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***HEAVY METAL POLLUTION OF FISH  
AND FISH OILS FROM SOME COASTAL AND INLAND  
WATERS OF GHANA***

**A THESIS SUBMITTED TO THE  
DEPARTMENT OF NUTRITION AND FOOD SCIENCE UNIVERSITY  
OF GHANA - LEGON**



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**IN PARTIAL FULFILMENT OF THE  
REQUIREMENTS FOR THE AWARD OF  
AN *M.Phil.* DEGREE IN NUTRITION.**

**AUGUST, 1998**

**ABSTRACT**

While fish and fish oil promote good health, increasing environmental pollution may introduce heavy metals into the fish which may render them injurious to health. Nine commonly consumed fish samples in Ghana, five from marine sources and four from freshwater sources were analysed for their heavy metal contents. The heavy metals are Cadmium (Cd), Lead (Pb), Mercury (Hg), Arsenic (As) and Selenium (Se). The fish samples are Herring (*Sardinella* species), Redfish (Red mullet), Mackerel species, Tuna species and Anchovies all from coastal waters and Tilapia (*Oreochromis niloticus*), *Blolo* (*Chrysichthys nigrodigitatus*), Catfish (*Heterobranchus* species) and One- mouth- thousand (*Serrathrissa leonensis*) from fresh waters. Oil extracted from four fish samples were also analysed for their heavy metal contents.

The fishes were selected from four environmental zones designated heavy industrial (James Town - Accra and Tema), light industrial (Apam and Elmina), river/lake (Weija and Kpong) and mining environment (Obuasi and Dunkwa). For each environmental zone, two locations were chosen based on industrial and/or fishing activities in the area. The analysis was done on the head, bone, flesh, whole fish and scales for those who have it in order to ascertain the distribution of the metal in the fish body. The metal contents were analysed with Atomic Absorption Spectrophotometer (AAS)

Generally the bone had the highest content of the heavy metals. It was followed by the head, the scale, and then the flesh. The total metal levels in the whole fish was higher than that in the flesh alone. Analysis of variance showed significant difference ( $p= 0.03$ ) in the levels of each heavy metal in the fish parts. There was a significant correlation ( $r=0.67$  and  $p=0.01$ ), between the Cadmium levels in the flesh and bone. The rest of the metals did not show any significant correlation in their distribution in the flesh and the bone.

Mercury levels occurred as the highest heavy metal in all parts of the fish followed by Arsenic and Lead whose levels were close. Cadmium levels were lowest in the fish tissues studied. The ranges of the metal in the body of all the fish samples are as follows; Mercury 25 - 300 $\mu\text{g/g}$  dried weight of fish, Lead 2.44 - 36.6 $\mu\text{g/g}$ , Arsenic 3.26 - 36.96 $\mu\text{g/g}$  and Cadmium 0.3 - 2.8 $\mu\text{g/g}$ . Selenium analysed in some of the fishes had levels slightly higher than Arsenic and lead in the flesh. Selenium levels ranged between 8.0 - 70  $\mu\text{g/g}$ .

The heavy metal contents of the fish oils were as follows; Cadmium ranged from 0.34ug/g in the Mackerel oil from Tema to 0.70ug/g in Herring oil from James Town. Lead was 6.12ug/g in Tuna from Tema to 35.56 ug/g in Mackerel, also from Tema. Mercury ranged from 25ug/g in Tuna and Tilapia from Tema and Weija respectively to 75ug/g in Herring from James Town. Arsenic ranged from traces in Tilapia and Tuna to 28.6ug/g in Mackerel from Tema.

Water sources of the fish were also analysed for their heavy metal contents. The coastal water samples had higher metal levels than the fresh water samples. For the coastal water samples heavy metal ranges were: Cd 0.6 - 0.13ppm, Pd 0.17 - 0.36ppm, Hg 8.87 - 10.8ppm, As <1.0 - 2.3ppm. For the fresh waters the metal ranges were: Cd 0.02 - 0.7ppm, Pb 0.08 - 0.12ppm, Hg 2.25 - 5.6ppm, and Arsenic; only traces.

The heavy metal levels in the fishes caught from heavy industrial coastal waters were slightly higher than those from light industrial coastal waters but only Arsenic and Mercury showed a significant difference ( $p < 0.05$ ).


The content of lead in Tilapia and *Blole* from non mining areas (RL) were significantly different ( $p < 0.05$ ) from those from the mining environment. Analysis of variance showed no significant difference ( $p > 0.05$ ) between the heavy metal levels in the oil, flesh and water except for Cadmium levels. There was no significant correlation ( $p > 0.05$ ) between the heavy metals in the flesh and water sample, water and oil and also the oil and flesh.

Comparison of the levels of the metal in 100g of flesh of each fish to safe margins established by FAO/WHO revealed that the levels in the fish were higher than the safe margins. The only exception is Cadmium, whose safe levels may be exceeded after an intake of 1000g of the flesh of the fish.

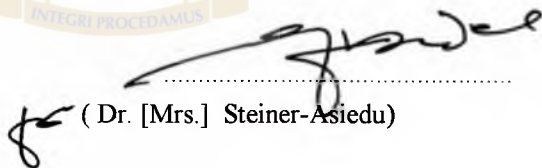
The research revealed that no matter the source of the fish the level of the heavy metal in the fish is high enough to warrant alarm and action to reduce the level of pollution in the waters and the fish.

**DECLARATION**

This Research was conducted by me and presented under the supervision of Dr. (Mrs.) Steiner-Asiedu of the Department of Nutrition and Food Science, University of Ghana - Legon.



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## **DEDICATION**

To Georgina, Elorm, Edem and My Daddy, for their sacrifices, love and support in the course of this research.

## **ACKNOWLEDGEMENT**

My first thanksgiving goes to God for the ability to carry out this work. I also wish to thank Georgina (my wife) for her support and encouragement. My special thanks go to Dr. (Mrs.) Steiner-Asiedu for her effective supervision. I owe much gratitude to NUFU project for the immense financial assistance given for the research. My final thanks go to Mr. Saakwa of Ecological laboratory and Dr. Ankrah of Chemical Pathology unit of NMIMR for their assistance in the use of the Atomic Absorption Spectrophotometer (AAS). I also wish to acknowledge the encouragement given me by all the lecturers of the Department of Nutrition and Food Science - University of Ghana, Legon.

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## CHAPTER 1

### 1.0 INTRODUCTION

#### 1.1 BACKGROUND INFORMATION

In recent times there has been a heightened global concern about the environmental impact of human activities. These activities have led to heavy pollution of land, air and water bodies. The pollution is pronounced in the coastal and inland waters where industrial and domestic liquid wastes end up. The 22nd December 1996 issue of Daily graphic reported that some fishermmen have been using chemical explosives for fishing which might lead to pollution of the waters.

The marine and fresh waters serve as the main source of fish and fish products. Apart from being a cheap and major source of protein in the diet, recent evidence has shown that fish and fish oils have other health promoting effect on humans. (Dyerberg *et al*; 1978; Belzing *et al*, 1993). Fish oils are rich sources of omega-3 (n-3) polyunsaturated fatty acids (PUFA) e.g. eicosapentaenoic (EPA) and docosahexaenoic acids (DHA). These PUFAs have been shown to decrease hyperlipidemia - high blood lipids (Goodnight *et al*, 1982), and decrease levels of cancer promoting prostaglandin PGE<sub>2</sub> (Karmali *et al*, 1984). They reduce platelet thromboxane synthesis, a potent risk factor for stroke through blockage of cerebral arteries (Von Schacky *et al*, 1985). They also reduces leukotrienes and hypoxo fatty acids, risk factors involved in asthma (Frankel 1984). They have been implicated in decreasing intravascular leakage of albumin in diabetics (Jensen *et al*, 1989), in improving learning behaviour and visual acuity of infants (Neuringer *et al*, 1984), and in possible protective effect against obesity (Belzing *et al*, 1993).

Due to the above benefits of fish it is important to protect the waters which contain the fishes. There is therefore the need for monitoring pollution in our water resources and fish. Water pollution by substances such as industrial wastes which may contain Arsenic (As), Lead (Pb), Mercury (Hg) and Cadmium (Cd) will result in pollution of the fish, the consumption of which will affect human health. Some of the hazards posed by these pollutants include neuro and nephrotoxicity (Dietrich, 1991) and bone fracture (Buchet *et al* 1990). Thus the benefit of the fish to the population must be preserved by controlling the possible factors that might introduce

poisonous compounds. To ensure effective reduction of these pollutants and for safety assurance there is the need for regular evaluation of the levels of these pollutants in the rivers, lakes, lagoons and the fish caught from them.

The strong advocacy for the increased intake of fish oils, rich in n-3 PUFAs may not achieve its desired effect of improving health if its safety in terms of heavy metal pollution is not taken seriously. The safety evaluation of fish and fish oils before and after processing will help establish the maximum benefit or otherwise that could be derived from the use of fish oils as dietary supplement and for therapeutic purposes. It is against this background that this study was initiated.

## 1.2 OBJECTIVES

### BROAD OBJECTIVE:

To investigate the extent of heavy metal pollution of fish and fish oils from selected Ghanaian coastal and inland waters.

### SPECIFIC AIMS:

1. To determine the levels of heavy metals e.g., Pb, Cd, As, Hg and Se in sampled fishes caught in Ghana's coastal and inland waters.
2. To determine the distribution of the metals in the body i.e., head, bone, flesh or muscle and scales where possible.
3. To determine the levels of these metals in the oils extracted from the fish.
4. To determine whether or not the amounts reach toxic levels by comparing it to safe-margins.
5. To ascertain the degree of the heavy metal pollution in some of the waters from which the fish were caught by analysing for the metal content.
6. To ascertain whether the level of Se is adequate enough to exert any protective effect against the toxicity of some of the heavy metals.

### **1.3 IMPORTANCE OF THE RESEARCH**

It is hoped that the data generated will serve as the basis to sound alarm on the possible dangers Ghanaians may be exposed to in the case of abnormal levels of heavy metals in the fish consumed.

Secondly the data collected could serve as baseline information for future evaluation and monitoring of these heavy metals in our waters and fishes.

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 FISH IN NUTRITION AND HEALTH

##### 2.1.1 Fish as food

Fish is a rich source of high quality protein and it is the major source of the protein in the diet of most people especially those in the low income group since it is cheaper than meat and poultry. Fish is also a good source of some vitamins and minerals. Cod liver oil has been given as supplement for vitamins A, D and E. Fish has been recommended for inclusion in the weaning foods for children to reduce protein energy malnutrition (PEM). Marine foods including fish are rich sources of iodine in the diet.

##### 2.1.2 Dietary fat and health

Dietary fat is known to be involved in the aetiology and progress of certain diseases, such as Ischaemic heart disease (Leaf & Werber, 1988), cancer (Karmali *et al.* 1984), and stroke (Dyerberg *et al.*; 1978). It is also known that saturated fat and cholesterol promote heart diseases. Dietary unsaturated fatty acid, however reduced hyperlipidemia, a potent risk factor influencing heart diseases (Kinsella, 1987).

The strong advocacy for increased consumption of polyunsaturated fatty acids (PUFA) in vegetable oils to reduce serum cholesterol, triglyceride and low density lipoprotein (LDL) has resulted in the consumption of high amounts of linoleic acid and other omega-6 (n-6) PUFAs. Recent evidence suggest that consumption of excessive amount of w-6 PUFAs may predispose individuals to various disease conditions such as thrombosis (Connor, Hoak & Warner, 1963), Psoriasis (chronic inflammatory disease characterised by whitish lamination scales on the knee, elbow and scalp), Asthma, and Arthritis in addition to enhanced tumour growth, metastasis and cancer (Kinsella, 1987).

### 2.1.2.1 Benefits of fish oil

Fish oils which are rich in n-3 PUFA appear to be more effective in reducing hyperlipidemia than vegetable oils. They are more effective inhibitors of fatty acid synthesis and lipoprotein formation in the liver and they enhance the catabolism of lipoproteins. In addition, the n-3 PUFAs of fish oils may directly affect the risk of cardiovascular disease through their impact on platelet function (Goodnight *et al*, 1982).

Stroke caused by thrombosis and blockage of cerebral arteries are precipitated by the excessive production of thromboxane which causes excessive platelet aggregation. Dietary n-3 PUFAs of fish oils significantly reduce platelet thromboxane synthesis without impairing prostacyclin synthesis. Some n-3 PUFAs e.g. eicosapentaenoic acid (EPA) are converted to a potent anti aggregating prostacyclin isomer (Von Schacky *et al*, 1985).

Cumulative evidence indicates that several cancers, particularly mammary tumours are facilitated if not stimulated by n-6 PUFAs which are converted to PGE<sub>2</sub> a tumour growth-promoting prostaglandin. Dietary n-3 PUFAs effectively reduce the production of PGE<sub>2</sub> in animals and resultant reduction in growth of certain tumours (Karmali *et al*, 1984). Recent evidence indicates that compounds generated by lipoxygenase in pulmonary tissues, such as leukotrienes and hydroxy fatty acids are potent factors involved in asthma (Frankel, 1984). By reducing the synthesis of these agents, dietary n-3 PUFAs may reduce the incidence of asthma.

Omega-3 PUFA rich in fish oil has been implicated in decreasing leakage of albumin in diabetics (Jensen *et al*, 1989), improvement in learning behaviour and visual acuity in infants (Neuringer *et al*, 1984) and possible protective effect against obesity (Belzing *et al*, 1993). Due to these benefits, fish oil is now being used as nutritional supplement and for therapeutic purposes, especially in the developed countries.

## 2.2 SOURCES OF POLLUTANTS IN FISH

### 2.2.1 Source of the metals

Heavy metal pollution in marine and fresh waters come from inflow of industrial waste from mines and factories. Flood waters flowing over soils rich in some of these heavy metals may leach them into the streams, rivers and the coastal waters. Agriculture chemicals added to the soil can lead to leaching of heavy metal into the waters, e.g. Phenyl mercuric acetate [PMA], (Imura *et al*, 1972).

Mercury pollution caused a physiological disorder called *Minamata* disease in Japan. This was due to accumulation of waste water from chemical works mainly of acetaldehyde markers containing Hg compounds. This settled in the bottom of rivers and the sea near estuaries. There was then a formation of methyl mercury which is taken into the food chain participated in by humans. Some fish used as human food also possess the ability to form methyl mercury (MM). Since animals higher in the food chain accumulate more Hg than those lower the chain, Tuna a fish ranked higher in the food chain have a high ability to form methyl mercury (Imura *et al*, 1972). Cadmium pollution also cause a disease called *Itai-itai* disease in Japan. The pollution was caused by effluent from mines (Imura *et al*, 1972). Nickel can be introduced into fish oil when being used as Nickel catalyst in hydrogenation of fish oils (Kinsella, 1987). Lead enters our waters from petroleum products from car exhausts and auto mechanic workshops into streams and rivers.

### 2.2.2 Forms of the heavy metals in aquatic organisms

In an aquatic environment, metals may exist as simple or complex ions in solution, associated with inorganic or organic particles of varying size and as chelates or colloids (Phillips, 1980). Most trace metals are taken up by aquatic organisms in the ionic form. The concentration of free cadmium ions appears to be the most important determinant of the extent of its uptake by fish (Louma, 1983). Mercury and lead exist in both organic and inorganic forms. Their organic

form is usually the methylated molecule synthesised by micro-organisms (Phillips, 1980). The lipophilic nature of methyl mercury and tetramethyl lead allows their accumulation by fish. The uptake of methyl mercury from food and water which resembles that of the organochlorines, occurs easily, and it is subsequently transported to lipid-rich tissues (Phillips, 1980). At higher trophic levels greater concentrations of methyl mercury occurs in the tissue of fish (Louma, 1983). Lead pollution may result from Pb fuels and Pb containing chemicals.

### **2.3 EFFECT OF PROCESSING ON HEAVY METAL LOAD IN FISH AND FISH OILS**

The metal content of fish oil is influenced by the metal content of the fish tissue used as raw material and the production and storage condition of the oil. The phospholipid content of the oil increases with longer storage (Lunde, 1973), and during production, these compounds carry metals into the oils. Thus, as the storage time of the raw fish prior to oil extraction is lengthened, the content of heavy metals in the extracted oil increases (Lunde, *et al* 1976). Although few studies of the metals content of fish oils before and after processing are available, processing oils for edible purposes appears to reduce the metal content (Elson, *et al* 1981).

The degree of reduction is dependent on the metal present. The removal of the bulk of a metal is usually accomplished in one refining or processing step (Elson, *et al* 1981)). Metals that are complexed to phospholipids are removed most easily by degumming and alkaline refining since these steps remove phospholipids (Elson & Ackman, 1978). Further processing steps are less likely to remove metals that are tightly bound to oil constituents and organometallic compounds (Elson, *et al* 1981). The FAO/WHO standards of acceptable metal content in oils have not been met after processing (Elson & Ackman, 1978). Trace metals, minerals, pesticides are removed by degumming, alkaline refining and by bleaching. Selenium is significantly lowered by hydrogenation and de-odorization. Alkaline refining removes arsenic and reduces lead by 40% (Elson & Ackman, 1978).

## 2.4 HEALTH IMPLICATION OF HEAVY METAL POLLUTION

### 2.4.1 Reported outbreak of heavy metal poisoning.

There has been reported cases of heavy metal poisoning in Iraq, Belgium, Japan and Sweden at various times. In Iraq there was an outbreak of methyl mercury poisoning in 1973 in which seed wheat treated with methyl mercury fungicide was accidentally consumed by poor farmers and their families. This led to numbness of the extremities, cerebella incoordination and loss of vision due to brain damage. In Belgium, people living in communities where there is historical Cd pollution from non-ferrous metal refinery suffered hypercalcemia particularly in the old women (Buchet *et al*, 1990). Japanese living in the Minamita Bay were found to suffer from mercury poisoning due to waste water from chemical works mainly of acetaldehyde markers containing mercury compounds (Imura *et al*, 1972). In Sweden mercury poisoning was reported in subject suffering from lack of coordination movement, loss of vision and other neurological affects (Johnels and Westermark, 1969).

### 2.4.2 Metal Toxicity

The concentrations of lead, mercury, and cadmium have increased greatly in aquatic environments (Kinsella, 1987). Excessive intakes of lead and mercury can damage the central and peripheral nervous systems and kidney function (Sims, *et al*, 1977).

#### 2.4.2.1 Lead toxicity

Lead in particular is an extremely poisonous heavy metal. In humans high concentrations of lead in the blood cause mental disorders. Children are the most likely to be affected, especially in their first two years of life when concentration of as low as 10ug/dl can impair mental development (Rotenberg *et al*, 1989). Lead poisoning has been implicated in poor brain development and low academic performance in school age children. Elevated blood-lead levels in school children are associated with comparatively low IQ, poor performance in tests of information processing, and low achievement scores e.g. in reading (Ernesto, 1990). Chronic

lead poisoning, 'saturnismo' can cause neurotoxicity, by inhibiting the release of neurotransmitters (Dietrick, 1991). It also has adverse impact on growth and can cause perpetual changes. Lead intake increases the urinary excretion of Zinc. Zinc deficiency also enhances lead absorption (Lauweys *et al*, 1983).

An important consequence of iron deficiency is an increased risk of lead poisoning in children exposed to high levels from chipped lead paints or other environmental exposure to excessive lead. Iron deficiency leads to increased lead absorption in the gut (Six and Goyer, 1972). Increased lead levels are found in children in many cities with high lead pollution from automobile fumes. In the developing countries where about 30% of children are at risk of iron deficiency anaemia their risk of lead poisoning is heightened. Lead toxicity can lead to lead-induced hypertension in some human subjects.

#### **2.4.2.2 Cadmium toxicity**

Chronic exposure to cadmium causes emphysema, anaemia, kidney dysfunction and spontaneous fractures (Kinsella, 1987). In addition, epidemiological investigations have implicated cadmium as a carcinogen (Koller, 1980). Both lead and cadmium have been associated with deaths due to heart disease (Kinsella, 1987). Tobacco is a plant which contain a substantial amount of Cd so that Cd uptake is virtually doubled in a pack-a-day smoker. Cadmium toxicity affect kidney and bone. Cd pollution has led to hypercalcemia particularly in old women in Belgium (Buchet *et al*, 1990). Cadmium has been reported to induce toxic free-radical species producing lipid peroxidation and causing liver damage (Gil, *et al*, 1989).

### 2.4.2.3 Selenium, Mercury, and Arsenic toxicity

Excessive and toxic concentrations of selenium may be found in cereals grown on selenium rich soils. Its toxicity may lead to loss of hair and nails, lesions of the skin, nervous system and teeth. Mercury toxicity can affect the brain and Central Nervous System (CNS). Arsenic toxicity can also affect the liver and kidney.

### Heavy metal - nutrient interactions

Lead intake increases the urinary excretion of Zinc. Zinc deficiency also enhances lead absorption (Lauweys *et al*, 1983). Lead has also been implicated in the metabolism of calcium. It has been shown to block calcium transport by calcium channels (Simons, 1986a; Simons & Pocock, 1987), act as substitutes for calcium in Ca-Na-ATP pump (Simons, 1986b), competes for calcium-binding protein sites (Fullmer, 1986), competes with uptake by mitochondria (Parr and Harris, 1976) and binds to second messenger calcium receptor e.g., Calmodulin and Proteinkinase C, (Habermann *et al* 1983). It has been suggested that increased vascular reactivity in lead-induced hypertension is due to increased proteinkinase C and lead-induced changes in cellular calcium metabolism.

Iron deficiency leads to increased lead absorption in the gut (Six *et al*, 1972). Cadmium interacts with the metabolism of Ca, Zn, and Fe. Cadmium toxicity affect kidney and bone. In Kidney it produces proximal tubular dysfunction so that there is a decrease in resorption of amino acids, glucose, phosphates and low molecular weight proteins (Buchet et al, 1990). Deficiency of Calcium, vitamin D, Zinc and Iron may increase Cadmium Toxicity. Cadmium has inhibitory effect on intestinal Ca transport stimulated by vitamin D. The interaction occurs also in the bone. Cadmium and Zn interactions are related to metallothioneins ( a group of low molecular weight proteins that bind Zn and Cu involved in their transport and storage. A report suggests that cadmium preferentially binds to membrane sulfhydryl groups and affects cellular thiols (Muller *et al* 1988). Cadmium is also proposed to cause cell membrane lesions and subsequent altered

membrane permeability involving lipid peroxidation (Kinter and Pritchard 1977). Cadmium have been implicated in cancer through free radical mechanism.

