pike from four lakes (Lanskie, Pluszne, Dluzek and Maroz) located in the Olsztyn Lake District (Northeastern Poland) from 1999-2000. In their study, there were negative correlations reported between the Zn content in the muscle of perch and body weight or total length.The authors also reported positive correlation between body size and Zn level in the muscle of Pike. Negative relationships between fish length and Zn levels have been reported by Canli and Atli (2003).

A total of nine species were subjected to regression studies. The results are shown in Figures 4.46- 4.54. Out of the nine species considered, three species (*Pomadasys rogerii, Galeoides decadactylus* and *Priacanthus arenatus*) showed no significant relationship between Zn content and fish body weight and total length. *Sardinella aurita* and *Sardinella maderensis* showed significant negative correlations between Zn content and fish body weight but there were no significant trend noted between Zn levels and the total length of both species. For *Lutjanus campechanus*, a significant negative trend was noted between fish body length and Zn content but the body weight and Zn level were not significantly correlated. The remaining three species (*Arius latiscutatus*, *Pagrus caeruleostictus* and *Thunnus Obesus*) recorded significant negative correlations between fish Zn content and body weight and total length. There were no significant positive trend noted between fish size and Zn content. It thus appears that zinc does not undergo biomagnification.



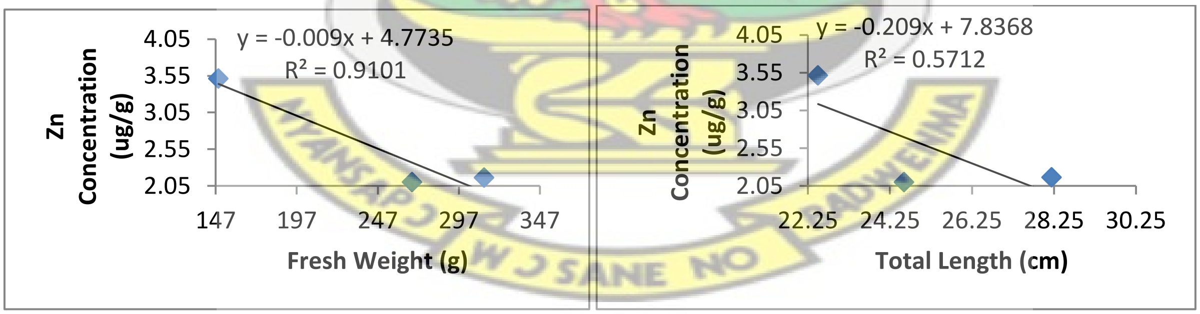
(A) (B)

Figure 4.46: Relationship between zinc concentration and body weight (A) and total length (B) for *Pomadasys rogerii*



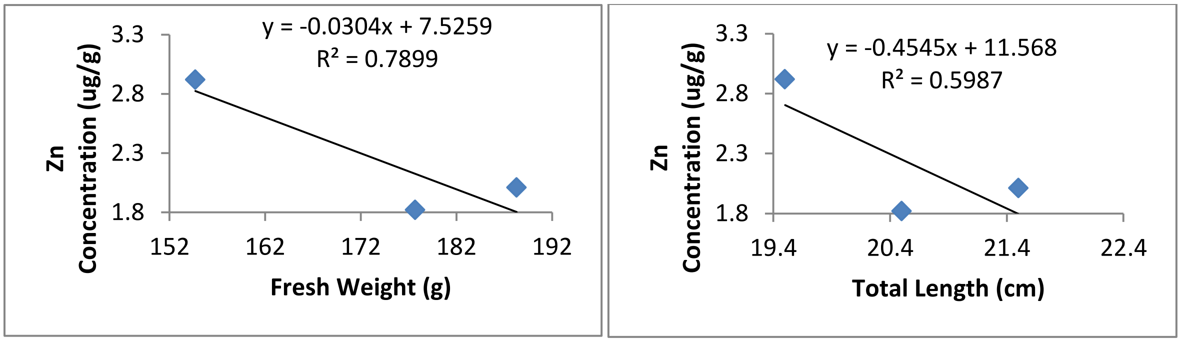
(A) (B)

