KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI

COLLEGE OF SCIENCE

TOTAL MERCURY LEVELS IN FRESHWATER FISH FROM SOME INLAND WATERS IN GHANA

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A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY

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BY

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DECLARATION

It is hereby declared that this thesis is the outcome of research work undertaken by the author. Any assistance obtained has been duly acknowledged. It is neither in part nor whole been presented for another degree elsewhere.

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DEDICATION

To my parents, Mr. Godlieb Kofi Agorku and Margret Atono Afi Tuani.

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First of all, I want to give credit and thanks to God almighty who by his grace has brought me this far. When the Lord defines a work, He provides willing and capable hands to accomplish it. I therefore acknowledge with ineffable and profound gratitude the immense assistance given by Professor Anthony Apeke Adimado, my project supervisor and instructor for his guidance, criticisms and suggestions.

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ABSTRACT

Total mercury (Hg) concentrations were determined in fish from three reservoirs in Ghana, namely, Lake Bosomtwi, Kpong Reservoir and Akosombo Reservoir. A total of one hundred and sixty five (165) fish samples covering nine (9) species were collected and analysed for total mercury.

A mixture of HNO_3, H_2SO4 and $HClO_4$ were used for complete oxidation of organic tissues followed by Hg detection using the Cold Vapour Atomic Absorption Spectrometry (CVAAS) technique using an automatic mercury analyzer.

Mercury concentration ranged from ND to 70.30 ng/g wet weight for *Tilapia multifaciata*, 65.56 to 47.48 ng/g wet weight for *Tilapia discolour* and 6.56 to 47.48 ng/g wet weight for *Tilapia bosomana* from Lake Bososmtwi. Poor correlations were observed between mercury concentration and fresh weight, and total length for *Tilapia bosomana* , *Tilapia multifaciata* and *Tilapia discolour* respectively.

Total mercury concentration ranged from 20.00 to 42.00 wet weight for *Synodontis sp.* and ND to 28.00 ng/g wet weight for *Tilapia zilli* from Akosombo Reservoir. *Synodontis sp.* showed good correlation between mercury concentration and fresh weight (R^2=0.6852) whereas *Tilapia zilli* showed a poor correlation.

Mercury concentration ranged form 10.70 to 1014.73 ng/g wet weight for *Pelmatochromis guntheri* (mean=158.79 ng/g), 26.38 to 79.03 ng/g wet weight for *Chrysichthys auratus*

(mean=40.71 ng/g), 141.24 – 207.59 ng/g wet weight for *Apistogramma trifasciatum* (mean=169.68 ng/g), 9.68 – 10.68 ng/g wet weight for *Tilapia zilli* (mean=10.50 ng/g) and 15.15 – 75.90 ng/g wet weight for *Amphilus grammatophorus* (mean=29.50 ng/g) from Kpong Reservoir. There was poor correlation between mercury concentration and fresh weight (r^2 = 0.1675) and total length (r^2 = 0.0170) for *Pelmatochromis guntheri. Chrysichthys auratus* also recorded a poor correlation between mercury concentration and fresh weight (r^2 = 0.0146) and total length (r^2 = 0.0509). *Apistogramma trifasciatum* showed a good correlation between mercury concentration and fresh weight (r^2 = 0.9626) and total length (r^2 = 0.9764). *Tilapia zilli* showed a poor correlation for mercury concentration and fresh weight (r^2 = 0.0854) and total length (r^2 = 0.0254).

Apart from one sample of *Pelmatochromis guntheri* which recorded a higher mercury concentration (1014.73 ppb) above the WHO acceptable limit for total mercury in fish, all the results obtained are below the WHO threshold limit of 500ppb. The results obtained from this research showed that fish from the three reservoirs are unlikely to constitute a significant health threat to the public because of consumption of fish.

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ABBREVIATIONS

AAS	Atomic Absoption Spectrophotometer
CVAAS	Cold Vapour Atomic Absoption Spectrophotometry
ICPAES	Inductively Coupled Atomic Emission Spectrometry
ND	Not Detectable

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CHAPTER ONE

1.0 INTRODUCTION

Mercury (Hg) is a poisonous naturally occurring element that can be found throughout the environment. Human activities have also increased the amount of mercury in many parts of the environment including the atmosphere, lakes and streams. Mercury emissions into the environment can be characterized by the following sources: Natural sources which include volcanic emissions, degassing from the earth's crust and oceans cycling of geological bound mercury and anthropogenic sources which include artisanal gold mining, laboratories, municipal waste, combustors in industries, chlor-alkali plants, agricultural activities, commercial and industrial boilers and construction of hydroelectric dams (Heindryckx, 1974).

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While there are three forms of mercury (elemental, inorganic, and organic), (Goldman, *et al.*, 2001) the organic form, methyl mercury (MeHg), is the most toxic (Ercal *et al.*, 2001). Micro bacteria convert the inorganic Hg in the water and sediments into highly toxic methyl mercury. This highly neurotoxic form accumulates in aquatic organisms, including fish (Lutter *et al.*, 2002). Methyl mercury can accumulate at higher concentrations, and biomagnify, in aquatic and land-based organisms to concentrations that can adversely affect organisms in higher levels of the food chain, including humans. Mercury has become so common that in 1997, mercury contamination accounted for more than 97% of all fish-consumption advisories in Canada. (USEPA, 2001).

Mercury poisonings have been caused by consumption of contaminated fish, such as in the case of Minamata disease. It is named after a Minamata Bay, a body of water in Japan where, in the

early 1950s was polluted by industrial effluent containing methylmercury. Fishes from this water body were found to contain high concentrations of methyl mercury. Local villagers ate the fish began to exhibit signs of neurologic damage such as visual loss, extremity numbness, hearing loss, and ataxia. Babies exposed to the methyl mercury in uterus were the most severely affected members of the village. Furthermore, because mercury was also discovered in the breast milk of the mothers, the babies' exposure continued after birth (Yoshino et al., 1966, Irukayama *et al.*, 1977).

A research study on Hg levels in fish obtained from different parts of the world reported various levels. For instance, Hg levels determined in fish from Caroni River in the French Guyana revealed a range of about 0.5μg/g to 1.7μg/g (Keith, 1991). As a result, organization such as the US Food and Drug Administration (FDA) set an Action Level of 1 mg /kg (wet mass) for concentration of MeHg in fish. Fish containing concentrations of MeHg above this level were considered to be hazardous for human consumption and could not be sold in interstate commerce. Canada and several US states developed consumption advisories of 0.5μg/g for MeHg in fish. In Taiwan, the guideline level of MeHg was set at 2.0μg/g for fish (WHO, 1990). Studies have shown that concentrations of methylmercury in aquatic invertebrates, fish, and piscivorous, or fish-eating, wildlife were commonly elevated in newly flooded reservoirs (Rosenberg *et al.*, 1997, Hall *et al.*, 1998 & Porvari *et al.*, 1998). For example, a flooding experiment conducted in the Experimental Lakes Area of Ontario, Canada led to the decomposition of vegetation (Paterson *et al.*, 1998), which depleted oxygen and imposed anoxic conditions over the inundated sulphate, stimulating microbial sulfate reduction and mercury methylation. Bioaccumulation, at higher levels in the food chain, was evident in the seston and planktonic food web (Paterson *et al.*, 1998).

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Another study at La Grande 2 reservoir in Northern Quebec, revealed that mercury concentrations in benthic insects, caged fish (which fed primarily on the benthic insects), and nestling tree swallows (which fed on the caged fish) increased after flooding (Bodaly *et al*., 1999 Gerrard *et al*., 2001). Mercury concentrations in fishery resources of new impoundments, or reservoirs, may remain substantially elevated for decades after flooding (Bodaly *et al*., 1992, Ramsey *et al*., 1990).

The flooding waters in Lake Winnipeg Regulation Churchill-Nelson River Diversion Project resulted in the decomposition of organic matter in reservoirs; and thus, increased sedimentation caused by erosion of shoreline (Bodaly, *et al*., 1992). Metallic mercury was released from the soil into the water, and was metabolized by bacteria, converting it to the highly toxic form, methyl mercury.

Elevated levels of mercury have been found in numerous occasions on and nearby the bodies of water affected by Manitoba Project. In 1991, 20 years after the initial damming, elevated mercury levels were found in fish from Sipiwesk Lake of Manitoba and the discovery resulted in the closure of the commercial fishery. The cause of the increased levels, based on scientific evidence, pointed to the link between hydro impoundment and elevated mercury levels (Cross Lake Environmental Impact Assessment Study, 1986). The bioaccumulation of methyl mercury found in numerous studies links the contamination of fish with the construction of hydroelectric dam.

At Southern Indian Lake, catches were monitored routinely and, in 1979, monitoring indicated a substantial rise in mercury concentrations in all fish species, with northern pike and walleye exceeding the Canadian marketing limits. Mercury contamination in white fish continued until

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1982, and elevated levels are expected to persist in pike for many decades as a result of damming (Ramsey, *et al.*, 1990).

Gold mining activities are quite widespread in Ghana and the potential contamination by mercury used for recovery of gold has become a matter of great concern. Once mercury is exposed to the atmosphere it can enter the biogeochemical cycle or it can be transported long distances through the atmosphere. In recent times, mercury contamination in the world over has attracted attention from both scientist and policy makers due to it persistence in the environment and health effects such as irritability, fits of anger, lack of energy, fatigue, low self-esteem, drowsiness, decline of intellect, low self-control, nervousness, memory loss, depression, anxiety, shyness/timidity and insomnia. Little work, however, has been done to study environmental mercury contamination in Ghana in fresh water bodies (Adimado *et al.*, 2002). This study seeks to determine mercury in freshwater fish from some inland waters in Ghana, namely, Kpong Reservoir, Akosombo Reservoir and Lake Bosomtwi.

The River Volta is 1,600 km long, from where the Black Volta rises in Burkina Faso. It is Ghana's largest river and drains 70 per cent of the country's land. The Volta River is dammed at Akosombo and Kpong to produce electricity. Lake Volta is an artificial lake on the river, which covers 9,500 square kilometres. Lake Volta is 400 km long. Lake Bosomtwi, located in the south-central region of Ghana, is the country's largest and deepest natural lake. Formed by a meteor, it has a diameter of 10 kilometers and a maximum depth of 86m in the centre. Fishing and irrigation activities are extensively undertaken in both waters.

1.1 Research Objectives

The objectives of this project are:

- To find the total mercury concentrations in various species of fish from selected freshwater bodies in Ghana.
- To evaluate the correlation between total mercury concentrations and factors such as size and length of fishes.
- To check whether the levels of mercury in fresh water fish are at levels of potential human health concern and whether consumption advisories should be issued.

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1.2 Justification of objectives

People are exposed to methylmercury primarily by eating fish. Mercury toxicity is well established in the scientific literature and its dangers to people have been well-known and several cases of mercury toxicity in the environment have been reported (USEPA, 2001). The most serious occurred in Minamata Bay area of Japan from 1953-1960. Mercury, released into the bay from manufacturing plants contaminated fish and shellfish. Mercury levels of 5-20 ppm were found in seafood eaten by 111 people diagnosed with "Minamata disease". Of these, 45 died as an apparent result of the poisoning (Yoshino *et al.*, 1966, Irukayama *et al.*, 1977). Monitoring of Hg levels in fish has since then become a matter of great concern in the world.

Considerable data exist on mercury accumulation in fish in lakes across Minnesota and some lakes in Wisconsin and Alaska. Some fish had mercury concentrations as high as 3.6 ppm. As a result of these elevated mercury levels, fishing was banned (Koeman *et al.*, 1975). In Eastern Africa, total mercury concentrations were measured in fish from Houston bay, Napoleon Gulf in

northern Lake Victoria between 1998 and 2000. Total mercury concentration in *Lates niloticus* (Nile Perch) and *Oreocchromis niloticus* (Nile tilapia) ranged from 10.6 to 77.5 ng/g and from 15.0 to 44.5 ng/g wet weight respectively (Xun *et al.*, 1987). Studies completed by Hydro-Quebec have linked hydroelectric development in northern Quebec to increased level of Hg in nearby ecosystems. Hg in fish passing through turbines into downstream river showed significantly high levels of Hg due to hydro turbulence and run-of waters. Mercury concentration recorded in 230 fish samples from Amazona hydroelectric reservoir recorded levels higher than 0.5mg Hg/kg fresh weights (Rosenberg *et al.*, 1997). There is therefore the need to monitor levels of Hg in fish meant for consumption from hydroelectric reservoirs and compare levels with an artificial lake in Ghana.

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There is an extensive body of literature documenting a positive relationship between fish mercury concentration, size and length within an individual water body (Lange *et al.*, 1994). Mercury in fish measured in Deep Creek pickerel in 1992 showed that the fish examined was 48cm long and contained 0.98 mg Hg/kg whereas those with length 20cm long had average Hg concentration of 0.3 mg/Kg (Paul *et al.*, 2004).

Due to the lack of research and adequate data on mercury contamination of the Aquatic Ecosystem of Ghana, this research seeks to determine the levels of mercury in fish from Kpong Reservoir, Akosombo Reservoir and Lake Bosomtwi in Ghana.

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2.0 LITERATURE REVIEW

2.1 Properties of Mercury and its Compounds

Mercury (Hg) can exist in a wide variety of states. Mercury exists in three different forms namely: Elemental mercury, inorganic mercury and organic mercury. The different chemical and physical forms of Hg element all have their intrinsic toxic properties and different applications in industry, agriculture, and medicine, and require a separate assessment chemistry texts (Romeo *et al.*, 1999, Cotton & Wilkinson, 1972). Mercury, along with cadmium and zinc, falls into Group IIb of the Periodic Table. In addition to its elemental state, mercury exists in the + 1 (mercury (I)) and +2 (mercury (II)) states in which the mercury atom has lost one and two electrons, respectively. The chemical compounds of mercury (II) are much more numerous than those of mercury (I). In addition to simple salts, such as chloride, nitrate, and sulfate, mercury (II) forms an important class of organometallic compounds. These are characterized by the attachment of mercury to either one or two carbon atoms to form compounds of the type RHgX and RHgR' where R and R' represent the organic moiety. The most numerous are those of the type RHgX, where X may be one of a variety of anions. The carbon-mercury bond is chemically stable. It is not split in water or by weak acids or bases. The stability is not due to the high strength of the carbon-mercury bond (only 15-20 cal/mol and actually weaker than zinc and cadmium bonds) but to the very low affinity of mercury for oxygen. The organic moiety, R, takes a variety of forms, some of the most common being the alkyl, the phenyl, and the methoxyethyl radicals. If the anion X is nitrate or sulfate, the compound tends to be "salt like" having appreciable solubility in water; however, the chlorides are covalent non-polar compounds that are more soluble in organic solvents than in water. From the toxicological standpoint, the most important of these organometallic compounds is the subclass of

short-chain alkylmercurials in which mercury is attached to the carbon atom of a methyl, ethyl, or propyl group.

An expert committee, considering occupational hazards of mercury compounds, distinguished two major classes of mercury compounds -organic" and "inorganic" (MAC Committee, 1969). Inorganic mercury compounds included the metallic form, the salts of mercury (I) and mercury (II) ions, and those complexes in which mercury (II) was reversibly bound to such tissue ligands as thiol groups and protein. Compounds in which mercury was directly linked to a carbon atom by a covalent bond were classified as organic mercury compounds. This distinction is of limited value because the toxic properties of elemental mercury vapour differ from those of the inorganic salts and furthermore, the short-chain alkylmercurials differ dramatically from other mercurials that fall within the definition of organic mercury. From the standpoint of risk to human health, the most important forms of mercury are elemental mercury vapour and the short-chain alkylmercurials(MAC Committee, 1969).

Mercury in its metallic form is a liquid at room temperature. Its vapour pressure is sufficiently high to yield hazardous concentrations of vapour at temperatures normally encountered both indoors and outdoors under most climatic conditions. For example, at 24°C, a saturated atmosphere of mercury vapour would contain approximately 18 mg/m^3, a level of mercury 360 times greater than the average permissible concentration of 0.05 mg/m^3 recommended for occupational exposure by the National Institutes of Safety and Health, USA (NIOSH, 1973). Apart from the noble gases, mercury is the only element having a vapour, which is monatomic at room temperature. However, little is known about the chemical and physical states of mercury

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found in the ambient air and in the air where occupational exposure occurs (MAC Committee, 1969).

Calomel or mercury (I) chloride (Hg_2Cl_2) is the best known mercury (I) salt. Widely used in the first half of this century in teething powders and in anthelmintic preparations, the low toxicity of this compound is due principally to its very low solubility in water. Mercury (I) forms few complexes with biological molecules. However, in the presence of protein and other molecules containing SH groups, it gives one atom of metallic mercury and one mercury (II) ion. In general, equilibrium is established between Hg^0, Hg_2^{++} and Hg^{++} in aqueous solution. The distribution of mercury between the three oxidation states is determined by the redox (oxidation-reduction) potential of the solution and the concentration of halide, thiol, and other groups that form complexes with Hg^{++}. Extra halide and thiol compounds, added to solution, form complexes with mercury (II) ions and the mercury (I) chloride splits to restore the equilibrium between Hg^0, Hg_2^{++} and Hg^{++}. The split results in the formation of one atom of mercury for every mercury (I) chloride molecule dissociated.

The mercury (II) ion, Hg^{++}, is able to form many stable complexes with biologically important molecules. Mercury (II) chloride (corrosive sublimate), a highly reactive compound, readily denatures proteins and was extensively used in the past century as a disinfectant. It is soluble in water and, in solution, forms four different complexes with chloride, $HgCl^+$, $HgCl_2$, $HgCl_3^-$ and $HgCl_4^{2-}$. It has been suggested that the negatively charged chlorine complexes are present in sea water (Clarkson, 1972).

Phenylmercury compounds have a low volatility. However, the halide salts of methyl-, ethyl-, and methoxyethylmercury can give rise, at 20°C, to saturated mercury vapour concentrations of the order of 90, 8, and 26 mg/m^3, respectively (Swensson & Ulfvarsson, 1968). In the case of methylmercury this saturated vapour concentration is several orders of magnitude greater than the maximum allowable concentration in the working atmosphere. Methylmercury dicyandiamide, previously widely used as a fungicide, has a much lower vapour pressure, being 340 times less volatile than the chloride salt.