Selenium has been shown to protect against acute heavy metal toxicity of mercury, cadmium and silver (Pariezek and Ostadalova, 1967). Selenium plays an important role in cell glutathione peroxidase in reducing cancer due to free radicals.

The interaction between Ca, Fe, and Zn lead to lowered cognitive and behaviour effect on children. Cadmium interaction with Zn and Fe may lead to Nephrotoxicity of the kidney and the interaction between Hg and Se does affect the Central nervous System.

## **2.6 SAFE MARGINS FOR HEAVY METALS**

To avoid ill-health one need not consume food items which contain substances that are toxic to the body. Any material that accumulates in the body will be dangerous to consume as compared to those that can be excreted very fast, A number of factors come into play and among them are the toxicity effect of the substance and how it is metabolised in the body. For metals it is important to note that the metals can be in different chemical forms such that some are poisonous than others. Our main interested in the amount of the element present nevertheless, it is important to take note of the toxic effect of the amount in relation to safe levels of consumption. The safe levels can be used to indicate the maximum intake of a substance that a person can take without poisoning. In order to find the safe levels for different substances, - the Joint FAO/WHO Codex Alimentaire Commission (Codex Alimentaire), was formed to look into all kinds of contaminants in foods.

The FAO/WHO Joint Expert Committee on Food Additives also evaluates food additives and contaminants. Maximum intake of contaminant is given by different values: Provisional Tolerable Weekly Intake (PTWI) and Maximum Tolerable Daily Intake (MTDI). PTWI is the amount of a substance (amount/kg body weight) that a person can be exposed to for the

whole of his life without any toxic effect of poisoning. The word Provisional means that the values are temporal because there is not enough data. The word Tolerable is an induction of the fact that contaminant in foods are not allowed but if one is exposed to them one should be able to tolerate them in small amounts. Maximum Tolerable Daily Intake (MTDI) is used for the essential elements which in higher concentrations can be toxic e.g. Copper and it is expressed in weight of element/ kg body weight.

The joint FAO/ WHO Expert Committee on Food Additives have proposed the following safe margins for the heavy metals (Aune 1992):

**Table 1 FAO/WHO Safe margin For Heavy Metals**

Heavy Metal		ug/kg bwt PTWI	60kg bwt (mg) PTWI
Cadmium	Cd	7.0	0.42
Lead	Pb	5.0	0.30
Arsenic	As	2.0	0.12
Mercury	Hg	5.0	0.30
MethylMercury		3.3	0.20
Selenium			2.5 - 3.0*

PTWI: Provisional Tolerable Weekly Intake

\*MTDI: Maximum Tolerable Daily Intake

bwt: Body weight

In fish products 50ug/kg is maximum permitted levels (MTDI) for lead.

## 2.7 SAFETY OF FISH OILS

There are three safety problems with fish oils, these include,

- i) Autoxidation -peroxidation due to high unsaturation and the products have been associated with cellular damage (Longani & Davis,1980).
- ii) Contamination of the fish oil with toxic chemicals, e.g., Dichloro Diphenyl trichloroethane (DDT), Polychlorinated biphenyl compounds (PBC ) etc.
- iii) Pollution from heavy metals such as Pb, Cd, , Ag, etc.

### 2.7.1 Autoxidation

Unsaturated fatty acids in the presence of free radical initiators and atmospheric oxygen undergo autoxidation. This process can be initiated by the presence of metal ions especially transition metals such as Cu, Cd, Ag, Fe, etc. The process can also be initiated by ultraviolet light as well

as some enzymes (Fankel, 1984; Kinsella, 1987). The autoxidation leads to rancidity and development of off-flavours. The peroxides formed from the oxidation reaction can prove toxic (Pra *et al* 1992). The consumption of oxidised oil led to the inflammation of the intestinal tract, damage to the mucous membrane of the stomach and the intestines, and severe ulceration as well as decreased cellular respiration and enzyme inhibition (Lang, 1965).

Autoxidation can be prevented or reduced by adding antioxidants such as several isomers of vitamin E in vegetable oils. Other antioxidants that can be used include Butylated hydroxytoluene, (BHT) and Butylated hydroxy anisole (BHA). Autoxidation can be inhibited by storing fish oil at low temperatures, limiting exposure to oxygen and contact with metallic ions (Kinsella, 1987). Haem pigment is an active catalyst for fish oxidation.

The contamination of fish may also come from agrochemicals. Heavy metal pollution may come from various sources.

## **2.8 FISH OIL PROCESSING**

### **2.8.1 Extraction**

Processing fish for edible oil requires that the fish raw material be of superior quality, thus it must be undamaged and chilled from the time of catch to prevent deterioration. The steps involved in the extraction of the oil include: Cooking, Filtering, Centrifuging, and Washing. The whole fish is minced and then cooked. The cooking causes protein denaturation, breaking of tissue and release of the oil. Undercooking results in reduced yield and overcooking causes excessive breakdown of muscles tissue. Cooking is done at 90°C for 15 minutes (Young, 1982). The boiled fish is filtered using a strainer or press filter. The oil and stick-water are then centrifuged, and then the oil decanted. The oil obtained is washed with hot water 90-95°C to remove trace amounts of protein and then dried under vacuum. The quality of the crude oil obtained is dependent on the storage and handling of the fish prior to processing, the efficiency of the processing plant and its handling and storage after processing (Kinsella, 1987). Solvent extraction can also be used to extract oil from fish.

### **2.8.2 Refining**

The crude oil contains certain soluble impurities including metals, pigments and, chemicals, free fatty acids, as well as insoluble impurities such as moisture, dirt, and rust. It also contains colloidal impurities which are largely made up of proteins. The refining process depends on the use of oil as industrial or edible oil. The refining for edible oil begins with Degumming. The oil in the container is agitated slowly at about 25°C to provide homogenous product. Eighty percent of phosphoric acid is added to remove insoluble phosphatides in the acid layer. The sludge is centrifuged and the oil is neutralised with caustic soda (i.e. 15-18% NaOH). The NaOH added neutralises the free fatty acids to about 0.01-0.03% (Kinsella, 1987). It also reacts with impurities making them soluble and removable in the aqueous layer. The oil is washed with water to remove the soap and then centrifuged.

### **2.8.3. Bleaching**

After refining, the oil is bleached with earth, clay or activated charcoal to remove pigments and reduce oxidation products, soaps, phosphorous, odorous substances and trace elements. The bleaching earth contains Mg, Ca, Fe and Na which are activated with mineral acids that increase bleaching activity and oil retention. The clay is removed by filtration under vacuum. In some cases the oil is deodorised by steam distillation under vacuum.

To be used as nutritional supplements, or in therapeutic applications, the oil has to be carefully refined and its Vitamins A and D contents reduced and supplemented with antioxidants and then packaged to minimise autoxidation.

## CHAPTER THREE

### 3.0 MATERIALS AND METHODS

#### 3.1 ENVIRONMENTAL AREAS FROM WHICH FISH WERE SAMPLED

The research is aimed at assessing environmental impact on the levels of heavy metals in fish, therefore fish were sampled from the following four environmental zones,

Heavy Industrial zone - Accra and Tema

Light Industrial zone - Apam and Elmina

Lake/River - Weija and Kpong

Mining Environment - Obuasi and Dunkwa

The zones were selected based on the relative industrial and fishing activities taking place. Tema and Accra have the highest number of industries and fishing harbours. These were designated high industrial zones. Apam and Elmina are far from the industrial towns but have busy fishing harbours hence were designated light industrial zone. Weija is about 10 km from Accra but has a large dam for water treatment and also used for fishing. The Weija lake serves as a source of Tilapia fish for a lot of people in Accra. Kpong lake is an extension of the Volta lake and about 35km from an industrial town that has a lot of fishing activities. These two areas were designated River / Lake zone. Dunkwa is a mining town supplied by the Ofin river into which effluent of the mining activities is discharged. The river serves as source of fish for the people of Dunkwa and its surrounding villages. There is not much fishing activities in Obuasi which is one of Ghana's busiest mining towns but some of the inhabitants of the area have fish pond for fish farming. These two towns were designated mining environment.

#### 3.2 Fish samples

Based on information from a market survey and data from Fisheries Department of Ministry of Food and Agriculture (MOFA), the following fishes were sampled due to their relative abundance and relatively high consumption in Ghana.

**Marine Fish**Herring (*Sardinella* species)

Mackerel Species

Tuna Species

Redfish (Red mullet)

Anchovies

**Freshwater Fish**Tilapia (*Oreochromis niloticus*)Catfish (*Clarias and Heteroblancus sp*)One-mouth-thousand (*Sierrathrissa leonensis*)'Blolo' (*Chrysichthys nigrodigitatus*)**3.3 Fish sample handling from landing sites.**

The fishing harbours or landing sites were visited early in the morning to get the fish as fresh as possible to reduce deterioration. The fish samples were bought directly from fishermen and retailers at the landing site. The samples were put in clean labelled polythene bags and kept chilled in ice chests with frozen ice packs. They were kept frozen at  $-20^{\circ}\text{C}$  until ready for analysis in the lab. Mean weight and lengths of the fishes were taken by weighing 3 - 4 pieces of the fish and dividing by the number of pieces. The length of the fish was taken by measuring the length from the tip of the mouth to the tip of the tail with a tape. This was done for 4 different pieces and the mean calculated.

**3.4 Preparation of fish sample for analysis**

Between 3 to 5 pieces of each species were thawed and then grilled in an oven at  $220^{\circ}\text{C}$  for 20 to 30 minutes depending on size of the fish. This rendered the fish tender and soft. The head, bone and flesh were separated. Each part was weighed. The parts were ground in a mortar and samples taken for moisture content determination. A sample of wholefish of each fish was treated just like the other parts. The rest of the ground samples were dried in an oven at  $105^{\circ}\text{C}$  overnight. Five grammes of each dried samples was acid digested using Nitric and Perchloric acids, for Atomic Absorption Spectrophotometer (AAS) analysis. Digestion procedure see

**Procedure for wet ashing ( NFS. Dept. acid digestion procedure)**

Five grams of dried fish sample was weighed into digestion tube. Then 50 ml of HNO<sub>3</sub> acid was added and heated strongly in a fume chamber till brown notrous fumes were removed. Then 15ml perchloric acid was added and heating continued till white fumes were all removed and solution turns almost colourless. The tube was cooled and distilled water was added to remove remaining white fumes. The resulting solution was made up to 100ml with dilled water.

To determine the distribution of the heavy metals in the fish, analysis was done on whole fish, head, bone, muscle, and scales for those who had. Samples of the water from which the fish were caught were also analysed for heavy metals. The water samples were collected by dipping the container into the water body. The container is a clean plastic bottles washed with de-ionised water and dried.

**3.5 EXTRACTION OF THE FISH OIL**

After four unsuccessful attempts to extract fish oil using a method described by Kinsella, 1987 for edible fish oil, the method of solvent extraction was used to extract enough for metal content analysis. Petroleum ether was used because that was readily available. Oil was extracted from fishes with appreciable quantities of oil e.g. Tuna, Mackerel, Herring and Tilapia. The whole fish was grilled in an oven at 220°C for 20 minutes and then blended. The blended fish was then put in a 250ml separating funnel and 40ml Petroleum ether was added and shaken to extract the oil. It was left to stand overnight. The mixture was centrifuged and the organic layer decanted and evaporated to obtain the oil. On the average about 400g of the fish yielded about 10ml of oil.

**3.6 AAS DETERMINATION**

AAS determination was done at Ecological laboratory(Ecolab), Department of Geography and Resource Development, and Noghuchi Memorial Institute of Medical Research (NMIMR), University of Ghana.

### 3.6.1 Preparation of Standard Solutions

1000ppm Standard solutions for the analysis of the AAS of various metals were prepared as follows;

Cd - (hydrated Cadmium chloride -  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ ), - 0.203g dissolved in 100ml distilled water.

Se - (Selenium dioxide -  $\text{SeO}_2$ ) - 0.1405g dissolved in 100ml distilled water

Hg - (Mercuric nitrate -  $\text{Hg}[\text{NO}_3]_2$ ) - 0.1618g dissolved in 100ml distilled water.

Each in 100ml distilled water was acidified with  $\text{HNO}_3$ .

As - (Standard Arsenic nitrate was provided by the NMIMR laboratory),

Pb - (Standard Lead nitrate was provided by the NMIMR laboratory )

### 3.6.2 INSTRUMENT CONDITIONS AND ASSAY SETTINGS

The AAS instruments used had specific conditions which needed to be set for reading each metal absorption. The specific condition for each elements is showed below in Table 2.

Model of instrument (Ecolab) - PERKIN ELMER AAS - MODEL 3110 USA.

" (NMIMR) - SHIMAZU AA - 630-12 JAPAN

Type of lamps used    electrodeless discharge lamp ( EDL ) and hollow cathode lamp (HCL)

**Table 2      Assay settings**

<u>SETTINGS</u>	<u>LEAD</u>	<u>CADMIUM</u>	<u>MERCURY</u>	<u>ARSENIC</u>	<u>SELENIUM</u>
Wavelength (nm)	283.3	228.8	253.7	194	196
Slit width (nm)	1.9	0.7	0.7	0.7	2.0
Lamp Current (mA)	6	240	210	400	280
Sensitivity (ppm)	0.77	0.028	0.25	1.0	0.59
Sensitivity Check	20	1.5	200	45	30
Lamp type	HCL	EDL	EDL	HCL	EDL
Replicate reading	3	3	3	3	5
Linear range(ppm)	10	2	300	100	200
Instrument used	SHIMAZU	PERKIN ELMER	PERKIN ELMER	SHIMAZU	PERKIN ELMER

**Calculation of heavy metals in (ug/g) dried fish.**

The values read on the AAS were in ppm (parts per million) which is equivalent to ug/ml or mg/L.

The total volume of digest was 100ml. The total weight of heavy metal in the digest is (ppm x 100) = 100ug. The weight of dried fish digested was 5g, hence weight of metal/gramme of dried fish is ( ppm x100/5) equivalent to {ppm x 20ug/g dried fish).

**Data analysis**

For statistical analysis Microsoft Excel version 4.0 1985-1992, Epi Info version 5.01, 1991, Statgraphic version 4.2 1985-1989, software programmes were used. Excel was used for all the graphic works while Statgraphics and Epi Info were used for most of the ANOVA and correlation analysis.

The reported levels of heavy metal in the analar grade perchloric and nitric acids used for the digestion are as follows:

**Perchloric acid,**

Arsenic 0.000005%  
Lead 0.000005%  
Cadmium 0.000005%

**Nitric acid**

Arsenic 0.000002%  
Lead 0.000002%

The low levels of the metals in the reagent can only contribute an insignificant amount to the high levels of the metals in the analysis hence they cannot be sources of errors in the analysis.

## CHAPTER FOUR

### 4.0 RESULTS

The results of the analysis are presented in the tables below.

**Table 3: Heavy metal content of fish, (ug/g of dried fish)**

**from Heavy Industrial area: James Town & Tema**

<u>Sample/loc*</u>	<u>Parts</u>	<u>Cd</u>	<u>Pb</u>	<u>Hg</u>	<u>As</u>	<u>Se</u>
Redfish/ JT	W	1.2	11.6	128	14.8	34
"	F	0.6	9.8	20	6.5	22
"	H	1.8	16.2	162	13.9	52
"	B	2.2	17.2	228	34.8	70
"	S	1.8	12.6	182	20.5	56
Tuna/JT	W	0.8	16.2	74	19.7	10
"	F	0.6	4.3	58	19.1	14
"	H	1.4	27.3	146	20.0	32
"	B	1.8	42.9	208	26.0	20
Herring/JT	W	1.2	9.3	158	15.4	16
"	F	0.6	6.1	70	9.3	Trace
"	H	1.8	10.7	218	19.1	34
"	B	2.0	36.6	220	40.5	26
"	S	2.0	36.6	224	29.3	32
Redfish/TM	W	1.4	8.0	158	13.5	20
"	F	0.8	3.4	74	14.8	8
"	H	1.6	13.5	170	15.5	56
"	B	2.2	19.0	134	27.9	28
"	S	1.8	16.2	150	12.6	30
Tuna/TM	F	1.4	8.8	98	4.2	Trace
"	H	3.0	9.8	192	19.7	Trace
"	B	2.0	19.0	300	23.3	52
Mackerel/TM	W	2.2	9.8	154	9.3	Trace
"	F	1.8	4.3	124	9.3	Trace
"	H	2.6	19.0	208	22.3	20
"	B	2.6	22.7	200	15.4	8

**Table 3: continued**

<b><u>Sample/loc*</u></b>	<b><u>Parts</u></b>	<b><u>Cd</u></b>	<b><u>Pb</u></b>	<b><u>Hg</u></b>	<b><u>As</u></b>	<b><u>Se</u></b>
Herring/TM	W	2.6	8.0	182	9.3	Trace
"	F	1.6	6.1	118	9.3	Trace
"	H	2.8	9.3	288	27.0	Trace
"	B	3.2	15.3	254	10.2	12
Anchovies/TM	W	1.4	16.2	124	12.6	Trace

\*Loc - location, JT - James Town; TM- Tema,

W- wholefish, F-flesh, H- head, B- bone and S- scale.

Trace - levels below sensitivity of metal

**TABLES 4: Heavy metal content of fish, (ug/g of dried fish)  
from Light Industrial areas, Apam & Elmina.**

<u>Sample/loc*</u>	<u>Parts</u>	<u>Cd</u>	<u>Pb</u>	<u>Hg</u>	<u>As</u>	<u>Se</u>
Mackerel/AP	W	1.6	6.1	104	7.9	Trace
"	F	1.2	2.4	68	3.3	Trace
"	H	2.2	8.9	184	15.8	14
"	B	2.6	11.6	160	35.6	50
Herring/AP	W	2.2	8.9	162	14.4	14
"	F	1.2	8.0	92	9.3	Trace
"	H	2.6	12.6	240	18.6	26
"	B	2.8	10.7	232	30.7	28
"	S	2.6	9.3	244	28.4	32
Emule/AP	W	1.2	7.0	110	13.5	8
"	F	1.0	5.2	68	1.9	Trace
"	H	2.0	8.9	168	17.2	14
"	B	2.4	10.7	262	19.5	40
Redfish/EL	W	1.2	8.0	222	10.1	Trace
"	F	0.6	7.0	144	10.1	Trace
"	H	1.6	16.2	256	29.5	Trace
"	B	1.6	9.3	288	29.9	18
"	S	1.6	16.2	266	11.0	10
Tuna/EL	F	0.6	5.2	50	19.8	**
"	H	1.0	16.2	100	24.2	**
"	B	1.6	35.6	75	26.0	**
Herring/EL	W	1.2	19.0	50	11.0	**
"	F	1.2	14.4	25	8.4	**
"	H	1.6	23.6	150	26.9	**
"	B	2.0	28.2	125	37.0	**

AP - Apam; EL - Elmina

\*\* Could not be analysed because of break down of AAS at the Ecolab.

**Tables 5: Heavy metal content of fish, (ug/g of dried fish),  
from River / Lake, (Weija & Kpong)**

<u>Sample/loc</u>	<u>Parts</u>	<u>Cd</u>	<u>Pb</u>	<u>Hg</u>	<u>As</u>	<u>Se</u>
Tilapia/WJ	W	0.8	17.2	146	11.6	Trace
"	F	0.4	12.7	50	9.8	Trace
"	H	1.0	22.7	134	19.5	14
"	B	1.8	39.2	210	21.7	42
"	S	1.0	37.4	122	19.5	10
Blolo/KP	W	0.8	24.5	50	7.9	**
"	F	0.8	22.7	50	6.1	**
"	H	1.6	28.2	100	13.6	**
"	B	1.2	28.2	100	26.0	**
"	F	0.4	8.0	50	4.4	**
"	H	1.2	12.6	75	26.5	**
"	B	1.2	19.0	125	13.6	**
1-M-T*/KP	W	0.6	24.5	125	20.2	**
Tilapia /KP	W	0.9	8.0	100	12.3	**
"	F	0.7	3.4	50	4.8	**
"	H	1.4	9.3	125	10.1	**
"	B	1.1	11.6	200	22.9	**
"	S	0.7	9.3	100	15.9	**

WJ - Weija ; KP - Kpong,

\*1-M-T - One -mouth-thousand (*Sierrathussa leonesis*)

\*\* Could not be analysed because of break down of AAS at the Ecolab.

**TABLES 6: Heavy metal content of fish, (ug/g of dried fish) from Mining Environment, Obuasi and Dunkwa**

<u>Sample/loc</u>	<u>Parts</u>	<u>Cd</u>	<u>Pb</u>	<u>Hg</u>	<u>As</u>
Tilapia/OB	F	0.6	5.2	50	18.5
"	H	1.7	20.8	150	25.5
"	B	1.8	15.3	150	26.0
Tilapia/DK	W	1.3	7.0	150	28.2
"	F	0.6	6.1	75	6.2
"	H	1.0	26.4	150	19.8
"	B	1.4	39.2	200	33.9
"	S	1.1	15.9	100	17.6
Catfish/DK	F	0.3	8.0	50	1.3
"	H	0.9	25.1	100	19.8
"	B	1.2	17.2	175	5.7
Blolo/ DK	F	1.0	9.3	50	5.7
"	H	1.3	11.6	90	14.1
"	B	1.5	16.2	250	18.2

OB - Obuasi; DK - Dunkwa

**Table 7: Mean  $\pm$  SD values of heavy metal in the flesh of each fish species.**

<b><u>Sample</u></b>	<b><u>Cd ug/g</u></b>	<b><u>Pb ug/g</u></b>	<b><u>As ug/g</u></b>	<b><u>Hg ug/g</u></b>
Redfish	0.67 $\pm$ 0.1	6.7 $\pm$ 3.2	10.5 $\pm$ 4.2	79.0 $\pm$ 62
Tuna	1.4 $\pm$ 1.4	6.1 $\pm$ 2.3	14.4 $\pm$ 8.8	68.7 $\pm$ 25
Herring	1.2 $\pm$ 0.4	8.7 $\pm$ 3.9	9.1 $\pm$ 0.5	76.3 $\pm$ 39.3
Mackerel	1.5 $\pm$ 0.4	3.4 $\pm$ 1.3	6.3 $\pm$ 4.3	96.0 $\pm$ 39.4
Tilapia	0.9 $\pm$ 0.6	11.2 $\pm$ 7.5	13.0 $\pm$ 8.9	87.5 $\pm$ 47.9
Catfish	0.4 $\pm$ 0.1	8.0 $\pm$ 0.0	2.9 $\pm$ 2.2	50.0 $\pm$ 0.0
Blolo	0.9 $\pm$ 0.9	16.0 $\pm$ 9.5	5.9 $\pm$ 0.3	50.0 $\pm$ 0.0
1-M-T*	0.6	24.5	20.2	125.0
Anchovies*	1.4	16.2	12.6	124.0

\*Whole fish levels (including bone and head). There are no  $\pm$ SD values because only single samples of this fish were analysed.