Figure 4.47: Relationship between zinc concentration and body weight (A) and total length (B) for *Galeoides decadactylus*



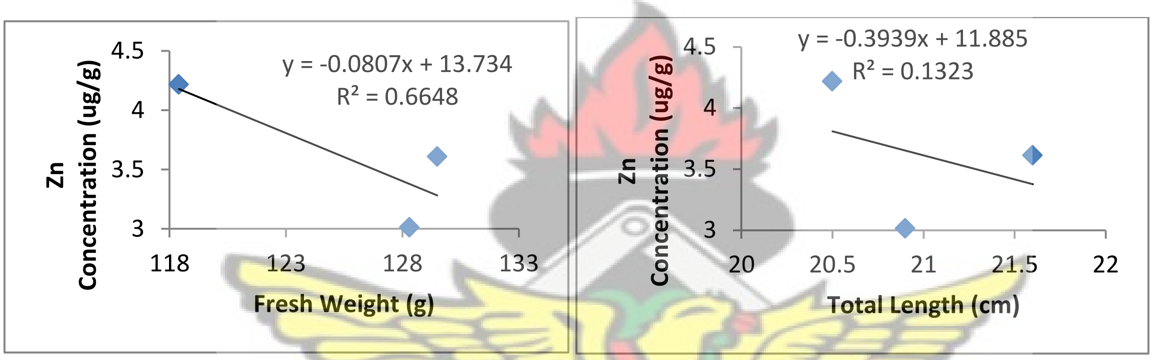
(A) (B)

Figure 4.48: Relationship between zinc concentration and body weight (A) and total length (B) for *Arius latiscutatus*



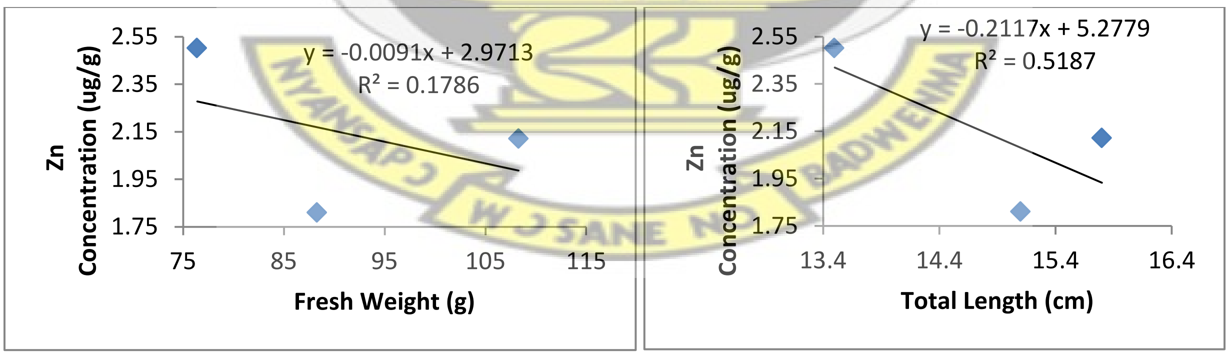
(A) (B)

Figure 4.49: Relationship between zinc concentration and body weight (A) and total length (B) for *Pagrus caeruleostictus*



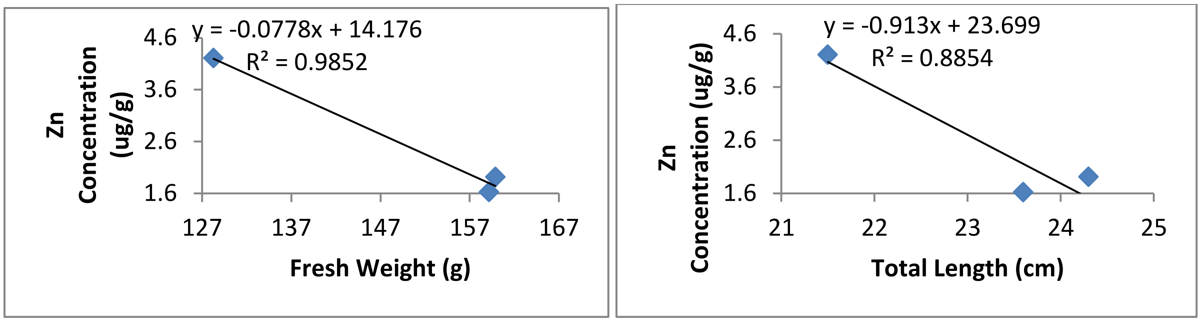
(A) (B)