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Although the carbon-mercury bond is chemically stable, in the living animal, the bond is subject to cleavage (Clarkson, 1972). The nature of the R radical is all important. If R is a phenyl or methoxyalkyl group, rapid breakdown occurs in animal tissues so that most of the organic compound has disappeared within a few days. Short-chain alkylmercurials undergo the slowest breakdown *in vivo* with methylmercury being the most stable. Differences in the stability of the carbon-mercury bond play an important role in determining the toxicity and mode of action in man. The rapid breakdown of phenyl- and methoxymercury results in toxic effects similar to those of inorganic mercury salts. The relative stability of the alkylmercurials is one important factor in their unique position with regard to toxicity and risks to human health.

The organic and inorganic cations of mercury, in common with other heavy metal cations, will react reversibly with a variety of organic ligands found in biologically important molecules. The chemical affinity of mercury (II) and of its monovalent alkylmercury cations for a variety of biologically occurring ligands is so great that free mercury would be present *in vivo* at concentrations so low as to be undetectable by present methods.

2.2. MERCURY TOXICITY, ABSORPTION, DISTRIBUTION AND EXCRETION

2.2.1 Toxicity

The health effects of mercury exposure depend on its chemical form (elemental, inorganic or organic), the route of exposure (inhalation, ingestion or skin contact), and the level of exposure. Humans generally take up mercury in two ways: (1) as methylmercury (CH3Hg+) from fish consumption, or (2) by breathing vaporous mercury (Hg0) emitted from various sources such as metallic mercury, dental amalgams, and ambient air. Our bodies are much more adapted for reducing the potential toxicity effects from vaporous mercury, so health effects from this source are relatively rare.

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2.2.1.1 Toxicity of Inorganic/ Elemental Mercury Compounds

The toxicity of inorganic and elemental mercury depend on the length and type of exposure. For example, if you were to accidentally swallow liquid elemental mercury from a broken fever thermometer, little mercury would be absorbed. However, if you were to inhale the vapour from that mercury spill, it would be more easily absorbed into your body, potentially causing health problems. At higher concentrations, mercury vapour can cause damage to the mouth, respiratory tract and lungs, and can lead to death from respiratory failure. Long-term exposure to low concentrations causes symptoms similar to those of methyl mercury. Occupational exposures to elemental mercury vapour have been the subject of recent reviews (NIOSH, 1973). Many studies dating back to the 1930s have related the frequency of signs and symptoms of mercury poisoning to exposure.These studies, involving observations of more than one thousand individuals, indicate that the classical signs and symptoms of elemental mercury vapour poisoning (objective tremors, mental disturbances, and gingivitis) may be expected to appear after chronic exposure of workers to air concentrations of mercury above 0.1 mg/m^3 (Bidstrup *et al.*, 1951, Friberg,

1951, Smith *et al.*, 1949, Smith *et al.*, 1970,). The industries involved included the chloralkali industry, the manufacture of thermometers and graduated scientific glassware, the repair of DC electrical meters, the mining and milling of mercury, the manufacture of artificial jewellery, the felt hat industry and others (NIOSH, 1973). Most of the publications referred to above do not report time-weighted average exposures and few give information as to the physical and chemical forms of mercury in the atmosphere. Different methods of measurement of mercury in air were employed some of which measured only mercury vapour, while others attempted to include particulate forms of mercury. Most of the studies, if not all, assumed that exposure occurred only during the working day. However, evidence has now come to light that, in certain industries, metallic mercury may be entrapped in the clothing and contaminate the home, particularly in those industries actually handling liquid metallic mercury .

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Effects of elemental mercury vapour, other than those designated as classical mercurialism, have been reported (Smith *et al.*, 1970). The study of Smith and co-workers involved observations on 567 workers exposed to mercury in chloralkali plants. The air concentrations of mercury (measured by a mercury vapour meter) ranged from less than 0.01 to 0.27 mg/m^3 and time-weighted averages were calculated for each worker. A significant increase in the frequency of objective tremors was noted at mercury levels in air above 0.1 mg/m^3 in agreement with previous reports on occupational exposure. However, a significant increase was observed at mercury concentrations in air of 0.06-0.1 mg/m^3 in such non-specific signs and symptoms as loss of appetite, weight loss, and shyness.

Studies related to assessment of the occurrence of a so-called "asthenic-vegetative syndrome" or "micromercurialism" have been reported (Friberg & Nordberg, 1972). This syndrome may occur in persons with or without mercury exposure. For a diagnosis of mercury-induced asthenic vegetative syndrome (Friberg & Nordberg, 1972) required that not only neurasthenic symptoms should be present but as supporting evidence three or more of the following clinical findings; tremor, enlargement of the thyroid, increased uptake of radio-iodine in the thyroid, labile pulse, tachycardia, dermographism, gingivitis, haemotological changes, and excretion of mercury in the urine which was above normal or increased 8-fold after medication with unithiol.

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2.2.1.2 Toxicity of Organic Mercury compounds

Mercury can change from one form to another in the environment. Methyl mercury tends to accumulate to some degree in all fish, but especially in the predatory fish. Methyl mercury is absorbed through the intestines and distributed throughout the body. It readily enters the brain, where it may remain for a long period of time.

Epidemics of poisoning in the general population due to exposure to phenyl- and methoxyethylmercury compounds have not been reported.Two outbreaks of poisoning due to elemental mercury vapour occurred in the 19th century, one due to a fire in the mercury mines in Idria, the other being caused by spillage of metallic mercury in a British warship in the early 1800s (Bidstrup, 1964). Fernandez *et al.*, (1966) have reported that, in the village of Almaden, the site of the large mercury mines in Spain, air mercury levels exceeded 0.1 mg/m^3. However, there were no reports about the health status of the population in the village.

Methyl- and ethylmercury compounds have been the cause of several major epidemics of poisoning due either to the consumption of contaminated fish or to eating bread prepared from

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cereals treated with alkylmercury fungicide. The two major epidemics of methylmercury poisoning (Katsuna, 1968) and in Niigata (Niigata, 1967) in Minamata Bay in Japan were caused by the industrial release of methyl- and other mercury compounds into Minamata Bay and into the Agano River followed by accumulation of the mercury by edible fish. The median level of total mercury in fish caught in Minamata Bay at the time of the epidemic was estimated as 11 mg/kg fresh weight and in the Agano River in Niigata as less than 10 mg/kg fresh weight (Swedish Expert Group, 1971). A recent report (Tsubaki, 1971) indicates that follow-up observations on exposed people in Niigata revealed a much larger number having mild signs and symptoms than the original 46 that had been reported. These milder cases may only have had paraesthesia. By 1971 a total of 269 cases of methylmercury poisoning had been reported in Minamata and Niigata, of which 55 proved fatal. By 1974, more than 700 cases of methylmercury poisoning had been identified in Minamata and more than 500 cases had been identified in Niigata (Tsubaki, 1975). The two Japanese epidemics have led to intensive studies on the effects of methylmercury on man and have resulted in important conclusions concerning dose-response relationships (Swedish Expert Group, 1971).

Epidemics resulting in the largest number of cases of poisoning and of fatalities have been caused by the ingestion of contaminated bread prepared from wheat and other cereals treated with alkyl- (methyl- or ethyl-) mercury fungicides. The largest recorded epidemic took place in the winter of 1971-72 in Iraq resulting in the admission of over 6000 patients to hospital and over 500 deaths in hospital (Bakir *et al.*, 1973). Reports on these epidemics have resulted in interesting clinical findings but quantitative studies relating exposure to effects have been reported only on the recent epidemic in Iraq (Bakir *et al.*, 1973, Mufti *et al.*, 1976, Shahristani *et*

al., 1976). In the Iraqi outbreak, the mean methylmercury content of the wheat was 7.9 mg/kg with most samples falling between 3.7 and 14.9 mg/kg. The mean methylmercury content of wheat flour samples was 9.1 mg/kg with a range of 4.8-14.6 mg/kg in 19 samples (Bakir *et al.*, 1973). In an epidemiological survey of a heavily affected village, Mufti *et al.* (1976) reported that the average total ingested dose of a group of 426 people was about 150 mg of mercury but some people may have consumed as much as 600 mg. The average daily intake of contaminated loaves was 3.2 loaves although individual variation was large, some people eating up to 10 loaves per day. The daily intake of methylmercury would vary greatly. The average daily intake of mercury in this village would be 80 μg/kg assuming a body weight of 50 kg for the population, with extremes of daily intake attaining 250 μg/kg. In the most severely affected group, reported by Bakir *et al.* (1974), the highest daily intake of mercury was about 130 μg/kg body weight. The average period of consumption for groups of patients reported by Bakir *et al.* (1973) ranged from 43-68 days. Mufti *et al.* (1976) reported mean consumption periods in villages to be about 32 days but some people continued for up to 3 months. Birke *et al.* (1972) has reported on families in Sweden consuming fish containing mercury levels of 0.3-7 mg/kg. Daily intake ranged up to approximately 5 μg/kg body weight. In two cases, intake was as high as 10-20 μg/kg. The highest recorded blood level of mercury was 1.2 μg/g of red cells or approximately 60 μg/100 ml of whole blood. A total of 188 people were referred to in these studies.

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2.2.2. Absorption

Generally, organic mercurials are absorbed much more rapidly than are inorganic forms. However, approximately 80% of mercury vapor is absorbed following inhalation exposure. Data on the inhalation absorption of organic mercury are limited and inconclusive. Metallic mercury

and mercurous salts (e.g., Hg_2Cl_2) are poorly absorbed (<0.10%) following oral exposure (Friberg and Nordberg, 1973). Absorption of mercuric chloride by adult mice was reported to be only 1 to 2% (Clarkson, 1972) but 1-week-old mice absorbed 38% of the orally administered compound. Gastrointestinal absorption of inorganic salts of mercury from food is <15% for mice and about 7% for humans (Goyer, 1991). Organic mercury compounds (methyl- and phenylmercury) have been shown to be readily absorbed (>80%) by humans and animals following oral exposure (ATSDR 1989, Goyer, 1991).

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2.2.3. Distribution

Being lipid soluble, mercury vapor readily enters the red blood cells and the central nervous system following inhalation exposure. The kidneys will exhibit the greatest concentration of mercury following exposure to inorganic mercury salts. Organic mercury is readily distributed throughout the body but tends to concentrate in the brain and kidneys (ATSDR 1989, Goyer, 1991). Mercury is known to bind to microsomal and mitochondrial enzymes resulting in cell injury and death. Mercury in renal cells localizes in lysosomes (Madsen and Christensen, 1978). Following 23-month exposure, neither inorganic nor organic mercury levels were increased in hair and urine of female workers exposed to mercury vapour concentrations of <0.02 mg Hg/m^3 (Ishihara and Urushiyama, 1994). However, the concentrations of inorganic as well as organic mercury were increased in the plasma and organic mercury levels were increased in erythrocytes. Petersson *et al.* (1991) administered ^{203}Hg-labeled methyl mercury intraperitoneally to rabbits twice weekly for nine weeks. After one week of treatment, the highest concentration of ^{203}Hg was detected in the fur with substantially lower levels being found in the kidney, liver, brain, muscle, and blood. Inorganic mercury levels in the liver of the rabbits increased with time after

cessation of treatment. Yoshida *et al.* (1991) reported that substantial concentrations of metallothionein-associated mercury were found in the kidneys and livers of neonate guinea pigs exposed to mercury vapor for 120 minutes on the day of birth. Metallothionein synthesis increased in the liver but not in the kidneys. Animal data indicate that all forms of mercury cross the placenta and that mercury levels may be 2-fold greater in maternal levels with fetal red blood cells containing mercury levels 30% higher than maternal red blood cells (Goyer, 1991). The placenta provides no barrier for methyl mercury thereby allowing easy access to the developing brain and development of subsequent neurological disorders characteristic of foetal exposure to methyl mercury (Rice *et al.*, 1996).

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2.2.4 Metabolism

Mercury is not destroyed by metabolism but rather converted to different forms and oxidation states. The metabolism of mercury and mercury compounds appears to be similar for animals and humans (ATSDR, 1989) and involves an oxidation-reduction cycle. Inhaled mercury vapour is rapidly oxidized to the divalent form in red blood cells (Halbach and Clarkson, 1978). Oxidation of elemental mercury also occurs in the lungs of humans and animals (Magos *et al.*, 1973, Hursh *et al.*, 1980), and some evidence suggests hepatic-mediated oxidation (Magos *et al.*, 1978). Animal studies have provided some data suggesting that the divalent inorganic mercury cation may be further reduced to elemental mercury (Clarkson and Rothstein, 1964, Dunn *et al.*, 1981). Organic \mercury compounds are also converted to divalent mercury by cleavage of the carbon-mercury bond (Goyer, 1991) with subsequent metabolism occurring via the oxidation reduction cycle. Aryl mercury compounds (e.g., phenylmercury) undergo this conversion more readily than do the short-chain (methyl) mercury compounds. No evidence of demethylation of

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methyl mercury by the brain of rabbits was noted following parenteral administration of the compound (Petersson *et al.*, 1991).

2.2.5 Excretion

The urine and faeces are the primary routes for the excretion of inorganic mercury by humans (ATSDR, 1989). Following brief exposure of humans to inorganic mercury, urinary excretion accounts for 13% of the total body burden, whereas this value increases to 58% for long-term exposure. For inorganic mercury, the urinary levels do not parallel blood levels (ATSDR, 1989). Henderson *et al.* (1974) identified three forms of mercury in the urine of occupationally-exposed individuals: elemental mercury, a reducible mercuric-cysteine complex, and a large complex in which the mercury can only be released following organic destruction. The data available for elemental mercury and mercury vapour indicate half-life for these forms to be 35 to 90 days (Goyer, 1991). The biologic half-life for inorganic mercury salts is about 40 days.

Faecal elimination is an important excretory route following exposure to organic mercury compounds (Norseth and Clarkson, 1970). However, Petersson *et al.* (1991), using ^{203}Hg-labeled methyl mercury administered intraperitoneally to rabbits twice weekly for nine weeks, showed that 12 weeks after cessation of treatment 54% of administered dose had been excreted in the urine and only 5% had been excreted in the faeces.

The elimination of organic mercury compounds generally follows first-order kinetics with whole body clearance times and blood clearance times being longer than for inorganic mercury. The biologic half-life for methyl mercury is about 70 days. Some evidence suggests that females tend

to excrete organic mercury faster than males (Aberg *et al.*, 1969, Miettinen, 1973). Additional excretory routes include saliva, bile, and sweat (ATSDR, 1989).

Experiments in animals indicate that elimination of inorganic mercury by the gastrointestinal tract depends on the dosage and the time after exposure. The faecal route is dominant soon after exposure. The urinary route is favoured when high doses are given (Prickett *et al.*, 1950, Rothstein & Hayes, Nordberg and Skerfving, 1972). Data obtained on rats subjected to a single exposure of labeled ^{203}Hg vapour indicated that about 4 times more mercury was eliminated in the faeces than in the urine (Hayes and Rothstein, 1962). In prolonged exposure of rats, the proportion changed in favour of urinary excretion (Gage, 1961). In workers exposed to mercury vapour, the output of mercury in urine slightly exceeded that in the faeces (Tejning and Ohman, 1966). High individual variation and great fluctuation from day to day were the principal features of urinary excretion in workers under similar exposure conditions (Goldwater *et al.*, 1963, Jacobs *et al.*, 1964). There is evidence that, on a group basis, urinary excretion is roughly proportional to exposure (air concentration) to elemental vapour (MAC, 1969). Occupational exposure of at least 6 months, 5 days per week at average air concentrations of mercury of 0.05 mg/m^3, should lead to average urinary concentrations of mercury of about 150 µg/litre.

Piotrowski *et al.* (1975) have reported changes in urinary rates of excretion in workmen following exposure to elemental mercury vapour.They noted that urinary excretion could be described by a two-term exponential equation with rate constants equivalent to half-times of 2 and 70 days. The short half-time compartment accounted for about 20-30% of the excretion rate under conditions of steady-state excretion. Piotrowski *et al.* (1975) suggested that there is variation in urinary mercury excretion in individuals and that this can be greatly reduced by

collecting the urine samples at the same time in the morning. Mercury exhalation found in animals after exposure to the elemental vapour (Clarkson & Rothstein, 1964) has also been confirmed in man (Hursh *et al.*, 1975). This pathway of excretion accounted for about 7% of the total excretion of mercury in volunteers following inhalation of a tracer dose. Recent observations indicate that the concentration of mercury in sweat may be sufficiently high to be taken into account in the overall mercury balance in workers exposed to elemental mercury vapour (Lovejoy *et al.*, 1974).

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The faecal route is most important in the elimination of mercury after acute or chronic dosing with methylmercury. Studies on human volunteers (Miettinen, 1973) indicate that approximately 90% of the elimination takes place via the faeces. This proportion does not change with time after exposure. Concentrations of total mercury in urine showed no correlation with blood mercury in people heavily exposed to methylmercury (Bakir *et al.*, 1973).

2.3 Mercury Levels in the Environment

Reliable data on Hg concentrations in the air are scarce. Recent information suggests a background level of about 2ng/m^3 in the lower troposphere of the northern hemisphere and about 1 ng/m^3 in the southern hemisphere, at least over oceanic areas. In European areas remote from industrial sources, such as the rural parts of the southern Sweden and Italy, concentrations most often lie in the range from 2 to 3 ng/m^3 in summer and from 3 to 4 ng / m^3 in winter. In urban air the concentrations could be higher.

Deposition with precipitation is a major factor in removing mercury from the atmosphere. The lowest concentrations of mercury in rain water, around 1 ng/litre, have been reported from a coastal site in Japan and from the islands of Samoa. Most other values reported lie in the range between 5 and 100 ng/litre.

Recent measurements of mercury in aquatic systems have given the following concentration ranges, which may be considered representative for dissolved mercury:

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Open ocean	0.5-3 ng/litre
Coastal sea water	2-15 ng/litre
Rivers and lakes	1-3 ng/litre

Local variations from these values are considerable, especially in coastal sea water and in lakes and rivers where mercury associated with suspended material may also contribute to the total load.

