# CONCENTRATION LEVELS OF COPPER (Cu), ZINC (Zn), CADMIUM (Cd) AND LEAD (Pb) IN SURFACE WATER, BOTTOM SEDIMENT, AND BLACK CHIN TILAPIA (*Sarotherodon melanotheron*) OF FOSU LAGOON, CAPE COAST

BY

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## DECLARATION

I hereby declare that this thesis is the result of my own work except references cited that have been duly acknowledged. It has never been submitted for the award of any degree.

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**DEDICATION**

This work is dedicated to my wife Felicia Fosu-Amankwah, Mr. and Mrs. Fosu-Gyiabour, Prof. and Mrs. Awusabo-Asare, Dr. A. K Amankwah, Juliet, Yaw Fosu-Gyiabour, Kwame Fosu-Boamah, Kwame Fosu-Boateng and Adwoa Fosu-Dufie.

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# ABSTRACT

Fosu lagoon, located in Cape Coast in the Central Region of Ghana, serves as a source of livelihood and a great cultural heritage for the people of Cape Coast. However, due to the numerous domestic and artisanal activities surrounding the lagoon coupled with poor waste management practices, the quality of the lagoon is impaired. Therefore, the need for overall assessment of the pollution status of the lagoon and its aquatic life cannot be overemphasized. Surface water, sediment and black chin tilapia, *Sarotherodon melanotheron* (whole fish) samples were collected from five sampling stations in relation to sections of the lagoon: upper section, middle section and lower section, guided by human activities surrounding the area, within the period of October 2008 to February 2009. The concentrations of some heavy metals (Cu, Zn, Pb and Cd) in the aforementioned environmental media were determined using Atomic Absorption Spectrometry (AAS). Copper and Cd concentrations in the water column exceeded the British Columbia Guidelines for the protection of marine or estuarine life by 23 and 138.3 times respectively. However, Zn concentration in the water column was 0.56 times lesser, whilst Pb was below the detection limit of the analytical method used. The pollution levels of the heavy metals in the sediment were assessed by the Pollution Load Index (PLI) approach. The PLI calculated for the sediment compartment of the lagoon had values less than 1, suggesting that no section of the sediment compartment was polluted by the metals studied. However, the trend of pollution (PLI) of the lagoon was in the order: lower section > middle section > upper section. Copper and Zn concentrations in the black chin tilapia (*Sarotherodon melanotheron*) were above the Provisionally Maximum Tolerable Daily Intake (PMTDI and the Provisional Tolerable Weekly Intake

(PTWI) set by (FAO/WHO) Joint Expert Committee on Food Additives, but Cd and Pb were below detection limits. No significant relationships were observed between the monthly concentrations of the metals in fish, water and/or sediment. Signs of pollution were observed, which is basically from anthropogenic sources.

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# CHAPTER ONE

# GENERAL INTRODUCTION

## 1.1 Background

Coastal lagoons are vulnerable ecosystems of great ecological significance and important wild life areas because of their biodiversity (Uysal *et al.*, 2008). Lagoons in Ghana form such important vulnerable ecosystems, as they house a wide variety of fishes, shrimps, crabs, molluscs and polychaete species. Some of these lagoons have been recognized both nationally and internationally as migratory waterbird habitats (Ntiamoa-Baidu, 1991), whilst some may serve as nursery areas for juveniles of marine fish and shrimp. Lagoons like the Abby Lagoon and Volta Estuary house manatee (*Trichechus senegalensis*) which attracts so much socio-cultural interest in Ghana as high priced meat as well as a river goddess associated with wealth and beauty. These lagoons also provide benefits such as fish for human consumption, tourism, aesthetics, cultural heritage and a source of employment to the coastal population (Gordon, 1998). Despite the numerous benefits derived from lagoons, they are threatened by the activities of humans, which coupled with poor management result in pollution and subsequent degradation of the waters.

Trace elements, especially the so called 'heavy metals', are among the most common environmental pollutants and their occurrence in water and biota indicate the presence of natural or anthropogenic sources (Singh *et al.*, 2005; Papafilippaki *et al.*, 2008). The main natural sources of metals in aquatic systems are the weathering of rocks as well as from anthropogenic sources such as mining and disposal of industrial and urban wastes into water bodies (Pardo *et al*., 1990 Boughriet *et al*., 1992; Klavins *et al*., 2000; Yu *et al*., 2001; Singh *et al*., 2005).

Zinc (Zn), copper (Cu), lead (Pb) and cadmium (Cd) are common pollutants, which are widely distributed in the aquatic environment. In aquatic systems, these metals can result from direct atmospheric deposition, geologic weathering or through the discharge of agricultural, municipal, residential or industrial waste products (Dawson and Macklin, 1998). For instance, domestic, industrial and clinical use and disposal of Cd, Pb, Zn and Cu containing compounds may find their way into water bodies. Heavy metals in aquatic systems may exist as dissolved free ions or form organic complexes with humic and fulvic acids (Spencer and MacLeod, 2002). Additionally, many metals such as Pb associate readily with particulates and become adsorbed or co-precipitated with carbonates, oxyhydroxides, sulphides and clay minerals. Consequently, sediments accumulate contaminants and may act as long-term stores for metals in the environment (Spencer and MacLeod, 2002). For instance, elevated concentrations of Pb, Cu, Cd and Zn have been reported in water, sediment, biota, etc. in different parts of the world. Bertin and Bourg (1995) documented the extent of Cd, Pb and Zn contamination in the Lot River basin in the areas of Southwest France. Cahill and Unger (1993) reported high levels of Cu, Pb, Zn, Cr and Cd in sediments collected from the west branch of the Grand Calumet River, USA. Chen and Hung (1995) found that sediments from the lower stream of the Kaohsiung River, Taiwan were heavily contaminated with Cu, Pb and Cd.

Heavy metals are among the most dangerous groups of anthropogenic environmental pollutants due to their potential toxicity and persistence in the environment (Nyarko *et al.*, 2006). Owing to their toxicity, persistence and tendency to accumulate in water and sediment, heavy metals when occurring in higher concentrations become severe poisons for all living organisms (Has-Schön *et al.*, 2006). Exposure of sediment-dwelling organisms to heavy metals may then occur via uptake of interstitial waters, ingestion of sediment particles and via the food chain (Spencer and MacLeod, 2002). However, the bioavailability of metals is determined by abiotic (e.g. pH, conductivity, temperature, complexation) and biotic (e.g. exchange surfaces, feeding habits) factors (Chowdhury and Blust, 2002; Clearwater *et al.*, 2002). Fishes are likely to bioaccumulate these metals through their feeding relationships and thus represent a potential risk, not only to the fishes themselves but also to piscivorous birds and mammals, including humans (Adams *et al.*, 1992). Bioaccumulation is the process in which a chemical pollutant enters the body of an organism and is not excreted but rather collected in the organism's tissues (Zweig, *et al.*, 1999).

The presence of unacceptable levels of Hg and Pb in the tissues of the African catfish, *Clarias gariepinus,* from River Niger has been reported (Lawani and Alawode, 1996). Omeregie *et al.* (2002) also reported enhanced levels of Pb, Cu and Zn in *Oreochromis nilotica* (Nile Tilapia) from River Delimi, Nigeria. Higher concentrations of Cd, Cu, Fe, Mn and Zn have been shown to bioaccumulate in muscle, liver and gill tissues of *O. nilotica* and *C. gariepinus*, cultured in some disused mining lakes (Akueshi *et al.*, 2003). The chronic exposure of fish to sub-lethal trace metal levels causes' disturbed ion regulation, reduced swimming speed and reduced growth, among others (Sorensen, 1991; Hollis *et al.*, 1999; Alsop *et al.*, 1999). Copper and Zn are among the essential group of metals required for some metabolic activities in organisms. However, Cu is inherently toxic at high levels (Awofolu *et al.,* 2004). Also, Cu is toxic at very low concentration in water and is known to cause brain damage in mammals (Department of Water Affairs and Forestry, 1996). Zinc has been found to have low toxicity to man, but prolonged consumption of large doses can result in some health complications such as fatigue, dizziness, and neutropenia (Hess and Schmid, 2002). Some literature sources have also revealed that Zn could be toxic to some aquatic organisms such as fish (Alabaster and Lloyd, 1980). Cadmium is a persistent environmental toxicant (Lauwerys and Hoet, 2001) and its exposure to humans occurs through consumption of contaminated food or water or by inhalation of tobacco smoke or polluted air (Hogervorst *et al.*, 2007). In addition to its well-known nephrotoxicity, chronic exposure to low-level Cd has been associated with a number of pathologies, such as end-stage renal failure, early onset of diabetic renal complications, osteoporosis, deranged blood pressure regulation, and increased cancer risk (Jarup *et al.*, 1998). Cadmium has also been found to be toxic to fish and other aquatic organisms (Rao and Saxena, 1981; Woodworth and Pascoe, 1982). Gabriel *et al.* (2006) and Staessen *et al.* (1994) have also recorded cases of neurotoxicity and tubular renal dysfunction as a result of consumption of food contaminated with lead and cadmium.