Figure 4.50: Relationship between zinc concentration and body weight (A) and total length (B) for *Sardinella maderensis*



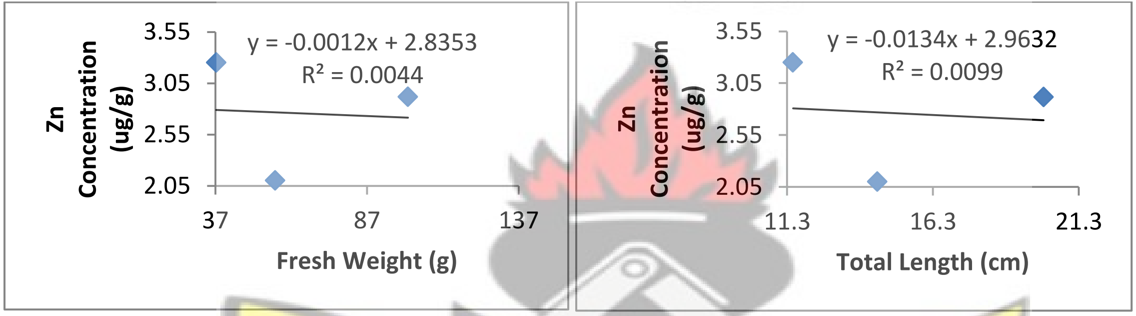
(A) (B)

Figure 4.51: Relationship between zinc concentration and body weight (A) and total length (B) for *Lutjanus campechanus*



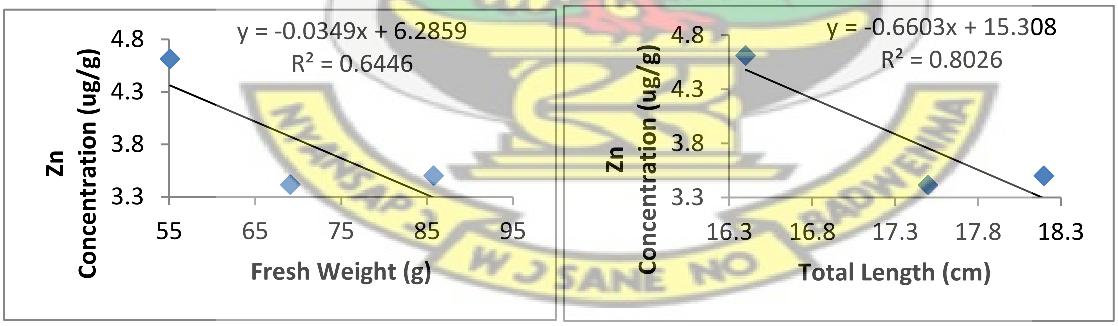
(A) (B)

Figure 4.52: Relationship between zinc concentration and body weight (A) and total length (B) for *Thunnus Obesus*



(A) (B)

Figure 4.53: Relationship between zinc concentration and body weight (A) and total length (B) for *Priacanthus arenatus*



(A) (B)

Figure 4.54: Relationship between zinc concentration and body weight (A) and total length (B) for *Sardinella aurita*

Zinc is an essential element in human diet. A deficiency of zinc is marked by retarded growth, loss of taste and hypogonadism, leading to decreased fertility. Excess Zn intakes can also result to symptoms of acute toxicity (Sivapermal *et al*., 2007). In this study, risks to human health from zinc contamination of fish were assessed by comparing estimates of dietary exposure with the Provisional Tolerable Weekly Intake (PTWI) recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). For zinc, the PTWI guideline of 7000 µg/kg body weight/week which is equivalent to 1000 µg/kg body weight/day (PTDI) was used in this study (JECFA, 2003). Data on the amount of fish consumed by an average Liberian adult per day or week is not available; thus the daily consumption rate of 32.57 grams of fish or 228 g/week (USEPA, 2012) was adopted from the American food consumption index and used in the health-risk assessment. The average zinc intake from all the fish species in this study was much lower than the recommended value as shown in Table 4.12.