The mercury content in minerals forming ordinary rock and soils is usually very low. The normal levels in igneous rocks and minerals seems to be less than 50 μg/kg, and in many cases is less than 10 μg/kg. Due to the strong binding of mercury to soil particles, including organic matter, only small amounts of the metal are present in soil solution; reported averages range between 20 and 625μg/kg soil. Background levels in sediments are approximately the same as levels in

unpolluted surface soils. Average concentrations in ocean sediments probably lie in the rage between 20 and 100 μg/kg (Das *et al.*, 1980).

2.4 METHYLATION OF MERCURY

The mercury cycle is a complex biogeochemical system involving both biotic and abiotic transformations (Winfrey *et al.*, 1990). The production of methylmercury (CH_3Hg^+) is of particular interest because methylmercury is more toxic and mobile than the precursor Hg^{2+} ion and because methylmercury bioaccumulates in food chains. Because mercury cannot be broken down into an innocuous by-product, remediation of mercury-contaminated sites is dependent upon gaining an understanding of the factors that make mercury bioavailable and mobile. Controls on mercury methylation in natural environments such as lakes are not well understood.

Mercury accumulated in the tissues of fish is usually in the form of methylmercury, while the source is usually inorganic mercury (Huckabee *et al.*, 1979). Several hypotheses of how and where methylation occurs have been proposed. The main hypotheses are:

(a) biological methylation, bacterial in origin, which produces methylmercury in the environment,

(b) methylation by microorganisms associated with branchial mucus of the fish or in the fish gut, and

(c) methylation in the fish's liver (Thellen *et al*, 1981).

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It is generally agreed that methylation by fish, other than by bacteria associated with the fish, either does not occur or accounts for only an insignificant amount of the methylmercury produced. There is good evidence for methylation by bacteria in aquatic systems.

Abiotic mercury methylation in natural environments appears to be of minor importance. In contrast, microbial mercury methylation has been shown to occur in a variety of marine, estuarine, and lacustrine environments. Several previous studies have indicated that sulfate-reducing bacteria are the primary mercury methylators in freshwater and estuarine anoxic sediments (Gilmour *et al.*, 1991, 1992). Bacteria that process sulfate (SO_4^{2-}) in the environment take up mercury in its inorganic form, and through metabolic processes convert it to methylmercury. At this point, the methylmercury-containing bacteria may be consumed by the next higher level in the food chain, or the bacteria may release the methylmercury to the water where it can quickly adsorb to plankton, which are also consumed by the next level in the food chain.

Factors influencing microbial methylmercury production include microbial community composition, mercury availability, carbon availability, and the abundance of electron acceptors such as sulfate.

The methylation of inorganic mercury in the sediment of lakes, rivers and other waterways, as well as in the ocean, is a key step in the transport of mercury in aquatic food chains.

Things to note about methylation:

(a) Mono-methylmercury is the predominant product of biological methylation near neutral pH,

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(b) The rate of methylation is greater under oxidizing conditions than under anaerobic conditions,

(c) The output of methylmercury doubles for a ten-fold increase in inorganic mercury,

(d) Temperature affects methylation as a result of its effect on overall microbial activity,

(e) Higher microbial growth rate increases mercury methylation,

(f) Methylation rates are inhibited by the addition of sulfide to anaerobic systems.

The formation of new or enlarged artificial lakes considerably increases the production of methylmercury, although this increase was found to be short-lived in new lakes in Finland. A similar problem of increased mercury in new lakes, which was taken up by fish and fish-eating mammals, occurred in the scheme to divert the Churchil River in Manitoba, Canada. Methylation rates in one lake, which had been flooded 20 years previously, had returned to normal. Methylation rates in the new lake, which had flooded arboreal forest, were high and were expected to remain high for decades. The source of mercury in all of these artificial lakes appeared to be natural rather than anthropogenic in origin. Anaerobic conditions after the flooding of large amounts of organic material and the subsequent increase in microbial activity are thought to be the causes of the increase availability of mercury through methylation (Koeman *et al*, 1975).

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2.5 SOURCES OF ENVIRONMENTAL POLLUTION

Sources of environmental Hg pollution include natural occurrence, artificial Hg pollution and degassing of geologically bound mercury.

2.5.1 Natural Occurrence

A review by the Joint FAO/WHO Expert Committee on Food Additives (1972) quotes the major source of mercury as the natural degassing of the earth's crust and quotes figures in the range of 25 000-150 000 tonnes of mercury per year. These figures originate from a paper by Weiss *et al.* (1971) on concentrations of mercury in Greenland ice that was deposited prior to 1900. The most recent calculations on natural sources of mercury have been published by Korringa & Hagel (1974). These authors also made use of the figures of Weiss *et al.* (1971) to calculate the annual amount of mercury reaching the earth's surface due to precipitation of rainfall and arrived at a figure of approximately 30 000 tonnes. It was admitted that the sources of this atmospheric mercury are not yet clearly established but that volcanic gases and evaporation from the oceans are probably significant sources. It was also calculated by these authors that the run-off of mercury from rivers having a "natural mercury" content of less than 200 ng/litre would account for approximately 5000 tonnes of mercury per year. Measurements of the concentrations of mercury in air attached to aerosols (Heindryckx *et al.*, 1974) indicate that soil dispersion to the atmosphere is not an important source of mercury. Significant local contamination may result from natural sources of mercury.

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2.5.2 Industrial Production

According to a recent review by Korringa & Hagel (1974), world production averaged about 4000 tonnes per year over the period1900-1940. Production in 1968 was 8000 tonnes per year and, in 1973, attained 10 000 tonnes per year. Although considerable yearly fluctuations were noted, the average rate of increase since 1950 has been about 2% per year. Recent concern over environmental problems related to the use of mercury seems to have stabilized production rates

and to have led to a dramatic fall in the price of mercury. For example, according to figures quoted by Korringa & Hagel (1974), the1966 price was $452 per flask (a flask is 34.5 kg), the 1969 price had risen to $510.00 but by 1972 it had fallen dramatically to $202 per flask.

It is difficult to estimate the amount of mercury released into the environment as a result of the mining and smelting of this metal. High levels of mercury in lake and stream waters have been attributed to the dumping of materials and tailings (Wallace *et al.*, 1971). It has been estimated that stack losses during smelting operations should not exceed 2-3%. Thus, based on a production figure for mercury of 10 000 tonnes in 1973, one might expect to find losses to the atmosphere of the order of 300 tonnes per year.

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2.5.3 Uses of Mercury

Wallace *et al.* (1971) have attempted to give a picture of the use of mercury in the USA. They note that 26% of the mercury mined is not reusable. They pointed out, however, that at least from the theoretical point of view most of the remaining mercury (i.e. 74% of the mercury mined) is reusable. To what extent these theoretical possibilities are attained is debatable at the present moment. Korringa & Hagel (1974) took a more pessimistic point of view and conclude that there is every reason to assume that by about 1975 all the 10 000 to 11 000 tonnes of mercury produced per year due to mining operations will finally find its way into the environment, predominantly via the atmosphere.

Average consumption patterns for industrialized countries have been summarized by Korringa & Hagel (1974) as follows: chloralkali plants, 25%; electrical equipment, 20%; paints, 15%;

measurements and control systems, such as thermometers and blood pressure meters, 10%; agriculture, 5%; dental, 3%; laboratory, 2%; and other uses including military uses as detonators, 20%. This pattern of consumption in industrialized countries is similar to that published by D'Itri (1972) for the consumption in the USA in 1968. Included in "other uses" are mercury compounds in catalysts, preservatives in paper pulp industries, pharmaceutical and cosmetic preparations, and in amalgamation processes. The use of mercury in the paper pulp industries is dramatically declining and it was banned in Sweden in1966 (Swedish Expert Group, 1971). Hasanen (1974) has reported that no mercury compounds have been used in the paper pulp industry in Sweden and Finland since 1968.

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2.5.4 Contamination by Fossil Fuels, Waste Disposal, and Miscellaneous Industries

Industrial activities not directly related to mercury can give rise to substantial releases of this metal into the environment. The most significant source is probably the burning of fossil fuels. Heindryckx *et al.* (1974) calculated the following approximate figures based on reports published in 1971 (Joensuu, 1971): the combustion of coal and lignite, 3000 tonnes per year; the refining and combustion of petroleum and natural gas, 400 tonnes per year; the production of steel, cement, and phosphate, 500 tonnes per year. Korringa & Hagel (1974) made similar calculations from published material (Joensuu, 1971, Cardozo, 1972, Weiss *et al.*, 1971). They estimated for the year 1970, an annual release of 3000 tonnes of mercury from coal burning, 1250 tonnes from mineral oil, and 250 tonnes from the consumption of natural gas. They expected that, by 1975, a total of 5000 tonnes of mercury would be emitted from burning fossil fuels.

Smelting of metals from their sulfate ores should contribute some 2000 tonnes annually and the making of cement and phosphate and other processes involving heating should have contributed another 5000 tonnes per year by 1975.

D'Itri (1972) points out that the disposal of sewage might be an important source of environmental mercury. Calculations from data in the literature indicate that somewhere between 200 and 400 kg of mercury per million population may be released from sewage disposal units. This would amount to approximately 40-80 tonnes per year for the entire population of the USA. He further points out that sewage sludge can retain high amounts of mercury according to published studies from Sweden (6-20 mg/kg). This sludge is sometimes used as a fertilizer resulting in widespread dispersal of mercury or is sometimes heated in multiple hearth furnaces when most of the mercury would probably be released into the atmosphere. If the United States production is taken as being roughly 30% of world consumption, one might extrapolate the sewage release figure for the United States to indicate that something of the order of 1000 tonnes of mercury may be released from sewage systems on a global scale.

The anthropogenic release of mercury has been well summarized in a recent article by Korringa & Hagel (1974) and will be briefly stated here. The total global release of mercury is taken as the sum of the global production (following their pessimistic view that all will be released into the environment) plus the release from fossil fuels and natural gas and release from non-mercury related industries.

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It was calculated that by 1975 the total anthropogenic release of mercury on a global scale would be about 20 000 tonnes per year. These figures should be compared with a minimum estimated release of 25 000 to 30 000 tonnes per year from natural sources. The latter figure may, in fact, be as high as 150 000 tonnes per year, given the uncertainties in calculations on the natural global release of mercury.

2.6 ENVIRONMENTAL TRANSPORT, DISTRIBUTION, AND TRANSFORMATION

Jenson & Jernelov (1972) have suggested different types of cycle for the distribution of mercury. One cycle is global in scope and depends upon the atmospheric circulation of elemental mercury vapour. The other cycle is local and is based on an assumed circulation of volatile dimethylmercury compounds. In the global cycle most of the mercury is derived from natural sources whereas the local cycle is predominantly concerned with man-made release.

2.6.1 Distribution between Media - the Global Mercury Cycle

Recent calculations on the global circulation of mercury have been reported by Korringa & Hagel (1974). Their calculations are based principally on data giving mercury levels in ice samples collected in Greenland and in the Antarctic as reported by Weiss *et al.* (1971). The circulation of mercury from natural sources was calculated using a figure of 0.06 μg of mercury per kilogram of Greenland ice samples collected prior to the year 1900. Using a reported figure for the global precipitation of water as 5.2×10^5 km^3 per year, they estimated that minimum transport from the atmosphere to the earth should have been about 30 000 tonnes annually, prior to 1900. The contribution by dust particles was regarded as insignificant, an assumption now supported by the findings of Heindryckx. (1974). Based on a published figure of 4.1×10^5 km^3

for annual precipitation over the oceans, these authors estimated the annual delivery of mercury to the oceans as 25 000 tonnes. Korringa & Hagel (1974) also calculated the contribution of the man-made release of mercury to the atmospheric transport cycle. They assumed that 16 000 tonnes of mercury is now released per year to the atmosphere from man-made sources and that the mercury is returned to the continental land surfaces and would soon re-evaporate to the atmosphere. The 16 000 tonnes per year would eventually find its way into the oceans and thus the annual delivery to the oceans from both natural and man-made sources would be 25 000 plus 16 000 tonnes which on a proportional basis should increase the background level from the 0.06 µg/kg observed prior to the 1900s in Greenland ice to a predicted level of 0.1 µg/kg. However, they point out that since most of the man-made release is probably in the northern hemisphere, the present level in Greenland ice should be somewhat higher than 0.1 µg/kg. They note that this estimate agrees well with the observations of Weiss *et al.* (1971) who found present levels in Greenland ice to range from 0.09 to 0.23 µg/kg with an average of 0.125 µg/kg. Thus, from these rough estimates, it would appear that present day "background" levels in rainwater, and presumably in the atmosphere, have a substantial component related to man-made release (approximately one-third). Observations on "background" mercury levels in the atmosphere tend to confirm the quantitative features of this global picture (Heindryckx, 1974). These authors assume that 50 000 tonnes are released each year from the continental land masses, that the mercury mixes up to a height of 1 km and that, in effect, the 50 000 tonnes are located over the continental land masses that account for 30% of the earth's surface. The assumption of the location of this mercury over the land masses is not in contradiction with the calculations of Korringa & Hagel (1974). It assumes only that the atmosphere above the land masses is in steady state, and receives 50 000 tonnes of mercury a year as evaporation and loses 50 000 tonnes per

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year to the atmosphere over the oceans. With these assumptions, Heindryckx, (1974) concluded that the background continental levels of mercury vapour plus aerosols should be 10 ng/m^3. The assumed mixing height of 1 km is probably the maximum level and they suggest that the actual level of mercury in air would lie between 1 and 10 ng/m^3. These figures are in good agreement with the published air levels as by Korringa and Hagel (1974). They note that this figure does not change substantially if one takes into account the fact that most of the mercury in river water is adsorbed to suspended matter with a mercury content of 200-500 µg/kg and that some 10^{10}-10^{11} tonnes of sediment are carried each year to the oceans. In fact, river transport of mercury to the oceans may be less than 5000 tonnes per year. Heindryckx, (1974) noted that the concentrations of mercury in the North Sea and in the coastal areas around the North Sea were far less than would be predicted if all the mercury in the rivers entering this area were, in fact, delivered into the oceans. Presumably a considerable amount of mercury observed in river water is retained in sediments in the rivers and estuaries and does not reach the ocean by normal flow of the river. Thus it would appear that the major pathway of global transport of mercury is metallic mercury transported in the atmosphere.

An important conclusion from these calculations on the global cycle of mercury is that the concentration of mercury in the oceans should not change substantially in the foreseeable future, and that the mercury concentration in the oceans has not changed significantly since the beginning of the industrial era. The amount of mercury in the oceans has been calculated as 70 million tonnes using a figure for total ocean volume of 1.37 x 10^9 km^3 and taking the average mercury content of ocean water as 50 ng/litre. Thus contrary to what has been observed for the mercury content of the atmosphere, it will be a long time before the mercury content in sea water

is significantly increased. Since water is thought to remain in the surface layers of the ocean for 10-50 years, these authors concluded that the mercury resulting from man-made activities should be well distributed in the water of all the oceans and therefore should not lead to high local concentrations.

The origin of mercury released by natural processes is not well established. Volcanic emissions are a possible source in view of the high concentrations of mercury vapour reported in the vicinity of volcanoes (Weiss *et al.*, 1971). The general "degassing" of the earth's surface is probably a major source (Weiss *et al.*, 1971). Korringa & Hagel (1974) have raised the possibility that evaporation from the oceans may make a contribution to the mercury present in the atmosphere in view of the substantial quantities of water vapour that evaporate (4.48×10^5 km^3). However, it seems unlikely that mercury would evaporate at the same rate as water in view of the fact that it is believed to be in a complex form in the oceans.

The mechanisms of volatilization of mercury from the land masses are not well understood. Presumably release of mercury from volcanoes is due to the high temperatures associated with volcanic activity. Vostal (1972) has suggested two major mechanisms, firstly the reduction of mercury in soils by a chemical process depending on the local redox potential, and secondly reduction by the activity of microorganisms. The quantitative importance of these two processes is not known. Mercury-volatilizing microorganisms are known to exist and have been identified (Magos *et al.*, 1964, Tonomura & Kanzaki, 1969).

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2.6.2 Environmental Transformation-the Local Mercury Cycle

Mercury is present naturally in the environment and released from manmade sources in a variety of chemical and physical states. The principal mercury ore is cinnabar, which is mercury sulfide. Andersson (1967) has shown that mercury in soils is complexed to the organic (humus) content. Metallic mercury may be discharged into the environment from natural sources as discussed above and also from man-made sources such as chloralkali plants. Varieties of organomercurial compounds are also discharged into the environment as a result of human activities. Both the inorganic forms of mercury (such as metallic mercury vapour and cinnabar) and the organic forms of mercury are subject to conversion in the environment. Jensen & Jernelov (1972) have summarized the major pathways of transformation. The inorganic forms of mercury (Hg^0 and HgS) undergo transformations in the environment mainly by oxidation-reduction reactions. Mercury vapour is oxidized to ionic divalent mercury (Hg^{2+}) in water in the presence of oxygen. Concentrations as high as 40 g/litre have been attained when water saturated with oxygen was exposed to mercury vapour (Wallace *et al.*, 1971). As pointed out by Jensen & Jernelov (1972) the oxidation of metallic mercury to inorganic divalent mercury is greatly favoured when organic substances are present in the aquatic environment.

Ionic mercury, once present in water, is capable of forming a wide variety of complexes and chelates with organic materials. Of considerable importance is its reaction with the sulfide (S^{2-}) ion to form highly insoluble mercury (II) sulfide. This reaction is likely to occur in anaerobic aquatic environments owing to the presence of hydrogen sulfide gas. This sulfide complex of mercury is highly stable and will not normally become involved in transformation under anaerobic conditions. However, in the presence of oxygen, the insoluble mercury (II) sulfide can

become oxidized to the soluble sulfite and sulfate salts of mercury which allow the metal to ionize and enter subsequent chemical reactions. In addition to the oxidation of metallic vapour, inorganic mercury (Hg^{2+}) can be formed by the breakdown of a variety of organic mercury compounds. The alkoxyalkylmercury compounds are very unstable in acid conditions and it has been reported (Jensen & Jernelov, 1972) that, in humid soil (pH = 5), methoxyethylmercury has a half-life of only 3 days. Aryl- and alkylmercury compounds can all be degraded in the environment by chemical and physical processes and by biologically mediated processes.