It has largely been suggested by environmentalists that metal speciation may be more important than total concentrations of heavy metals in assessing the potential toxicity and mobility of contaminant metals released into the fluvial environment through either natural or anthropogenic processes (e.g. Barona *et al.*, 1999; Buykx *et al.*, 2000; Bird *et al.*, 2005). However, the importance of total concentrations of heavy metals in assessing metal pollution in aquatic systems cannot be downplayed (Adomako *et al.*, 2006), especially where baseline data is unavailable.

Measuring heavy metals in aquatic organisms may be a bioindicator of their impact on organisms and ecosystem health (Acker *et al.*, 2005). Most monitoring programs only measure contaminant levels in the environment, i.e. levels in water, sediment, and/or suspended matter (e.g. Doodo and Adjei, 1995; Gilbert *et al.*, 2006). For example, Cd levels in *Anodonta grandis* correlated with dissolved Cd at the sediment-water interface, but not with the total Cd concentration in the sediment (Tessier *et al.*, 1993). Hickey *et al.* (1995) reported that no significant correlation existed between total sediment Hg and As concentrations and freshwater mussels *Hydrinella menziesi* (Unionacea) tissue levels. In another study, Cd concentrations in the sediment were also not found to be useful in predicting Cd bioavailability. Therefore, the assessment of bioaccumulated metals in an organism should be made together with determination of metal concentrations in water and sediment.



### 1.2 Problem Statement

Fosu lagoon provides a source of livelihood for over 417 fisher men and their families, and also serves as a river god and a major cultural heritage for the people of Cape Coast. Despite the numerous benefits derived from this lagoon, it is saddled with environmental problems/challenges. The lagoon is heavily polluted and has been declared a "dead zone" by the United Nations Environmental Program (UNEP, 2006). Studies so far by Doodo and Adjei (1995) and Gilbert *et al.* (2006) on the lagoon were on heavy metals enrichment in the sediments. Furthermore, in the 2006 research report of the Environmental Protection Agency EPA), Cape Coast, it was concluded that the lagoon was generally polluted with most of the commonly known cations, with values being extremely high.

However, little attention has been paid to the comparative study of metal concentrations and distributions in sediments, surface water and fish, although it had been recommended by the EPA, Cape Coast that further analyses be conducted on the fishes, vegetation and other aquatic life.

This study therefore seeks to provide more information on the extent of pollution as well as the ecological health status of the lagoon.

### 1.3 General Objective

The main objective of the study is to determine the extent of some heavy metals (Zn, Cu, Cd and Pb) pollution of the Fosu Lagoon.

#### 1.3.1 Specific Objectives

- Determine the levels of cadmium (Cd), lead (Pb), copper (Cu) and zinc (Zn) in surface water of the Fosu lagoon as well as temperature, electric conductivity and pH.

- Determine the levels of Cd, Pb, Cu and Zn in the bottom sediment and in black chin tilapia (*Sarotherodon melanotheron*) from the Fosu lagoon.
- Determine the relationship of these metals between the fish and the other media (i.e. surface water and bottom sediment).
- Determine the sections of the lagoon which is more polluted.
- Compare the concentrations of the heavy metals present in black chin tilapia obtained from Fosu Lagoon with the PMTDI and the PTWI values set by Food and Agriculture Organization/World Health Organization (FAO/WHO) for the safe consumption limits of food.

## CHAPTER TWO

## LITERATURE REVIEW

### 2.1 Heavy Metals

The definition of a 'heavy metal' is not clear. However, in many texts, metals with a density > 4 or 5 g/l are considered as being heavy metals. This definition would include the lanthanides and actinides that, chemically, have distinct properties. The classification preferred by many researchers is that of Nieboer and Richardson (1980), in which elements with a density > 5 g/l are grouped into three classes: A, B and borderline (Wilkinson *et al.*, 2003).

Table 1: Classification of selected essential and non essential metal ions into classes A, B and borderline (based on Nieboer and Richardson, 1980)

| Class A | Borderline | Class B |
|---|---|---|
| Cs | Zn | Cd |
| Mn | Pb | Cu |
| Sr | Fe | Hg |
| | Cr | Ag |
| | Co | |
| | Ni | |
| | As | |
| | Sn | |
| | V | |

Class A elements have a preference for ligands containing O (e.g. Mn, density 7·42 g/l). Class B elements show a preference to form ligands with N or S (e.g. Cd, density 8·65 g/l). Borderline elements are of intermediate nature between classes A and B (Table 1).

There are known sixty heavy metals (Suciu *et al*., 2008) that can be grouped as essential and non-essential. Essential heavy metals are the metals with known biological or metabolic importance (e.g. Cu, Zn, etc.) whilst the non-essential heavy metals have no known biological or metabolic importance (e.g. Cd, Pb, Hg, etc).

Human activities have increased the levels of heavy metals in many of the natural water systems, which have raised concerns regarding metal bioaccumulation and human health hazards. With increasing public concern regarding environmental contamination, there is a growing need to monitor, evaluate, manage and remediate ecological damage (Kureishy, 1993).

**2.2 Water Pollution**

Pollution, as defined by a 1991 GESAMP (IMO/FAO/UNESCO/WMO/WHO/IAEA /UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution) report, is the introduction by man, directly or indirectly, of substances or energy into the environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of sea water and reduction of amenities. Pollutants released into aquatic systems may be chemical, physical or biological in nature. Common aquatic pollutants include human or animal waste, disease producing organisms, radioactive materials, agricultural chemicals (i.e., pesticides, herbicides and fertilizers), acid rain, high-temperature water discharge from power plants, and toxic or heavy metals such as lead (Pb), cadmium (Cd) and mercury (Hg).

Sources of these pollutants into water bodies may either be from point sources or non-point sources. Point sources involve the discharge of substances from factories, sewage systems, power plants, underground coal mines and oil wells. Non-point sources, which are poorly defined and scattered over broad areas, may include agricultural run-off (from animal and crop lands), storm water drainage (from streets, parking lots and lawns) and atmospheric deposition (from air pollutants washed to earth or deposited as dry particles).

### 2.2.1 Pollution Monitors in Surface Water

Surface water has been used by many researchers to assess the extent of heavy metals pollution in riverine, marine or coastal waters (Braungardt *et al*., 2003; Turner *et al*., 2004; Awofolu *et al*., 2005; Eletta, 2007; Kar, *et al*., 2008; Begum *et al*., 2009; Netpae and Phalaraksh, 2009).

Kar *et al*. (2008) detected concentrations of Fe (0.025–5.49 mg/L), Mn (0.025–2.72 mg/L), Zn (0.012–0.370 mg/L), Ni (0.012–0.375 mg/L), Cr (0.001–0.044 mg/L), Pb (0.001–0.250 mg/L), Cd (0.001–0.003 mg/L) and Cu (0.003–0.032 mg/L) in the surface water of river Ganga in West Bengal, India. Begum *et al*. (2009) also detected concentrations of Cr (0.22–2.5 2$\mu gL^{-1}$), Ni (1.00–6.40 2$\mu gL^{-1}$), Cd (1.02–4.9 2$\mu gL^{-1}$) and Pb (0.66–7.2 $\mu gL^{-1}$) in surface water of Madivala lake, Bangalore India. However, the concentration of heavy metals in surface water is affected by several factors.

### 2. 2. 2 Factors That Affect Heavy Metals Availability in Surface Water

Changes in physical and chemical features of the aquatic system may influence the solubility and mobility of metals in that system (Gundersen and Steinnes, 2003). The solubility of heavy metals in surface water is controlled by the water pH (Osmond *et al.*, 1995), water temperature (Iwashita and Shimamura, 2003), the river flow or estuarine mixing (Neal *et al.,* 2000b; Iwashita and Shimamura, 2003; Olías *et al.,* 2004) and the redox environment of the aquatic system (Osmond *et al.,* 1995; Iwashita and Shimamura, 2003). A lower pH increases the competition between metal and hydrogen ions for binding sites. A decrease in pH may also dissolve metal-carbonate complexes, releasing free metal ions into the water column (Osmond *et al.*, 1995).

During estuarine mixing, pH rise causes metals to precipitate as hydroxide, $CO_3^{2-}$ (Braungardt *et al*., 2003; Achterberg *et al*., 2003). Salinity and electrical conductivity (EC) are related and are useful parameters for water quality assessment. As the concentration of salts in the water increases, electrical conductivity rises. Conductivity is also affected by temperature; the warmer the water, the higher the conductivity (USEPA, Voluntary Estuary Monitoring Manual, 2006).