The Hazard Quotient (HQ) in the studied species ranged from 0.001 to 0.003; which is extremely low when compared to results from other studies in Literature (Al Sayegh *et al*., 2012; Fathi *et al*., 2013). The species with the highest reported mean concentration of Zn was *Scomberomorus tritor* (6.013 µg/g). If an adult consumes 32.57g/day of *Scomberomorus tritor*, he would take in approximately 195.843 µg/day (1370.904 µg/week) of iron. This amounts to a weekly intake (WI) of 19.584 µg/kg body weight/week for a 70 kg person; which is far below the JEFCA (2011) recommended Provisional Tolerable Weekly Intake (PTWI) of 7000 µg/kg body weight/week. To exceed the PTWI, an adult would have to consume more than 81.5 Kg of *Scomberomorus tritor* per week; which is very unlikely.

The dietary intake of fish estimated from the present study is well below FAO/WHO guideline limits. Thus consuming the tested fish species at the stipulated rate is unlikely to pose any known health risk to the population of Monrovia considering zinc.

Table 4.14: Mean dietary intake of Zinc

	Species	Zn Conc. (µg/g)	WCR (g/person/wk)	Weekly Intake (WI) (µg/kg body weight/wk)	Hazard Quotient (HQ)
1	*A. vulpes*	3.811	228	12.413	0.002
2	*A. latiscutatus*	2.591	“	8.439	0.001
3	*C. taeniops*	1.783	“	5.807	0.001
4	*C. chrysurus*	2.093	“	6.817	0.001
5	*E. lacerta*	2.735	“	8.908	0.001
6	*E. senegalensis*	3.242	“	10.560	0.002
7	*E. goreensis*	4.972	“	16.195	0.002
8	*E. alletteratus*	4.113	“	13.397	0.002
9	*G. decadactylus*	3.466	“	11.289	0.002
10	*H. jaguana*	2.772	“	9.029	0.001
11	*L. gibbosus*	3.922	“	12.775	0.002
12	*L. campechanus*	2.144	“	6.983	0.001
13	*P. caeruleostictus*	2.251	“	7.332	0.001
14	*P. rogerii*	1.992	“	6.488	0.001
15	*P. arenatus*	2.757	“	8.980	0.001
16	*P. elongatus*	4.621	“	15.051	0.002
17	*P. senegalensis*	4.271	“	13.911	0.002
18	*S. aurita*	3.840	“	12.507	0.002
19	*S. maderensis*	4.015	“	13.077	0.002
20	*S. colias*	5.021	“	16.354	0.002
21	*S. tritor*	6.013	“	19.585	0.003
22	*S. setapinnis*	3.242	“	10.560	0.002
23	*S. carpenteri*	4.986	“	16.240	0.002
24	*S. fiatola*	5.721	“	18.634	0.003
25	*T. obesus*	2.578	“	8.397	0.001
26	*T. goreensis*	4.902	“	15.967	0.002
27	*T. maxillosus*	5.922	“	19.289	0.003
28	*T. lepturus*	2.396	“	7.804	0.001
29	*T.C. crocodilus*	2.268	“	7.387	0.001

Note: PTWI (µg/kg body weight/wk) = 7000
WCR = weekly consumption rate

4.7 Hazard Index

The total health hazard represented as hazard index (HI) to the population of Monrovia due to Hg, Pb, Cd, Cu, Zn and Fe exposure from fish intake was in the range 0.042 - 0.541. The Hazard index for each fish species in this study is presented in Table 4.15. *Albula vulpes* recorded the highest HI (0.541) followed by *Euthynnus alletteratus* (0.402). *Epinephelus goreensis* (0.042) recorded the lowest HI in this study. The observed range of hazard quotient (HQ) and hazard index (HI) is lower than the acceptable safe risk level (HI≤1). Therefore, our results infer that consumption of these fish species at the present rate might not be hazardous to the population of Monrovia with respect to observed levels of Hg, Pb, Cd, Cu, Zn and Fe alone or in combination of each other.