**Tables 8: Heavy metal content of fish oil (ug/ml oil)**

<b><u>Type of fish oil</u></b>	<b><u>location</u></b>	<b><u>Cd</u></b>	<b><u>Pb</u></b>	<b><u>Hg</u></b>	<b><u>As</u></b>
Herring	JT	0.70	10.72	75	15.4
Mackerel	TM	0.40	35.56	Trace	28.6
Tuna	TM	0.35	6.12	25	Trace
Tilapia	WJ	0.50	9.28	25	Trace

**TABLES 9: Heavy Metal levels of water sources of fish,  
[ug/ml (ppm) of water]**

<u>Water source</u>	<u>water</u>	<u>Cd</u>	<u>Pb</u>	<u>Hg</u>	<u>As</u>	<u>Se</u>
James Town	marine	0.13	0.26	8.7	1.8	2.9
Tema	marine	0.13	0.35	8.7	2.3	1.8
Elmina	marine	0.13	0.17	10.8	1.7	1.0
Apam	marine	0.06	0.26	9.8	Trace	2.2
Kpong (Volta)	lake	0.02	Trace	5.6	Trace	Trace
Weija (Densu)	lake	0.07	0.12	4	Trace	Trace
Obuasi (Nyam)	stream	0.02	0.08	2.25	Trace	**
Obuasi	fishpond	0.04	Trace	5.0	Trace	**
Dunkwa (Ofin)	river	0.02	0.08	3.75	Trace	**

**Table 10: Heavy metal content of flesh (mg/100g)<sup>1</sup>**

<u>Sample</u>	<u>Cd</u>	<u>Pb</u>	<u>As</u>	<u>Hg</u>
Redfish	0.03	0.34	0.52	3.95
Tuna	0.07	0.31	0.72	3.43
Herring	0.06	0.43	0.45	3.81
Mackerel	0.08	0.17	0.31	4.80
Tilapia	0.05	0.56	0.65	4.38
Catfish	0.18	0.40	0.14	2.50
Blole	0.05	0.80	0.29	2.50
1-M-T	0.03	1.23	1.01	6.25
Anchovies	0.07	0.81	0.63	6.20
<b>*PTWI</b>	<b>0.42</b>	<b>0.30</b>	<b>0.12</b>	<b>0.30</b>

\*FAO/WHO safe margins 1992.

<sup>1</sup> flesh with moisture content of 50%

## 5.0 DISCUSSION

### 5.1.0 Distribution of Heavy Metals in fishes from Heavy Industrial area, James Town and Tema.

Fish was sampled from James Town in Accra and Tema and the distribution of the heavy metals Lead (Pb), Mercury (hg) etc. is presented in Table 4. All the fish types contained an amount of the heavy metals that are of major health concern. The highest was mercury and the lowest was cadmium.

#### 5.1.1 Cadmium levels in Redfish from James Town (JT)-Accra

The levels of Cadmium in this fish ranged from 0.6 to 2.2ug/g (Table 4). The bone contained the highest levels of Cd (2.2ug/g) followed by the head and the scale ((1.8ug/g). The head and the scale had the same amount of Cd levels. The next highest Cd levels occurred in the wholefish (1.2ug/g). The flesh had the lowest levels of Cd with value 0.6ug/g. The flesh contained about a quarter of Cd as the bone but about a third in the head and the scale. This trend revealed that the more the skeletal structure (i.e. bone content), the greater the Cd levels.

#### 5.1.2 Mercury levels in Redfish from JT

The distribution of Hg in the Redfish showed a similar pattern as Cd distribution. Thus the bone had the highest levels of 228ug/g, followed by the scale (182ug/g), head (162ug/g), the wholefish (128ug/g) and then the flesh (20ug/g). The Hg levels in the flesh was less than a fifth of that in bone and about a quarter that in the head, scale and the whole fish.

### 5.1.3 Arsenic levels in Redfish from JT

The same trend was shown in the distribution as for Cd and Hg. The highest occurred in the bone (34.81ug/g) and the lowest in the flesh (6.5ug/g). The As levels in the flesh was about a fifth of that in the bone. The level in the Head was (13.9ug/g) and the scale was (20.47ug/g).

### 5.1.4 Lead levels in Redfish from JT

Lead, like the other metals occurred highest in the bone, head and scale and lowest in the wholefish and flesh. The levels were bone 17.16ug/g, head 16.24ug/g, scale 11.6ug/g and flesh 9.8ug/g. The level in the flesh was about half the amount in the bone.

### 5.1.5 Selenium levels in Redfish from JT

Selenium distribution in the Redfish showed the same trend as the other metals. The Se content in the flesh (22ug/g) was about a third of that in bone (70ug/g) and about half the level in head (52ug/g) and scale (56ug/g).

### 5.1.6 Heavy Metal levels in Redfish from JT

Mercury level was highest in the bone (228ug/g), followed by Selenium (70ug/g), Arsenic (34.81ug/g), Lead (17.16ug/g) and Cadmium as the lowest. Cadmium levels (0.6 - 2.2 ug/g) were negligibly low as compared to Hg (20 - 228ug/g). Selenium levels in the flesh of Redfish was higher than those of the other metals. This implies that Selenium could effectively compete with these element for absorption in the gut and hence may offer some protection against toxicity of these elements if only the flesh of the redfish is consumed. The levels of Selenium in the head was also higher than the levels of Arsenic, Lead and Cadmium in the head of the redfish but not Mercury. The mercury level in the head was about four times the selenium level in the head.

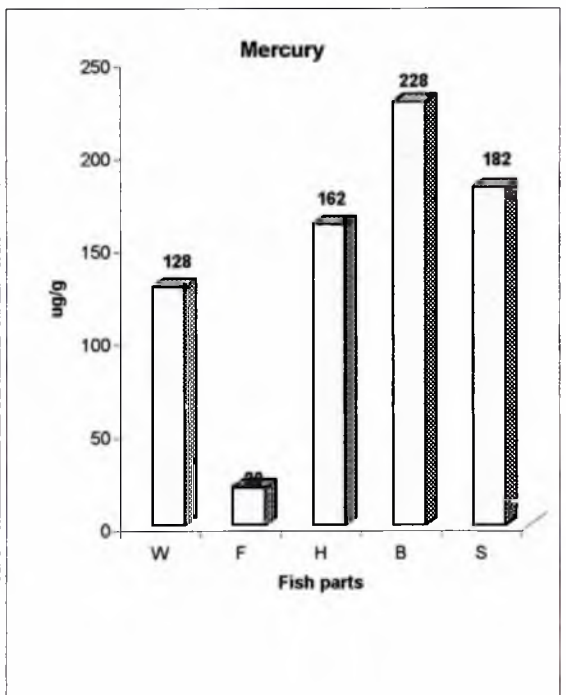
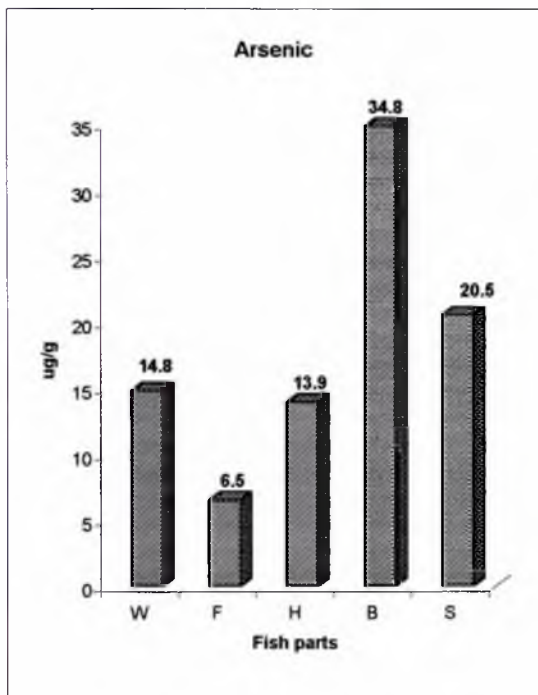
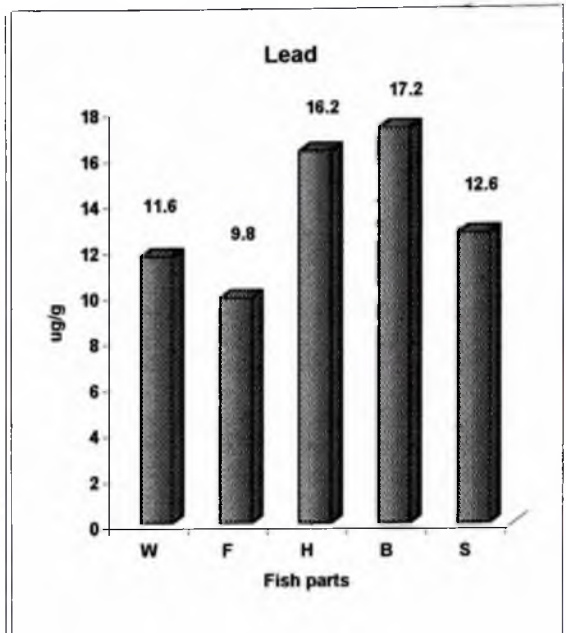
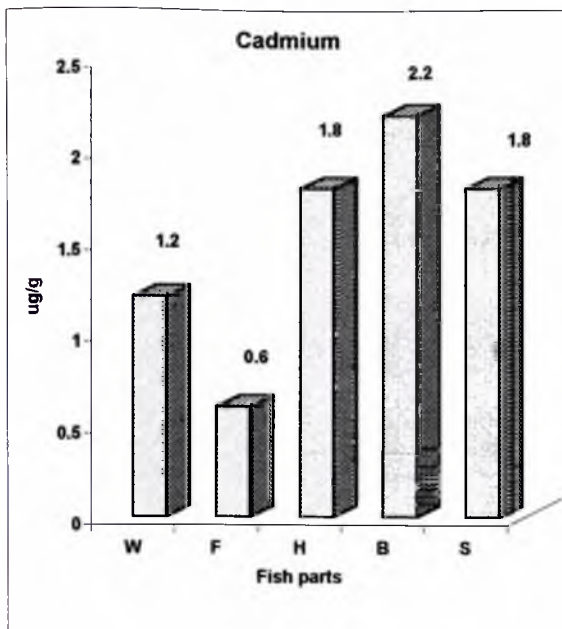
**Fig.1: Distribution of Heavy metal in redfish from James Town. The fish parts are, Wholefish (W), Flesh (F), Head (H), Bone (B) and Scale (S).**

Cadmium (Cd) levels

Lead (Pb) levels

Arsenic (As) Levels

Mercury (Hg) levels



## 5.2 Heavy Metal levels in Herring from JT

For each of the herring parts mercury had the highest levels (220ug/g) followed by arsenic then Se, Pb and finally Cd (Table 4). The Hg levels in the bone (220ug/g), Head (218ug/g) and scale (224ug/g) were virtually the same. The Mercury content in the flesh (70ug/g) was about a third of the levels in the head and bone. Arsenic levels in the flesh (9.3ug/g) was about a quarter of that in the bone (40.47ug/g) and half the level in the head (19.07ug/g). Selenium level in the flesh of the herring was negligible hence may not be able to offer any protective effect against the other heavy metals. The levels in the wholefish, the head, bone, and scale were respectively, 16, 34, 26, and 32ug/g. The selenium levels in the wholefish and the head are higher than the Pb levels in these parts of the fish. The Pb levels in the Wholefish and the head were respectively 9.34 and 10.72ug/g.

## 5.3 Heavy Metal levels in Tuna From JT

The heavy metal distribution in the Tuna fish from James Town (JT) showed the same trend as the distribution in the Redfish from JT. The highest levels occurred in the bone followed by the head with the lowest in the flesh. Selenium level in the bone (20ug/g) was lower than that in the head (32ug/g) and the level in the flesh (14ug/g) was more than half that in the bone but was about half the level in the head.

The Mercury level in the flesh of Tuna was about a quarter that of the bone and about half that of the head. The Arsenic content in the flesh (19.07ug/g) was very close to the level in the head (20.0ug/g). The relatively high level of As in the flesh seemed to have reflected in the level of As content of the wholefish since the flesh forms more than half the weight of the whole fish. Cadmium levels in the Tuna was negligibly small when compared to the Hg content. The Se level in the flesh (14ug/g) was higher than the Cd (0.6ug/g) and Pb (4.28ug/g) levels. But this level is less than half the amount of Hg and also lower than Arsenic level in the flesh. The

Selenium level in the flesh of Tuna can effectively compete with Cd and Lead for absorption and thereby reduce the toxicity of lead and Cadmium but not Mercury and Arsenic. This can only be achieved when more of the flesh is consumed with less consumption of the bone.

#### **5.4.1 Cadmium levels in Redfish, Tuna and Herring from JT**

Cadmium levels in the flesh of all the three fish species from James Town were the same. Thus, the flesh of Redfish, Tuna and Herring contained the same Cd levels of 0.6ug/g dried sample. The wholefish of Redfish and Herring contained the same amount of Cd (1.2ug/g). Similarly the head of Redfish and Herring contained the same levels of Cd (1.8ug/g). Generally, Redfish and Herring contained higher levels of Cd distribution in their body than Tuna. Cadmium level in the bone of Redfish, 2.2ug/g was slightly higher than that in the bone of Herring which was 2.0ug/g. Analysis of variance showed no significant differences ( $p=0.2$ ) in the levels of Cadmium from the various fish sources.

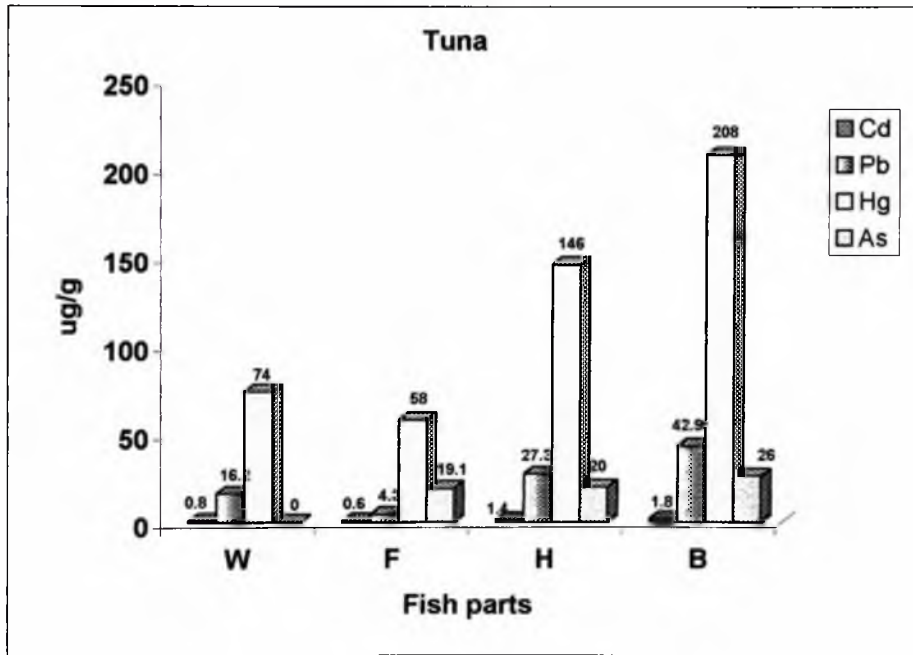
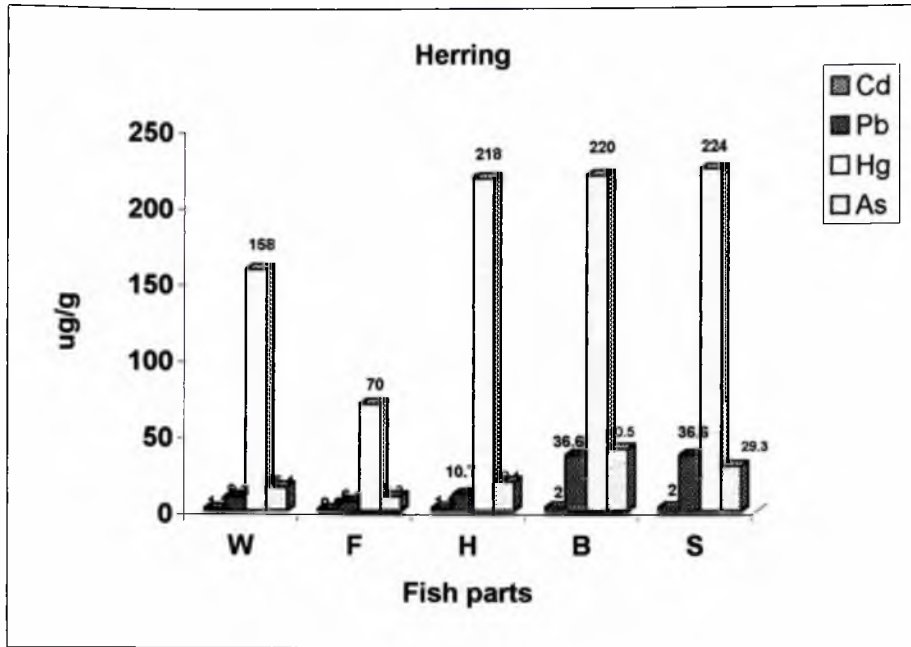
#### **5.4.2 Mercury levels in Redfish, Tuna and Herring from JT**

The flesh of all the fish contained the lowest levels of Hg. The flesh of the Redfish had the lowest amount of 20ug/g. This was less than half the Hg levels in the flesh of Tuna and Herring which had Hg levels of 58 and 70 ug/g respectively. The head and the bone contained the highest levels of Hg. The Herring and Redfish had slightly higher Hg levels than the head and bone of Tuna. The Hg levels in bone of Redfish was slightly higher than that in bone of Tuna and Herring.

**Fig. 20 Heavy metal levels in Tuna and Herring from James Town**

Herring

Tuna



#### **5.4.3 Arsenic levels in Redfish, Tuna and Herring from JT**

The lowest level of arsenic occurred in the flesh just as in the other metals. The flesh of Tuna, Herring, and Redfish contained respectively 19.07ug/g, 9.3ug/g and 6.5ug/g. The level in Redfish was about a third while that of Herring was about half that in Herring. The levels in the bone were Herring (40.47), Tuna (26.0) and Redfish (17.16 ug/g). Thus the levels in Tuna and Redfish were about half that in bone of the Herring. The levels in the head were Tuna 20.0, Herring 19.07 and Redfish 13.9ug/g. The scale of Redfish and Herring contained appreciably high Arsenic contents and this had contributed to the high levels in the wholefish. The levels in the scale were: 20.47 (Redfish) and 29.30ug/g (Herring). The levels in the wholefish were: 14.8 (Redfish) and 15.35 ug/g (Herring).

#### **5.4.4 Selenium levels in Redfish, Tuna and Herring from JT**

Selenium levels were generally low as compared to Hg and As. Among the fishes caught from JT the highest level occurred in the Redfish. The levels were lowest in the flesh. There was no detectable level of Se in the flesh of Herring, but the level in flesh of Tuna was appreciably low when compared to the level in the Redfish. There were relatively high levels in the head and bone in both the Tuna and Herring. The level in the head was higher than that in the bone. This was one of the metals which had higher level in the head than the bone. The Se levels in the head of Tuna and Herring were respectively 32 and 34 ug/g, while the levels in the bone were 20 and 26 ug/g respectively.

#### **5.4.5 Lead levels in Redfish, Tuna and Herring from JT**

The highest level of Pb occurred in the bone of Tuna with a value of 42.92ug/g followed by bone of Herring with a value of 36.0ug/g. The lowest content occurred in the flesh of Tuna, 4.28ug/g followed by the flesh of Herring (6.12ug/g) and then the flesh of redfish (9.8ug/g).

The flesh of Redfish had the highest Pb level among the flesh of the other fish species. The head of Tuna had the highest amount of Pb (27.28ug/g), followed by redfish head (16.24ug/g) and finally the head of herring had Pb content of 10.72ug/g. The scale of herring had the same content of Pb as the bone, but the Pb levels in the scale of Herring (36.6ug/g) was more than twice the level in the scale of redfish (12.56ug/g). The wholefish of Herring had the lowest Pb levels (9.34ug/g), followed by Redfish (11.6ug/g) and lastly Tuna with a value of 16.24ug/g.

#### **5.5.1 Heavy metal levels in Redfish from Tema**

The distribution of Heavy metals in Redfish from Tema showed a similar trend as the Redfish from JT. The flesh contained the lowest levels of all the heavy metals. The head and bone just like the other fish contained the highest levels of the heavy metals. The mercury levels were high as compared to Se, As, Pb and Cd. The Hg level in the flesh was appreciably high when compared to the flesh of other fishes. The level of Hg in the whole fish was greater than the level in the bone. This was not the usual case in the other fishes. This may be due to the high level in the flesh since the flesh makes up more than 50% of the total weight of the whole fish (Fig. 10).

The Arsenic distribution in the redfish from Tema was very unusual in that the levels in the wholefish, flesh and head were comparable with the amount in the flesh slightly higher than the level in the wholefish and the scale. The values were: whole fish 13.49, flesh 14.8, head 15.35, bone 27.91 and scale 12.56ug/g. The Hg levels in the flesh was very high when compared to As and Cd levels. The Hg content in the flesh (74ug/g) was about half the level in the head (170ug/g), bone (134ug/g) and the wholefish (158ug/g). Cadmium levels were comparatively very low as compared to the other metals. The flesh had the lowest content of 0.8ug/g with the highest occurring in the bone (2.2ug/g) and the head (1.6ug/g).