## 2.3 Sediment

Although water is commonly employed as a pollution indicator by heavy metals, sediment can also provide a deeper insight into the long-term pollution state of the water body. Sediment has been described as a ready sink or reservoir of pollutants including trace metals where they concentrate according to the level of pollution (Becker *et al*., 2001; Onyari *et al*., 2003). Several researchers (e.g. Binning and Baird, 2001; Sin *et al*., 2001; Awofolu *et al*., 2005; Gilbert *et al*., 2006) have therefore used bottom sediment to assess the extent of heavy metal pollution in aquatic environment. Binning and Baird (2001) detected mean heavy metals concentrations of Cr (20.3 μg/g), Pb (32.9 μg/g), Zn (35.9 μg/g), Ti (99.3 μg/g), Mn (114.9 μg/g), Sr (173.8 μg/g), Cu (6.82 μg/g and Sn (630.5μg/g) in the sediment of the Swartkops estuary, and Cr (11.9 μg/g), Pb (24.7 μg/g), Zn (45.0 μg/g), Ti (39.1 μg/g), Mn (119.4 μg/g), Sr (36.6 μg/g), Cu (9.51 μg/g) and Sn (586.4 μg/g) in the sediment of Swartkops river, Eastern Cape, South Africa. Sediment analysis allows contaminants that were adsorbed by particulate matter, which escaped detection by water analysis, to be identified (Greaney, 2005). Concentrations of heavy metals in sediment usually exceed the levels of the overlying water by 3 to 5 orders of magnitude (Defew *et al*., 2004). Singh *et al*. (2005) observed considerably higher concentrations of heavy metals in the sediments of Gomti River–a tributary of the Ganges, India than those obtained in the river water. He attributed this occurrence to the neutral to alkaline nature of the river water, saying, most of the heavy metals have precipitated and settled as carbonates, oxides and hydroxide bearing sediments, hence the elevated levels. Similar trends of heavy metals concentrations in water and sediment were also observed by Rios-Arana *et al*. (2003) when he conducted an assessment of arsenic and heavy metal concentrations in water and sediments of the Rio Grande at El Paso-Juarez metroplex region, Texas.

### 2.3.1 Factors Affecting Heavy Metals Availability in Sediment

Heavy metals accumulation from the overlying water to the sediment is dependent on a number of external environmental factors such as pH, ionic strength, anthropogenic input, the type and concentration of organic and inorganic ligands, and the available surface area for adsorption caused by the variation in grain size distribution (Davies *et al*., 1991).

Diagenetic processes in the sediments can change and redistribute these contaminants between the solid and the dissolved phases, but most of the elemental contaminants are immobilized through sedimentation (Hanson *et al.*, 1993). The sulphides of Cd, Cu, Pb and Zn are highly insoluble and considered to be less mobile and less bio-available to benthic organisms (Carignan and Tessier, 1995; Ankley *et al.*, 1996). Depending on the amount of sulphides present in the system, the mobility could be very low, if all trace metals are removed from the porewater phase and immobilized as solid sulphides minerals (Griethuysen *et al.*, 2002). Fine grained particles in sediment usually act as effective collectors and carriers of dissolved metals from the water column to the sediments and thus result in elevated concentrations of heavy metals in sediment. In Ghar El Melh Lagoon, Tunisia, 55 to 65% of heavy metals in the sediment was associated with fine particles of diameter 40 μm or less (SCET, 1999). Small particles with large surface-area-to-mass ratios allow more adsorption than an equivalent mass of large particles with small surface-area-to-mass ratios. Reduced adsorption can increase metal bioavailability by increasing concentrations of dissolved metals in associated water.

### 2.4 Fish

Fish forms an important component of human food, and it is therefore not surprising that numerous studies have been carried out on heavy metal pollution in different species of edible fish (Ramamurthy, 1979; Kureishi *et al.*, 1981; Lakshman and Nambisan, 1983; Radhakrishnan, 1994; Prudente *et al.*, 1997; Senthilnathan and Balasubramanian, 1998; Sultana and Rao, 1998; Kalfakakon and Akrida-Demertzi, 2000; Kucuksezgin *et al.*, 2001; Rashed, 2001; Lewis *et al.*, 2002; Benson *et al.*, 2007; Birungi *et al.*, 2007). Tay *et al.* (2005) detected the following mean metals concentrations (μg/g wet weight) and their standard deviations in *Egeria paradoxa galanata* (Shell fish): Fe (35.04 ± 2.54), Mn (16.74 ± 1.29), Cu (7.73 ± 0.47), Pb (0.42 ± 0.01), Zn (16.09± 0.17) and Cd (0.33 ± 0.16); in *Parapenaeopsis atlantica* (Shell fish): Fe (9.68 ± 1.72), Mn (7.27± 1.27), Cu (0.87± 0.01), Pb (0.08 ± 0.001), Zn (6.55 ± 0.28) and Cd (0.34 ± 0.01); in *Solar crumophthalmus* (Fin fish): Fe (7.62 ± 0.46), Mn (1.51± 0.80), Cu (11.91 ± 0.50), Zn (16.73 ± 1.06) and Cd (0.14 ± 0.09); and in *Panulirus regius* (Fin fish): Fe (9.24 ± 0.11), Mn (1.06 ± 0.23), Cu (14.18 ± 0.59), Pb (0.13 ± 0.15), Zn (14.58 ± 1.05) and Cd (0.08 ± 0.01) obtained from some coastal and inland waters in Ghana. Sallam *et al.* (1999) also detected heavy metal concentration ranges (in mg/kg wet weight) of Hg (0.26–0.391), Cd (0.28–0.053) and Pb (0.022–0.654) in *Bagrus orientalis* fish captured from River Nile, Egypt. However, heavy metals are taken up through different organs of the fish and many are concentrated at different levels in different organs of the body (Scharenberg *et al.*, 1994; Bervoets *et al.*, 2001). According to Kargin (1998), Ay *et al.* (1999), Liu *et al.* (2001), Wong *et al.* (2001), Bervoets and Blust (2003) and Yilmaz (2005), organs such as liver, gonads, kidney and gill have the tendency to accumulate enhanced levels of heavy metals than the muscles.

### 2.4.1 Black Chin Tilapia Fish (*S. melanotheron*)

*Sarotherodon melanotheron* is a dermesal (bottom-associated) species that inhabits fresh to brackish water. It is native to tropical West Africa, occurring from Senegal to Zaire and southern Cameroon (Trewevas, 1983; Robbins *et al.*, 1991). The species is common in quiet muddy brackwater habitats where aquatic vegetation is abundant (Jennings and Williams, 1992). They are broadly euryhaline, primarily inhabiting estuarine habitats such as mangrove marshes, and travel freely between fresh and saltwater environments

(Trewevas, 1983; Shafland, 1996). They frequent the saline lower reaches of streams and are also tolerant of hypersaline conditions that may arise in enclosed lagoons and impounded marshes (Page and Burr, 1991). Black chin tilapia exhibits an ontogenic dietary shift, switching from a more carnivorous habit as juveniles to an adult diet that focuses mainly on detritus, algae, periphyton and the organisms and material inhabiting fouling submerged hard surfaces (Hensley and Courtenay, 1980; Diouf, 1996). This characteristic behaviour of the *S. melanotheron* satisfy the requirement for an organism to be used for monitoring contaminants as recommended in the UNEP/FAO/IAEA,(1993) MAP Technical Reports Series No. 77.



**2.4.2 Factors That Affect Heavy Metals Bioavailability in Fish**

Heavy metal accumulation in different species depends on the feeding habits (Amundsen *et al*., 1997; Romeo *et al*., 1999), size and length of the fish (Al-Yousuf *et al*., 2000) and more particularly their habitat (Canli and Atli, 2003). The accumulation patterns of contaminants in fish and other aquatic organisms also depend on both their uptake and elimination rates (Guven *et al*., 1999). A number of studies have shown that various factors such as season (Kargın, 1996), physical and chemical status of water, i.e. temperature, pH, salinity, electric conductivity, etc (Jezierska and Witeska, 2001) can as well play a role in the tissue accumulation of metals. Recent studies have shown that pH and especially salinity play an important role in the bioavailability of these metals to different organisms, including toxicity (Riba *et al*., 2003, 2004; Baldó *et al*., 2005). Romeo *et al*. (1999) showed that mercury (Hg) concentrations in edible muscles of pelagic fish species were lower than those of benthic fish species. Allen-Gil and

Martynovb (1995) observed a negative correlation between Pb and age of Pechora River Whitefish ($R^2$ =0.41; 0.0479).