Metal intake through fish and human health hazard reported in this study was compared with some other studies around the world and found to be lower than those reported from Malaysia (Fathi *et al.*, 2013), Slovenia (Al Sayegh *et al.*, 2012), Taiwan (Ling *et al.*, 2009), Puerto Rico (Mansilla-Rivera and Rodriguez- Sierra, 2011) , Southeast Gulf of California, Mexico (Soto-Jimenez *et al.*, 2010), but higher than those reported from Sicily (Copat *et al.*, 2012). The obtained HQ in this study was comparable with HQ reported from China (Zhuang *et al.*, 2013) and India (Kumar *et al.*, 2013).

Table 4.15**:** Hazard index (HI) to the population of Monrovia from some heavy metals through fish consumption, 2013

	Species	Hg HQ	Pb HQ	Cd HQ	Cu HQ	Fe HQ	Zn HQ	HI
1	*A. vulpes*	0.474	0.010	0.054	0.00020	0.001	0.002	0.541
2	*A. latiscutatus*	0.109	0.017	0.030	0.00087	0.001	0.001	0.159
3	*C. taeniops*	0.062	0.005	0.002	0.00018	0.002	0.001	0.072
4	*C. chrysurus*	0.044	0.012	0.061	0.00053	0.003	0.001	0.122
5	*E. lacerta*	0.086	0.023	0.161	0.00050	0.002	0.001	0.274
6	*E. senegalensis*	0.078	0.015	0.060	0.00020	0.002	0.002	0.157
7	*E. goreensis*	0.025	0.006	0.004	0.00169	0.003	0.002	0.042
8	*E. alletteratus*	0.283	0.007	0.107	0.00057	0.002	0.002	0.402
9	*G. decadactylus*	0.063	0.020	0.033	0.00014	0.001	0.002	0.119
10	*H. jaguana*	0.051	0.009	0.061	0.00032	0.001	0.001	0.123
11	*L. gibbosus*	0.111	0.004	0.107	0.00012	0.002	0.002	0.226
12	*L. campechanus*	0.113	0.013	0.003	0.00076	0.002	0.001	0.133
13	*P. caeruleostictus*	0.111	0.009	0.034	0.00024	0.002	0.001	0.157
14	*P. rogerii*	0.081	0.016	0.040	0.00095	0.002	0.001	0.141
15	*P. arenatus*	0.134	0.019	0.053	0.00035	0.002	0.001	0.209
16	*P. elongatus*	0.079	0.005	0.001	0.00010	0.002	0.002	0.089
17	*P. senegalensis*	0.102	0.010	0.004	0.00043	0.002	0.002	0.120
18	*S. aurita*	0.046	0.016	0.028	0.00278	0.004	0.002	0.099
19	*S. maderensis*	0.009	0.004	0.022	0.00242	0.004	0.002	0.043
20	*S. colias*	0.086	0.011	0.090	0.00039	0.001	0.002	0.190
21	*S. tritor*	0.061	0.004	0.026	0.00020	0.002	0.003	0.096
22	*S. setapinnis*	0.023	0.010	0.062	0.00124	0.002	0.002	0.100
23	*S. carpenteri*	0.147	0.016	0.114	0.00013	0.002	0.002	0.281
24	*S. fiatola*	0.036	0.005	0.054	0.00064	0.002	0.003	0.100
25	*T. obesus*	0.147	0.023	0.043	0.00050	0.002	0.001	0.217
26	*T. goreensis*	0.081	0.004	0.087	0.00009	0.001	0.002	0.175
27	*T. maxillosus*	0.028	0.011	0.034	0.00026	0.001	0.003	0.077
28	*T. lepturus*	0.035	0.033	0.074	0.00081	0.001	0.001	0.145
29	*T.C. crocodilus*	0.111	0.030	0.052	0.00025	0.001	0.001	0.195

4.8 Inter-metal correlations

Pearson moment correlation test was performed to investigate associations between metal concentrations in fish. The values of correlation coefficients between metal concentrations in fish are given in Table 4.16. The correlations showed a strong positive association between the concentrations of iron and copper (r = 0.771) in the studied species. There were significantly negative correlations reported for Pb-Zn (r = -0.506), Hg-Cu (r = -0.306), Hg-Fe (r = -0.258) and Pb-Fe (r = -0.286). There were moderate or weak correlations between concentrations of Hg-Cd, Pb-Cd, Cd-Cu and Fe-Zn. Correlations between Hg-Pb, Hg-Zn, Pb-Cu, Cd-Fe, Cd-Zn and Cu-Zn were non-significant.