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Divalent inorganic mercury (Hg^{++}) can undergo two important reactions in the environment. The first is the reduction to metallic mercury vapour, a reaction that will occur in nature under appropriate reducing conditions. As mentioned above, certain bacteria, particularly of the genus *Pseudomonas,* can convert divalent mercury into metallic mercury (Magos *et al.*, 1964). The formation of inorganic divalent mercury in nature and its reduction to metallic mercury vapour are probably key processes in the global cycle of mercury. The reduction to metallic mercury vapour must be the key step in the release of mercury because of degassing of the earth's surface. The oxidation of metallic mercury vapour to divalent ionic mercury must be the critical step in the uptake of mercury vapour in rainwater and in the oceans. Unfortunately, other than these crude generalizations, little is known of the details of the kinetics of these processes in nature.

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The second important reaction that ionic divalent mercury (Hg^{++}) undergoes in nature is its conversion to methylmercury and dimethylmercury compounds and the interconversions between these compounds. These reactions play a critical role in the so called "local cycle" of mercury and are worth further discussion. Some countries, particularly those in Scandinavia, that

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used methylmercury fungicides extensively, experienced a general rise in the mercury content of their agricultural products. High levels were also noted in some species of birds. The increase corresponded with the onset of the use of methylmercury fungicides. However, it was discovered that mercury levels in fish were also high and that these fish were obtained in areas where methylmercury compounds were not used (Jensen and Jernelov, 1969). It was subsequently discovered that methylmercury was the predominant form of mercury in fish regardless of the nature of the mercury pollutant. This was the first evidence that transformations of mercury compounds must occur in the environment and that, indeed, they must be of great significance. It has now been demonstrated that biological methylation of mercury occurs in the organic sediments of aquaria and in sediments from freshwater and coastal waters of Sweden (Jernelov, 1967, Jensen and Jernelov, 1967, 1969,).

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Two biochemical pathways of methylation of mercury have been identified, one anaerobic the other aerobic. The anaerobic pathway involves the methylation of inorganic mercury by methylcobalamine compounds produced by methanogenic bacteria in a mildly reducing environment (Wood *et al.*, 1968). The process is non-enzymic and is strictly anaerobic. The aerobic pathway has been described by Landner (1971) in studies of *Neurospora crassa.* His findings indicate that methylmercury bound to homocysteine becomes methylated by those processes in the cell normally responsible for the formation of methionine. In other words, the methylmercury-homocysteine complex is methylated by "mistake".

Despite the fact that an anaerobic pathway for methylmercury production is well known, it seems unlikely that significant amounts of methylmercury are formed in the aquatic environment under

anaerobic conditions. The chief reason for this, as pointed out by Jensen & Jernelov (1972), is that, in natural water when oxygen is exhausted, hydrogen sulfide is formed and divalent mercury becomes bound up as mercury (II) sulfide. In this sulfide form, mercury is not available for methylation under anaerobic conditions (Jernelov, 1968), and methylation is slow even under aerobic conditions (Fagerstrom & Jernelov, 1971).

In an aquatic environment under aerobic conditions, it must be borne in mind that the upper sedimentary layers and sedimentary particles suspended in the water may be both aerobic and anaerobic,the exterior being well oxygenated and the interior deficient in oxygen. Thus both pathways, aerobic and anaerobic, are possible routes of methylation in water that is oxygenated.

The ability to methylate mercury is not confined to a limited number of species of microorganism. Thus, conditions that promote bacterial growth in general, will lead to enhanced methylation of mercury. The highest rates of methylation in the aquatic environment are, therefore, seen in the uppermost part of the organic sediments and on suspended organic material in water (Jernelov, 1973).

The formation of dimethylmercury from monomethylmercury compounds has been shown to occur in decomposing fish (Jensen & Jernelov, 1968), and from (originally) inorganic mercury in sediments. The anaerobic pathway using methylcobalamines is one means by which dimethylmercury can be synthesized. The reaction is greatly favoured by high pH whereas the formation of monomethylmercury is favoured by a low pH environment.

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The ability to methylate mercury at a high rate correlates with the resistance of the microorganism to concentrations of inorganic mercury (Jernelov, 1973). The observations, reviewed above, of the interconversion of the various mercury compounds in nature have led to a hypothesis for a local cycle (Jensen & Jernelov, 1972). Inorganic divalent mercury is formed either by the oxidation of metallic mercury vapour by physico-chemical processes or by the cleavage of the carbon-mercury bond in organomercurial compounds either chemically or enzymatically. The divalent ionic mercury becomes attached to sediments either suspended in the water or in the sedimentary layers. The upper sedimentary layers are biologically active but it is postulated that, with the passage of time, large quantities of inorganic mercury will penetrate down to the inorganic mineral layers of the sediments where the mercury should remain inactive. In the surface layers of the sediment, part of the inorganic mercury becomes methylated. Methylation significantly increases the ability of mercury to cross biological membranes. This is why aquatic organisms contain mainly methylmercury. If conditions of pH are appropriate, dimethylmercury will be formed. Dimethylmercury is water insoluble, possesses a very high volatility, and is postulated to diffuse from the aquatic environment into the atmosphere. Once in the atmosphere, it is subject to removal by rainfall. If the rainwater is acidic, the dimethylmercury is converted to monomethylmercury compounds and is thereby returned to the aquatic environment completing the cycle. In the presence of mercury (II), dimethylmercury is converted to two methylmercury molecules (Jensen & Jernelov, 1969).

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2.6.3 Speciation

The following speciation among mercury compounds has been proposed by Lindquist et al. (1984), where V stands for volatile, R for water-soluble or particle-borne reactive species, and NR for non-reactive species (Hg^0 is elemental mercury):

V: Hg^0, $(CH_3)_2Hg$

R: Hg^{2+}, HgX_2, HgX_3^-, and HgX_4^{2-}, with X = OH^-, Cl^- and Br^-.

HgO on aerosol particles. Hg^{2+} complexes with organic acids.

NR: CH_3Hg^+, CH_3HgCl, CH_3HgOH and other organomercuric

compounds, $Hg(CN)_2$. HgS and Hg^{2+} bound to sulfur in fragments of humic matter.

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The main volatile form in air is elemental mercury but dimethylmercury may also occur (Slemr *et al.*, 1951).Uncharged complexes, such as $HgCl_2$, CH_3HgOH etc., occur in the gaseous phase, but are also relatively stable in fresh water (snow and rain as well as standing or flowing water). $HgCl_4^{2-}$ is the dominant form in seawater.

2.6.4 Interaction with Physical or Chemical Factors

The interaction of mercury with physical or chemical factors has been referred to frequently in the previous section, so that only a brief summary will be given here. In terms of the global distribution of mercury, such physicochemical factors as temperature, pH, redox potential, and chemical affinities for the organic materials in soil will interact to determine the degree of volatility of mercury under specific local conditions and the rate of release of mercury from the earth's crust as elemental mercury vapour. The interplay between these factors is so complex that studies of mercury volatilization from soil and from the earth's crust, in general, do not lend themselves easily to experimental work. Once in the atmosphere, metallic mercury is liable to

both physical and chemical interactions. Physically it may be adsorbed on to particulate materials in air. Metallic mercury vapour should distribute more or less evenly between air and water providing it remains in the unoxidized metallic state (Hughes, 1957). However, the reported levels in rainwater are higher than the background level by a factor of at least 2 or 3. This is no doubt a consequence of the oxidation of metallic mercury to ionic mercury in the water in the presence of oxygen. Once deposited in the ocean from rainwater, any remaining metallic mercury should be liable to oxidation to ionic mercury whereupon it will undergo rapid chemical combination with various chemical compounds in ocean water.

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2.6.5 Bioconcentration

The short-chain alkylmercurials, especially methylmercury compounds, have a strong tendency to bioaccumulation since they possess a group of properties that makes them unique among the mercury compounds. Methylmercury is very efficiently absorbed through biological membranes. In mammals, absorption of methylmercury from food is virtually complete. Methylmercury is degraded much more slowly into inorganic mercury than are the other classes of organomercurial compounds. It is excreted from living organisms much more slowly than other mercury compounds. It possesses a very high chemical affinity for the sulfhydryl group. Since this group occurs mainly in proteins in living organisms, methylmercury, once it has entered the organism, is soon convened to a non-diffusible protein-bound form. However, even though most of the methylmercury is bound to protein, a small fraction remains in a diffusible form. Methylmercury rapidly equilibrates between diffusible and non-diffusible binding sites and thus retains its mobility within animal tissues.

In view of its ability to accumulate in living organisms, one would, in general, expect to see higher concentrations of methylmercury at higher trophic levels in natural food chains. Qualitatively, this generalization appears to be true but quantitative predictions are not possible because of the complex interplay of a host of factors that influence the accumulation and movement of mercury in food chains. For example, remarkably large species differences exist in biological half-times which vary from approximately 7 days in the mouse, to 70 days in the monkey and man, 500 days in seals, and over 1000 days in some species of fish (Clarkson, 1972).

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The accumulation of methylmercury in food chains in freshwater systems has been proposed as a three-step process by Fagerstrom & Larsson. The first step is an accumulation by bottom fauna that are in closest proximity to the active sedimentary layers where the methylmercury is formed. Accumulation in the bottom fauna, including plankton, would be followed by accumulation in species such as the roach and finally in the large carnivorous fish such as the northern pike. The authors point out that the relative importance of uptake of methylmercury directly from water through the gill membranes, as opposed to intake from food, should depend upon the trophic level of the fish. The higher the trophic level the more important the intake from food. However, for the overall food chain, uptake through the gills is the key process. If for some reason there is a dramatic change in the environmental layers of methylmercury, the authors predict that it would take from 10-15 years for the levels in the top predators to readjust to the new environment.

These generalizations on freshwater species should be expected to apply to oceanic fish. The remarkably high levels of methylmercury seen in swordfish and tuna fish are due to a variety of factors. First these species are large carnivorous fish at the end of a food chain. They live for a relatively long time compared with other species of fish and it is well established that methylmercury levels show a positive correlation with age (and or weight) of the fish. They are highly active fish having insatiable appetites. Because of their activity, large quantities of oceanic water pass through the gill membranes each day. Thus it is possible that tuna fish, swordfish and related species have a high intake of methylmercury both from their food supply and from the surrounding water. Accumulation of mercury in the terrestrial and aquatic food chains (Fagerstrom & Larsson, 1990) results in risks for man mainly through the consumption of: game birds in areas where methylmercury fungicides are in use; fish from contaminated waters, especially predator species, tuna fish, swordfish and other large oceanic fish even if caught considerably off shore; other seafoods including muscles and crayfish; fish-eating birds and mammals; and eggs of fish-eating birds.

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2.7 Analytical Methods for the Determination of Total mercury in Fish

Methods of analysis are usually classified according to the type of instrument used in the final measurement. Measurement of the very low levels of mercury found in the non-contaminated environment makes special demands both on the skills of the analyst and the resources of the method employed. Several research papers exist concerning methods of determining mercury. Several recent reviews have appeared (Swedish Expert Group, 1971, Wallace *et al.*, 1971, D'Itri, 1972, NIOSH, 1973, CEC Working Group of Experts, 1974). The most frequently used methods for measurements of total mercury are colorimetric (dithizone), flameless atomic absorption, and

neutron activation. The flameless atomic absorption method has become the "work-horse" for measurement of environmental samples. Difficulties might arise in the measurement of mercury owing to the fact that it is strongly bound to the organic materials in most samples. Many procedures require the destruction of organic materials by wet oxidation or by high temperatures. Loss of mercury by volatilization may occur. If the wet oxidation is too mild the result will be inadequate recovery. A high reagent blank may be introduced by the chemicals used for oxidation. In certain procedures involving atomic absorption or neutron activation the digestion of the sample or heating of the sample is not necessary. These procedures have the advantage of having a low blank but problems of variable recovery or interference may arise.

The determination of mercury by colorimetric measurement of a mercury dithizonate complex has been the basis of most of the methods in the 1950s and in the 1960s. The above procedures all make use of wet oxidation of the sample followed by extraction of mercury in an organic solvent as a dithizonate complex and finally the colorimetric determination of the complex itself. Selectivity for mercury is obtained by adjusting the conditions of extraction. Copper is the metal most likely to interfere with mercury measurement by dithizone.

The dithizone procedure has an absolute sensitivity of about 0.5 μg of mercury. A sample size of 10 g is suitable for most digestion procedures so that mercury can be determined at the 0.05 mg/kg level in most foodstuffs and tissues.

The quoted recovery rates for the dithizone procedure from foodstuffs and tissues are in the range of 85-99% and the reproducibility can yield a coefficient of variation of as low as 2%. On

account of its long history of use, the dithizone procedure has been used to measure mercury in virtually all types of environmental samples including air, water, food, tissues, and soils. It suffers from the disadvantage that it is time consuming and its sensitivity is not high when compared with atomic absorption procedures.

Magos (1971) has described a reduction technique that selectively determines total and inorganic mercury in biological samples without digestion of the material. This technique has been modified by Magos & Clarkson (1972) to permit determination of mercury in blood samples at the low levels found in unexposed populations (0.1-1.0 µg/100 ml). The technique has a sensitivity of approximately 0.5 ng of mercury. The relative standard deviation was 2% and the recovery rates were quoted as being close to 100%. The technique has the advantage of high speed (each determination taking less than 2 minutes), high sensitivity, and the apparatus involved is light, portable, and suitable for field applications. Its widest application to date has been in the measurement of mercury in biological samples in the large Iraq outbreak (Bakir *et al.*, 1973). Since the procedure does not require digestion of the biological sample, internal standards are used in each determination. The rates in this procedure must be checked for each new biological matrix.

The atomic absorption techniques are subject to interference. The most common interfering substances are benzene and other aromatic hydrocarbons that absorb strongly in the 253.7 nm region. The combustion-amalgamation method has undergone a series of developments to avoid difficulties due to interfering substances. All these methods have sensitivities down to the 1 µg/litre level and avoid the risk of interference from other substances. However, as pointed out

by Burrows (1975), care must be taken in the design and operation of the combustion tube to avoid losses of volatile mercury derivatives.

Procedures for neutron activation analysis of total mercury have recently been reviewed by Wallace et al. (1971), Swedish Expert Group (1971) and Burrows, (1975). The method is based on the principle that when natural mercury (a mixture of stable isotopes) is exposed to a high flux of thermal (slow) neutrons, it is converted to a mixture of radioactive isotopes, principally ^{197}Hg and ^{203}Hg, which have decay half-lives of 65 hours and 47 days, respectively. After the sample has been irradiated with neutrons, a precise weight of carrier mercury is added and the sample subjected to digestion and organic destruction. On completion of digestion, mercury is isolated by electrodeposition on a gold foil and the radioactivity is determined with a gamma counter. The use of carrier mercury corrects for any losses of mercury during the digestion, extraction, and isolation procedures. The limit of detection is 0.1-0.3 ng of mercury. The sample size is 0.3 g giving a concentration limit of 0.3-1 μg/kg in most biological samples.

In general, the analyst is faced with three major options in the use of neutron activation procedures; *(a)* destruction or non-destruction of the sample, (destruction and isolation of the mercury is usually required in samples containing less than 1 μg of mercury); *(b)* the choice of isotope ^{197}Hg (if the longer-lived isotope, ^{203}Hg, is used the sample may be allowed to stand to avoid interference from short-lived elements activated along with the mercury, however, ^{203}Hg requires a more intense neutron flux or a longer irradiation time to achieve the same activity as the ^{197}Hg); *(c)* the choice of detector (the sodium iodide (thallium) detector does not have as high a resolution as the germanium (lithium) detector, although its sensitivity is significantly higher).

Interference may come from the following elements, produced at the same time as the radioactive mercury isotopes, ^{24}Na, ^{82}Br, ^{32}P, and ^{75}Se. Interference from these isotopes may be avoided by chemical isolation of the radioactive isotope. However, ^{75}Se may not be completely removed by the isolation procedures and might interfere if the sodium iodide (thallium) detector is used. The better resolution of the germanium (lithium) detector allows correction for ^{75}Se interference through use of other lines in the ^{75}Se spectrum. For samples containing more than 1 μg of mercury, the required selectivity can be achieved without destruction of the sample, i.e., by instrumental analysis only. One procedure is to measure the ^{203}Hg isotope, after allowing the sample to stand for approximately one month to eliminate interference due to sodium, phosphorous and bromine. Another procedure is to make use of the discriminating germanium (lithium) detector when the gamma irradiation from the radioactive isotope may be determined to the exclusion of most of the interfering radioactivity.

Compared with other methods reviewed here, the neutron activation procedure has the following advantages; (1) high sensitivity (approximately 0.5 μg/kg); (2) no reagent blank; (3) independence from the chemical form of the element; and (4) non-destructive instrumental methods applicable to samples containing 1 μg of mercury or more. It has the disadvantages that it cannot be adapted to field use and, that if there are large numbers of samples, special radiation facilities and data processing are required. It is generally agreed that the neutron activation procedure finds its most important use as a reference method against which other procedures can be checked.

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A variety of other instrumental techniques, such as X-ray fluorescence, mass spectrometry, and atomic fluorescence, for the measurement of total mercury have been reviewed by Burrows (1975). In general, some of these methods may have a potentially higher sensitivity or selectivity for mercury. The fact is that, at the time of writing, these procedures have not yet found useful application in the measurement of mercury in environmental samples.

2.7.1 The Cold Vapour (CV) Technique

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

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Two reducing agents usually employed for CV analysis are tin (II) chloride ($SnCl_2$) and sodium borohydride ($NaBH_4$). The reaction between mercury (II), $SnCl_2$ and $NaBH_4$ are described by equations 2 & 3 respectively.

Equation 1:

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

Equation 2:

$$BH_4^- + H^+ + 3H_2O \rightarrow H_3BO_3 + 8H^+ + Hg^{2+} \rightarrow Hg^0 + 4H_2$$

But of these two reactions, the borohydride technique is limited to open systems because of the production of hydrogen gas.

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CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Apparatus

All glassware used were soaked in detergent solution for about sixteen hours; rinsed and soaked in 10% (v/v) HNO_3 for another sixteen hours. They were rinsed with distilled water followed by 0.5% (w/v) $KMnO_4$ and finally rinsed with distilled water before use.

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Automatic Mercury Analyzer Model HG-5000 (Sanso Seisakusho Co., Ltd, Japan), equipped with mercury lamp operated at a wavelength of 253.7 nm was used for the determinations. The signals were obtained on a Yokogawa Model 3021 strip chart recorder.