Widianarko *et al.* (2000) investigated the relationship between trace metals (Pb, Zn and Cu) concentration and fish (*Poecilia reticulata*) size and found that there was a significant decline in Pb concentrations with the increase in size, whereas concentrations of Cu and Zn did not depend on body weight.

It is well known that one of the most important factors that play a significant role in heavy metal accumulation in marine animals is the metabolic activity (Heath, 1987; Langston, 1990; Roesijadi and Robinson, 1994). It is also known that the metabolic activity of a young individual is normally higher than that of an older individual. Thus, metal accumulation has been shown to be higher in younger individuals than the older ones (Douben, 1989; Canli and Furness, 1993b; Widianarko *et al.*, 2000 and Nussey *et al.*, 2000).

Temperature may also affect quantities of metal uptake by an organism, because biological process rates (as noted above) typically double with every $10^0$ C temperature increment (Prosi, Luoma, 1983). Because increased temperature may affect both influx and efflux rates of metals, net bioaccumulation may or may not increase (Luoma, 1983).

### 2.5 Bioavailability of Metals

A brief summary of some factors controlling bioavailability of specific metals of interest is provided below.

### 2.5.1 Cadmium

The redox potential of sediment-water systems exerts controlling regulation on the chemical association of particulate cadmium, whereas pH and salinity affect the stability of its various forms (Kersten, 1988). In anoxic environments, nearly all particulate cadmium is complexed by insoluble organic matter or bound to sulfide minerals. Greenockite (CdS) has extremely low solubility under reducing conditions thereby decreasing cadmium bioavailability. Oxidation of reduced sediment or exposure to an acidic environment results in transformation of insoluble sulfide-bound cadmium into more mobile and potentially bioavailable hydroxide, carbonate, and exchangeable forms (Kersten, 1988). Studies of lake and fluvial sediment indicate that most cadmium is bound to exchangeable site, carbonate fraction, and iron-manganese oxide minerals, which can be exposed to chemical changes at the sediment-water interface, and are susceptible to remobilization in water (Schintu *et al.*, 1991). In oxidized, near neutral water, $CdCO_3$ limits the solubility of Cd (Kersten, 1988). In a polluted river, cadmium was the most mobile and potentially bioavailable metal and was primarily scavenged by non-detrital carbonate minerals, organic matter, and iron-manganese oxide minerals (Prusty *et al.*, 1994).

Elevated chloride contents tend to enhance chloride complex formation, which decreases the adsorption of cadmium on sediment, thereby increasing cadmium mobility (Bourg, 1988) and decreasing the concentration of dissolved Cd and bioavailability (Luoma, 1983).

### 2.5.2 Copper

In a river polluted by base-metal mining, copper is most efficiently scavenged by carbonate minerals and iron-manganese oxide minerals and coatings, and is less mobile than cadmium, lead and zinc (Prusty *et al.*, 1994). In most other situations, lead is less mobile than copper. Elevated chloride contents decrease adsorption of copper on sediment due to the formation of chloride complexs such as $CuCl_4^{2-}$, which results in greater solubility and mobility (Bourg, 1988; Gambrell *et al.*, 1991). In systems with high total copper contents, precipitation of malachite controls dissolved copper contents at low pH (Bourg, 1988; Salomons, 1995).



### 2.5.3 Lead

The main sources of lead in the aquatic environment are leaded gasoline and mining (Prosi, 1989). Leaded gasoline results in introduction of organometallic lead compounds, which eventually reach surface water through the atmosphere. Mining also releases inorganic lead compounds into the aquatic environment. Both organic and inorganic forms of lead pose serious health risks to all forms of life (Ewers and Schlipköter, 1990). Inorganic lead compounds (sulphide, carbonate and sulphate minerals) are commonly abundant in sediment but have low solubilities in natural water. Naturally-occurring lead in mineral deposits is not very mobile under normal environmental conditions, but becomes slightly more soluble under moderately acidic conditions. In the aquatic environment, total dissolved lead abounds in water and pore water control primary uptake by organisms. Lead bioaccumulation is primarily dependent on the amount of active lead compounds (predominantly aqueous species) in the environment and the capacity of animal species to store lead (Prosi, 1989). Particulate lead may contribute to bioaccumulation in organisms. For humans, particles that are inhaled but not exhaled are especially important. Variations in physiological and ecological characteristics of individual species lead to different enrichment factors and tolerances for each organism. Studies of bottom dwelling organisms suggest that iron-rich sediment inhibits lead bioavailability (Luoma, 1983). In a study of lake and fluvial sediment, most lead was bound to a carbonate fraction or to iron-manganese oxide minerals, both of which respond to chemical changes at the sediment-water interface, and are susceptible to remobilization in water (Schintu *et al.*, 1991). In a polluted river environment, lead is most efficiently scavenged by non-detrital carbonate and iron-manganese oxide minerals and is less mobile than cadmium (Prusty *et al.*, 1994).

**2.5.4 Zinc**

In slightly basic, anoxic marsh sediment environments, zinc is effectively immobilized and not bioavailable (Gambrell *et al.*, 1991). Substantial amounts of zinc are released to solution if this sediment is oxidized or exposed to an acidic environment. Very high concentration of soluble zinc are present under well oxidized conditions and at pH 5 to 6.5, whereas low concentration of soluble zinc are present at pH 8 under all redox conditions and at pH 5 to 6.5 under moderately and strongly reducing conditions (Gambrell *et al.*, 1991). In polluted river environments, most zinc is scavenged by non-detrital carbonate minerals, organic matter and oxide minerals and is less mobile than cadmium (and perhaps less mobile than lead) (Prusty *et al.*, 1994). Elevated chloride contents decrease adsorption of zinc on sediment (Bourg, 1988).

**2.6 Relationship between Heavy Metals Concentrations in Water/Fish/Sediment**

Heavy metals in flora or fauna reflect the concentration of these metals in the environment. This assertion holds within one system with a clear concentration gradient. It is more likely that tissue levels reflect environmental levels since environmental characteristics, and as a consequence of bioavailability, will be comparable (Tessier *et al*., 1984; Miller *et al*., 1992). Ashraf *et al*. (1991) observed no correlation between the trace metal contents in water, sediment and fish when they undertook a study of trace metals in fish, sediment and water from three freshwater reservoirs on the Indus River, Pakistan. Amundsen *et al*. (1997) also found no correlation between the water, sediments and fish. Thus clear relationships between total environmental metal concentrations and levels in organisms are seldom found (Luoma, 1983; Tessier *et al*., 1984; Van Hattum *et al*., 1991; Allen-Gil *et al*., 1995; Pollet and Bendell-Young, 1999 and Bervoets *et al*., 2001)

**2.7 Essential Metals**

**2.7.1 Essentiality of Zinc**

Most biochemical roles of Zn reflect its involvement in a large number of enzymes or as a stabilizer of the molecular structure of subcellular constituents and membrane. Zinc participates in the synthesis and degradation of carbohydrate, lipids, proteins and nucleic acids. It has recently been shown to play an essential role in polynucleotide transcription and translation and thus in the processes of genetic expression. Its involvement in such fundamental activities probably accounts for the essentiality of Zn for all forms of life (WHO, 1996). There is also evidence that zinc inhibits human prostate cancer cell growth (Liang *et al*., 1999).

### 2.7.2 Essentiality of Copper

Copper is an essential element for both plants and animals. The essentiality of Cu was not recognized until 1928 when Hart *et al.* (1928), showed Cu to be essential for erythropoiesis in rats fed on a milk-based diet (IPCS, 1998).

In humans as well as animals, Cu is required for normal biological activity of many enzymes, haemoglobin formation and hair keratin (Prohaska and Gybina, 2004). For instance, ferroxidases are Cu enzymes found in plasma, with a function in ferrous iron oxidation ($Fe^{2+} \rightarrow Fe^{3+}$) that is needed to achieve iron's binding to transferrin (Hartmann and Evenson, 1992, Linder and Hazegh-Azam, 1996).

These enzymes serve critical functions in their respective organisms (Linder and Hazegh-Azam, 1996); however the distribution of the total body Cu among the tissues varies with the species, age and Cu status.

The essentiality of Cu is not limited to only humans/animals. It is also an essential micronutrient for normal plant nutrition (Larcher, 1995), as it forms a constituent of a number of plant enzymes (Fernandes and Henriques, 1991). Copper is required in small amounts (5–20 mg/kg) in plant tissue and is adequate for normal growth (Stevenson, 1986; IPCS, 1998).

## 2.8 Symptoms of Essential Metals Deficiency

### 2.8.1 Copper Deficiency

Copper deficiencies, either gene defects due to mutations or low dietary Cu intake, although relatively rare in humans, have been linked to mental retardation, anemia, hypothermia, neutropenia, diarrhea, cardiac hypertrophy, bone fragility, impaired immune function, weak connective tissue, impaired central-nervous- system (CNS) functions, peripheral neuropathy, and loss of skin, fur (in animals), or hair colour (Linder and Goode, 1991; Uauy *et al*., 1998, Cordano 1998, Percival, 1998).