### 5.5.2 Heavy Metal levels in Tuna from Tema

The flesh of Tuna formed more than 60% in weight of the whole fish. The levels of Cd, As and Se were very low when compared to Hg contents. The trend of distribution of heavy metals in the Tuna was similar to those of the other fishes, in which the metals occurred highest in the head and bone. The levels in the bone were appreciably higher than in the head. Mercury levels in the bone and head were respectively 300 and 197 ug/g, while As levels were 23.26 and 19.67 ug/g respectively. The level in the flesh was 4.19 ug/g. The only detectable level of Se occurred in the bone with a value of 52.0ug/g. The Cadmium levels were: flesh 1.4, head 3.0 and bone 2.0ug/g. The level of Hg in the flesh was about half the level in the head (i.e., 98 and 194 ug/g respectively). The levels of Pb ranged between 8.8ug/g in the flesh to 19.0ug/g in the bone. The head had 9.8ug/g. The amount in the bone was about twice the amount in the flesh and head.

The size of tuna obtained from Tema and Elmina were so big that it was not very easy working on the fish as a whole hence only the parts were analysed for heavy metals.

### 5.5.3 Heavy Metal levels in Mackerel from Tema

The distribution of the Heavy metal in the Mackerel conformed to the trend shown by the other fishes from JT and TM. The levels of As in the flesh and wholefish were comparable. The As level in the flesh and whole fish were respectively 9.30 and 9.33ug/g while the levels in the head and bone were 22.33 and 15.35ug/g respectively. The mercury distribution in the Mackerel did not show much variation as the Arsenic. The levels in the head and bone were comparable and the values were 208 and 200 ug/g respectively. Cadmium and Selenium levels in the Mackerel were negligible as compared to Hg levels. The highest occurrence of Se was in the head. The levels in the flesh and Wholefish were undetectable, but the levels in the head and bone were 20 and 8ug/g respectively.

#### 5.5.4 Heavy Metal levels in Herring from Tema

As in the other fishes the bone and head contained the highest levels of the heavy metals, followed by the flesh and the whole fish. In each part of the fish, Hg levels were highest, but the head had slightly higher Hg content than the bone. The levels of the As in both the flesh and wholefish were the same.

The Arsenic levels in the head and bone were respectively 26.98ug/g and 10.23ug/g and the wholefish and flesh had the same levels of 9.3ug/g. The Arsenic level in the head was more than twice the level in bone and the level in the flesh was very close to that in the bone. The mercury levels in the head and bone were 288 and 254ug/g respectively. The Cadmium and Selenium levels were very low as compared to Hg content. Cadmium levels in the wholefish, flesh, head and bone were respectively, 2.6ug/g, 1.6ug/g, 2.8ug/g, and 3.2 ug/g. The Selenium content was detected only in the bone with the value of 12ug/g. Lead levels occurred lowest in the flesh and highest as usual in the bone with values of 6.12 and 15.32ug/g respectively. The content of the whole fish was 7.96ug/g and the head was 9.28ug/g.

#### 5.5.5 Heavy Metal levels in Anchovies from Tema

Anchovies are often eaten whole due to their relatively small size. Therefore the whole fish was analysed without considering its parts. Mercury levels occurred as the highest metal followed by Lead and Arsenic. The lowest occurring metals were Cd and Se. The levels were; Hg, 124 ug/g and As, 12.56 ug/g, while Cd level was 1.4ug/g and Pb 16.24ug/g. Selenium level was below the sensitivity of the method so could not be detected. These levels are higher than those observed in sprats in Norway. The levels in Norwegian sprat are; Arsenic 2.5, Cadmium 0.14, Mercury 1.0 and Lead 0.27 (Kaare *et al*, 1975).

### 5.5.6 Heavy Metals in the flesh of fish from James Town and Tema

In all the fish from the two locations, Hg was the predominantly occurring metal. The flesh of redfish from James Town (JT) had the following levels of the various metals Cd 0.6, As 6.5, Pb 9.8, Se 22 and Hg 20ug/g. Those of Redfish from Tema (TM) are; Cd 0.8, As 14.8, Pb 3.36, Se 8.0 and Hg 74ug/g. The redfish from TM had more than twice the level of Mercury in the flesh than that from JT. Selenium in the flesh of the redfish from JT was also more than three times the level in the flesh of redfish from TM. There were more Pb in the flesh of redfish from JT than the redfish from TM. The Pb level in the flesh from JT was about three times the level in redfish from TM. The Arsenic level in the flesh of TM Redfish was about twice the level in the flesh of redfish from JT.

Herring from JT had the following levels of the various metals; Cd .06, Pb 6.12, As 9.3, and Hg 70ug/g. The levels in herring from TM were: Cd 1.6, As 9.3, Pb 9.28, and Hg 118ug/g. Generally, there were slightly higher levels of the metal in Herring from TM than those from JT. In the flesh of Herring from both locations, no selenium was detected. The Arsenic levels in the Herring from both locations were the same. The mercury level in the flesh of TM herring was about one and a half times the level in the flesh of Herring from JT.

Tuna from JT showed the following levels of the various metals, Cd 0.6, Pb 4.28, Se 14 As 20 and Hg 58.ug/g. For Tuna from TM, the levels are; Cd 1.4, Se 0, As 4.19, Pb 8.88 and Hg 98ug/g. The levels of Cd, Pb, and Hg were higher in the flesh of Tuna from TM than that from JT. But the Tuna from JT had higher levels of Se and As than the flesh of Tuna from TM. No Selenium was detected in the flesh of Tuna from TM. Among the fishes analysed from JT and TM, Mackerel from TM had the highest levels of Cd and Hg in the flesh with values of 1.8 and 154ug/g respectively.

### **5.6.0 Distribution of Heavy Metals in fishes from Light Industrial area, Apam and Elmina.**

Apam and Elmina are both in the Central region of Ghana. They are about 60km apart. Apam is nearer to Accra than Elmina which is also closer to Takoradi another industrial town. The fish samples obtained from these two towns included Mackerel, Herring, *Emule*, Redfish and Tuna. The levels of heavy metals is recorded in Table 5.

#### **5.6.1 Heavy Metal levels in Herring from Apam**

The distribution of heavy metals in the fish showed similar trend as the herring from Heavy industrial areas (e.g. Tema and James Town). Mercury levels were the highest followed by As, Se, Pb and Cd. The levels of Hg in the head, bone and scale were almost the same with slightly higher levels in the scale and head than the bone. The level in the flesh (92ug/g), was about half those in the head (240ug/g), bone (232ug/g), and scale (244ug/g). The level in the wholefish was very high (162ug/g). This was expected considering the levels in the other parts of the fish.

The Arsenic level was highest in the bone (30.7ug/g), followed by the scale (28.37ug/g) and the head (18.6ug/g). Arsenic level in the flesh was lowest (9.3ug/g) and this seemed to have reflected in the relatively low level in the wholefish (14.42ug/g). There was virtually the same level of Se in the head, bone and scale. The levels were 26, 28 and 32ug/g respectively. The flesh had undetectable levels of Se but the level in the whole fish (14ug/g), was more than half the amount in the head. The levels of Pb in the fish ranged from 7.96 to 12.56ug/g. This showed a narrow range as compared to the other metals which ranged between 9.3 and 30.7ug/g. The Pb values were flesh 7.96ug/g, wholefish 8.88ug/g, scale 9.29ug/g, bone 10.72ug/g and head 12.56ug/g. In this, fish the bone had lower Pb levels than the head.

### 5.6.2 Heavy Metals in Mackerel from Apam

The trend of heavy metal distribution in the other fish was also repeated in the Mackerel. The head had the highest level of Hg followed by the bone and the flesh having the lowest level. The mercury levels were head 184ug/g bone, 160ug/g and flesh 68ug/g, but the wholefish had 104 ug/g. Arsenic level was highest in the bone with a value of 35.36ug/g. The level in the head, (15.81ug/g) was about half that in the bone. The level in the whole fish (7.91ug/g) was lower than the value in the head. The level in the flesh 3.26ug/g was appreciably low as compared to the level in the wholefish. Selenium levels in the mackerel were detected only in the head and bone, and the values were 14ug/g in the head and 50ug/g in the bone. Cd levels were even negligibly low as compared to Hg levels. The values were whole fish 1.6, flesh 1.2, head 2.2 and bone 2.2 ug/g. Lead levels were relatively low with the highest occurring in the bone with value 11.64ug/g. The other levels were: head 8.88ug/g, wholefish 6.1ug/g and flesh 2.44ug/g. The selenium level in the head of the fish was more than the Pb level in the head of the fish and also more than twice the level of Pb in the wholefish. The level of selenium in the bone alone was high enough to compete effectively with lead in the fish for absorption in the gut, thereby possibly reducing the toxicity of the lead.

### 5.6.3 Heavy Metal levels in Emule from Apam

Mercury was the highest occurring heavy metal in the *emule* with levels ranging between 68 and 262ug/g. The bone had a value of 262ug/g. The levels in the head and wholefish were 168 and 110ug/g respectively. The level in flesh was 68ug/g. The As levels were slightly higher than the Pb levels. The Arsenic levels ranged from 1.86ug/g in the flesh and 19.53ug/g in the bone. The lead levels ranged between 5.2ug/g in the flesh and 10.72ug/g in the bone. Lead level in the wholefish was 7.04ug/g and that in the head is 8.88ug/g.

Selenium could not be detected in the flesh but levels in head and bone were appreciably high. The levels were, head 14ug/g and bone 40ug/g with wholefish having selenium level of 8.0ug/g.

The Cadmium levels which were very low ranged between 1.0ug/g in flesh and 2.4ug/g in the bone. The levels were; flesh 1.0ug/g, wholefish 1.2ug/g, head 2.0ug/g and bone 2.4ug/g.

#### **5.6.4 Heavy Metal levels in Redfish from Elmina**

Mercury occurred as the highest heavy metal in this fish with values ranging from 144ug/g in the flesh to 288ug/g in the bone. Apart from the flesh, all the other parts of the fish had Hg levels above 200ug/g. The levels were: flesh 144ug/g, wholefish 222ug/g, head 256ug/g and scale 266ug/g. Arsenic was the next highest occurring metal in the fish with levels ranging from 10.12ug/g in the flesh to wholefish and 29.92ug/g in the bone. The levels in the flesh and scale (11.0ug/g) were comparable while the levels in the head (29.48ug/g) and bone (29.92ug/g) were also comparable. The levels of Pb ranged from 7.04ug/g in the flesh to 16.24ug/g in scale. The levels in the wholefish was 7.96ug/g, head 16.22ug/g, bone and 9.28ug/g. The levels in the flesh and wholefish were close.

Selenium was detected only in the bone and scale. The values were bone 18ug/g and scale 10ug/g. The same levels of Cd were observed in the head, bone and scale with a value of 1.6ug/g, while the levels in the wholefish and the flesh were 1.2 and 0.6 ug/g respectively. The level of Cd in the flesh was half the level in the wholefish and about a third the level in the head, bone and scale.

#### **5.6.5 Heavy Metal levels in Tuna from Elmina**

In this fish also, mercury occurred as the highest element with values ranging from 50 and 100ug/g. The level in the flesh was 50ug/g. The level in the bone was 75ug/g, while the level in the head was 100ug/g. Thus the head had the highest level of the metal. Arsenic levels ranged between 19.8 and 25.96, showing a narrow range of distribution. The highest occurred as 25.96 and closely followed by head with the value 24.2ug/g. The level in flesh was 19.8, which was appreciably high when compared to other fishes. The lead levels ranged from 5.2 to

35.56ug/g. The level in the flesh was 5.2ug/g and the head was 16.24, while the bone was 35.56ug/g. The level in the bone was more than twice the level in the head and about seven times the amount in the flesh. The Cd levels were flesh 0.6, head 1.0 and bone 1.6ug/g.

#### **5.6.6 Heavy Metal levels in Herring from Elmina**

Cadmium levels occurred as the lowest heavy metal. The values ranged from 1.2ug/g in the flesh to 2.0 ug/g in the bone. The level in the head and whole were respectively 1.6 and 1.2ug/g. The level of Arsenic occurred highest in the bone with the value of 36.96 and lowest in the wholefish with a value of 8.36ug/g. The level in the head was 26.84 and the flesh was 11.0ug/g. The amount in the bone was about four times the amount in the flesh. The level in the flesh was higher than in the whole fish. The Pb levels were as follows; flesh 14.4, wholefish 19.0, head 23.6 and bone 28.2ug/g. The range was 14.4 to 28.2ug/g. This showed a narrow range when compared to the distribution of Arsenic in the same fish. For Arsenic the range was 8.36 to 36.96. Mercury was the highest occurring heavy metal in this fish just as in the other fishes. The levels ranged from 25ug/g in the flesh to 150ug/g in the head. The values for the bone and wholefish were 125 and 50ug/g respectively.

#### **5.6.7 Heavy Metal levels in Herring from Elmina and Apam**

Cadmium levels in Herring from Apam were generally higher than that in Herring from Elmina. But the levels in the flesh from both towns were the same with a value of 1.2ug/g. The Arsenic levels ranged between 9.3ug/g and 30.7ug/g in the fish from Apam but ranged between 8.36ug/g and 36.96ug/g in the fish from Elmina. Thus the fish from Apam had a higher As level in the flesh than the fish from Elmina but had lower level of Arsenic in the bone than herring from Elmina. The Pb levels ranged from 7.96ug/g to 12.56ug/g in Herring from Apam while that for Herring from Elmina ranged from 14.4 to 28.2ug/g. Thus the level of Pb in the flesh of Herring from Elmina was higher than the level in the bone of the Herring from Apam.

### **5.7.0 Distribution of Heavy Metals in fishes from Fresh water, River and Lake - (Weija, Kpong)**

The Weija lake is a fresh water body and it is about 10km away from Accra an industrial town. It is less than 8km from the Tetegu beach in the western part of Accra. Tilapia is the major fish in the lake. The distribution of the heavy metals in the fish conformed to the trend in the other fish samples analysed. The highest levels occurring in the bone, head and scale.

Kpong is more than 60km from Tema industrial town. The only industrial activity at Kpong is a hydroelectric dam. The dam serves as source of various species of fish. Tilapia, *blolo*, catfish etc. were analysed for their heavy metal contents. The levels of the heavy metals are recorded in Table 6. The sizes of anchovies and one-mouth-thousand fish were so small that they are almost always eaten whole without dismembering them therefore they were analysed as whole fish only.

#### **5.7.1 Heavy metal levels in Tilapia from Weija**

The levels of Cd ranged from 0.4 to 1.8ug/g. The level in the flesh was 0.4ug/g, the wholefish was 0.8ug/g, and the head and scale was 1.0ug/g and in the bone it was 1.8ug/g. The level in the flesh was about a quarter of the level in the bone but a half in the wholefish. Selenium was detected only in the head, bone and the scale with levels as 14, 42, and 10ug/g respectively.

Mercury levels ranged from 50ug/g in the flesh to 210ug/g in the bone. The level in the wholefish was 146ug/g, in the head it was 132ug/g and the scale the value is 122ug/g. The high level in the bone has raised the level in the wholefish to about three times the level in the flesh. Arsenic levels also ranged from 9.7ug/g in the flesh to 21.86ug/g in the bone. The level in the wholefish was 11.63ug/g, with the head and scale having the same value of 19.53ug/g. The lead levels occurred lowest in the flesh as in most of the fishes with the value of 12.56ug/g, while the highest level was observed in the bone with a value of 39.24ug/g. The highest level in the bone was about three times the level in the flesh. The levels in the whole fish was 17.16 and the head

was 22.68ug/g with the scale having a value of 37.4 ug/g. Arsenic showed a wider range of distribution in the fish as compared to the lead level in the same fish.

### **5.7.2 Heavy metal levels in *Tilapia* from Kpong**

The distribution of Cadmium in the fish was flesh 0.7, head 1.4, bone 1.1, scale 0.7 and wholefish 0.9ug/g. The level in the head was slightly higher than the level in the bone. The flesh and the scale had the same level of Cadmium. Mercury level ranged from 50ug/g in the flesh to 200ug/g in the bone. The contents of the head, scale and whole fish were 125, and 100ug/g respectively. The Arsenic level in the *Tilapia* ranged from 4.84ug/g in the flesh to 22.88 ug/g in the bone. The level in the head was 10.12ug/g, scale 15.88ug/g and the wholefish was 12.32ug/g. The level in the flesh was about a third of the level in the wholefish but about a fifth the level in the bone. Lead levels occurred lowest in the flesh with a value of 3.36ug/g followed by the wholefish with a value of 7.96ug/g. The head and the scale had the same amount of lead with a value of 9.28ug/g. The bone contained 11.64ug/g of the lead.

### **5.7.3 Heavy metal levels in *Blole* from Weija**

Cadmium levels in this fish occurred highest in the head, instead of the bone as in the case of most of the fishes analysed, and with a value of 1.6ug/g. The flesh and wholefish had the same level of Cadmium with a value of 0.8ug/g. The level in the bone was 1.4ug/g. The level in the flesh was half of the amount in the head.

Mercury levels ranged from 50 to 100ug/g. The flesh and wholefish had the same level of 50ug/g. The bone had the same level as the head with a value of 100ug/g. The levels in the flesh and the wholefish were about half of the levels in the head and bone. Arsenic levels in the *Blole* fish were: flesh 6.16ug/g, wholefish 7.92ug/g, head 13.64ug/g and bone 25.96ug/g. The level in flesh was about a quarter the amount in the bone. The Lead levels ranged from 22.68 in the flesh to 28.2ug/g in the bone and head. The level in the wholefish was 24.52ug/g. There was a narrow

range in the distribution showing nearly even distribution of the lead in this fish. The fish had the highest lead level in the flesh among all the fish samples analysed.

#### **5.7.4 Heavy metal levels in Catfish from Kpong**

In the catfish the heavy metal levels ranges were: Cd 0.4 to 1.2ug/g, As 4.4 to 6.52ug/g, Pb 7.96 to 12.56ug/g, while Hg levels ranged from 50 to 125ug/g. The distribution of Cadmium were: flesh 0.4ug/g, head and bone 1.2ug/g. The distribution of As was: flesh 4.4ug/g, head 26.52ug/g and bone 13.64ug/g. The level in the head was about twice the level in the bone. The distribution of the Pb was, flesh 7.96ug/g, head 12.56ug/g and bone 125 ug/g. The levels of mercury were: flesh 20ug/g, head 75ug/g and bone 125ug/g. The level in the bone was more than double the level in the flesh.

#### **5.7.5 Heavy metal levels in 'One-Mouth-Thousand' (*Sierrathrissa leonensis*) from Kpong**

One-mouth-thousand is a tiny fish having a length not more than 4cm which is often fried. It is a delicacy along the Volta lake. Its consumption is gaining ground as one can see some in big towns like Accra being eaten with *abolo* a traditional fermented maize flour product. Several of it is taken at a time to fill the mouth hence the local name one-mouth-thousand (about 50 pieces weigh 10g). Since it is taken whole, analysis was done only on the wholefish. The level of the various heavy metal were: Cd 0.6ug/g, Pb 20.24ug/g, As 24.24ug/g and Mercury 125ug/g. The Pb and As level were very close but were relatively high as compared to the levels in the other fishes.

### **5.8.0 Distribution of Heavy metals in fishes from Mining Environment, Obuasi and Dunkwa**

Obuasi is a mining town with very little fishing activities except for few people who have fishponds. Tilapia from one of such fishponds was analysed. There is a stream that runs through the town called *Nyam*. No fish was obtained at the time of the visit but the water sample was analysed for heavy metals. Dunkwa is also a mining town. The river Ofin runs through the town and the waste from the mining activity flows into the river. The river is a major source of fish for the people. Some of the fish caught in the river were Tilapia, Catfish and Blolo. Samples of these fishes and the water were analysed for heavy metals. The contents of the heavy metals in the fish are shown in Table 7 below.

#### **5.8.1 Heavy metal levels in Tilapia from Obuasi**

The ranges of heavy metal level in the Tilapia from the fishpond were as follows; Cd from 0.6 to 1.8ug/g and Arsenic from 18.48 to 25.96ug/g. Lead levels fell between 5.2 and 20.84ug/g, while mercury level ranged from 50 to 150ug/g. For Cadmium, the distribution was; flesh 0.6ug/g, head 1.7ug/g and bone 1.8ug/g. The level in the bone was about three times the level in the flesh. The level in the head and bone were very close. The Pb distribution was; flesh 5.2ug/g, head 20.84ug/g and bone 15.32ug/g. The level in the head was clearly higher than the level in the bone. Arsenic levels were 18.48ug/g in the flesh, 25.52ug/g in the head and the bone 25.96ug/g. The head and bone had nearly the same levels of Arsenic. Mercury level in the flesh was 50ug/g and in the head and bone the value was 150ug/g. In this fish the heavy metals in the head and bone were very close.

#### **5.8.2. Heavy metal levels in Tilapia from Dunkwa**

The ranges of the various metals in the Tilapia were: Cd 0.6 to 1.4ug/g, As 6.16 to 33.88ug/g, Pb 6.12 to 26.24 and Hg 75 to 200ug/g. The distribution of Cadmium was; flesh 0.6ug/g, head

10.ug/g, wholefish 1.3ug/g, bone 1.4ug/g and scale 1.1ug/g. The distribution of As was: flesh 6.16, head 19.8, wholefish 28.16ug/g scale 17.6ug/g and bone 33.88ug/g. The lead levels were: flesh 6.12ug/g, wholefish 7.04ug/g, head 26.36ug/g and bone 39.24ug/g with scale having a value of 15.29ug/g.

Mercury distribution was: flesh 75ug/g, bone 200ug/g and scale 100ug/g. Apart from the Pb levels in which the level in the head was far higher than the level in the wholefish, all the other metals had the same or more levels in the wholefish than the head. The levels of Cd and Hg in the flesh were about half the level in the bone, but for As and Pb the levels were about a quarter the level in the bone.

### **5.8.3 Comparison of Heavy metal levels in Tilapia from Dunkwa and Obuasi**

The flesh of Tilapia from both Dunkwa and Obuasi had the same level of Cadmium with a value of 0.6ug/g but the bone and head of Tilapia from Obuasi had higher Cd levels than the Dunkwa Tilapia. The level of mercury in the flesh of Dunkwa Tilapia was higher than the level in the Obuasi Tilapia. The Dunkwa Tilapia had higher Hg in the bone (175ug/g) than the Obuasi Tilapia (150ug/g).