Digestion apparatus was thick walled long neck 50 ml volumetric flasks and a hot plate with a temperature range of 150-350^{0}C.

3.2 Reagents

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

Mercury stock standard solution (1000 mg L^{-1}) was prepared by dissolving 0.677 g of $HgCl_2$ in the acid mixture HNO_3-H_2SO_4-$HClO_3$ (2+10+2) in a 50ml digestion flask with heating on a hot plate at a temperature between 150 and 250^0 C until the solution became clear. The solution was

then diluted to 50ml with water. Blank solutions were also prepared in the ratio of 1 : 1 : 1 : 5 distilled water : HNO_3 : $HClO_3$: H_2SO_4 for use as a diluent. The working solutions were freshly prepared by diluting an appropriate aliquot of the stock solution through intermediate solutions using the blank solution. Stannous chloride solution (10% v/v) was prepared by dissolving 10 g of the salt in 100 ml 1M HCl. The solution was aerated with nitrogen gas at 50 ml min^{-1} for 30 min to expel any elemental mercury from it.

3.3 Sampling and Sample Preparation

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The fish species were collected from random commercial catches in villages along Akosombo Reservoir and Kpong Reservoir both in the Eastern region and Lake Bosomtwi in the Ashanti Region depending on the species available for sale. Samples obtained were therefore reflective of species meant for consumption. A total of one hundred and sixty five (165) fishes covering nine (9) species were obtained. The samples were sorted out by species, placed in clean plastic bags and stored on ice in an ice chest. They were then transported to the laboratory, identified and kept in a freezer at -2^0C prior to preparation for chemical analysis. The samples were washed with distilled water, dried in tissue paper and the length and body weight of each was taken after defrosting in the laboratory. A portion of the edible muscle tissue was removed from the dorsal part of each fish, homogenized and stored in clean-capped glass vials and kept in a freezer until analysis.

3.4 Digestion Procedure

The fish samples were digested for total mercury determination by an open flask procedure as shown in chart 3.0 below developed at the National Institute for Minamata disease (NIMD) in

Japan by Akagi and Nishimura (1991). The accuracy of this method has been verified at NIMD through interlaboratory comparison exercise and by participating in the analyses of Certified Reference Materials (CRMs) supplied by the International Atomic Energy Agency (IAEA). In the procedure, 0.5 g of homogenized fish sample was weighed into 50 ml volumetric digestion flask and a mixture of 1 ml H_2O, 2ml NHO_3-$HClO_3$ (1:1) and 5ml H_2SO_4 was added. The mixture was then heated at a temperature between 150^0C and 250^0 C until the solution was clear. The sample solution was then cooled and diluted to 50 ml with double distilled water. A blank and standard solution digest using 20, 50, and 100 µl of 1µg ml^{-} standard Hg solution were subjected to the same treatment. The concentrations of the standard solution digest obtained were 25, 50 and 100ng.

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Sample (0.5g in 50ml digestion flask)

↓ H_2O, 1ml

↓ HNO_3: $HClO_4$ (1:1), 2ml

↓ H_2SO_4, 5ml

↓ Heat at 200^o C ± 5^o C for 30min

Cool to room temperature

Digested Sample

↓ H_2O, make up to 50ml

Sample Solution, 5ml

↓ 10% $SnCl_2$, 0.5ml

AAS (Analyzer)

Chart 3.0 Analytical procedure for total mercury in fish samples

3.5 Determination of mercury

Determination of mercury in all the digests was carried out by cold vapour atomic absorption spectrophotometer using an automatic Mercury Analyzer Model HG-5000 (Sanso Seisakusho co., Ltd, Japan) developed at NIMD. The analyzer is an instrument designed specifically for the measurement of mercury using the cold vapour technique. It makes use of the batch mercury cold vapour generation system. The analyzer consists of an air circulation pump, a reaction vessel, $SnCl_2$ dispenser, an acidic gas trap and a four –way stop-cock with tygon tubes to which is attached a ball valve. The operations of the ball valve and the air circulation pump are controlled by a microprocessor. A schematic diagram of the system is shown in Fig 3.0. During the determination, a known volume of the sample solution normally 5 ml is introduced into the reaction vessel using a micropipette (1-5 ml). The reaction vessel is immediately stopped tightly and 0.5 ml of 10 %(w/v) $SnCl_2$-$2H_2O$ in 1MHCl is added from a dispenser for the reduction reaction. During this time, air is circulated through the four-way stopcock to allow the mercury vapour to come to equilibrium and the acidic gases produced by the reaction also swept into the sodium hydroxide solution. After 30 seconds the four-way stopcock is rotated through 90^0 and the mercury vapour is swept into the absorption cell. Response was recorded on the strip chart recorder as a very sharp peak. Peak heights were used for computations. Standards used for calibration of the analyzer included solutions containing 0.0, 0.5, 1.0 and 2.0 ng Hg ml^{-1}. Quality assurance samples analyzed included method (digestion) blanks, replicate samples, pre-digestion spikes, and post-digestion spikes.

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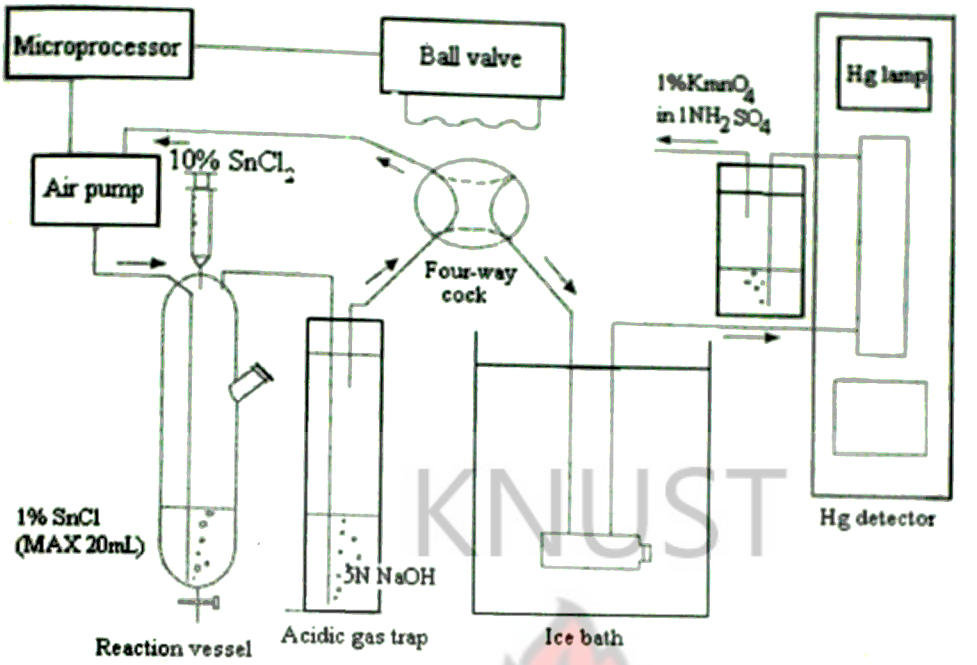

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Fig. 3.0 Apparatus for mercury analysis by Cold Vapour Atomic Absorption Spectrometry

3.6 Determination of Recovery

Recovery of mercury was determined by adding 20, 50, and 100 µl of 1µg ml^{-} standard Hg solution to 0.5g of samples of two different fish species. To each sample was added 1 ml distilled water, 1 ml HNO_3, 1 ml $HCLO_3$ and 5 ml H_2SO_4. The mixture was then heated at a temperature of $200 \pm 5\ ^0$C for about 30 minutes. The sample solution was then cooled and diluted to 50 ml with distilled water. The resulting solutions were analyzed for mercury concentration.

3.7 Determination of Detection Limit

The detection limit of the analyzer was determined using two standard solutions of 0.04 and 0.1ng ml^{-1} and a blank. The peak height was obtained for each standard alternately, fourteen times. A blank reading was made between was made between each standard reading. The sequence was: blank, 0.04ng ml^{-1} standard, blank, 0.1ng ml ml^{-1} standard: the sequence is repeated. The average peak height of the two blanks obtained immediately before and after each standard was obtained and subtracted from the standard reading. The mean and standard deviation for the set of corrected peak height of the standards was calculated and substituted in the formula for the calculation of the detection limit.

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3.8 Quality Assurance

For quality assurance the instrument was calibrated based on a linear four-point calibration curve (0.0, 0.5, 1.0, and 2.0 ppb). Standard calibration curves with an r^2 = 0.9999 were run during measurements. To monitor the calibration curve, a continuing calibration verification standard and blank sample was analyzed at a 10 percent frequency and at the end of each analytical batch. To verify the quality of the analytical results obtained, matrix spike/matrix spike duplicates were analyzed with each analytical batch of 10 samples or more. For each run, a triplicate sample and three blanks were carried through the procedure. An analytical spike recovery was done by spiking 20, 50, and 100 µl of 1µg ml^{-} standard Hg solution to samples of two different fish species, which were taken through the digestion procedure. A matrix spike recovery was also complete for the digestion procedure used by adding 20, 50, and 100 µl of 1µg ml^{-} standard Hg solution to the pre-digest sample, which was then digested. To assess the precision of the overall

procedure, 6 replicate analyses of muscle tissues of fish were conducted. All sample analyses were performed in duplicate by the instrument.

3.9 Statistical Analysis

The data obtained in this study were subjected to statistical analyses using SPSS for Windows Statistical Package Version 10.0. Linear regression analysis was conducted using the following variables: mercury concentration in fish, fish length and fish weight.

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CHAPTER FOUR

4.0 Results and Discussion

4.1 Total Mercury Concentrations in Different Fish Species

The accuracy of the technique used in this study was determined by carrying out recoveries. Recoveries were between 96% and 110% with coefficient of variation between 2% and 7%. The detection limit of the analytical technique used in this study was 0.01 ppb.

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Results of Hg concentrations, fresh weight and total length of fish from the three reservoirs are presented in tables 4.20 to 4.35. The range of total mercury concentrations in the edible muscles of fish analysed from Lake Bosomtwi, Akosombo Reservoir and Kpong Reservoir are ND to 70.30, ND to 42.0 and 9.68 to 1014.73 ng/g wet weight respectively. The mean fresh weight (g) for *Tilapia multifaciata* (n=30), *Tilapia discolour* (n=39) and *Tilapia bosomana* (n=16) from Lake Bosomtwi were 41.90, 27.88 and 17.17 respectively. Mean fresh weight (g) of fish from Kpong Reservoir were 112.43, 170.41, 22.03, 152.31 and 171.91 for *Pelmatochromis guntheri* (n=9), *Chrysichthys auratus* (n=10), *Apistogramma trifasciatum* (n=3), *Tilapia zilli* (n=9) and *Amphilus grammatophorus* (n=4) respectively. Total mercury concentration in the edible muscle tissue of all the fish tested ranged from ND to 1014.74 ng/g wet weight. Apart from one specie of *Pelmatochromis guntheri* which contained the highest Hg concentration (1014.74 ng/g), all the samples studied showed mercury concentrations below the World Health Organisation (WHO) limit of 0.5ugg-1 wet weight. Total mercury concentration in fish depends on the fish species and the concentrations also varied with factors such as total length of fish and fresh weight of fish. The five most significant factors that control mercury accumulation in freshwater fish were

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reported by Meili *et al.* (1991) and Lindguist (1991) as organic matter, pH, seasonal changes, regional variations and hydrologic conditions. In this study, there was a significant variation between mercury concentration, fish length and fresh weight of fish. Table 4.0 provides mean mercury concentration and mean weights for the various fish samples.

Though growth rate data in fish from the studied reservoirs are not available, variations suggest that all the fish are not necessarily growing at the same rate. The difference in growth rate may influence Hg bioaccumulation rate. If fish are growing more slowly, then it should be expected that the concentration of Hg in the muscle tissue would be higher as bioaccumulation is more a factor of age than size. Thus, slow growth rate may lead to a higher concentration for a fish of a particular size. There is no data available for Hg concentration and background Hg levels to ascertain trends of Hg levels in the reservoirs studied. This study would therefore serve as the basis for future reference.

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Table 4.0 Total Hg concentrations (ng/g) in fish muscle samples from Lake Bosomtwi, Akosombo Reservoir and Kpong Reservoir.

Species Name	Sampling Site	Sample Size (n)	Fresh weight Range (g)	Mean Weight (g)	Hg Concentration Range (ng/g)	Mean Hg Concentration (ng/g)
Tilapia multifaciata	Lake Bosomtwe	30	26.20-53.51	41.90	ND-70.30	8.27
Tilapia discolour	Lake Bosomtwe	39	8.34-65.21	27.88	65.56-47.48	17.12
Tilapia bosomana	Lake Bosomtwe	16	12.89-20.68	17.17	1.89-49.37	21.14
Tilapi zilli	Akosombo Reservoir	39	93.41-252.71	148.09	ND-28.00	15.97
Synodontis species	Akosombo Reservoir	6	186.93-435.35	29.76	20.00-42.00	28.17
Pelmatochromis guntheri	Kpong Reservoir	9	57.17-175.19	112.43	10.70-1014.73	158.79
Chrysichthys auratus	Kpong Reservoir	10	135.00-307.8	170.41	26.38-79.03	40.71
Amphilus grammatophorus	Kpong Reservoir	4	20.90-23.80	22.03	141.24-207.59	169.68
Apistogramma trifasciatum	Kpong Reservoir	3	142.32-158.23	152.31	9.68-10.68	10.50
Tilapia zilli	Kpong Reservoir	9	92.00-217.20	171.91	15.15-75.90	29.50

ND= Not Detectable

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4.2 Total Mercury Concentration in Fish from Lake Bosomtwi

Results obtained for total mercury concentration, total length and total weight are presented in tables 4.10, 4.11 and 4.12. The level of mercury ranged between ND and 70.30 ppb. The highest level of 70.30 ppb and the lowest level below detection were found in *Tilapia multifaciata*. The levels of mercury obtained showed that within the same aquatic environment, fish of the same specie have different levels of mercury. The relationship between the weight of fish and their corresponding total mercury levels of the three species, *Tilapia bosomana, tilapia multifaciata and tilapia discolour* was determined by regression and their correlation coefficient obtained. Figures 4.0 to 4.6 describe the relationship between Hg concentrations on wet weight basis and fresh weight and total length of the three fish species from Lake Bosomtwi respectively.

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The range of mercury concentration in the muscle tissue for *Tilapia bosomana* (n=16) is 1.89 to 49.37 ppb. The mean Hg concentration evaluated was 21.14 ppb. There was, however, poor correlation between mercury concentration, fresh weight (r^2=0.302) and total length (r^2=0.1196) of fish respectively. This is in agreement with what was reported by Castilhos *et al.* (1998) for noncanivorous fish. The highest mercury level was found to be 70.303 ppb in *Tilapia multifaciata*. *Tilapia multifaciata* showed poor correlation between total mercury concentration and fresh weight (r^2=0.0081) and total length (r^2=0.0006).

The highest total mercury concentration in *Tilapia discolour* was found to be 47.48 ppb and the lowest concentration was found to be 6.56 ppb. *Tilapia discolour* showed a poor correlation between Hg concentration and fresh weight (r^2 =0.0477) and total length (r^2=0.0261). Thompson

(1985) also observed poor correlation between total length and Hg concentration for several fish species distributed along Tasmanian River.

The low levels of mercury in all the three species may be due to the fact that the rate of Hg contamination in Lake Bosomtwi by human activities may be very low. Also there are no tributaries which joined the lake which could carry any Hg contaminants to the lake, hence, the low level of mercury concentration in the fish from the lake. The rate of atmospheric deposition could also be very low since concentrations are low. Factors affecting methylation (e.g. organic matter and pH) could also be responsible for the low Hg concentration levels. The evasion of elemental mercury as a result of microbial activities could also represent a significant pathway for reducing the level of the metal in aquatic ecosystem.

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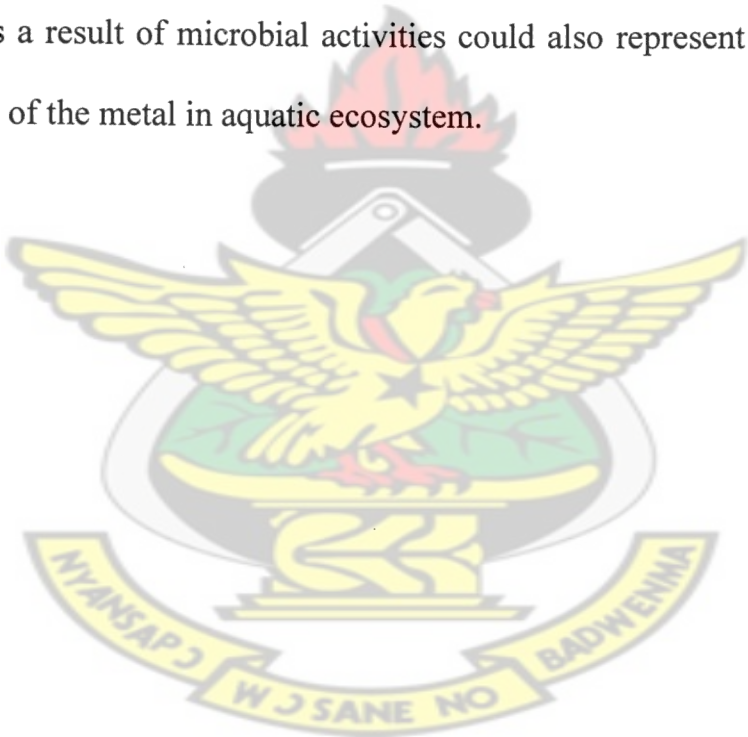

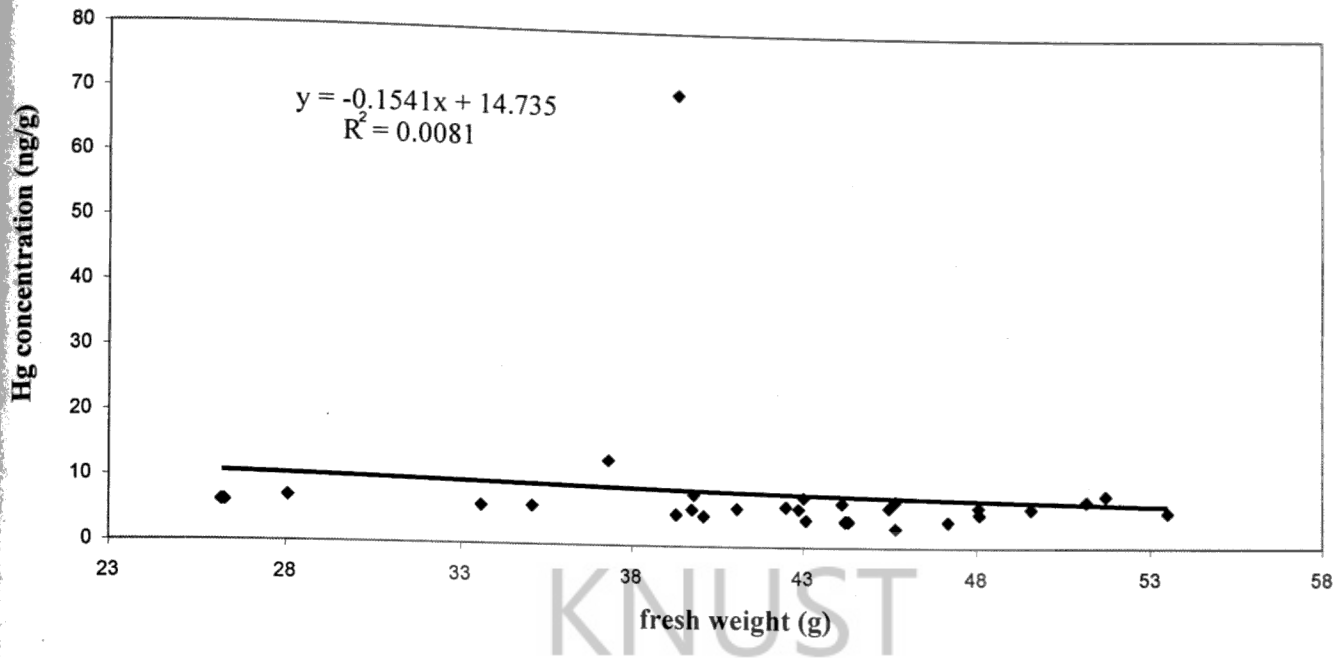

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Fig. 4.0 Relationship between Hg concentrations on wet weight basis and fresh weight for *Tilapia multifaciata* from Lake Bosomtwi.