Typical visible symptoms of Cu deficiency in plants, on the other hand, are stunted growth, distortion of young leaves, necrosis of the apical meristem, and wilting and bleaching of young leaves (IPCS, 1998). Copper deficiency results in insufficient lignification of the cell walls of the xylem vessels (IPCS, 1998) indicating that the degree of lignification is a good indicator of nutritional Cu status in plants.

### 2.8.2 Symptoms of Zinc Deficiency



Cases of severe Zn deficiency are now rare, but mild deficiency during periods of rapid growth, pregnancy, synthesis of new tissue, and in persons consuming plant-based diets, is not uncommon. Zinc deficiency also occurs in the presence of certain disease states such as malabsorption syndromes, renal and hepatic diseases, and in association with burns and alcoholism. Two genetic disorders, acrodermatitis enteropathica and sickle-cell disease, are associated with suboptimal Zn status.

Zinc deficiency has been classified into three syndromes (Henkin and Aamodt, 1983): acute, chronic and subacute Zn deficiency. The clinical symptoms range from neurosensory changes, oligospermia in males, decreased thymulin activity, decreased interleukin-2 production, hypogeusia and impaired neuropsychological functions (Penland, 1991) in mild or marginal deficiency, through to growth retardation, male hypogonadism, and delayed wound healing with moderate deficiency, and alopecia, mental disturbances, cell-mediated immune disorders and pustular dermatitis in patients with severe Zn deficiency (Prasad, 1988).

## 2.9 Toxicity of Heavy Metals

### 2.9.1 Cadmium Toxicity to Fish

Cadmium uptake from water by aquatic organisms is extremely variable and depends on the species and various environmental conditions such as water hardness (notably the calcium ion concentration), salinity, temperature, pH, and organic matter content (IPCS, 1992). Toxicity of Cd to both marine (Eisler, 1971) and freshwater (Roch and Maly, 1979) fish has been shown to be greater at higher temperatures.

Meteyer *et al.* (1988) observed that hatching was delayed by up to 3 days at the highest Cd concentration and the resulting treated larvae were shorter than controls, as sheepshead minnow (*Cyprinodon variegates*) eggs were exposed to Cd concentrations of between 0.39 and 1020 µg/litre from approximately 4 hours after fertilization. Furthermore, protective metal-binding proteins (metallothioneins) are induced by Cd in fish. A manifest symptom of Cd toxicity in freshwater fish is ionic imbalance with reduced plasma $Ca^{+}$, $Na^{+}$ and $Cl^{-}$. The probable explanation is that Cd is a potent inhibitor of ion – transporting enzymes. Verbost *et al.* (1988) showed that Cd inhibited Ca – ATPase in the cell membranes of fish gut. It probably does the same in the gills because Cd exposure has been shown to inhibit Ca uptake in the gills of the adult (Verbost *et al.*, 1987; Reid and McDonald, 1988) as well as in larvae (Wright *et al.*, 1985). Similarly, Cd has been shown to inhibit Na/K – ATPase in fish gills (Watson and Benson, 1987).

MacInnes *et al.* (1977) reported reduced gill tissue oxygen consumption in cunner (*Tautogolabrus adspersus)* exposed to Cd (0.05 or 0.1 mg/litre) for 30 or 60 days, reduced activity of aspartate aminotransferase and an increased activity of glucose-phosphate dehydrogenase in the liver of the fish after acute (24 h) or chronic (90 day) exposure to Cd. Acute exposure to 12.65 mg/litre led to significant hyperglycaemia and an increase in liver, kidney, and ovarian cholesterol levels. Chronic exposure to 0.63 or 0.84 mg/litre, by contrast, led to an enduring hypoglycaemia and diminished levels of cholesterol in tissues. Both acute and chronic exposure caused marked hypocholestrolaemia, glycogenolysis in the liver and brain and a rise in myocardial glycogen. Testis cholesterol was also depleted after 60 days in both acute and chronic exposures.

Sastry and Subhadra (1983) also observed reduced absorption of glucose and fructose from the gut, when catfish (*Heteropneustes fossilis*) was exposed to Cd in water at sublethal concentration of 2.3 µmol/litre, this effect was more pronounced after 30 days of exposure than after 15 days.

### 2.9.2 Cadmium Toxicity to Humans

The human body burden of Cd has increased over the past 100 years due to an increase in environmental and industrial pollutants (Thrush, 2000), leading to a range of health effects. Humans normally absorb Cd into the body either by ingestion or inhalation (Lauwerys, 1979). Cadmium is more efficiently absorbed from the lungs than from the gastrointestinal tract (ATSDR, 1989). The latter usually reflects the toxic action of a high body burden on the kidney and possibly the skeleton. The absorption efficiency is a function of solubility of the specific Cd compound as well as its exposure concentration and route. It is widely accepted that approximately 2% to 6% of the Cd ingested is actually taken up into the body (IPCS, 1992; ATSDR, 1997).

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

The effects of Cd on the kidney take the form of renal tubular dysfunction and subsequent pathological changes. The former is reflected by failure to reabsorb substances normally, and results in proteinuria, aminoaciduria, glucosuria and decreased renal tubular absorption of phosphate. Cadmium excretion and low molecular weight proteinuria are early indicators of renal Cd damage (WHO, 1996).

Individuals with severe Cd nephropathy may have renal calculi and exhibit excessive urinary loss of calcium. With chronic Cd exposure, urinary calcium may eventually decline to become less than normal. Associated skeletal changes probably related to calcium loss due to the Cd exposure include osteomalacia and osteoporosis. That is, bone changes associated with intense skeletal pains which are features of a syndrome nicknamed "itai-itai" observed in postmenoposal multiparous women living in the Fuchu area of Japan before and during the Second World War. Other features of the syndrome included severe body deformities and chronic renal diseases. Current estimates suggest that > 200 million people worldwide have osteoporosis and that the prevalence of this disease is escalating (Reginster and Burlet, 2006). Women are at greater risk of developing Cd toxicity than are men (Choudhury *et al.*, 2001).

Inhalation of Cd causes irritation and possibly an acute inflammatory reaction of the lungs. Long term exposure produces chronic bronchitis and increased susceptibility to infections, bronchiectasis and emphysema. Other pulmonary irritants, particularly cigarette smoke, a significant source of Cd, may exacerbate its toxic effects (WHO, 1996). IARC (1993), U.S. EPA (2005) and OEHHA (2005) have determined that there is sufficient evidence that Cd is carcinogenic to humans. OEHHA derived an inhalation potency factor based on inhalation studies in humans, but no oral studies in humans or animals were identified that were judged suitable for developing oral cancer potency for Cd.

The most important measure of excessive Cd exposure is increased Cd excretion in urine. Increased urinary Cd reflects recent exposure, an increased body burden and, in particular, an elevation of renal Cd. Urinary Cd measurement thus provides a good index of excessive Cd exposure.



### 2.9.3 Lead Toxicity to Fish

Adult trout exposed to Pb as part of their diet (0.86–1.77 µg/g) for 21 days experienced increased scale loss and accumulation of lead in their guts. When exposed to Pb for the same length of time through the water column (4.3–6.4 µg/L, hardness=100–106), trout experienced scale loss, reduced survival, and accumulation in gill and kidney tissues. A combination of dietary and water-borne lead exposure at the same concentrations resulted in lipid peroxidation in kidneys of adults and a decrease in the whole body potassium of juveniles (Farag *et al.,* 1994). Other documented sublethal responses include hematological, neurological, teratogenic, growth, and histological effects at lead concentrations of 8–119 µg/L and >1000 µg/L (hardness=42-353) during exposures from 3–16 weeks (Hodson *et al.*, 1984).

Concentrations of lead >10 µg/L (hardness=135) caused long-term effects such as: spinal curvature; anemia; caudal chromatophore degeneration (black tail); caudal fin degeneration; destruction of spinal neurons; γ-aminolevulinic acid (ALAD) inhibition in blood cells, spleen, liver, and renal tissues; reduced swimming ability; destruction of respiratory epithelium; elevated lead in blood, bone and kidney; muscular atrophy and paralysis; inhibition of growth; retardation of maturity; changes in blood chemistry; testicular and ovarian histopathology; and even death (U.S. EPA, 1985d). The effects of lead increase under rapid growth conditions, as illustrated by the increase of the rate of intoxication by lead, increased with growth rate, but not fish size (Hodson *et al*., 1982). In sexually maturing male rainbow trout exposed to 10 μg/L (hardness=128) for 12 days during spermatogenesis, spermatogonial cysts increased, spermatocytes declined, and the sensitivity of the reproductive cycle was suppressed as the transformation of spermatogonia to spermatocytes decreased (Ruby *et al*., 1993). In whitefish (*Coregonus sp*.) from contaminated lakes (0.5–4.5 μg Pb/L, hardness=10–20) γ-aminolevulinic acid (ALAD) activity was inhibited up to 88% when compared to fish from uncontaminated lakes. Inhibition of ALAD activity leads to problems with hemoglobin synthesis that can result in anemia. Higher blood glucose levels and lower plasma sodium content were also found in fish taken from lead contaminated lakes (Haux *et al*., 1986).