Table 4.16: Pearson's moment correlation coefficients (r) and levels of significance (p) for the relationship between the heavy metals in muscle tissue of fish species from markets in Monrovia, Liberia, 2013 (n=60)

Variable	Hg	Pb	Cd	Fe	Cu	Zn
Hg	1					
Pb	0.015	1				
Cd	0.213	0.221	1			
Fe	$-0.258^{b,c}$	-0.286^{a}	-0.155	1		
Cu	-0.306^{a}	-0.030	-0.249	$0.771^{a,b,c}$	1	
Zn	-0.048	$-0.506^{a,b,c}$	0.036	0.212	-0.012	1

Note: Significant correlations at P<0.05 are indicated as ^{a} mark, at P<0.01 are indicated as ^{b} mark and P<0.001 are indicated as ^{c} mark

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study determined the exposure of the population of Monrovia to heavy metals (Hg, Pb, Cd, Cu, Fe, Zn) through fish consumption. From the outcome of this research it could be concluded that:

- The concentration of mercury, cadmium, lead, copper, iron and zinc in the edible fish muscle tissue were generally below the FAO/WHO maximum permissible limits; except for one (1) sample representing 0.02% which had tissue mercury above the allowable limit of 0.50 µg g^{-1}.
- Mean total mercury concentrations in the muscle tissues of the studied species ranged from 0.014 to 0.727 µg g^{-1} wet weight. *Albula vulpes* (a predatory fish) recorded the highest mean THg concentration among all the species analyzed. Generally, mercury levels in the studied species increased with increasing body length and weight (for predatory species). Correlation between THg and fresh body weight and total length was significantly positive for eight (8) out of nine species analyzed. Hazard Quotient for THg in the studied species ranged from 0.009 to 0.474.
- Mean copper concentration in the fish sampled ranged from 0.101 to 2.990 µg g^{-1} wet weight. *Sardinella aurita* recorded the highest mean concentration of Cu. Correlation between Cu and fresh body weight and total length was insignificant for seven (7) out of nine species analyzed. Hazard Quotient for Cu in the studied species ranged from 0.00009 to 0.000278.

- Mean lead concentration ranged from 0.027 to 0.256 µg g^{-1} wet weight. *Trichiurus lepturus* recorded the highest mean concentration of Pb. Correlation between Pb and fresh body weight and total length was significantly negative for six (6) out of nine species analyzed. Hazard Quotient for Pb in the studied species ranged from 0.004 to 0.033.
- Mean cadmium concentration ranged from 0.002 to 0.347 µg g^{-1} wet weight. *Elops lacerta* recorded the highest mean concentration of Cd. Correlation between Cd and fresh body weight and total length was significantly positive for three (3) and significantly negative for two (2) out of nine species analyzed. The rest showed no correlation between Cd content and fish body size. Hazard Quotient for Cd in the studied species ranged from 0.001 to 0.161.
- Mean iron concentration in the studied species ranged from 2.122 to 6.804 µg g^{-1} on wet weight basis. *Sardinella maderensis* recorded the highest mean Fe concentration. Correlation between Fe and fresh body weight and total length was not significant for three (3) out of nine species analyzed. The rest showed no correlation between Fe content and fish body size. Hazard Quotient for Fe in the studied species ranged from 0.001 to 0.004.
- Zinc concentration in the sampled fish species ranged from 1.783 to 6.013 µg g^{-1} wet weight. *Scomberomorus tritor* recorded the highest mean Zn concentration. Correlation between Zn and fresh body weight and total length was insignificant for three (3) and significantly negative for two (2) out of nine species analyzed. The rest of the species showed no clear correlation trend. HQ for Zn in the studied species ranged from 0.001 to 0.003.