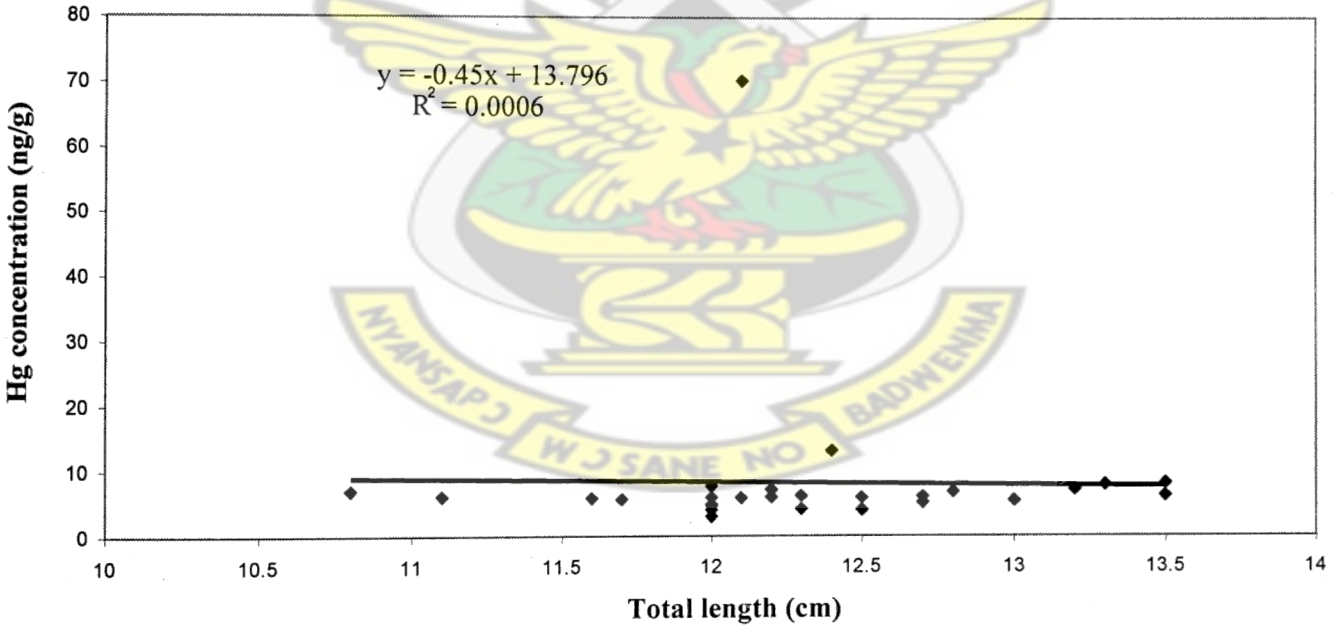

Fig. 4.1 Relationship between Hg concentrations on wet weight basis and total length for *Tilapia multifaciata* from Lake Bosomtwi.

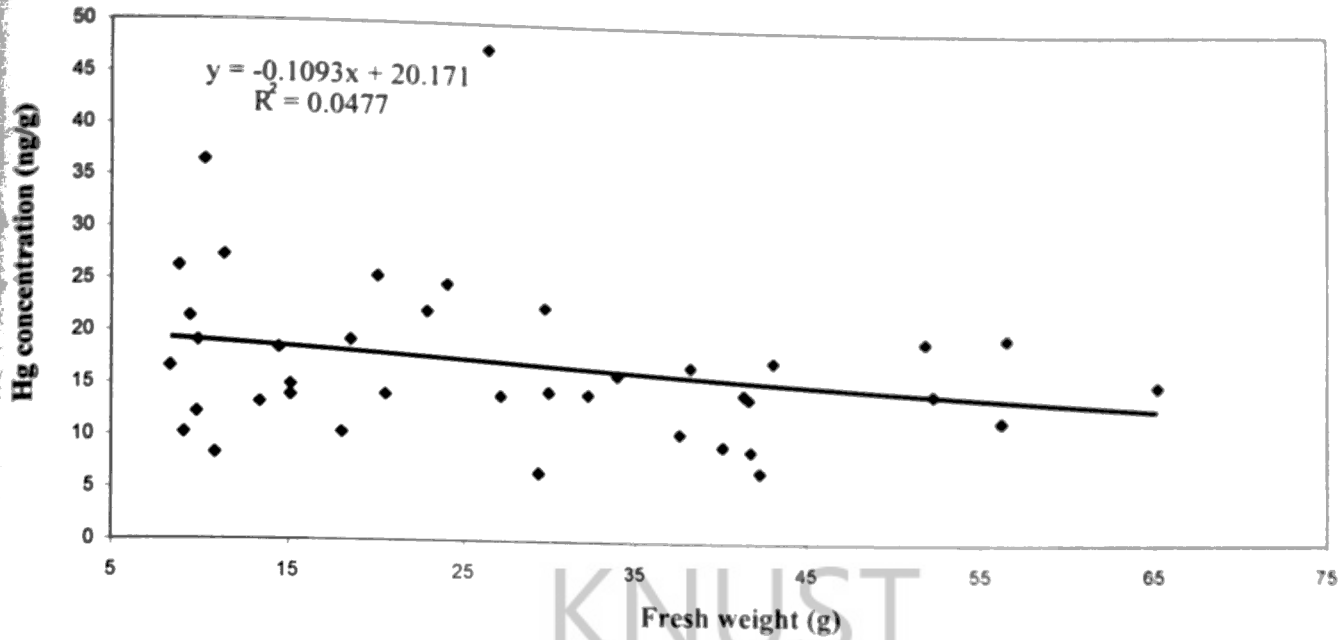

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Fig. 4.3 Relationship between Hg concentrations on wet weight basis and fresh weight for *Tilapia discolour* from Lake Bosomtwi.

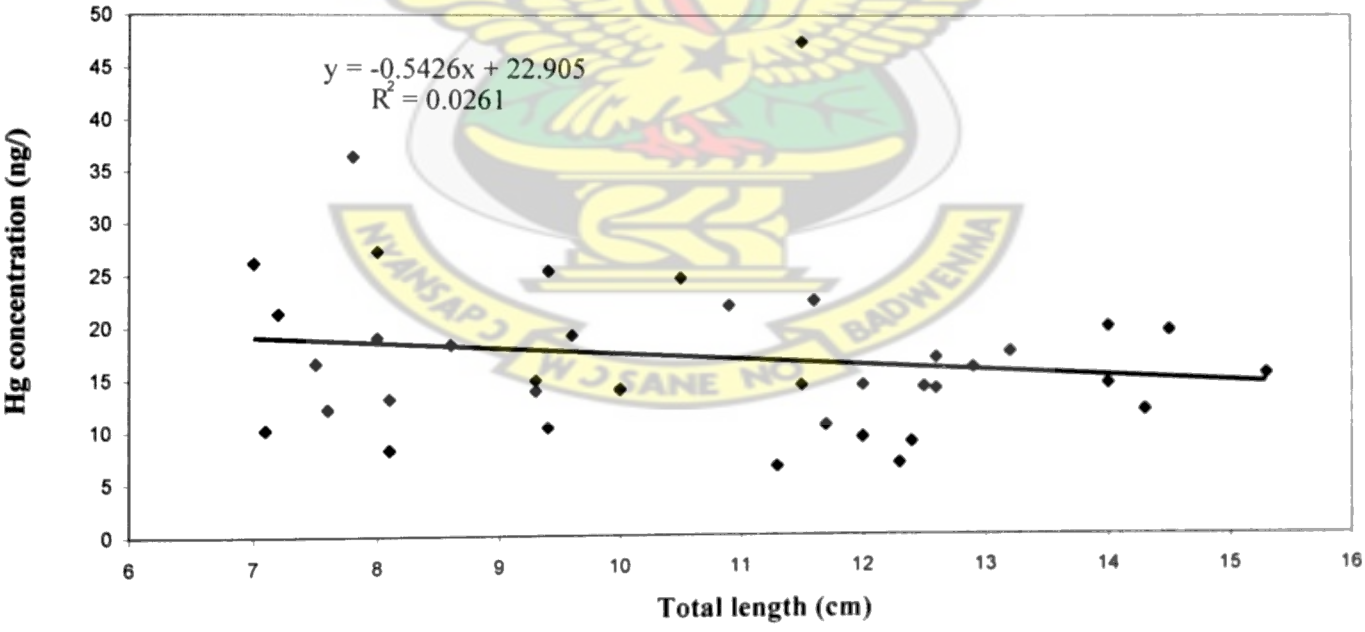

Fig. 4.4 Relationship between Hg concentrations on wet weight basis and total length for *Tilapia discolour* from Lake Bosomtwi.

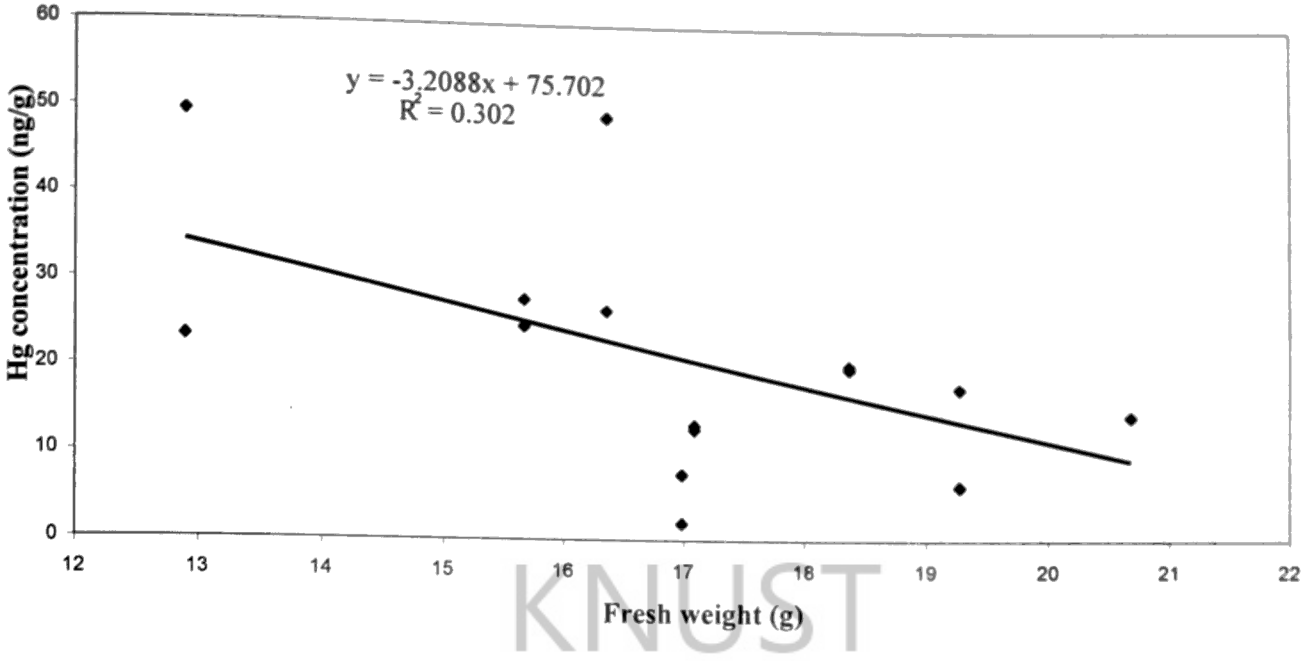

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Fig. 4.5 Relationship between Hg concentrations on wet weight basis and fresh weight for *Tilapia bosomana* from Lake Bosomtwi.

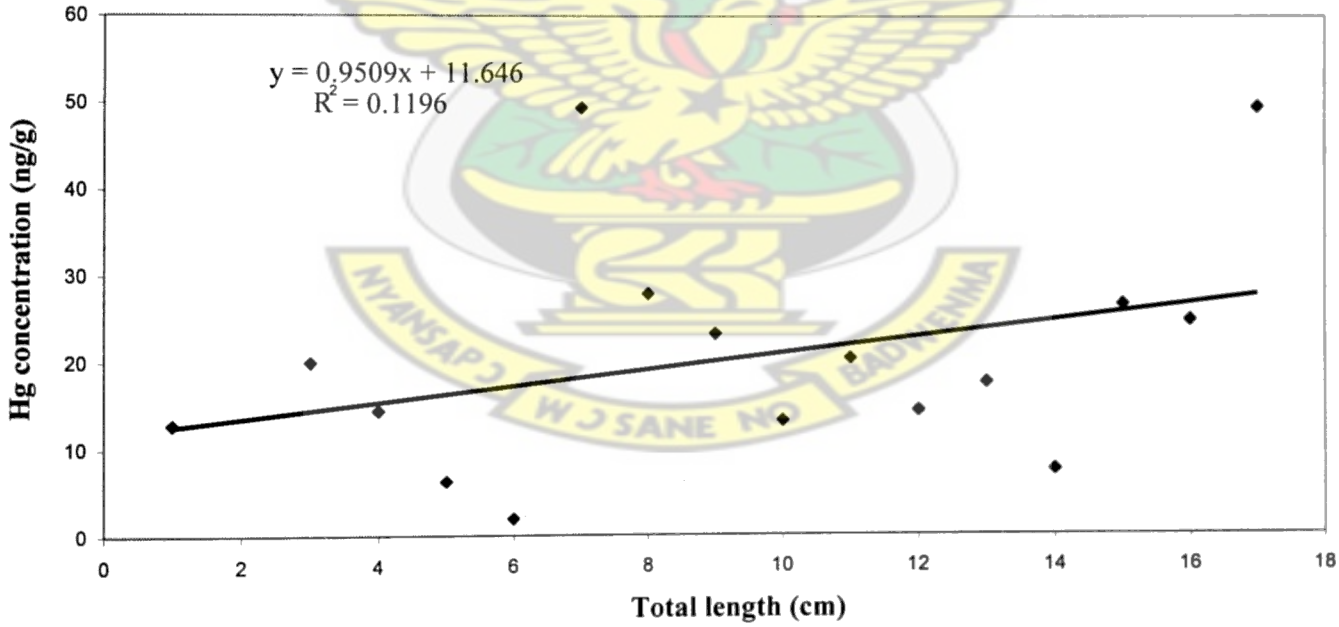

Fig. 4.6 Relationship between Hg concentrations on wet weight basis and total length for *Tilapia bosomana* from Lake Bosomtwi.

4.3 Total Mercury Concentration in Fish from Akosombo Reservoir

Tables 4.20 and 4.21 show the total levels of mercury concentrations in species of fish collected from Akosombo Reservoir. In all, forty five (45) fish samples were analysed which comprised of two species, *tilapia zilli* (n=39) and *synodontis sp.* (n=6). Generally, almost all fish contain some amounts of mercury of low toxicological concern. The results showed total mercury concentration range between ND to 42.00 ppb. S*ynodontis sp.* recorded the highest level of mercury of 42.00 ppb but for the lowest level recorded, both *Tilapia* and *Synodontis* gave ND levels. In areas where there is industrial mercury pollution, the levels of mercury in the fish can be quite high (Smith *et al.*, 1949, Friberg, 1951, Bidstrup *et al.*, 1951, Smith *et al.*, 1970). Fish absorb mercury from water as it passes over their gills and as they feed on aquatic organisms. The highest level of mercury 42.00 ppb wet weight recorded is by far less than the standard 500 ppb set by the World Health Organization (WHO) and hence does not pose health hazard.

There was a good relationship with regression, $r^2 = 0.6852$, between mercury concentration and fresh weight for *synodontis sp.* Total mercury decreased with increasing weight of fish. The mean concentration (ng/g) and mean fresh weight (g) evaluated is 28.17 and 29.76 respectively.

The highest mercury level recorded for *Tilapia zilli* is 28.00 ng/g wet weight. Fresh weights and mercury concentrations ranged between 93.41 to 252.71 g and ND to 28.00 ng/g respectively. The mean concentration evaluated is 12.28 ng/g. An inverse correlation (r^2=0.2118) was observed between mercury concentration and fresh weight.