Spinal deformities in rainbow trout resulted from exposure to lead concentrations of 18.9 and 101.8 μg/L (hardness=28 and 35, respectively). In juvenile rainbow trout, ALAD activity was inhibited. Red blood cells and blood iron content were also affected after 28 days exposed to lead levels of 13 μg/L (hardness=135). At 120 μg Pb/L (hardness=135) for 32 weeks, 30% of juvenile rainbow trout exposed had black tails caused by degeneration of caudal chromophores (U.S. EPA, 1985d).

### 2.9.4 Lead Toxicity to Humans

In humans, the toxic effects of Pb have been demonstrated at very low levels, and there is a suggestion that there may be no level of exposure below which Pb is harmless. Its toxic effects involve several organs and are the consequence of a variety of biochemical defects (WHO, 1996).

Lead is particularly toxic to the brain, kidneys, reproductive system, and cardiovascular system. Exposures can cause impairments in intellectual functioning, kidney damage, infertility, miscarriage, and hypertension (Silbergeld, 1996). Several studies have shown that Pb exposures can significantly reduce the Intelligent Quotient (IQ) of school-aged children; some estimates suggest that every 10-microgram-per-deciliter increase in Pb levels in the blood is associated with a 1- to 5-point decrease in the IQ of exposed children (Goyer, 1996). Lead exposures have also been associated with aggressive behavior, delinquency, and attention disorders in boys between the ages of 7 and 11 (Needleman *et al.*, 1996). In adults, Pb toxicity has been linked to increased blood pressure and hypertension, conditions known to increase the risk of cardiovascular disease.

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

### 2.9.5 Copper Toxicity to Fish

Copper is a common element in the environment and as a micronutrient, it is essential for growth and metabolism of all living organisms (Eisler, 1998). However, Cu can be toxic to many different species of organisms at concentrations above the micronutrient level.

Chronic effects of Cu to fish may include decreased growth (Hansen *et al.*, 2002b), changes in fish behavior, including olfactory responses, agonistic responses, avoidance and attraction and changes in swimming ability or swimming speed (Beaumont *et al.*, 1995).

Behavioral effects of elevated Cu exposure include coughing (Atchison *et al.*, 1987), inhibition of olfactory responses (Baldwin *et al.*, 2003), changes in swimming performance (endurance and speed) and avoidance (Giattina *et al.*, 1982).

A number of researchers have demonstrated the importance of olfactory cues for salmon returning to their natal stream (Atchison *et al.*, 1987). Atchison *et al.* (1987) reported that the addition of 44 μg Cu $L^{-1}$ resulted in avoidance by migrating Atlantic salmon. Furthermore, Cu exposure can damage cellular surface proteins, membrane structure or internal organelles. High concentrations (in the order of 50 μg Cu $L^{-1}$) may result in permanent damage to the olfactory cells in Chinook salmon (Hansen *et al.*, 1996b).

The mechano-sensory cells of the lateral line may also be damaged by Cu exposure, although recovery usually occurs within a few days, provided Cu concentrations are low (Hansen *et al.*, 1996b; Bettini *et al.*, 2006). Linbo *et al.* (2006) conducted experiments with zebra fish and showed damage to mechano-sensory cells following exposures of 20 μg Cu $L^{-1}$ and regeneration within 2 days in clean water. However, exposure to high concentrations (more than 20 μg Cu $L^{-1}$) resulted in permanent damage to mechano-sensory cells.

Waiwood and Beamish (1978) observed that critical swimming performance or the maximum velocity that a fish can maintain for a given period of time was impaired in rainbow trout (*Oncorhynchus mykiss*) exposed to 10 µg Cu $L^{-1}$. The effects on swimming performance were, however, greatest at low pH and in soft water.

Sandahl *et al*. (2006) exposed chum salmon (*Oncorrhynchus keta*) to different Cu concentrations, then measured responses to "predator" stimulant. They reported significant reductions in swimming speed for coho salmon exposed to 20 µg Cu $L^{-1}$.

### 2.9.6 Copper Toxicity to Humans



In humans, acute Cu toxicity is rare and usually results from contamination of foodstuffs or beverages by Cu containers or from accidental or deliberate ingestion of gram quantities of copper salts (Williams, 1982; IPCS, 1998). Following acute ingestion of copper salts (e.g., copper sulphate) in amounts that exceed approximately 1 g, systemic effects are generally observed. The effects include gastrointestinal mucosal ulcerations and bleeding, acute hemolysis and hemoglobinuria, hepatic necrosis with jaundice, nephropathy with azotemia and oliguria, cardiotoxicity with hypotension, tachyeardia and tachypnea, and central-nervous-system (CNS) manifestations, including dizziness, headache, convulsions, lethargy, stupor, and coma ( U.S. AF, 1990 ). Acute hemolytic anemia and kidney effects, indicative of renal tubular damage, were observed in a child 2 days after drinking a solution containing approximately 3 g copper sulfate (Walsh *et al*., 1977; RAIS 1992). Symptoms occurring immediately after ingestion are metallic taste in the mouth, abdominal pain, diarrhoea, and vomiting (ATSDR, 1990).

Although the chronic toxicity from long-term exposure to copper has not been investigated extensively, studies of patients with Wilson's disease, a genetic defect that results in accumulation of copper in tissues, provide information on the chronic toxicity of Cu. Wilson's disease may affect many organs and systems and is characterized by hepatic cirrhosis, brain damage and demyelination, kidney damage, and hemolytic anemia. Patients may also suffer from poor coordination, psychological impairment, tremors, disturbed gait, rigidity, and eye opacities (ATSDR, 1990; Goyer, 1991). An increased dietary intake of Cu may be partially responsible for a disease known as Indian childhood cirrhosis, which usually occurs in children, aged 6 months to 5 years. The disease is characterized by high levels of Cu in the liver, Mallory's hyaline inclusions in hepatocytes, intralobular fibrosis, and widespread hepatic necrosis with poor hepatic regeneration (U.S. AF, 1990).

A recent prospective population study of men residing in eastern Finland, an area with high levels of Cu in drinking water, established a positive correlation between serum Cu levels and risk of acute myocardial infarction (Salonen *et al*., 1991).

**2.9.7 Zinc Toxicity to Fish**

Malik *et al*. (1998) studied the effect of Zn toxicity on the biochemical composition of the muscle and liver of murrel (*Channa punctatus*). The selected specimen of murrel was exposed to a sub-lethal Zn concentration. They reported that the Zn exposure produced marked changes in the chemical composition of liver and muscle tissues. The metabolism of the fish decreased with the time of exposure and there was a decline in the calorific value of lipid, protein, and glycogen in muscle and liver.

Furthermore, treatment of fish with Zn results in substantial gill damage (Skidmore and Tovell, 1972). He observed that there was initial separation of epithelium, followed by occlution of central blood spaces and the enlargement of central and marginal channels.

Lamellar height progressively reduced and ultimately, central bloods were completely occluded. These changes resulted in a decrease in oxygen consumption and the ability to transport ions across the gill, thus increasing hypoxia, opercular amplitude, buccal amplitude, ventilation frequency and coughing frequency.

Numerous other physical and biochemical changes have been reported for Zn intoxicated fishes. These include (i) increase in production of lactic acid and pyrucic acid, thereby decreasing blood pH, (ii) dysfunction of kidney tissues and enzymes, (iii) decrease in growth, maximum size and fecundity, and (iv) alteration in schooling and reproductive behaviour (Moore and Ramamoorthy, 1984).



**2.9.8 Zinc Toxicity to Humans**

A number of reports outline the effect of acute exposure to Zn in humans. However, these reports are generally old and poorly documented, with inadequate characterization of the actual exposure levels, although some estimates of exposure have been made. For example, high concentrations of Zn in drinks (up to 2500 mg/litre) have been linked with effects such as severe abdominal cramping, diarrhoea, tenesmus, bloody stools, nausea, and vomiting in 300 people, and symptoms of dryness of the mouth, nausea, vomiting and diarrhoea in more than 40 people (Brown *et al.*, 1964). The amount of Zn ingested was estimated to be approximately 325–650 mg.