There was a narrow range of distribution of the As in the Obuasi Tilapia than the Dunkwa Tilapia. The flesh of Obuasi Tilapia had 18.48ug/g and the bone had 25.96ug/g of As while that for Dunkwa Tilapia was 4.84ug/g and 22.88ug/g respectively. There was also a wide difference between the level of As in the head of the fishes from the two locations. Obuasi Tilapia had 25.52ug/g while Dunkwa Tilapia had 10.12ug/g. The levels of As in the head and bone of the Obuasi Tilapia were virtually the same but in the Dunkwa Tilapia the difference between the head and bone was larger. Lead levels ranged from 5.2 to 20.84ug/g for Obuasi Tilapia and for Dunkwa Tilapia it was between 6.12 and 39.24ug/g. The range was wider for the Dunkwa Tilapia than the Obuasi Tilapia.

#### **5.8.4 Heavy metal levels in Catfish from Dunkwa**

The distribution of the Cd in the fish were, flesh 0.3, head 0.9, and bone 1.2ug/g. The levels in the flesh is about a quarter the level in the bone. The Arsenic levels were; flesh 1.32, head 19.8 and bone 15.72ug/g. Lead levels were: flesh 7.96, head 25.12 and bone 17.16ug/g. Mercury levels were: flesh 50, head 100ug/g and bone 175 ug/g. The As and Pb levels in the head were higher than the levels in the bone.

#### **5.8.5 Heavy metal levels in Blolo from Dunkwa**

The Cadmium levels ranged from 1.0ug/g in the flesh to 1.5ug/g in the bone. The level in the head was 1.3ug/g. The Arsenic levels ranged from 5.72.ug/g in the flesh to 18.48 in the bone. The level in the head was 14.08 ug/g. The level in the bone was about three times the level in the flesh. Lead levels ranged from 9.28ug/g in the flesh to 16.24ug/g in the bone with the level in the head being 11.24ug/g. In this fish the level in the bone was about twice the level in the flesh. Mercury levels were flesh 50, head 90 and bone 250ug/g. The mercury level in the bone was about five times the level in the flesh.

## **5.9.0 COMPARISON OF HEAVY METALS IN FISH FROM THE FOUR ENVIRONMENTAL ZONES**

The heavy industrial locations were Tema and James Town (Accra), while the light industrial locations from which fish was sampled were Apam and Elmina. The fish sampled from the heavy industrial and light industrial zones included Redfish, Tuna, Herring, Mackerel, Anchovies and *Emule*. Analysis of variance was done on all the samples at  $\alpha = 0.05$ . The mean levels of the heavy metals in the flesh are shown in Table 8.

### **5.9.1: MARINE FISH FROM HEAVY INDUSTRIAL (HI) AND LIGHT INDUSTRIAL (LI) ZONES.**

#### **5.9.1.1 REDFISH**

For the Redfish there was a significant difference in the distribution of the Cadmium in the parts of the fish ( $P = 0.003$ ). Though there were higher levels of Cd in the Redfish from heavy industrial areas than the redfish from light industrial areas these levels were not significantly different ( $P = 0.07$ ). Similarly analysis of variance revealed no significant difference ( $P = 0.9$ ) in the levels of Arsenic in the redfish from heavy industrial and light industrial areas, but there was a significant difference ( $P = 0.01$ ) in the distribution of the Arsenic in the fish parts. There was also no significant difference ( $P = 0.09$ ) in the levels of Lead in the redfish from both environmental areas.

The level of Mercury in the redfish from Elmina, a light industrial town, was higher in all the parts of the fish than in the redfish from Tema and James Town, a heavy industrial towns. This higher levels were significantly different ( $P = 0.001$ ) from the levels in the redfish from the heavy industrial areas. The levels of the various metals range from 0.6 to 2.2  $\mu\text{g/g}$  for Cadmium, 3.36 to 19.0  $\mu\text{g/g}$  for Pb, 6.3 to 34.8  $\mu\text{g/g}$  for Arsenic and 20. to 288  $\mu\text{g/g}$  for Mercury. These ranges are over and above the values reported for the Norwegian redfish. The values from the Norwegian redfish are; Cd 0.38 $\mu\text{g/g}$ , Hg 0.05 $\mu\text{g/g}$ , Pb 1.6 As 9.04 $\mu\text{g/g}$ , (Kaare and Olnf, 1975)

### 5.9.1.2 TUNA

There was no significant difference ( $P= 0.3$ ) in the contents of Cadmium in the Tuna from both heavy industrial and light industrial areas. Mercury levels also did not show any significant difference ( $P=0.80$ ) in its occurrence in the Tuna fish from both environmental areas. The observed differences in the levels of Arsenic in Tuna fish from the two environmental areas were not significant ( $P=0.19$ ). There was no significant difference ( $P=0.09$ ) in the distribution of Arsenic in the Tuna parts. Though there was a significant difference in the distribution of the lead levels in the Tuna fish parts ( $p-0.3$ ), the difference in the occurrence of Lead in the Tuna from heavy industrial and light industrial areas was not significant ( $P=0.09$ ). (See Figure 3 for graph of heavy metal content of the Tuna fish).

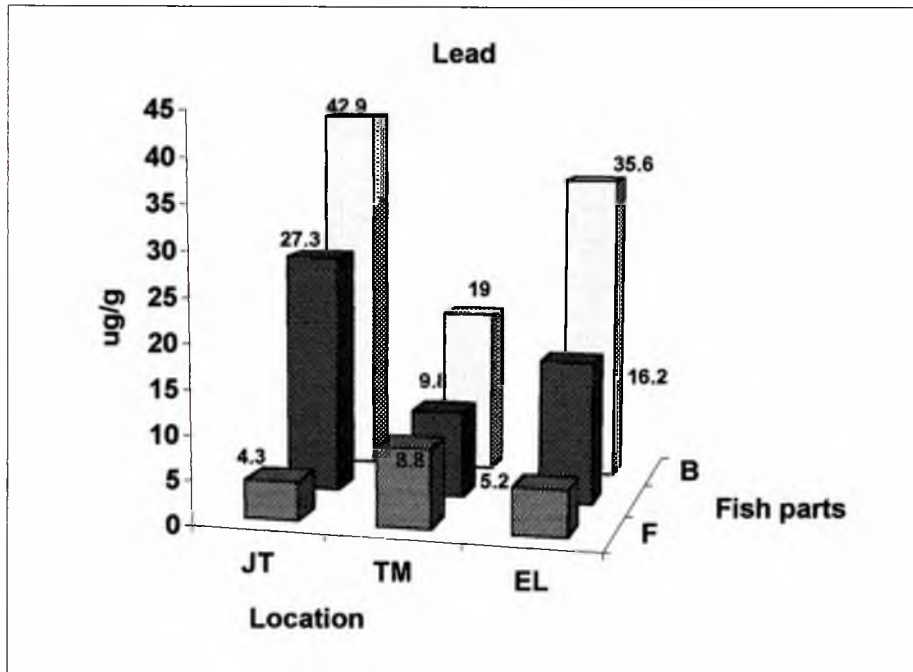
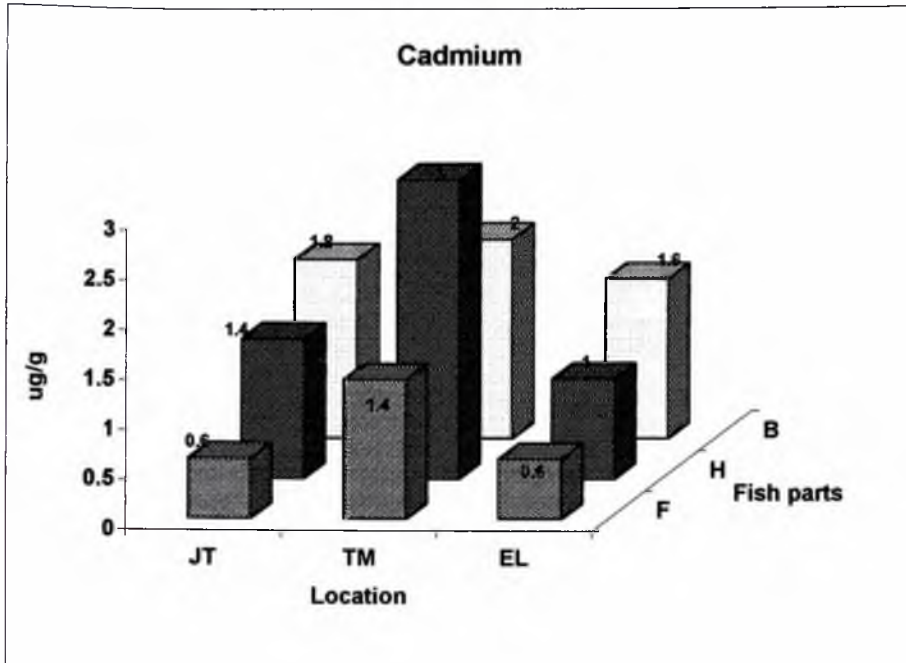
**Fig. 2: Heavy metal distribution in Tuna fish from James Town (JT), Tema (TM) and Elmina (EL) .the fish parts are flesh (F) head (H), and bone (B)**

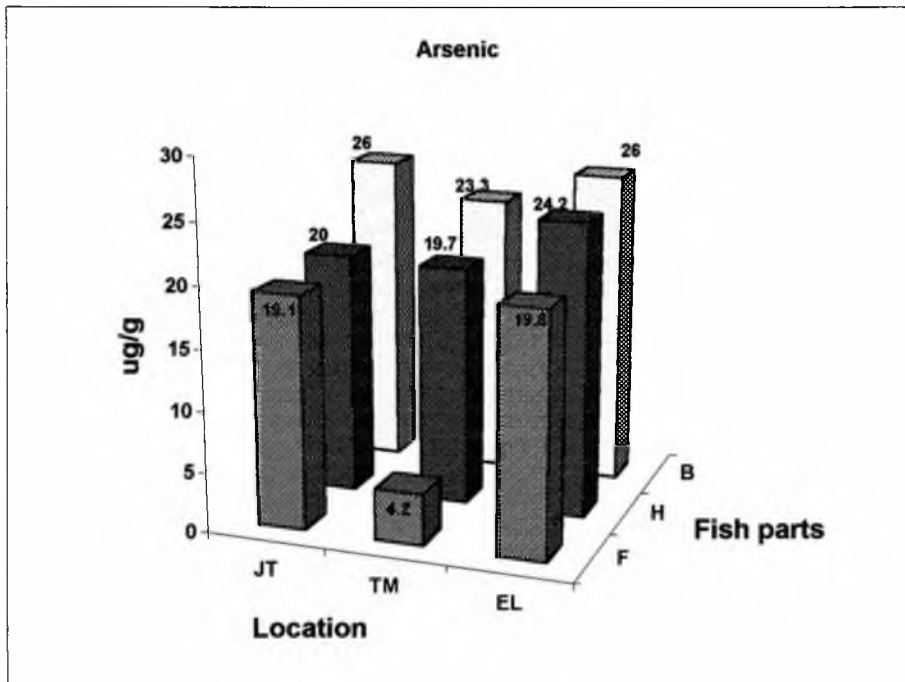
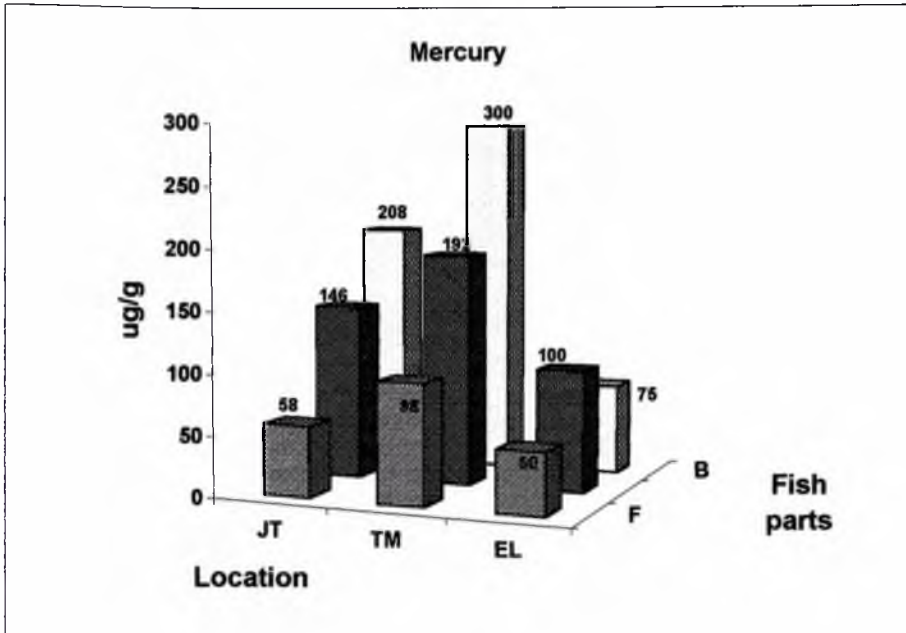
Cadmium (Cd) levels

Arsenic (As) levels

Lead (Pb) levels

Mercury (Hg) levels





### 5.9.1.3 HERRING

There was no significant difference ( $P=0.12$ ) in levels of Cadmium in the Herring from both heavy industrial and light industrial areas. Arsenic levels in the herring from heavy industrial and light industrial also showed no significant difference ( $P=0.4$ ). There was however a significant difference ( $P=0.02$ ) in the level of Mercury in the Herring from both heavy industrial and light industrial areas with the herring from heavy industrial having higher levels. The Lead levels showed no significant differences ( $P=0.9$ ) in the Herring from both environmental areas. The Arsenic in herring from the four locations ranged between 9.3 to 36.6 ug/g. The value is higher than those reported in Norway as 9.4ug/g (Kaare *et al* , 1975).

### 5.9.1.4 MACKEREL

Cadmium levels in the mackerel from both environmental areas showed no significant difference ( $P=0.07$ ). Similarly the Arsenic levels also showed no significant difference ( $P=0.8$ ). The observed differences in the Hg levels in this fish was significant ( $P= 0.008$ ), with the levels in the heavy industrial higher than the levels in the Mackerel from light industrial areas (Fig. 3). The Arsenic level in mackerel range between 9.3 and 35.56ug/g. The value for Cd, Hg and Pb reported in Norwegian Mackerel were respectively 0.026, 0.26, and 0.1ug/g (Kaare *et al* , 1975).

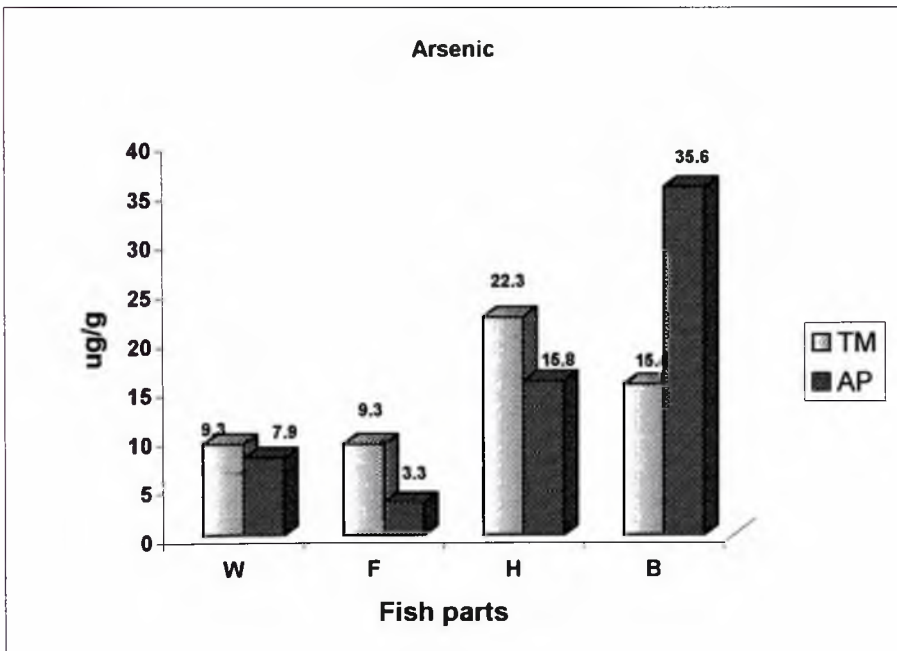
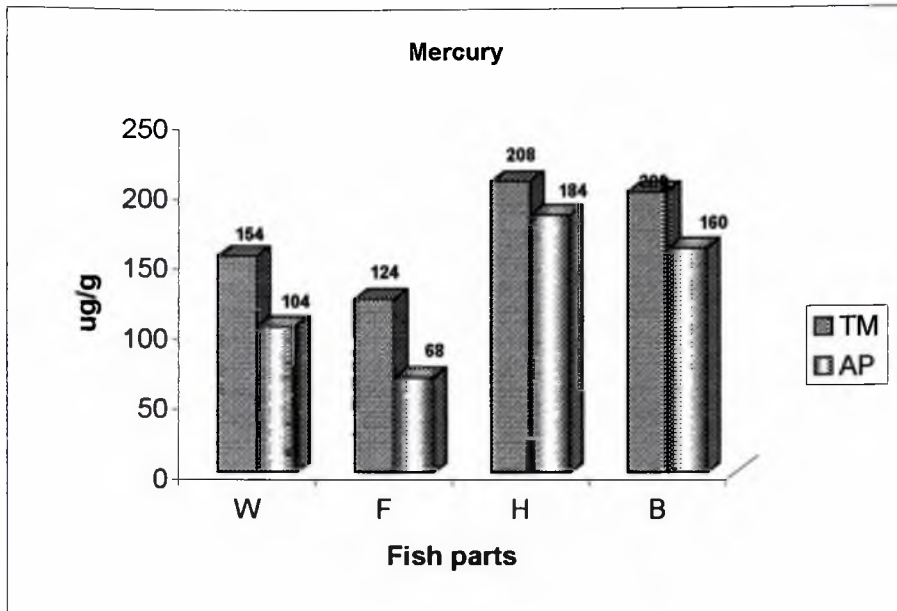
**Fig. 3 Heavy metal levels in Mackerel from Tema and Apam**

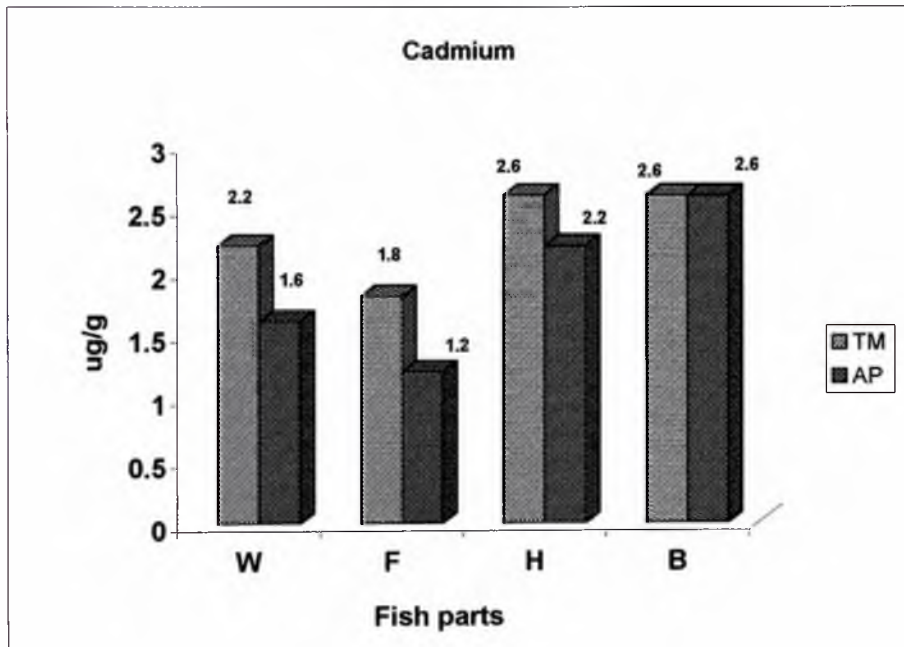
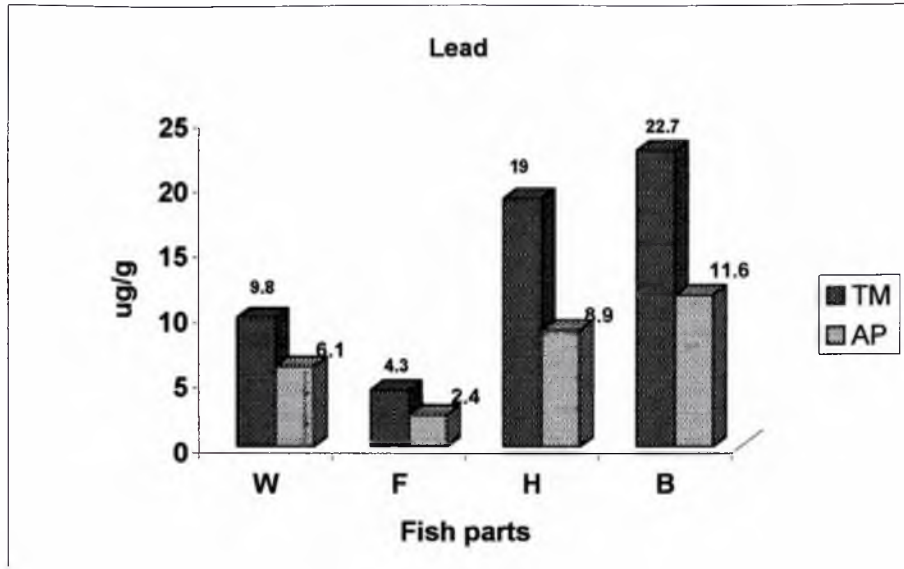
Hg levels