Synodontis granulosis is omnivorous at trophic level 3.0 whereas *Tilapia zilli* is herbivorous at trophic level 2.0. The relatively high Hg concentration in *Synodontis granulosis* can be attributed

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to its high trophic level compared to *Tilapia zilli*. The low levels of mercury in both fish may be attributed to many factors. Hydrologic condition plays a very important role in increasing Hg concentration in hydroelectric reservoirs. Increases in Hg levels in freshwater fish as a result of the construction of hydroelectric dams have been reported (Cross Lake Environmental Impact Assessment Study, 1986, Ramsey, *et al.*, 1990). However, no data is available in order to ascertain Hg trend as a result of the construction of Akosombo dam. Other factors such as pH, age of fish, organic matter, seasonal changes and regional variations also affects Hg levels in aquatic systems. Also the low level of mercury may be due to the fact that contamination due to human activities is insignificant. There is also no artisanal gold mining activity that employs the use of Hg around the reservoir.

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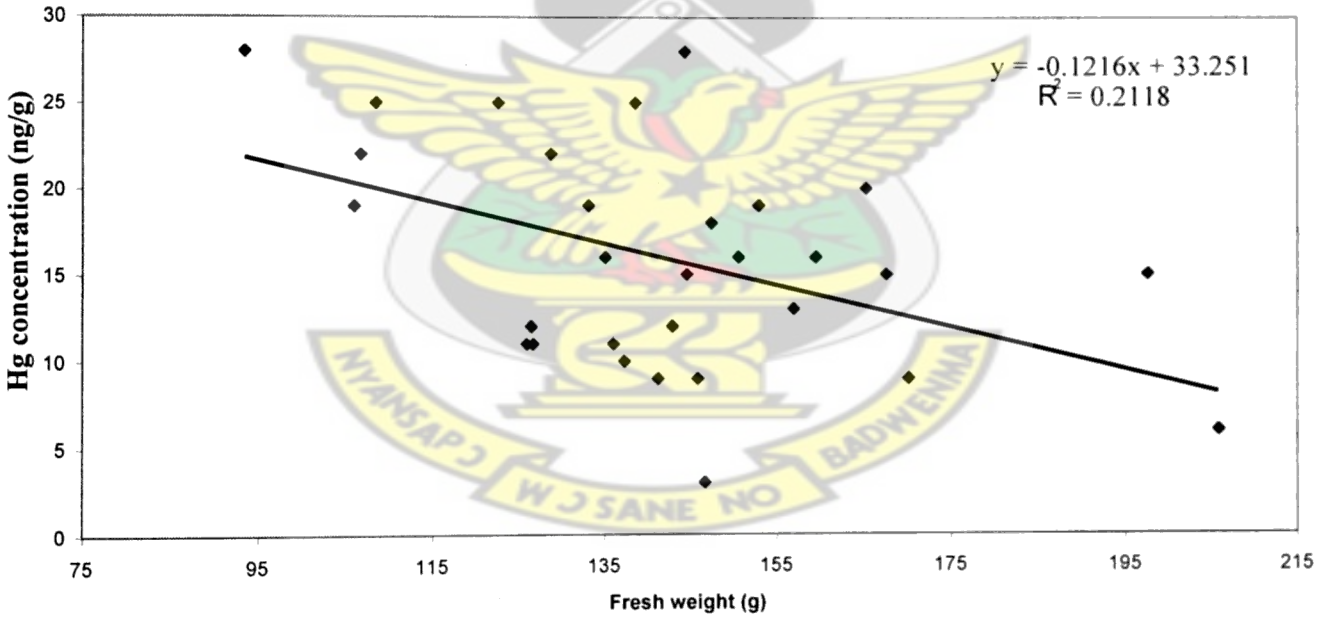

Fig. 4.7 Relationship between Hg concentrations on wet weight basis and fresh weight for *Tilapia zilli* from Akosombo Reservoir.

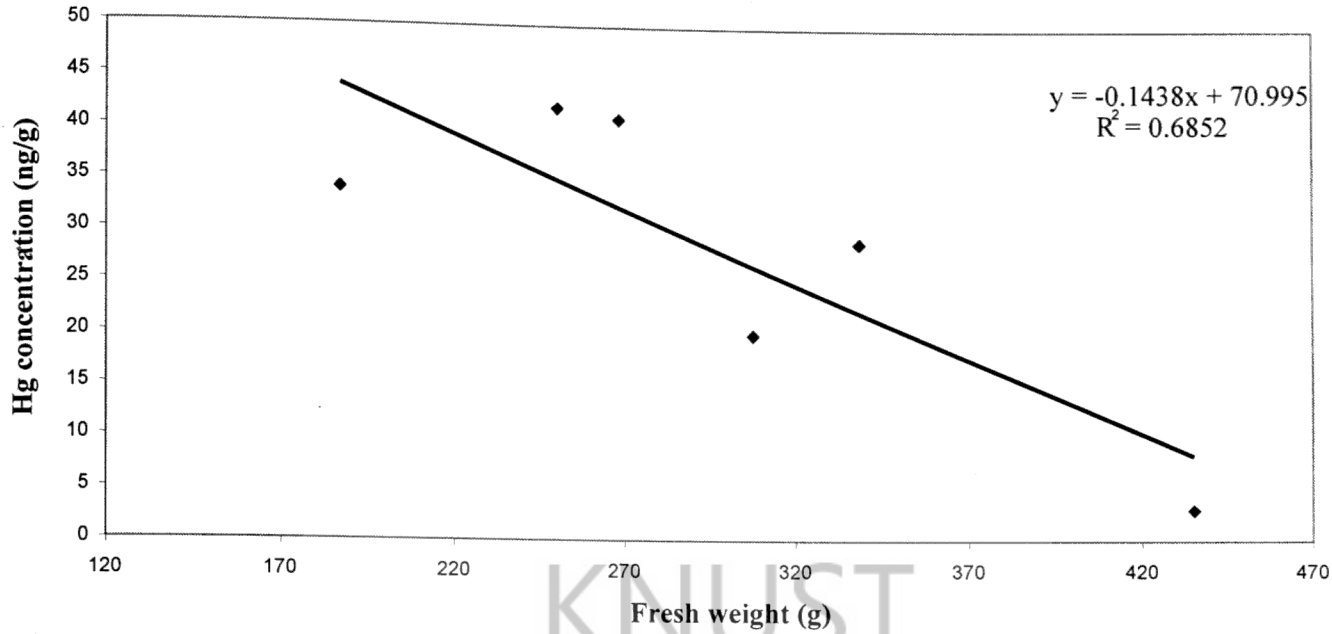

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Fig. 4.8 Relationship between Hg concentrations on wet weight basis and fresh weight for *Synodontis sp.* from Akosombo Reservoir.

4.5 Total Mercury Concentration in Fish from Kpong Reservoir

A total of five species representing thirty five fish samples from Kpong Reservoir were analysed for total mercury in the edible muscle tissue. The five species are *Pelmatochromis guntheri* (n=9), *Chrysichthys auratus* (n=10), *Apistogramma trifasciatum* (n=3), *Tilapia zilli* (n=9) and *Amphilus grammatophorus* (n=4). The mean mercury concentration recorded is 80.34 ng/g. One sample of *Pelmatochromis guntheri* recorded the highest mercury concentration of 1014.73ng/g. The range of mercury concentration recorded from Kpong reservoir is 9.68-1014.73ng/g. The range of mercury for *Pelmatochromis guntheri*, *Chrysichthys auratus*, *Apistogramma trifasciatum*, *Tilapia zilli* and *Amphilus grammatophorus* recorded are 10.70 to 1014.73, 26.38 to 79.03, 141.24 – 207.59, 9.68 – 10.68 and 15.15 – 75.90 ng/g wet weight respectively. The mean mercury concentration recorded for the species are 158.79, 40.71, 169.68, 10.50 and 29.50 ng/g

respectively. There is a poor correlation between mercury concentration and fresh weight (r^2 = 0.1675) and total length (r^2 = 0.0170) for *Pelmatochromis guntheri. Chrysichthys auratus* also recorded a poor correlation between mercury concentration and fresh weight (r^2 = 0.0146) and total length (r^2 = 0.0509). *Apistogramma trifasciatum* showed a good correlation between mercury concentration and fresh weight (r^2 = 0.9626) and total length (r^2 = 0.9764). *Tilapia zilli* showed a poor correlation for mercury concentration and fresh weight (r^2 = 0.0854) and total length (r^2 = 0.0254). This is in agreememnt with what was reported by Thompson (1985). Apart from one sample *Pelmatochromis guntheri* which recorded a higher mercury concentration above the WHO acceptable limit for total mercury in fish, all the results obtained are below the WHO threshold. Figures 4.9 to 4.14 describe the relationship between Hg concentration on wet weight basis and fresh weight and total length for the samples from Kpong Reservoir. Fish from Kpong recorded a higher mercury concentration as compared to fish from Akosombo. However, no data is available in order to ascertain Hg trends. Factors such as age of fish, pH, organic matter, seasonal changes and regional variation could also be responsible for the levels.

The results obtained for Akosombo and Kpong reservoir showed low Hg levels within the river systems as be the case reported in certain parts of the world (Bodaly *et al.*, 1999, Gerrard *et al.*, 2001, Ramsey *et al.*, 2001). For example, the levels of methyl mercury in fish from certain new reservoirs to produce electricity in northern Manitoba and northwestern Quebec in Canada have resulted in an increase in methyl mercury concentrations in fish (Bodaly *et al.*, 1999, Gerrard *et al.*, 2001). The Akosombo dam was constructed over 40 years ago. Theoretical models predict returns of MeHg concentrations to background levels after impoundment of certain reservoirs to be 20 years (Anderson *et al.*, 1995). Data collected sixteen years after impoundment of

Smallwood Reservoir in Canada showed that the Hg levels in flesh of non-piscivores were similar to background Hg levels while piscivores were still elevated above un-impounded lakes (Anderson *et al.*, 1995). There are no data available for Hg concentration and background Hg levels for the reservoirs for comparison. Overall, the average mercury concentration in *Tilapia zilli* shows substantial variability in both reservoirs. The large variability obtained for each of the reservoirs is caused by the variability in the size and length of the fish. This suggests that growth rate influence is not the only factor over fish concentration but the length-weight relationship also matters.

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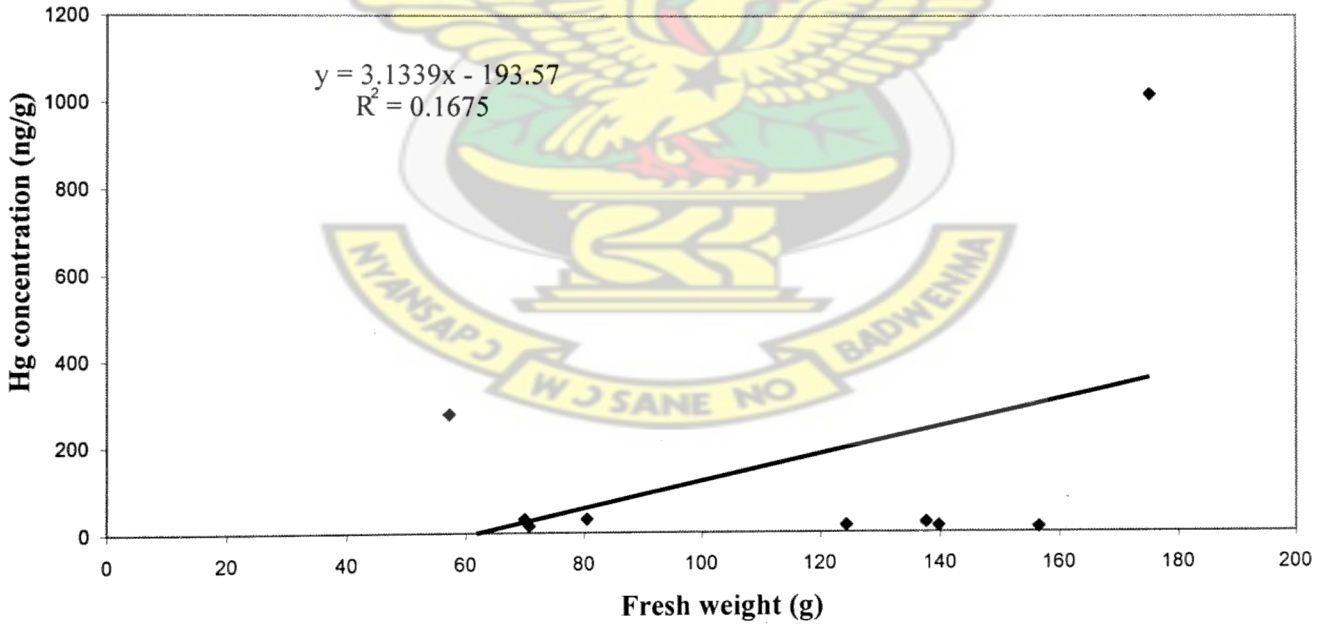

Fig. 4.9 Relationship between Hg concentrations on wet weight basis and fresh weight for *Pelmatochromis guntheri* from Kpong Reservoir.

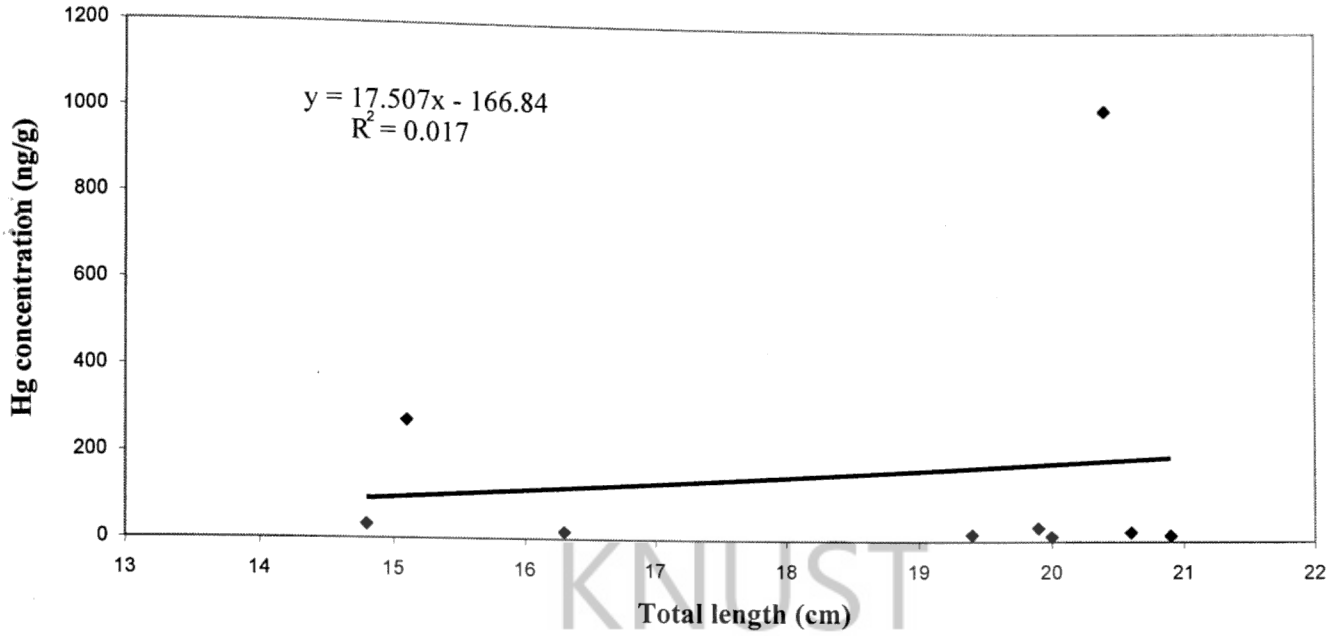

Fig. 4.10 Relationship between Hg concentrations on wet weight basis and total length for *Pelmatochromis guntheri* from Kpong Reservoir.

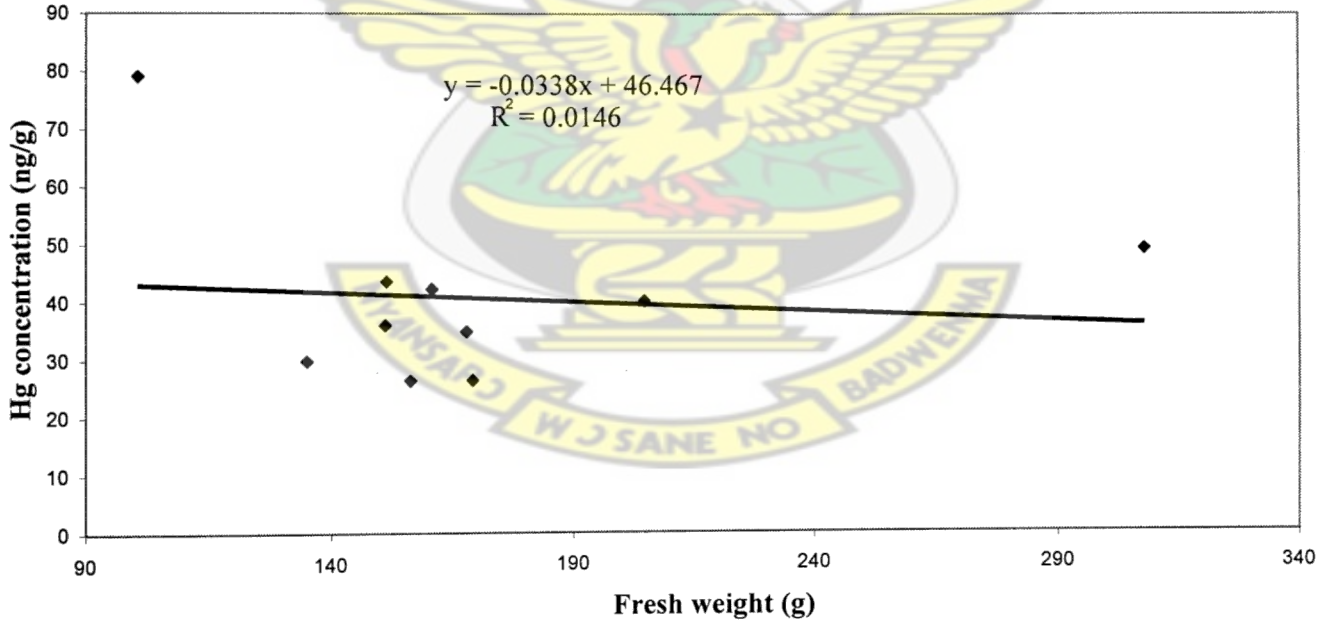

Fig. 4.11 Relationship between Hg concentrations on wet weight basis and fresh weight for *Chrysichthys auratus* from Kpong Reservoir.