Lethargy, along with drowsiness, unsteady gait, and increased serum lipase and amylase levels, was seen in an individual who had ingested 12 g of elemental Zn, equivalent to 150 mg/kg body weight, resulting in increases in blood Zn concentrations (Murphy, 1970). No gastrointestinal distress was reported and chelation therapy was effective in achieving clinical improvement and reducing blood Zn levels. Severe local burns, metabolic acidosis, hepatic damage, hyperamylasaemia, lethargy and hypertension resulting from the ingestion of Zn chloride/ammonium chloride soldering flux were reported in a 16-month-old boy who developed pancreatic exocrine insufficiency 5 months later (Knapp *et al*., 1994).

Excess hepatic Cu and Zn levels in a small number of Cree and Ojibwa-Cree children were associated with severe chronic cholestatic liver disease progressing to end-stage biliary cirrhosis in these children (Phillips *et al*., 1996).

An adverse lymphocytic response was reported in 11 healthy adult men who ingested 150 mg of elemental Zn twice a day for 6 weeks; the subjects also showed a reduction in the lymphocytic stimulation response to phytohaemagglutinin (up to 70% reduction at 6 weeks), chemotaxis (50% reduction) and phagocytosis of bacteria by polymorphonuclear leukocytes (50% reduction).

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

## 2.10 Review of Previous Work done at Fosu Lagoon

Gilbert *et al.* (2006), in a study of sediments of the Fosu Lagoon, observed that the concentrations of Cd and Ni in the lagoon sediment suggested greater contamination of the lagoon from industrial activities in the vicinity of the lagoon. Fifty percent of the sediment samples exceeded the established sediment Cd guidelines for the protection of aquatic life. The mean Cd concentration in the Fosu Lagoon sediment during the entire study was found to be 0.78 ± 0.33 mg/kg which exceeded the Canadian interim cadmium marine/estuarine sediment guideline for the protection of aquatic life of 0.7 mg/kg. There was a significant variation between the sampling sites as far as the sediment Cd concentration was concerned (CV = 43.7%).

There was no regular trend and much monthly variation in the Zn concentration in sediment, although site variations were very significant ($P < 0.0001$). Gilbert *et al.* (2006) observed that the highest Zn concentration in the sediment of the Fosu Lagoon was at a sampling point behind a recreational area of a secondary school where laboratory waste from the institution is discharged directly into the lagoon without treatment. This also supports an earlier investigation by Dodoo *et al.* (1995) that the input of Zn into the lagoon sediment is largely from the school laboratories. However, the Zn data collected during the survey period were two orders of magnitude lower than the Canadian interim zinc marine/estuarine sediment guideline for the protection of aquatic life of 124 mg/kg.

The Environmental Protection Agency (EPA), Cape Coast in a research report concluded that the lagoon was generally polluted with most of the commonly known cations and anions values being extremely high. Electric conductivities were recorded as 5920.0 µS/cm,3170.0 µS/cm and 3340.9 µS/cm respectively with a mean concentration exceeding the World Health Organization (WHO's) standard for good quality water of 1000 µS/cm,

However cyanide, manganese, nickel and copper were not detected in all the samples analysed (EPA Cape Coast, 2006).

## 2.11 Analytical Techniques

Trace metals have been determined in potable water (Holynska *et al*., 1996; Gulson *et al*., 1997; Garcia et al., 1999) and fresh and marine waters (Fatoki, 1993; Batterham *et al*., 1997 Fatoki *et al*., 2002 and Hall *et al*., 2002), using varieties of methods.

Atomic absorption spectrometry (AAS) has become by far the most commonly used method for trace metal analysis of environmental materials, i.e. water, soils, sediments and biological tissues (Atta *et al*., 1997; Allen-Gil and Martynovb, 1995; Amundsen *et al*., 1997; Canli and Atli, 2003; Dalman *et al*., 2006; Birungi *et al*., 2007 and Harikumar *et al*., 2009). The technique involves the absorption of light of a specific wavelength by atomic species of the element as it is excited in a flame or other thermal device. The amount of light absorbed by the atomic species is proportional to the concentration of the element present in the ground state. Thus, if the element can be atomized without excitation a high sensitivity can be achieved.

## CHAPTER THREE

## MATERIALS AND METHODS

### 3.1 Study Area

Fosu lagoon is a 'closed' type of lagoon located in Cape Coast, the Regional Capital of the Central Region of Ghana. According to the 2000 Population and Housing Census, Cape Coast has a population of 82,291(Special Report on Urban Localities, 2002). The Cape Coast township lies along the Atlantic Coast, between longitude $1^{o}$ 15' West of the Greenwich Meridian and latitude $5^{o}$ 5' North of the Equator. Fosu lagoon covers an area of about $0.68 km^2$, of which an estimated $0.097 km^2$ was covered with water hyacinth as at the time of the study (Figure.1).

The study area is situated within the tropical rain forest. Temperatures are high, ranging between 25 $^{o}C$ and 35 $^{o}C$ with little variation throughout the year. There are two wet seasons in a year; the major season is from April to July and the minor one from September to November. The dry season occurs between December and March during which dry, dusty winds blow from northeast to southwest, thus lowering the relative humidity. In the study area, the effect of these winds is felt most in January (Gilbert *et al*., 2006).

Several anthropogenic activities take place in and around the lagoon. Some of the surrounding activities include farming, car repairs, palm kernel extraction, welding and other small scale industrial activities. There are also domestic settlements, St. Augustine's Senior High School and the District Teaching Hospital (Figure.1). The waste generated from these settlements, industries or institutions are disposed off anyhow which eventually end up in the Lagoon (Pate1a and 1b). These activities are believed to be the cause of fish depletion in the lagoon.

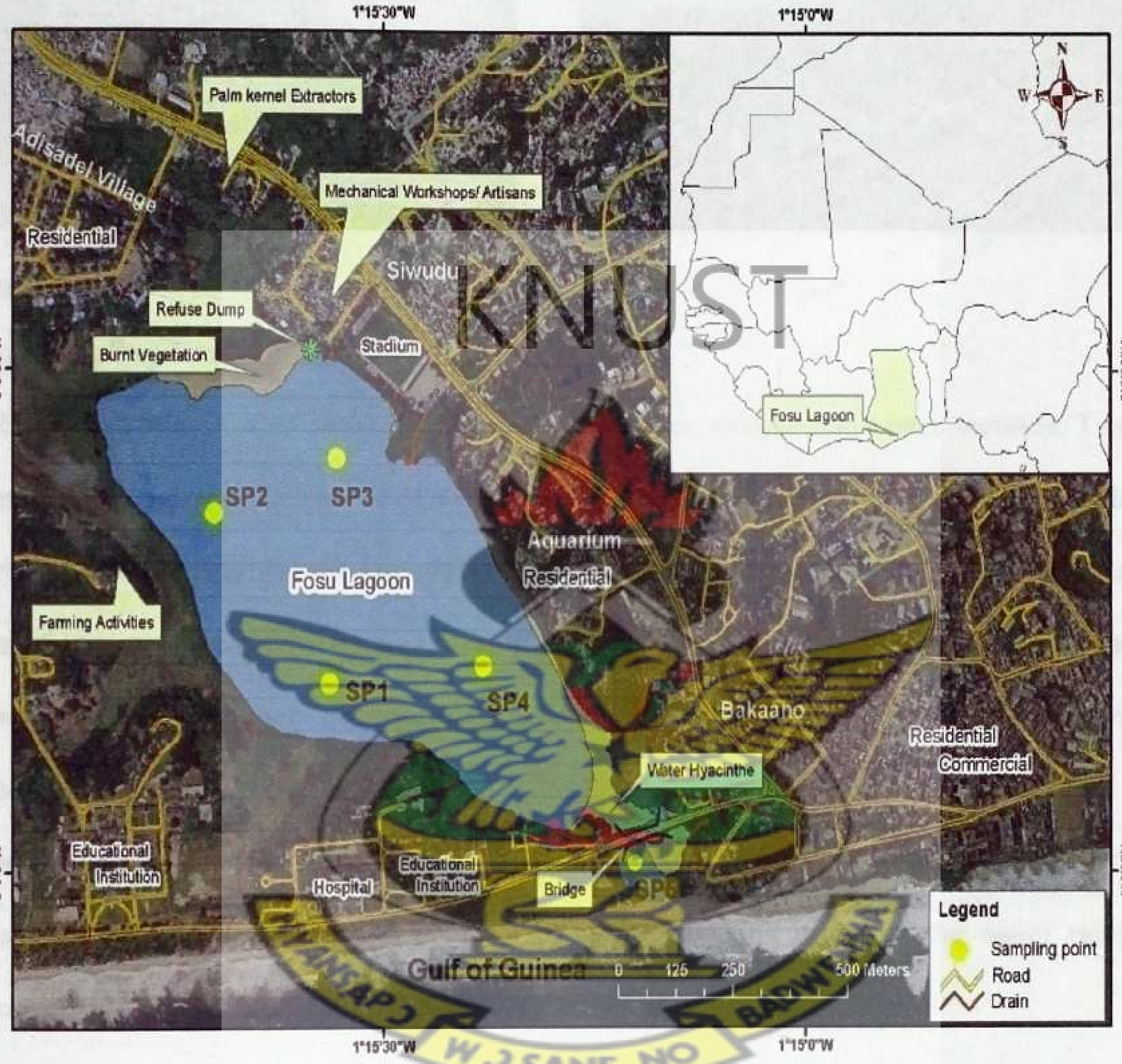



Figure 1: Map of Fosu lagoon, sampling sites and surrounding land use

Presently, the dominant specie of commercial value in the lagoon is the black chin tilapia (*S. melanotheron*).