As levels

Pb levels

Cd levels



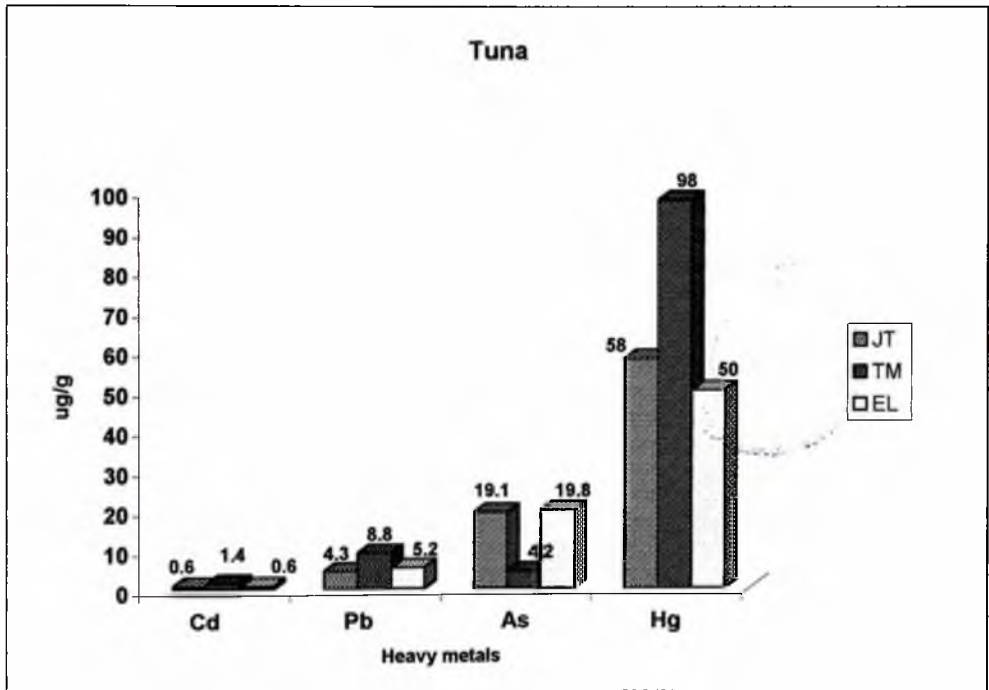
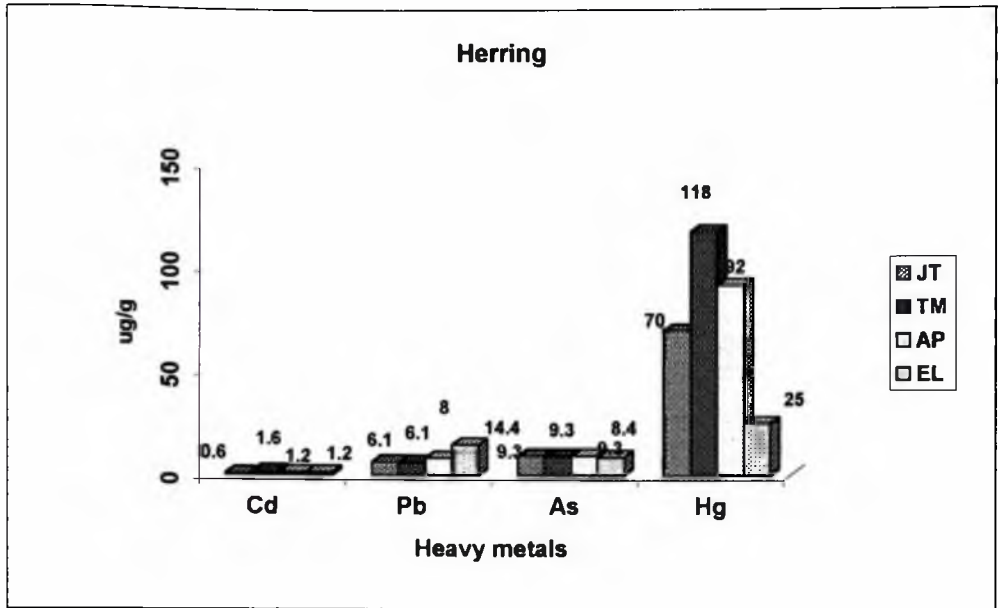


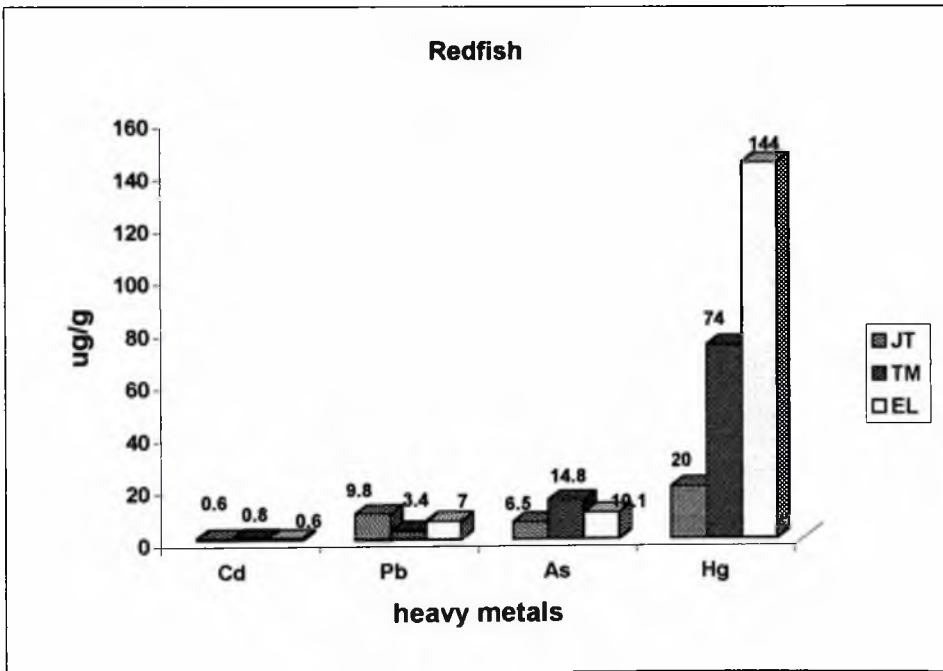
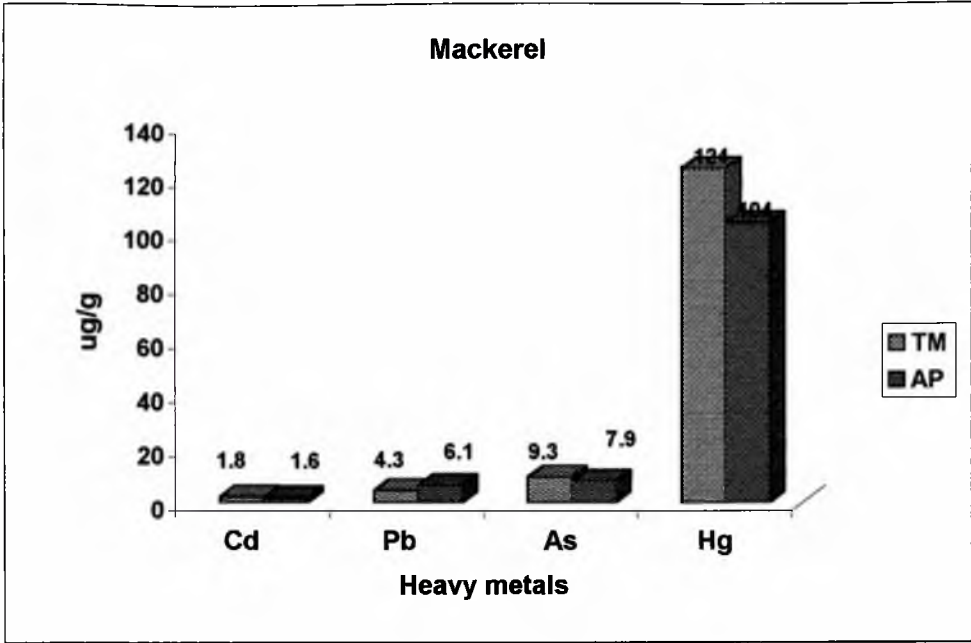
**Fig 4: Comparison of heavy metals of flesh of the fishes from marine sources: JamesTown (JT) Tema, (TM) Apam(AP) and Elmina (EL).**

Herring

Tuna

Mackerel





## **5.9.2 FISH CAUGHT IN FRESH WATER FROM MINING ENVIRONMENT (ME) AND NON-MINING ENVIRONMENT, RIVER/ LAKE (RL).**

The mining towns were Obuasi and Dunkwa and the non-mining towns were Weija and Kpong. The fish sampled from these waters were Tilapia, Blolo, Catfish and One-Mouth-Thousand.

### **5.9.2.1 TILAPIA**

There was not much variation in the levels of Cd in the fishes. In the head and bone of the fish from Obuasi the Cd levels were slightly higher. Weija and Obuasi fish had similar Cd levels in their bones. There was no significant difference ( $P=0.8$ ) in the distribution of Cd in the fish from these four towns. The Tilapia from Obuasi and Dunkwa had slightly higher levels of Arsenic than those from Weija and Kpong. However this observed difference was not significant ( $P=0.43$ ). There were also no significant difference ( $P= 0.09$ ) in the distribution of Arsenic in the fish parts.

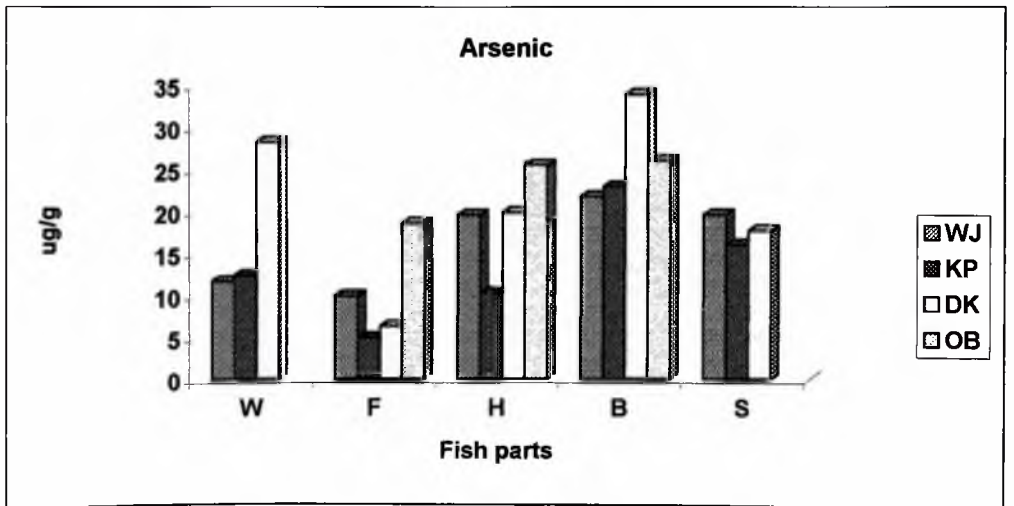
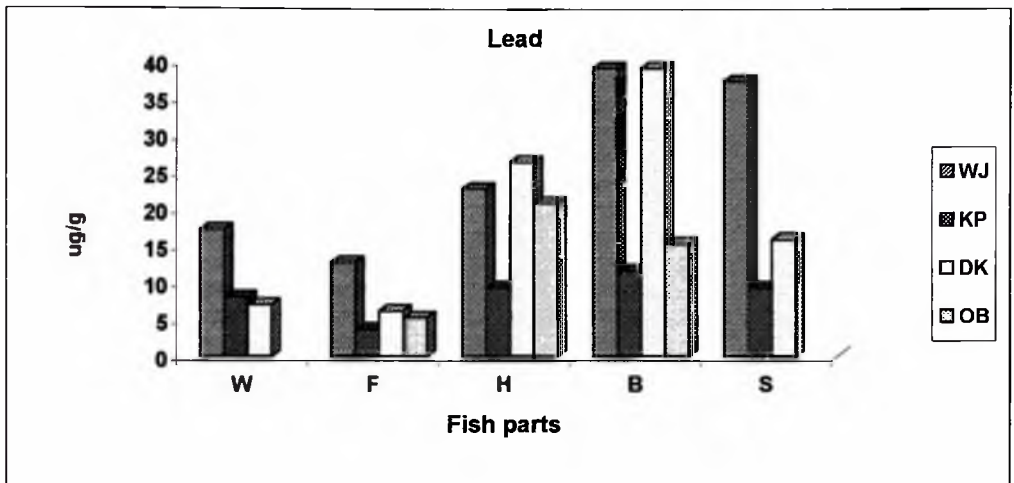
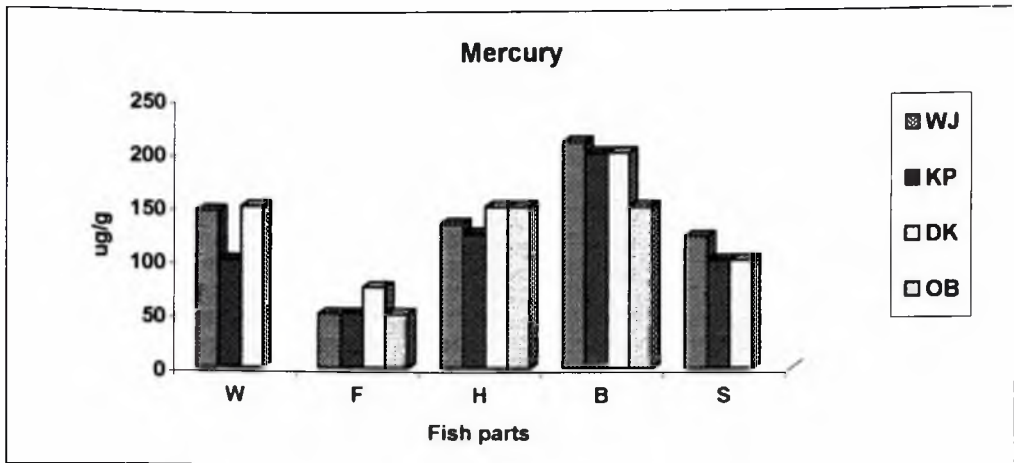
Lead distribution in the Tilapia from the four locations showed higher levels in the bone for the Weija and Kpong fishes than that for Obuasi and Dunkwa fish. The differences in the levels of the Pb in the fish parts were significant ( $P=0.01$ ). The level of lead in the Tilapia from the mining environment and the River/Lake was significantly different ( $P=0.007$ ). The level of mercury in the Tilapia showed significant difference in their distribution within the fish ( $P=0.001$ ). There was also a significant difference ( $P=0.03$ ) in the occurrence of mercury in the Tilapia from the various areas. The level in Weija and Dunkwa Tilapia was higher than the level in the Obuasi Tilapia.

**Fig. 5 Heavy metal levels in Tilapia from Weija (WJ), Kpong (KP), Dunkwa (DK) and Obuasi (OB) . The fish parts are wholefish (W), flesh (F), head (H), bone (B) and scale (S)**

Hg levels

Pb levels

As levels



### 5.9.2.2 BLOLO

The observed differences in the levels of Hg in the fishes from both environmental areas were not significant ( $P=0.4$ ). Arsenic levels also showed no significant differences ( $P=0.42$ ) in its levels from both environmental areas. The distribution of the Arsenic in the fish parts also showed no significant difference ( $P=0.4$ ). Lead occurrence in the Blolo fish from the various environmental areas showed significant difference ( $P=0.009$ ), with the fish from non-mining areas having higher values. Cadmium levels in the fish from the mining area showed no significant difference ( $P=0.59$ ) from the fish from non-mining areas. Similarly the mercury level in the Blolo from mining areas showed no significant difference ( $P=0.4$ ) from those from the non-mining area.

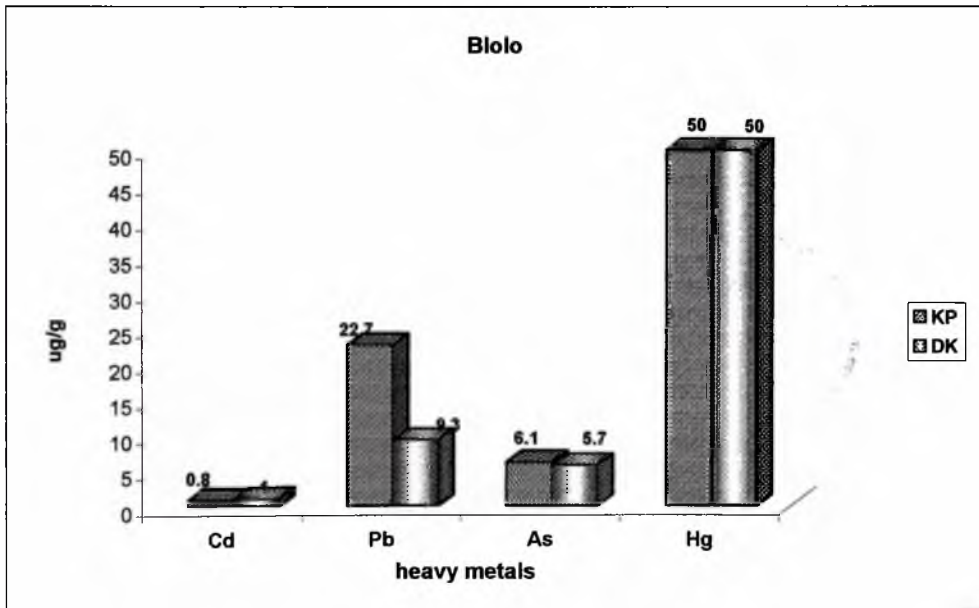
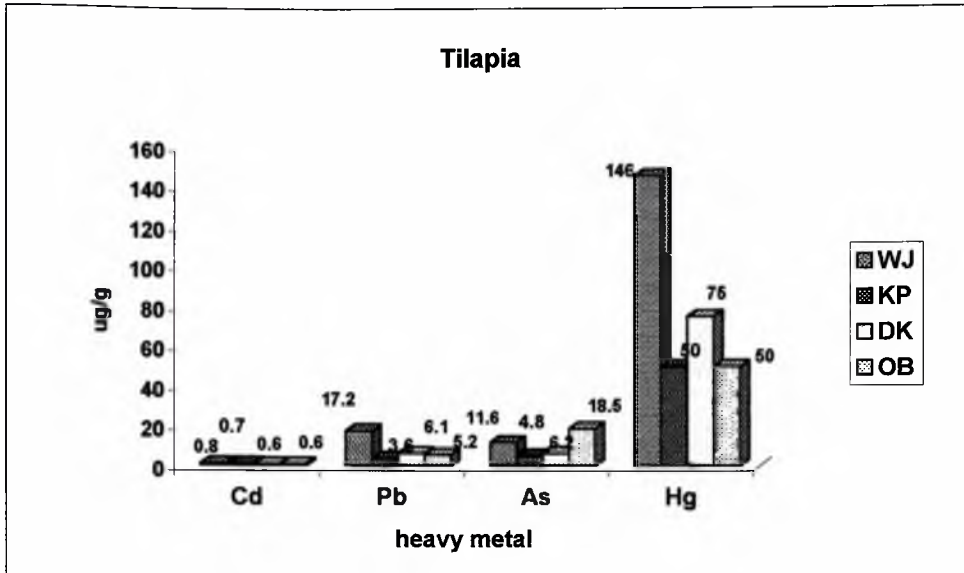
### 5.9.2.3 CATFISH

The level of Lead in the Catfish from mining environment was not significantly different ( $P=0.5$ ) from that from non-mining area. Similarly the occurrence of Arsenic showed no significant difference ( $P=0.06$ ) in the Catfish from mining and non-mining areas. Mercury levels also showed no significant difference ( $P=0.2$ ) in its occurrence in the catfish from the two environmental area. The observed differences in the occurrence of Cadmium in the Catfish from the two environmental areas were not significant ( $P=0.26$ ).

**Fig.6: Comparison of heavy metal levels in flesh of various fish samples from Weija (WJ), Kpong (KP) and Dunkwa (DK)**

Tilapia

Blolo



### 5.10.1 Heavy metal levels in fish oils

The fishes from which oil was extracted were Herring from James Town (JT), Mackerel from Tema (TM), Tuna from TM and Tilapia from Weija (WJ). The metal levels are shown in Table 8.

Mercury occurred as the highest metal, with cadmium as the lowest, just as in the other parts of the fish. Lead and Arsenic levels in the oils were comparable. Herring oil had the highest level of mercury (75ug/ml) and its value was about three times the levels in Tuna and Tilapia (25ug/ml). The mercury level in the Mackerel oil was lower than the sensitivity level of the method so could not be detected.

Cadmium levels ranged between 0.35 to 0.70ug/ml. Herring had the highest content with 0.70ug/ml, followed by Tilapia with 0.50ug/ml, and then Tilapia having 0.40ug/ml and finally Tuna with 0.35ug/ml. Arsenic levels detected in Herring and Mackerel oils were 15.4ug/ml for Herring and 28.6ug/ml for mackerel. Lead was detected in all four oils with the highest occurring in Mackerel and lowest in Tuna. The levels were Mackerel 35.56ug/ml, Herring 10.72ug/ml, Tilapia 9.28 ug/ml and Tuna 6.12ug/ml.

The levels of these metals in the oils extracted from the fishes can be considered appreciable when compared to their levels in parts of the fishes. For example the metal levels in the flesh of the Herring fish from JT were, Cd 0.6ug/g, Hg 70ug/g, As 9.3ug/g and Pb 6.12ug/g and the corresponding levels in the oil from the same fish were, Cd 0.7ug/ml, Hg 75ug/ml, As 5.4ug/ml and Pb 10.72ug/ml. Lead and mercury levels were highest in the oils extracted possibly due to the ability for the Mercury and Lead to be methylated into tetramethyl lead and methyl mercury (Imura *et al*, 1972).