- Pearson's moment correlation showed a strong positive relationship between copper and iron (r = 0.771) concentrations in the muscle of the tested fish species. There were also significant negative correlations reported for Pb-Zn (r = -0.506), Hg-Cu (r = -0.306), Hg-Fe (r = -0.258), Hg-Zn (-0.048), Pb-Fe (r = -0.286), Cd-Fe (r = -0.155), Cd-Cu (r = -0.249) and Cd-Zn (r = 0.036). There was no positive association noted between the toxic and essential heavy metals.
- The Hazard index due to Hg, Cd, Pb, Cu, Fe and Zn exposure from fish intakes was in the range 0.042 - 0.541. With the observed range of HQ and HI being lower than the acceptable safe risk level (HQ, HI≤1), this study has shown that consumption of the studied fish species (at the stipulated rate) from markets in Monrovia is unlikely to constitute health risks to the population with respect to observed levels of Hg, Cd, Pb, Cu, Fe and Zn alone or in combination. The relatively low hazard values suggest that the population of Monrovia is not at any imminent health risk due to excess heavy metals exposure from fish consumption.
- Based on the findings in this study, no fish consumption advisory is required.

5.2 Recommendations

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

- The number of fish samples tested for each species was limited by resources available and availability of fish during the sampling period. Ideally, more samples for each species would better reflect the heavy metal levels for each species. Subsequent research must be conducted with a larger sample size for each species. More emphasis should be placed on large predatory species in subsequent research.

- There is a need to identify the species of fish most commonly eaten within Monrovia and an indication of the approximate amounts per week or day of fish consumed.
- The species tested were the ones available during the period of sampling, but not all the species are available for the whole year period. Since seasonal variations in the availability of fish species are expected, some species that are commonly consumed by the population of Monrovia are not included in this study. Subsequent research must therefore factor in seasonal variations during sampling.

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Appendix I

List of Plates

Plate 1: *Sardinella maderensis* (Bonny)

Plate 2: *Sardinella aurita* (Sardine fish)

Plate 3: *Scomberomorus tritor* (Mackerel fish)

Plate 4: *Chloroscombrus chrysurus* (Porjoe)

Plate 5: *Stromateus fiatola* (Marry fish)

Plate 6: *Pagrus caeruleostictus* (Snapper)

Plate 7: *Epinephelus goreensis* (Black grouper)

Plate 8: *Pseudotolithus senegalensis* (Cassava fish)

Plate 9: Pseudotolithus elongatus (White boy)

Plate 10: *Galeoides decadactylus* (Butter nose)

Plate 11: *Arius latiscutatus* (Catfish)

Plate 12: *Albula vulpes* (Morlay)

Plate 13: *Priacanthus arenatus* (Chicken soup fish)

Plate 14: *Pomadasys rogerii* (Grunter)

Plate 15: *Seriola carpenteri* (Wakie)

Plate 16: *Selene setapinnis* (Big head Porjoe)

Plate 17: Trichiurus lepturus (Silver fish)

Plate 18: *Elops senegalensis* (Tenpound)

Plate 19: *Thunnus obesus* (Tuna fish)

Plate 20: *Scomber Colias* (Sea Mackerel)

Plate 21: *Trachinotus maxillosus* (Pompano)

Plate 22: *Cephalopholis taeniops* (Rock fish)

Plate 23: *Tylosurus crocodilus crocodilus* (Penten)

Plate 24: *Lepomis gibbosus* (Pumpkin fish)