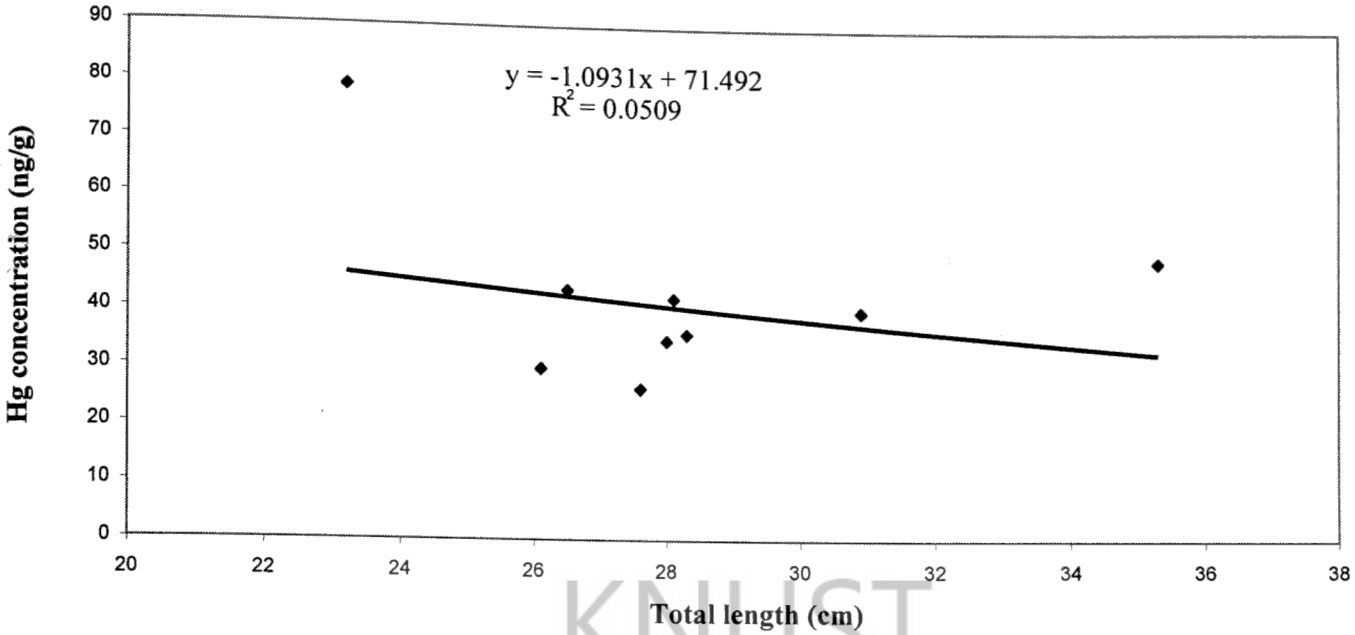

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Fig. 4.12 Relationship between Hg concentrations on wet weight basis and total length for *Chrysichthys auratus* from Kpong Reservoir.

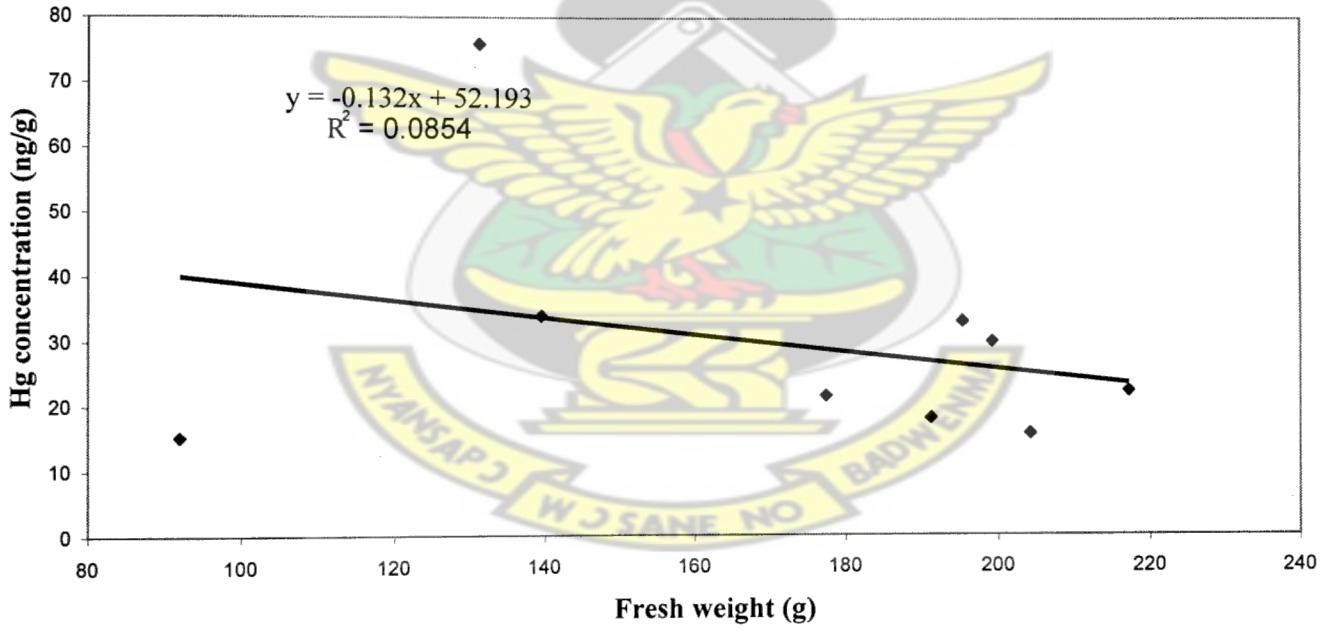

Fig. 4.13 Relationship between Hg concentrations on wet weight basis and fresh weight for *Tilapia zilli* from Kpong Reservoir.

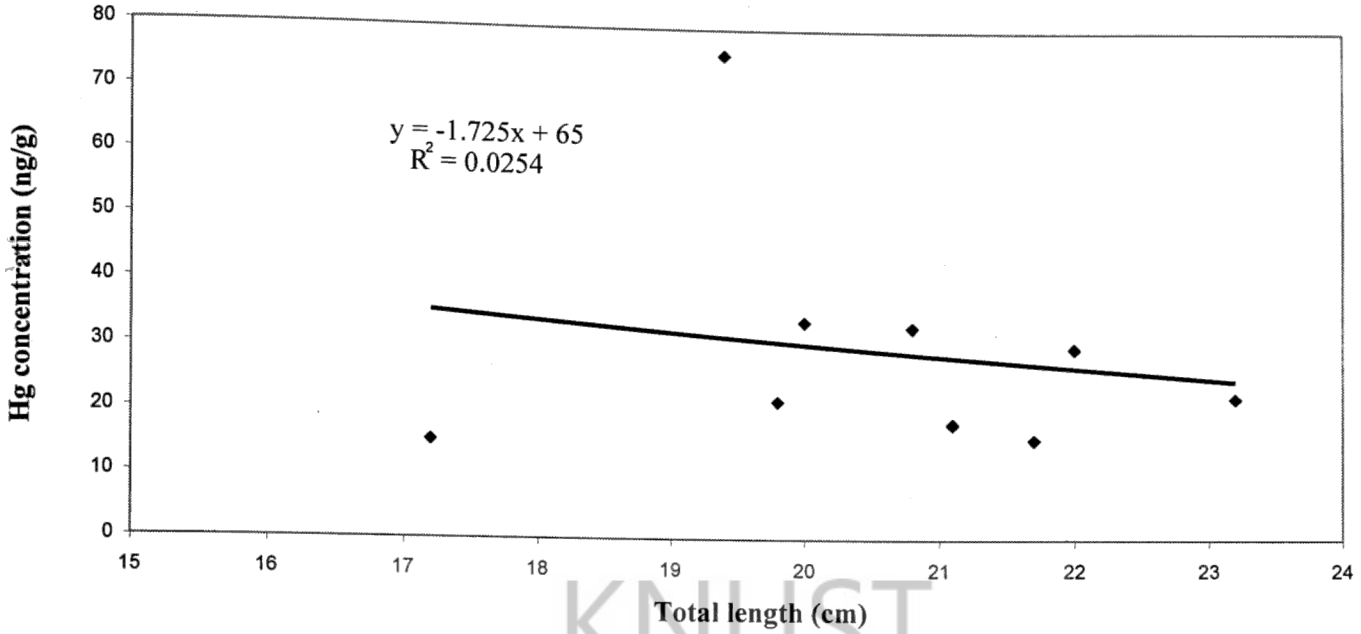

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Fig. 4.14 Relationship between Hg concentrations on wet weight basis and total length for *Tilapia zilli* from Kpong Reservoir.

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CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

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

The main objectives of this research were achieved by determining the total mercury (Hg) concentration in muscle tissues meant for consumption. This study reports mercury concentration levels in fish from Lake Bosomtwi, Kpong and Akosombo reservoirs. Apart from one sample of one of the specie which recorded a higher mercury concentration, all the concentrations are below the World Health Organisation (WHO) limit.

The concentration of total mercury in the edible muscle tissue of all the fish tested from Lake Bosomtwi, Kpong and Akosombo reservoirs ranged from ND – 70.30, ND – 42.00 and 9.68 – 1014.73 ng/g wet weight respectively. The results obtained showed that apart from one of the fish which recorded a high mercury concentration above the WHO threshold, fish from Lake Bosomtwi, Kpong and Akosombo reservoirs are unlikely to constitute a significant exposure of Hg to the public through consumption of fish.

The low concentrations of mercury in fish species obtained in this study suggest a relatively clean aquatic environment. There are no data, however, available for Hg concentration and background levels for comparison.

5.2 RECOMMENDATIONS

The following recommendations are made as a result of the outcome of research:

Monitoring of mercury concentration in fish in other fresh water bodies should be encouraged with special attention to rivers and lakes close to artisanal gold mining areas where mercury is used for amalgamation.

More samples should be tested over a longer period to ascertain if there are any trends.

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Analysis of the water for water quality parameters should be carried out to understand spatial patterns of mercury bioaccumulation, better standardization of mercury for fish size and age, better prediction of the likelihood of bioaccumulation and more information on factors controlling bioaccumulation in the aquatic eco-system of Ghana.

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Appendix I

Results from Lake Bosomtwi

Table 4.10 Results for *Tilapia multifaciata*

Sample Identity	Total length/cm	Total weight/g	T-Hg conc./ppb
TM1	12.1	41.089	5.830
TM2	12.1	40.526	ND
TM3	12.7	45.488	6.080
TM4	12.3	43.093	4.142
TM5	12.0	47.194	4.000
TM6	12.0	43.030	7.617
TM7	12.2	49.580	5.962
TM8	13.0	53.510	5.425
TM9	12.0	40.120	4.631
TM10	12.1	39.358	70.304
TM11	13.2	51.170	7.163
TM12	12.5	44.320	4.045
TM13	12.0	42.890	5.896
TM14	12.5	44.230	4.045
TM15	11.7	39.773	5.628
TM16	12.0	45.687	2.959

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TM17	13.3	39.821	7.877
TM18	12.4	37.324	13.071
TM19	11.6	33.603	5.852
TM20	12.8	44.148	6.789
TM21	10.8	28.075	6.918
TM22	12.5	35.087	5.874
TM23	13.5	51.719	8.106
TM24	12.3	42.519	6.176
TM25	12.0	39.300	4.832
TM26	12.7	48.087	5.116
TM27	12.2	45.677	7.135
TM28	13.5	48.069	6.250
TM29	11.1	26.286	6.045
TM30	11.1	26.197	6.068

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Table 4.11 Results for *Tilapia discolour*

Sample Identity	Total length/cm	Total weight/g	T-Hg conc./ppb
TD1	15.3	65.21	15.348
TD2	13.2	43.07	17.568
TD3	12.9	33.979	16.057
TD4	14.3	56.240	11.882
TD5	11.5	26.422	47.482
TD6	11.3	29.356	6.561
TD7	12.6	38.257	16.984
TD8	10.5	24.037	24.655
TD9	10.9	22.895	22.035
TD10	12.6	41.646	13.996
TD11	11.5	29.940	14.354
TD12	8.0	11.376	27.253
TD13	10.0	27.145	13.942
TD14	10.0	20.515	14.02
TD15	7.6	9.855	12.136
TD16	9.6	18.526	19.178
TD17	8.1	10.895	8.244
TD18	8.1	13.403	13.138
TD19	9.3	15.131	14.853
TD20	9.3	15.131	13.863

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TD21	8.6	14.456	18.346
TD22	8.0	9.911	18.994
TD23	7.1	9.122	10.173
TD24	7.2	9.462	21.321
TD25	7.5	8.343	16.534
TD26	7.0	8.835	26.155
TD27	7.8	10.291	36.396
TD28	14.0	56.535	19.955
TD29	14.5	51.853	19.580
TD30	14.0	52.315	14.468
TD31	11.7	37.633	10.512
TD32	12.0	41.363	14.354
TD33	12.0	40.149	9.338
TD34	12.3	42.293	6.866
TD35	12.4	41.756	8.895
TD36	12.5	32.250	14.159
TD37	11.6	29.723	22.512
TD38	9.4	20.059	25.382
TD39	9.4	18.030	10.334

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Table 4.12 Results for *Tilapia bosomana*

Sample Identity	Total length/cm	Total weight/g	T-Hg conc./ppb
TB1	10.5	17.091	12.766
TB2	10.3	18.37	19.984
TB3	10.2	20.684	14.443
TB4	10.1	19.275	6.250
TB5	9.4	16.988	1.894
TB6	9.5	16.356	49.321
TB7	9.3	15.670	27.847
TB8	8.3	12.893	23.234
TB9	10.5	17.091	13.276
TB10	10.3	18.370	20.425
TB11	10.2	20.684	14.443
TB12	10.1	19.275	17.708
TB13	9.4	16.988	7.576
TB14	9.5	16.356	26.634
TB15	9.3	15.670	24.753
TB16	8.3	12.893	49.373

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Results from Akosombo

Table 4.20 Results for *Tilapia zilli*

Sample Identity	Total weight /g	T-Hg Conc. /ppm
AT1	214.02	ND
AT2	252.71	ND
AT3	212.77	ND
AT4	209.03	ND
AT5	205.85	0.006
AT6	106.69	0.022
AT7	108.40	0.025
AT8	122.56	0.025
AT9	152.92	0.019
AT10	93.41	0.028
AT11	105.96	0.019
AT12	128.73	0.022
AT13	138.54	0.025
AT14	144.57	0.015
AT15	197.61	0.015
AT16	145.83	0.009
AT17	170.14	0.009
AT18	136.02	0.011

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AT19	144.30	0.028
AT20	126.61	0.011
AT21	115.80	ND
AT22	124.76	ND
AT23	167.58	0.015
AT24	129.05	ND
AT25	119.08	ND
AT26	135.05	0.016
AT27	134.50	ND
AT28	133.11	0.019
AT29	150.51	0.016
AT30	142.86	0.012
AT31	137.32	0.010
AT32	125.91	0.011
AT33	147.40	0.018
AT34	126.39	0.012
AT35	141.21	0.009
AT36	159.48	0.016
AT37	165.26	0.020
AT38	156.95	0.013
AT39	146.73	0.003

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Table 4.21 Results for *Synodontis species*

Sample Identity	Total fish weight /g	T-Hg Conc. /ppm
AS1	307.64	0.020
AS2	435.35	0.003
AS3	186.93	0.034
AS4	250.06	0.042
AS5	268.07	0.041
AS6	338.53	0.029

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RESULTS FROM KPONG

Table 4.30 Results for *Pelmatochromis guntheri*

Sample Identity	Total fish length /cm	Total fish weight /g	T-Hg Conc. /ppb
BA1	20.4	175.185	1014.728
BA2	20.9	139.763	14.2555
BA3	19.4	124.331	15.2386
BA4	20.6	137.752	21.4004
BA5	20.0	156.537	10.7002
BA6	19.9	69.943	31.2761

BA7	14.8	80.510	31.1867
BA8	16.3	70.703	15.7555
BA9	15.1	57.173	274.5275

Table 4.31 Results for *Chrysichthys auratus*

Sample Identity	Total fish length /cm	Total fish weight /g	T-Hg Conc. /ppb
BJ1	28.3	151.0	35.9743
BJ2	30.9	204.8	40.0573
BJ3	35.3	307.8	48.9237
BJ4	27.6	156.2	26.3832
BJ5	28.0	167.8	34.8075
BJ6	26.5	151.3	43.5388
BJ7	28.1	160.6	42.1656
BJ8	27.6	169.0	26.4271
BJ9	23.2	100.6	79.0328
BJ10	26.1	135.0	29.7923

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Table 4.32 Results for *Amphilus grammatophorus*

Sample Identity	Total fish length /cm	Total fish weight / g	T-Hg Conc. /ppb
BD1	32.2	23.8	207.590
BD2	27.7	21.1	141.244
BD3	27.3	20.9	172.707
BD4	28.8	22.3	157.177

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Table 4.33 Results for *Apistogramma trifasciatum*

Sample Identity	Total fish length /cm	Total fish weight /g	T-Hg Conc. /ppb
BC1	20.5	158.226	10.8432
BC2	21.0	156.383	10.9688
BC3	19.0	142.321	9.6794

Table 4.34 Results for *Tilapia zilli*

Sample Identity	Total fish length /cm	Total fish weight /g	T-Hg Conc. /ppb
BZ1	19.4	131.2	75.9022
BZ2	23.2	217.2	22.1946
BZ3	19.8	177.4	21.5220
BZ4	20.8	195.307	33.1181
BZ5	21.1	191.200	18.1014
BZ6	21.7	204.200	15.6278
BZ7	22.0	199.2	29.9606
BZ8	20.0	139.5	33.9551
BZ9	17.2	92.0	15.1515

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