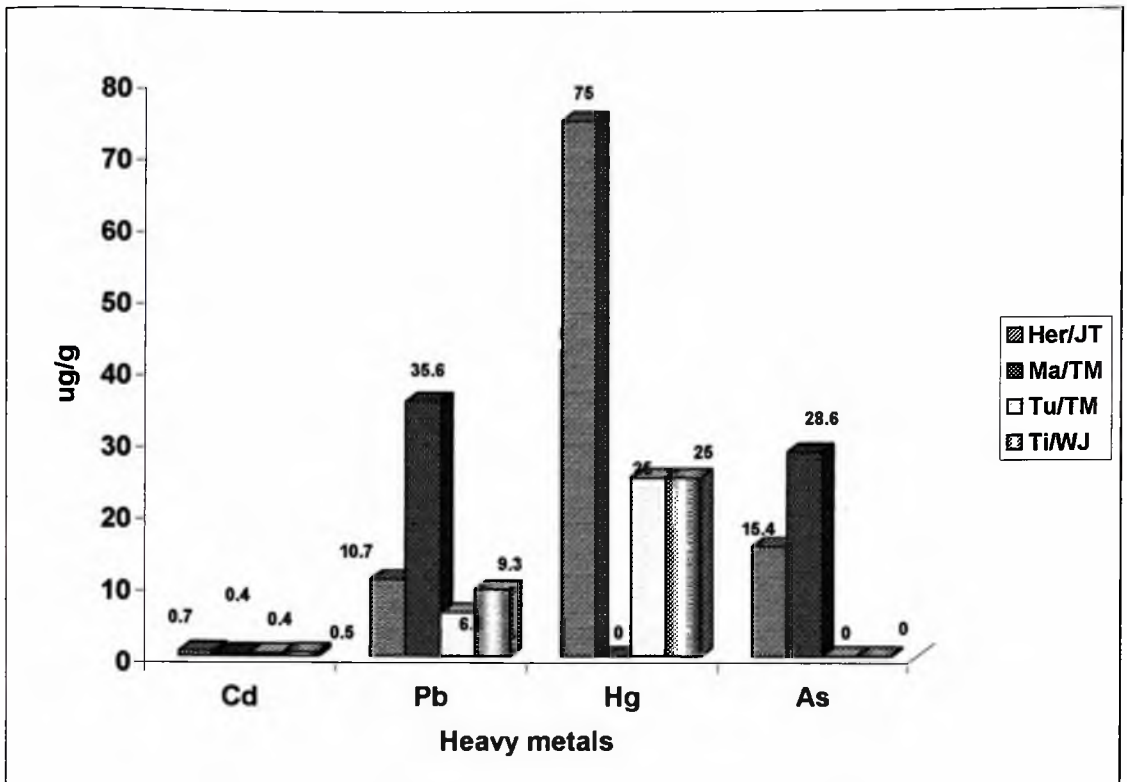
**Fig. 7: Heavy metal levels in fish oil from James Town, Tema and Weija**

He = Herring

Ma = Mackerel

Tu = Tuna

Ti = Tilapia



### 5.10.2 Water sources and their heavy metal contents.

The waters from which fishes were sampled include marine from Tema, James Town, Apam and Elmina, and fresh waters from mining areas including Dunkwa (river - Ofin) and Obuasi (Nyam stream and a fishpond), and non-mining areas - Weija and Kpong lakes. The heavy metal levels in the waters are reported in Table 9.

The Cadmium levels in the marine waters from Tema, James Town and Elmina were the same with a value of 0.13ug/ml. The level detected in the Apam water was about half the level in the other marine waters (0.6ug/ml). For the marine waters, selenium levels ranged from 1.0 to 2.9ug/ml. The level in James Town water was the highest, with a value of 2.9ug/ml, Apam the second highest of 2.2ug/ml followed by Tema with 1.8ug/ml and lowest in Elmina water with a value of 1.0ug/ml. Lead levels in the marine samples ranged from 0.17ug/ml in the Elmina sample to 0.35ug/ml in the Tema sample. The Apam and James Town water samples had the same Pb levels of 0.26ug/ml. Mercury levels were highest in Elmina water sample with a value of 10.8ug/ml followed by Apam with a value of 9.8ug/ml. The level in the Obuasi water sample was higher than the Dunkwa water sample with values 5.0 and 3.75ug/ml respectively.

For the fresh waters the level of mercury was highest in Kpong lake and Obuasi fishpond samples with values 5.6 and 5.0ug/ml respectively. The levels in the rest of the freshwaters were Weija lake 4.0ug/ml, Obuasi stream 2.25ug/ml and Dunkwa river Ofin 3.75ug/ml. No Arsenic was detected in any of the fresh water samples, thus the levels were below the sensitivity level of the metal. Lead levels in the freshwaters were detected in Weija, Obuasi and Dunkwa samples with values 0.12, 0.08, and 0.08ug/ml respectively. These values compare with some heavy metals analysed in some freshwaters in Amsterdam in Holland. The levels Pb and Cd in the Amsterdam Lakes were: 0.01 to 0.02 ug/ml for Cd and 0.26 and 1.38 ug/ml for Pb (Hans *et al*, 1995).

In general the marine waters had higher heavy metal levels than the freshwaters. For the marine samples there was no clear cut difference in the heavy metal levels between the heavy and light industrial areas since some metal were higher in the Light industrial areas than the heavy industrial areas and vice versa. The freshwaters also did not show any distinct differences in the levels of the heavy metals but the Obuasi stream and Dunkwa river showed slightly lower levels than the Weija and Kpong water samples. Apart from mercury levels the selenium content of the sea water was higher than the other heavy metals.

**Fig. 8: Heavy metal content of water from which fish was sampled**

JT = James Town

TM = Tema

WJ = Weija

AP = Apam

KP = Kpong

EL = Elmina

OB/S = Obuasi stream

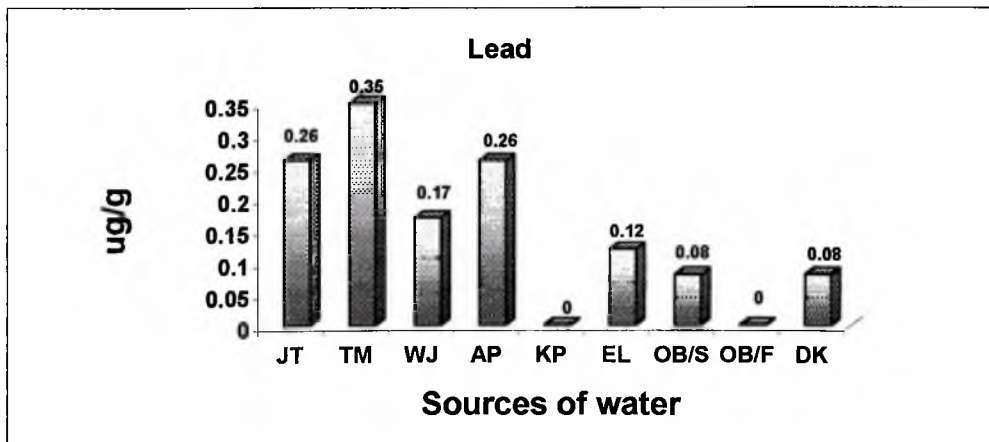
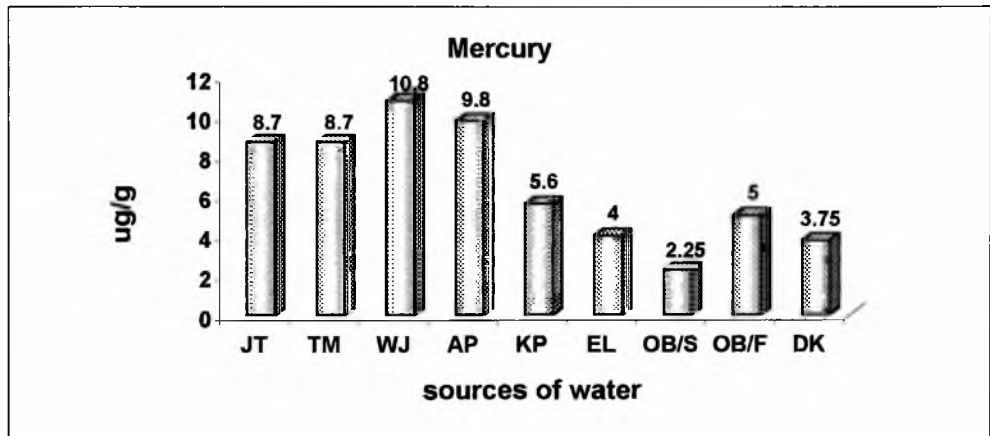
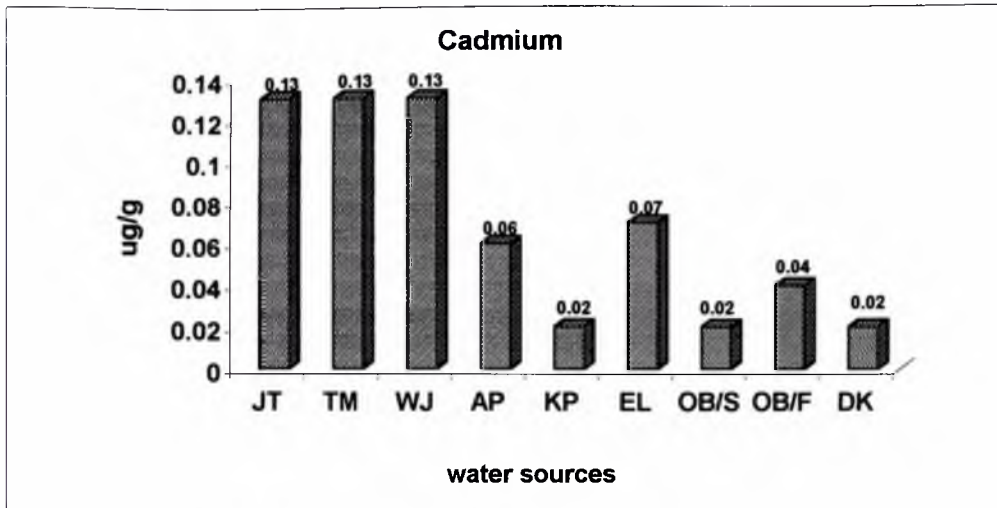
OB/F = Obuasi fish pong

DK = Dunkwa (river Ofin)

Cd levels

Pb levels

Hg levles



### 5.10.3 RELATIONSHIP BETWEEN HEAVY METAL LEVELS IN FLESH, FISH- OIL AND WATER SOURCES OF FISH.

The fish oil was extracted from fish samples from three towns; Tema, James Town and Weija. The fish samples were Herring from James Town, Mackerel from Tema, Tuna from Tema and Tilapia from Weija.

Analysis of variance (ANOVA) of the levels of Cd in the flesh, oils and water in these fish samples at  $\alpha = 0.05$ , showed a significant difference ( $P= 0.02$ ). There was no significant level of Cd in fish oils from the various fishes ( $p= 0.6$ ). The difference in the Cd content of oil and flesh was not significant ( $p= 0.2$ ). A correlation between the Cadmium levels in oil and flesh gave a strongly inverse relation ( $r= -0.6$ ) but the correlation was not significant ( $p= 0.58$ ). Cadmium levels in flesh and water showed a strong positive relation ( $r=0.656$ ). There was a nonsignificant inverse relation between the levels of Cadmium in the oil and water ( $r= -0.26$ ;  $p= 0.65$ ). Figure 9: shows a graph of the relationship.

Analysis of variance of Lead levels showed no significant difference in the flesh, oils and water ( $p= 0.075$ ). A correlation between Pb levels in flesh and oil showed a strong inverse relation ( $r= -0.8$ ) but the correlation was not significant ( $p=0.16$ ). Similarly a correlation between flesh and water content of Pb showed a strong inverse relation ( $r= -0.767$ ). But correlation between oil and water contents of Pb also showed positive weak relationship ( $r= 0.415$ ) which also not significant ( $p=0.12$ )

Possible explanation of the above observations is that the levels in the water are very low and since the concentration of these metals in the flesh require active transport mechanisms each fish might have varying degrees of absorbing and retaining the metal in its body. The fish also ingested these element from their foods and the levels of these metal may also be in varying degrees in their food sources.

Fig. 9: Heavy metal content of flesh, fish oil, and water. Oil

sources are Herring from James Town (He/JT), Mackerel from Tema (Ma/TM), Tuna from Tema (Tu/TM) and Tilapia from Weija (Ti/WJ).

F = Flesh

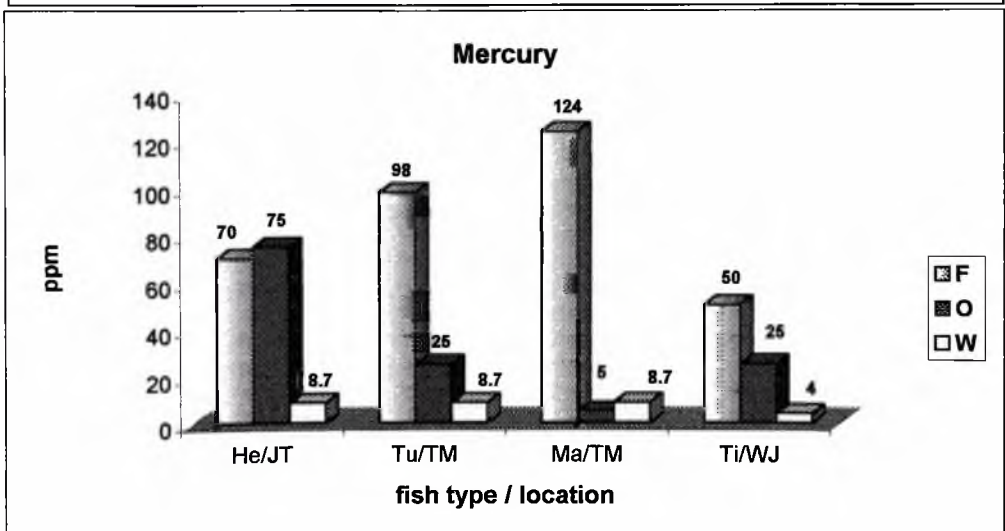
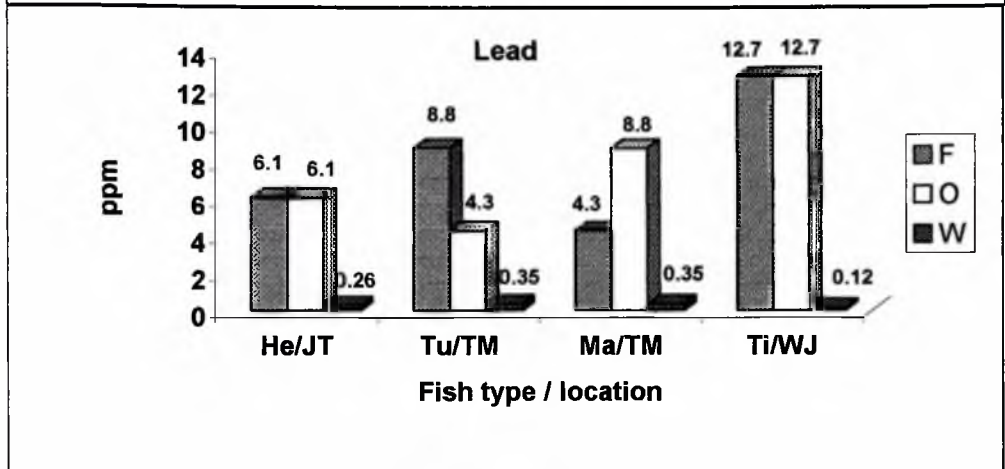
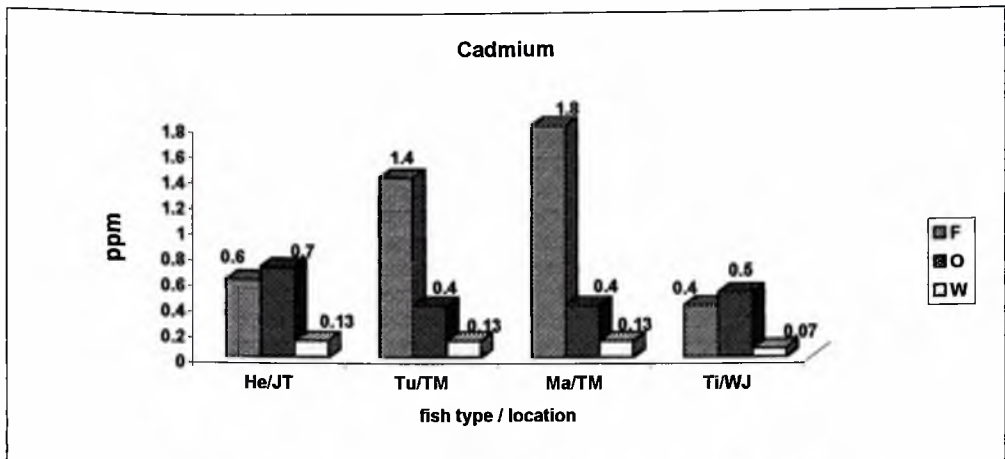
O = Oil

W = Water

Cadmium levels

Lead levels

Mercury levels



ANOVA of mercury levels in flesh and water showed a significant difference ( $p < 0.001$ ). A correlation between mercury levels in flesh and water showed a weak inverse relation ( $r = 0.223$ ). There was no significant correlation between mercury levels in flesh and oil ( $r = 0.2$ ;  $p = 0.7$ ). The level of the mercury in the oil was below the sensitivity levels of the metal so could not be quantified for statistical analysis. The correlation between the levels of heavy metals in the flesh and the bone of the fishes gave coefficient of correlation and p-values as follows: Cd,  $r = 0.674$ ;  $p = 0.016$ , Lead,  $r = -0.131$ ;  $p = 0.65$ , Hg,  $r = 0.249$ ;  $p = 0.35$  and As  $r = 0.282$ ;  $p = 0.35$ . These values suggest that only Cadmium distribution in the flesh and bone showed a significant relation to each other. Lead showed a non-significant inverse relation in both flesh and water, and flesh and oil.

Water levels of the metals were the lowest possibly because the volume of water from which samples were taken are vast. The fish species concentrated the metals in their body which is relatively small in size when compared to the vastness of the water body from which they were caught. Thus the large volume of the water seemed to have diluted the metal concentration.

#### **5.11.1 Intake of toxic levels of the heavy metals**

The flesh contained the lowest amounts of the heavy metals and forms about 60% (Fig 10) of the total weight of the whole fish hence a greater amount of the heavy metal that can be ingested will come from the flesh. The possible intake of the metals was then calculated based on the mean levels in the flesh of each fish species. The average moisture content of the flesh of the fish was 50% (Appendix 3).

The calculation of toxic intakes of the metals was based on the minimum amount of flesh (dry weight) per week that will give metal levels over and above the safe margin. Therefore 100g of flesh (dry weight) was used since it gave intake of the metals over and above the safe margins for most of the elements.

For a 100g of flesh of Redfish the amount of Cd ingested will be  $(0.67 \times 50)$ , 3.4ug or 0.0034mg for a 50% moisture content. When such an amount is consumed each day of the week the total intake per week will be 23.8ug (0.024mg). This amount is far below the FAO/WHO Provisional Tolerable Weekly Intake (PTWI) of 0.42mg for a 60 kg body weight (Aune 1992). For the highest Cadmium content of 0.77ug/g the corresponding amount in the 100g of the flesh will be 0.0038mg, while the lowest admium level of 0.56ug/g will give an amount of 0.0028mg/100g. The range of cadmium that may be ingested from the flesh of Redfish per week is 0.020 - 0.027mg. But if the weekly intake is increased to 1000g the average amount of Cadmium ingested will be 0.24mg which is still below the safe margin of 0.42mg.

Lead content in shell fish was reported to be in the range of 0.77 to 5.4mg/kg wet weight from the fjords in Norway, (Bines, 1994). The PTWI for lead by JEFCA is 0.05mg/kg body weight for adults and 0.025 mg/kg body wt. for children. For an adult of 60kg body weight this corresponds to 3mg per person per week. However it has been reported that the largest intake of lead is from cereals, fruits, berries, milk and meat. It is speculated that people who eat fruit and vegetables from gardens near heavy traffic roads could be at risk (Aune, 1992)

Cadmium content in shellfish ranged from 0.2 to 1.75 mg/kg wet weight. Tens years ago in Noeway, the values were about 80 to 90 % higher than what was expernced in 1994, (Bines, 1994). This reduction was due to the importance of environmental health programme that Norway initiated. The safe margin for Cadmium has been set very low because the biological half-life is long. JEFCA in 1988 set it at 7ug/kg bwt, (Aune, 1992).

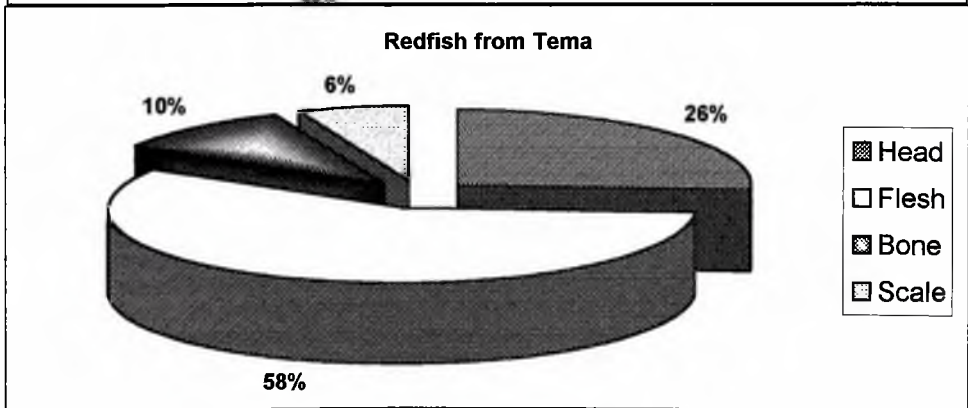
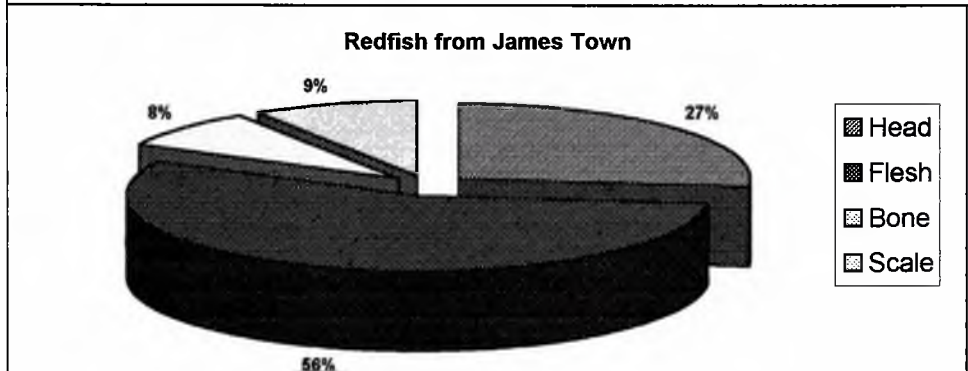
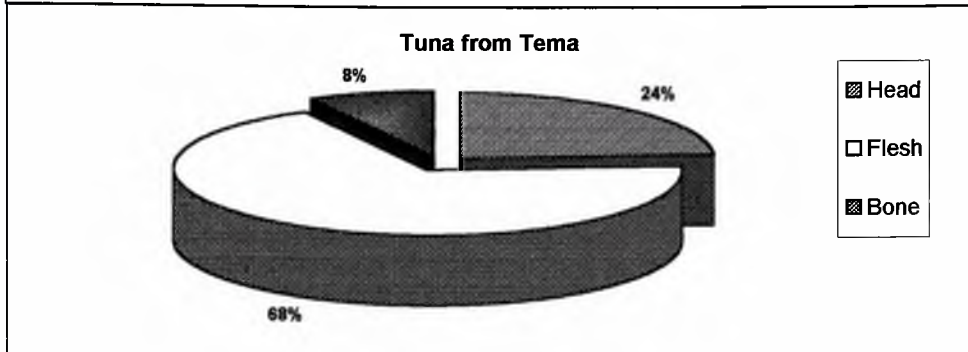
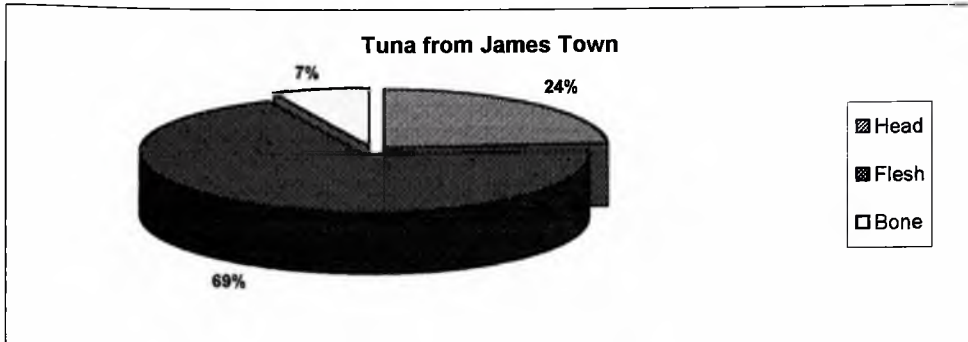
Fig 10: Fish parts by wet weight of Tuna without scales and Redfish with scale.