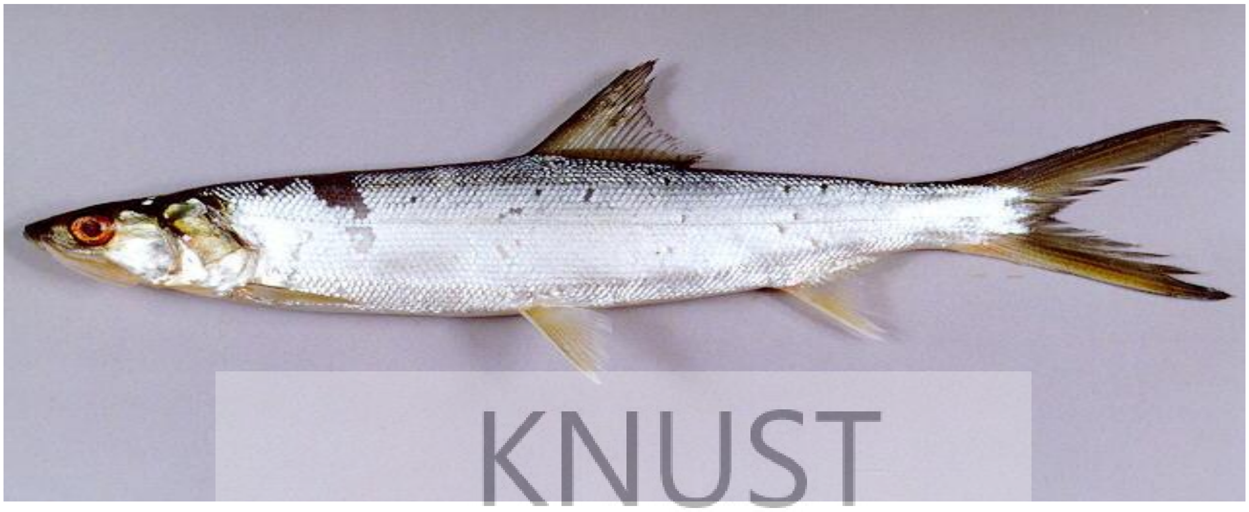

Plate 25: *Elops lacerta* (Shiny lady)

Plate 26: *Harengula jaguana* (Zipper fish)

Plate 27: *Lutjanus campechanus* (Red snapper)

Plate 28: *Trachinotus goreensis* (Small corvally)

Plate 29: *Euthynnus alletteratus* (Blood fish)

Appendix II

Plate 30: Arranging samples for mercury analysis

Plate 31: Mercury analysis using an automated Mercury Analyzer HG 5000

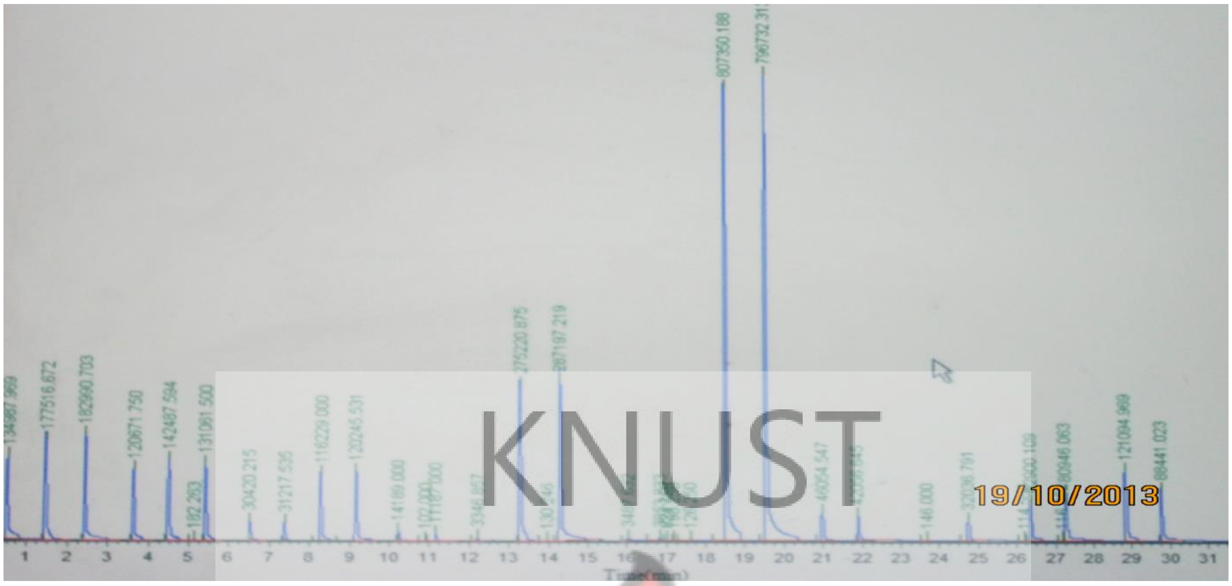

Plate 32: Peak heights from mercury analysis