Tuna from James Town

Tuna from Tema

Redfish from James Town

Redfish from Tema



For a mean mercury level of 79ug/g in flesh of Redfish the total intake of mercury per 100g of the fish is about 3950ug (3.95mg). Thus total intake of mercury from the flesh of Redfish is 3.95mg for every 100g of the fish consumed. If this amount alone is taken in a week it is over and above the PTWI of 0.32mg for a 60 kg body weight (Aune, 1992). The intake may be about 10 times higher than the safe margin.

For Arsenic levels of 10.47ug/g in the flesh of Redfish the total intake of the metal per 100g of the fish will be 523.5ug (0.524mg). Thus total intake of Arsenic from the flesh of redfish is 0.524mg for every 100g of the fish consumed. If this amount alone is taken in a week it is over and above the FAO/WHO PTWI of 0.12mg for a 60 kg body weight (Aune 1992). For 100g flesh of Redfish total lead intake will be 336.5ug. (0.34mg). This amount alone consumed in a week is just about the FAO/WHO PTWI of 0.30mg for a 60 kg body weight individual. For Mackerel, 100g of the flesh will contain 168ug (0.168mg) of Pb. This amount alone per week is below the FAO/WHO PTWI for a 60kg body weight individual. But if such an amount is consumed each day of the week the total intake will be 1.176mg which is higher than the PTWI for a 60 kg weight individual. The intake of each metal from 100g of the fish is reported in Table 10.

Comparison of the levels of heavy metals in 100g dry weight of fish and the safe margins set by FAO/WHO showed that all the heavy metals except Cadmium occurred over and above the safe margins. Thus if more than 100g of each fish is consumed the risk of ingesting toxic amounts of the heavy metals also increases. For Cadmium, if 1000g of fish is consumed in a week the amount ingested will still be below the safe margin. The comparison of the safe margins to the various heavy metals are shown in Figure 11, with the safe margins in the cross- shading.

**Fig. 11: Comparison of heavy metals in 100g of flesh for the various fishes to the safe margin. Safe margin in distinct shading.**

PTWI = Provisional Tolerable Weekly Intake

RDF = Redfish

TUNA = Tuna

HERR = Herring

MACK = Mackerel

TILAP = Tilapia

CATF = Catfish

BLO = Blolo

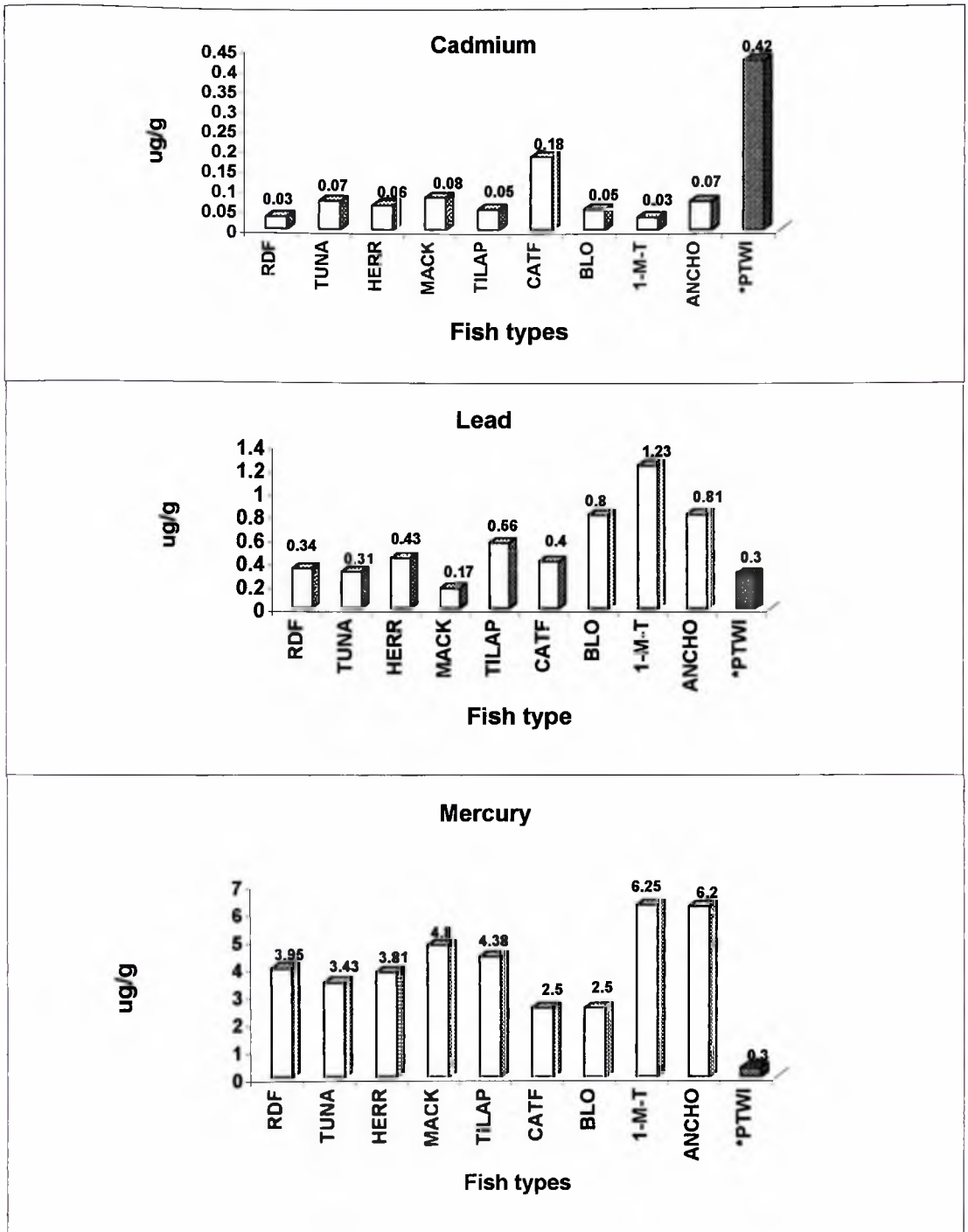
1MT = One-mouth-thousand

ANCH = Anchovies

Cadmium levels

Lead levels

Mercury levels



### 5.11.2 Impact of selenium on the toxicity of the heavy metals of the fish and oils

Selenium content in the fish analysed revealed low levels in the flesh but the levels in the bone and head are higher than the levels of Pb and As in the flesh of the fishes. The consumption of the flesh alone may allow the selenium to possibly reduce the toxicity of Pb and As by competing with them for absorption. But the consumption of the bone also introduces more heavy metal, hence the benefit the selenium is expected to offer may be nullified by the increased intake of the heavy metals from the bone (Pariezek and Ostadalova, 1967 ).

### 5.11.3 Calculation of total heavy metals in flesh of specific fishes for the year 1993.

Total fish catch for the following fish species in Ghana for the year 1993 and 1994 (Department of Fisheries, Ministry of Food and Agriculture [MOFA], 1996) is shown in Table 11 below.

The amount of heavy metals Cd, Hg etc., in this catch is estimated to give an indication of the health hazards and its implications to the population.

**Table 11: Total catch for 1993 and 1994**

<u>TYPE OF FISH</u>	<u>TOTAL CATCH IN METRIC TONNES FOR</u>	
	1993	1994
Herring ( <i>Sardinalla</i> Sp)	110438.1	90638.0
Tuna	36855.6	36973.3
Anchovies	81349.7	60519.3
Mackerel	8289.5	67312.5
Red mullet (redfish)	107.1	67.0

The average Cadmium content of the flesh of Mackerel caught was 1.5ug/g. This is equivalent to 1.5g/mt of fish weight. The total metric tonnes of Mackerel caught for 1993 was 8289.5. Hence the minimum level of Cadmium that may be ingested from Mackerel alone for 1993 was 8289.5

$\times 1.5g = 12434.24g$ . Considering moisture content of 50% the average amount of cadmium ingested from Mackerel in 1993 was  $(12434.24 \times 50\%) = 6217.12g$ . The break down of the other metals with respect to fish type are shown in Table 12.

**Table 1 : Mean levels of Heavy Metal in the flesh (dry weight).  
for 1993 catch.**

<u>HM/kg</u>	<u>Fish Type</u>				<b>TOTAL</b>
	<b>Herring</b>	<b>Mackerel</b>	<b>Tuna</b>	<b>Redfish</b>	
<b>Cadmium</b>	6.3502	6.217	25.799	0.036	38.4
<b>Mercury</b>	4,210.453	397.896	1265.437	4.231	5878.017
<b>Arsenic</b>	500.837	26.029	264.439	0.561	791.866
<b>Lead</b>	477.644	13.926	112.225	0.360	604.155

The average total amount of heavy metals possibly ingested from Herring, Tuna, Mackerel and Redfish caught in Ghanaian waters for 1993 are as follows: Cadmium 38.4kg, Mercury 5878.017kg, Arsenic 791.866kg, and Lead 604.155kg. If these high level of heavy metals are consumed by about eighteen million Ghanaians from only these four fish species while there is the likelihood of ingesting heavy metals from other sources it can then be said that there is an urgent need for an alarm to be sounded for relevant agencies to act immediately to lower the rising levels of these elements in our waters and fish stocks.

## CHAPTER SIX

### 6.0 CONCLUSION AND RECOMMENDATION

#### 6.1 Distribution of Heavy Metals in the fish

Generally the bone had the highest levels of the heavy metals. It is followed by the scale, the head and then the flesh. The total metal levels in the whole fish is higher than that in the flesh alone. This trend implies that the higher the content of skeletal bone the higher the level of the metal. This is expected since most of the metallic elements are incorporated in the bone matrix.

Analysis of variance showed significant difference ( $p= 0.03$ ) in the levels of each heavy metal in the fish parts. Mercury levels occurred as the highest heavy metal in all parts of the fish followed by Arsenic and Lead whose levels were comparable. Cadmium levels occurred as the lowest heavy metals. Selenium analysed in some of the fishes had levels slightly higher than Arsenic and lead in the flesh.

There was a significant correlation  $r=0.67$  and  $p=0.01$ , between the Cadmium levels in the flesh and bone. The rest of the metals did not show any significant correlation in their distribution in the flesh and the bone.

#### 6.2 Heavy metals in fish from different environmental zones.

The heavy metal levels in the fish caught from heavy industrial coastal waters were significantly higher than those from light industrial coastal waters, except for mercury which was higher in redfish from Elmina a light industrial area. There was significantly higher levels of Mercury in the Redfish caught from Elmina than those caught in the Tema and James Town waters ( $p= 0.001$ ).

There was no significant difference in the level of Cd, As, and Pb in the Redfish caught from heavy industrial areas (Tema and James Town ) and light industrial area (Elmina). There was no significant differences in the level of any of the heavy metals in Tuna fish caught from the two environmental areas. But the levels of Cd, Hg, and Pb in the bone and head were significantly higher than in the flesh.

The Herring from heavy industrial areas had significantly higher Hg levels than herring from light industrial areas. For the rest of the heavy metals there were no significant differences in their levels in the herring from the two environmental areas. The observed differences in the Hg levels in Mackerel was significant ( $P= 0.008$ ), with the levels in the heavy industrial areas higher than the levels in the Mackerel from light industrial areas.

The level of Lead in Tilapia from the Mining Environment (ME) and the River/Lake (RL) was significantly different ( $P=0.007$ ), with Weija Tilapia from RL having higher level. But there was no significant difference ( $P=0.07$ ) between the level in Obuasi, Dunkwa and Kpong Tilapia. There was also a significant difference ( $P=0.03$ ) in the level of Mercury in the Tilapia from the various areas. The levels in Weija and Dunkwa Tilapia were higher than the level in the Obuasi and Kpong Tilapia.

Lead levels in the *Blole* fish from the various environmental areas showed significant difference ( $P=0.009$ ), with the fish from non-mining areas having higher values.

None of the heavy metals in the Catfish caught from the two environmental areas showed any significant difference.

### **6.3: Heavy metal contents of fish oils.**

Mercury occurred as the highest metal with cadmium as the lowest just as in the fish parts. Lead and Arsenic levels in the oils were close. Herring oil had the highest level of the Mercury

followed by Tuna and Tilapia. The Mercury level in the mackerel oil could not be detected because it was below the sensitivity level of the method.

Herring had the highest level of Cadmium followed by Tilapia and finally Tuna. Arsenic levels detected in herring oil was about twice the level in mackerel oil. Arsenic was not detected in the Tuna and Tilapia oils. Lead was detected in all four oils with the highest occurring in mackerel and lowest in Tuna. The levels in herring oil was slightly higher than in the tilapia oil.

The levels of these metals in the oils extracted from these fishes were considerably high when compared to their levels in parts of the fishes. Lead and mercury levels were highest in the oils extracted possibly due to the ability for the mercury and Lead to be methylated into tetramethyl lead and methyl mercury, (Imura *et al*, 1972).

#### **6.4 Heavy metal contents of water sources of the fish**

In general the marine waters had higher heavy metal levels than the freshwaters. This may be attributed to the fact that all running waters end up at the beach. For the marine samples there was no specific trend in the heavy metals levels between the heavy and light industrial areas since some metals were higher in the light industrial areas than the heavy industrial areas and vice versa. Thus mercury was highest in the Elmina sample which was from a light industrial area while Pb was higher in Tema water sample which was classified as high industrial area. Apart from Mercury levels the Selenium contents of the seawater was higher than the other heavy metals. The metal ranges in the marine waters were as follows; Cd 0.6 - 0.13, Se 1.0 - 2.9, Hg 8.7 - 10.8, As 1.7 - 2.3, and Pb 0.17 - 23.5ppm.

The freshwaters also did not show any distinct trend in the levels of the heavy metals but the Obuasi stream and Dunkwa river from the Mining Environment showed slightly lower levels than the Weija and Kpong water samples, but these lower levels were not significantly different.

The heavy metal ranges in the freshwater were, Cd 0.02 – 0.07, Hg 2.25 – 5.6 and Pb 0.08 – 0.12ppm. No Arsenic was detected in any of the freshwater samples.

### **6.5 The relationship between the heavy metal contents of flesh, fish oil and water sources of fish.**

#### **Cadmium content**

There was a significant difference ( $P= 0.024$ ) in the levels of Cd in the flesh, oil and water in these fish samples. There was no significant difference in the level of Cd in fish oils from the various fishes ( $p= 0.6$ ). The difference in the Cd level in oil and flesh was not significant ( $p= 0.2$ ). A correlation between the Cadmium levels in oil and flesh gave a strongly inverse relation ( $r= -0.708$ ). Cadmium levels in flesh and water showed a positive relationship ( $r=0.656$ ). There was a weak inverse relation between the levels of Cadmium in the oil and water ( $r= -0.053$ ).

#### **Lead content**

There was no significant difference in Pb levels in the flesh, oils and water ( $p= 0.075$ ). A correlation between Pb levels in flesh and oil showed a relatively strong inverse relation ( $r = -0.694$ ). Similarly a correlation between flesh and oil content of Pb showed a strong inverse relation ( $r= -0.767$ ). But correlation between oil and water contents of Pb showed a relatively weak relationship ( $r= 0.415$ ).

#### **Mercury content**

There was a significant difference ( $p<0.001$ ) in the mercury levels in flesh and water. A correlation between mercury levels in flesh and water showed a weak inverse relation ( $r= -0.223$ ).

## 6.7 Toxic levels

Comparison of the levels of heavy metals in 100g of fish and the safe margins set by FAO/WHO showed that all the heavy metals except for Cadmium occurred over and above the safe margins. Thus any amount above 100g of each fish consumed increases the risk of ingesting toxic levels of the heavy metals. Selenium levels in the fishes analysed revealed low levels in the flesh but the levels in the bone and head were higher than the levels of Pb and As in the flesh of the fishes. The consumption of the bone may cancel the possible protective effect selenium can offer.

If this trend of high levels of the heavy metals continues there is a risk of increased incidence of the physiological disorders that are caused by the consumption of these heavy metals such as brain damage, poor growth, especially in school-aged children, and kidney and bone disorders in the elderly.

In spite of these alarming levels of heavy metals in the fishes, one good news is that the absorption of these metals is influenced by several factors which include the presence of other mineral nutrients such as calcium and phosphorus which occur in high levels in the diets rich in fish products.

## 6.8 RECOMMENDATIONS

The high levels of the metals found in these fish species call for an immediate action to monitor the inflow of these metals into our waters from which the fish concentrate them in their bodies. There is therefore the need for further investigation into the sources and entry points of the chemicals or wastes that carry these heavy metals into our waters.

For regular monitoring and evaluation, there is a need for such a study to be repeated every two or five years to ensure effective reduction in the levels of these hazardous elements from both the waters and the fish we consume.

To determine the actual effect of the ingestion of these high levels on the population, there is also the need for an investigation into the blood levels of these metals in the population, especially those living around these water bodies.

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**APPENDIX 2**

Table 14: Weight and lengths of the various fish samples studied.

Fish Type /loc	Head/g	Flesh/g	Bone/g	Scale/g	Whole/g	Lenth/cm
Redfish/TM	49	93.9	13.8	15	84.3	35
Redfish/JT	103.4	233.1	40.1	25	134	32
Herring/JT	24.4	128.2	10.7	24.8	55.3	25
Tilapia/WJ	39.3	102	16.8	23.8	83.5	25
Tuna/JT	112.6	283	42	-	103	20
Herring /TM	52.6	160.8	16.7	29.2	245	45
Tuna/TM	62	170.2	25		221.4	36
Tilapia/DK	42.6	125.3	41	35	150.2	28
Tuna/AP	80	263	19.7		213.8	42
Mackerel /TM	38	108	32	-	98.9	45
Mackerel/AP	56	156	29		120.1	38
Blole/KP	21	93	23	-	211.8	39
Blole/DK	39	196	32		169.3	45
Catfish/KP	49	209	36		132.5	34
Catfish/DK	37	156	29		142.2	42

**APPENDIX 3****Moisture content of fish samples.**

Sample/Loc.	Fish parts	Wt of fish/g	Moisture/g	% Moisture
Herring/AP	W	21.596	12.01	56
"	F	13.98	8.05	58
"	H	26.38	14.25	54
"	B	15.77	8.27	52
"	S	11.81	5.11	43
Tuna/TM	F	34.8	13.52	59
"	H	20.14	10.14	50
"	B	21.51	12.09	45
Mackerel	W	24.75	13.2	53
"	F	8.5	5.01	59
"	H	29.84	15.28	51
"	B	12.5	5.78	46
Herring/TM	W	20.73	12.06	58
"	F	20.23	11.85	59
"	H	23.43	12.34	53
"	B	17.29	7.92	46
Redfish/EL	W	12.02	6.03	50
"	F	24.43	12.8	52
"	H	43.38	21.02	48
"	B	21.13	9.52	46
"	S	21.13	9.52	45
Herring/EL	W	11.82	6.27	53
"	F	20.12	10.44	52
"	H	34.47	17.18	50
"	B	16.03	7.59	47
Tuna/EL	F	21.27	11.08	52
"	H	26.14	12.67	48
"	B	32.45	14.47	45
Redfish/JT	W	27.09	15.81	58
"	F	26.37	14.6	55
"	H	29.88	15.2	50
"	B	20.5	8.7	42
"	S	17.89	7.8	43

<b>Sample/Loc.</b>	<b>Fish parts</b>	<b>Wt. of fish/g</b>	<b>Moisture/g</b>	<b>% Moisture</b>
Tilapia/WJ	W	20.64	11.02	53
"	F	20.25	14.2	53
"	H	37089	17.95	47
"	B	16.6	7.4	45
"	S	25.57	11.05	43
Tuna/JT	W	42.2	22.2	53
"	F	32.19	16.76	52
"	H	26.15	13.05	50
"	B	16.53	8.41	50
Herring/JT	W	27.69	15.7	57
"	F	25.49	14.02	55
"	H	12.52	6.34	51
"	B	24.69	12.25	50
"	S	23.87	11.15	47
Redfish/TM	W	20.93	12.16	58
"	F	23.43	12.96	55
"	H	13.6	7.01	52
"	B	24.73	10.5	42
Anchovies	W	19.14	7.66	40
Mackerel	W	21.53	12.44	58
"	F	25.21	14.49	57
"	H	23.22	12.24	53
"	B	15.87	8.01	50
	<b>Mean % moisture</b>			<b>50.50</b>

**APPENDIX 5**

Map of Ghana showing locations from which fish were sampled.

JT = James Town

TM = Tema

WJ = Weija

AP = Apam

KP = Kpong

EL = Elmina

OB = Obuasi

DK = Dunkwa