 

lagoon.



**3.2 Sampling Design**

The lagoon was divided into three sections: the upper, middle and lower sections. Two sampling stations (SP2 and SP3) were chosen at the upper section; two at the middle section (SP1 and SP4) and one (SP5) at the lower section. These points were chosen based on ecological settings and human activities around the area. The names of the sampling sites with their corresponding co-ordinates as well as the site descriptions are shown in Table 2.

Sampling was done within the minor rainy season (October to December) and the dry season (January and February) in order to reduce flushing effect of the major rainy season.

Table 2: Sampling Points, Sampling Coordinates and Site Description

| Sampling Points | latitude | longitude | Site Description |
|---|---|---|---|
| SP2 | -1.2614 | 5.1087 | Adjacent to farm lands, thus receives drainage from surrounding farming activities. |
| SP3 | -1.2691 | 5.1097 | Near mechanical shops and palm kernel extractors, refuse damp and a point of urban drain discharge. |
| SP1 | -1.2592 | 5.1059 | Adjacent to District Hospital, Recreational Center and St. Augustine's Senior High School where untreated effluent is discharged into the lagoon. |
| SP4 | -1.2562 | 5.1062 | Close to domestic settlement, thus receives decomposable domestic waste as well as untreated effluent from urban drains. There are also some pig farms near this site. |
| SP5 | -1.2532 | 5.1029 | Near busy road, shallow and receives effluent that runs through a Goil filling station. This site is the "mouth" of the lagoon. However, it is separated from the ocean by a large sand bar and mostly invaded by water hyacinth. |

### 3.3 Materials and Reagents used for the Study

Materials used for the study consist of 750 ml plastic bottles, Eckman grab, Mettler Toledo MP125 pH meter with temperature correction, WTW (Water Treatment Works) conductivity meter LF92 model, acetone, nitric acid, polyethylene bags, test tubes, drag nets, basket traps, Teflon containers, tape measure, Petri dishes, 25 ml measuring cylinders and Mettler Toledo analytical balance AB204-S model.

The 750 ml plastic bottles were thoroughly washed with detergent, rinsed with tap water and then with distilled water before soaking in 5% $HNO_3$ for about 24 h. Finally it was rinsed with double distilled water before being used for sampling in order to get rid-off any contaminant.



### 3.4 Sample Collection

#### 3.4.1 Water Sampling

Surface water samples were collected from the five sampling points by hand, from a rowing boat by submerging 750 ml drinking water bottles approximately 20 cm beneath the water surface. Two sets of water samples were collected monthly from October 2008 to February 2009 in accordance with the method used by Adomako *et al.* (2006). Prior to sampling the bottles were rinsed with water from the study site several times.

#### 3.4.2 Sediment Sampling

Sediments were collected from all the five sampling stations at a depth of about three meters (3m) from the surface using an Eckman grab sampler. At each sampling site three sets of about 20 $cm^3$ of the bottom sediment samples were collected with the Eckman grab, as was done by Topouoglu *et al.* (2002). The sediment samples were packed in pre-cleaned polyethylene bags, labeled and placed in an ice chest, and transported to the Ghana Atomic Energy Commission (GAEC) laboratory, Accra for analysis. Sampling was done for five months (October, 2008 to February, 2009).

### 3.4.3 Fish Sampling

Fishermen were employed to catch fishes with drag nets and basket traps from selected sites. Black chin tilapia (*Sarotherodon melanotheron)* were sorted out from the catch and rinsed several times with distilled water to remove any adhering clay particles. These fishes were packed into pre-cleaned polyethylene bags and then placed in an ice chest and transported to the GAEC laboratory, Accra for analysis. However, no fish was obtained around sampling site SP5 as they were of very small sizes.



## 3.5 Field Measurements and Pretreatment of Water Samples

Conductivity, temperature and pH of surface water were measured. A buffered Mettler Toledo MP125 pH meter with temperature correction and WTW conductivity meter model LF92 were used for the measurement of the pH, temperature and conductivity of one set of the collected surface water (unfiltered) samples.

The content of the other bottles with unfiltered surface water samples were acidified to a pH < 2 with a minimum of 20 drops of 50% $HNO_3$ acid based on the procedure of Jain *et al.* (2005). The tightly sealed bottles were placed in an ice chest and transported to GAEC laboratory, Accra.

### 3.6 Sample Preparation

#### 3.6.1 Sediment Samples

Sediment samples were air dried at room temperature for three days. The sediment samples were pulverized using acetone cleaned mortar and pestle and thereafter sieved mechanically using a 0.5 mm sieve, following the procedure of Dalman *et al*. (2006). The prepared samples for the individual sampling sites were put together and thoroughly mixed to form a composite sample for each sampling site. These were packed into a pre-cleaned polyethylene zip lock bag and stored in a clean dry place before digestion.



#### 3.6.2 Fish Samples

Fish samples were thawed and the total weight (TW) and total length (TL) of ten selected fish samples measured to the nearest 0.1cm with a measuring tape. All measurements were taken from the tip of the maxilla to the tip of caudal fin ray and the values recorded. Each of the selected whole fish samples was rinsed with double distilled water and deep frozen. The frozen fishes were transferred into pre-cleaned Petri dishes and lyophilized at a temperature of 20°C at vacuum pressure of 2.380 mbar and freeze dried until a constant weight was achieved for each month's sample. The drying process took about 72 hours.

The dry-weight (dw) of the selected fish samples were taken and recorded. Individual dried fish (whole fish) samples were ground into powder with a thoroughly cleaned stainless steel blender, packed into a pre-cleaned and labeled polyethylene zip lock bags and kept in a cool dry place before digestion.

Determinations of whole body concentrations of trace elements were conducted, as it is important for assessing whole body burdens and accumulations relative to uptake by other tissues and it can also assist in determining potential dietary risks to natives that culturally utilize the entire fish (Higgins, 2001).

Prior to digestion, the Condition Factor ($CF_B$) which describes the physiological condition of the fishes according to Baur *et al.* (1988), Busacker *et al.* (1990), Voight, (2003) and Benson *et al.* (2007) was calculated using the equation;

$$CF_B = \frac{TW}{(TL)^3} \times 100$$

where $CF_B$ is the Condition Factor; TW is the total weight and TL the total length of the fish.



### 3.7 Decontamination of Digestion Vessels

Teflon containers, ten test tubes, 25 ml measuring cylinders required for measurements and digestion of samples were washed with detergent, rinsed with distilled water, soaked in 10% $HNO_3$ acid overnight and finally rinsed in re-distilled and de-ionized water and dried in an oven at 45°C for five minutes in order to get rid-off all contaminants. All reagents used in the digestion were analytical grade. Digestion was conducted according to the Milestone Digestion Cook book (updated in 2001).

### 3.8 Digestion of Water Samples

At GAEC laboratory, the acidified unfiltered water samples were kept in a refrigerator prior to analysis in order to stabilize the trace metal ions in the solution and as a precaution adopted to preserve the samples.

5 ml of unfiltered surface water samples for various sampling points were measured into separate Teflon containers, after which 6.0 ml of 65% $HNO_3$, 3.0 ml of 35% HCl and 0.25 ml of 30% $H_2O_2$ were added to each (in a fume chamber) and capped. They were

then placed on the rotor of the micro-wave oven and properly sealed. This was placed in an ETHOS 900 micro-wave labstation oven using the following step program of treatment: 250 W for 5 minutes during the 1st step, 0 W for 1 minute during the 2nd step, 250 W for 10 minutes during the 3rd step, and 450 W for 5 minutes during the final step. The rotor was removed from the oven and allowed to cool to room temperature. The digests were then transferred into a pre-cleaned 25 ml volumetric flask and topped-up with re-distilled water to 20 ml mark, sealed and stored for trace metal analysis. All samples were digested in duplicate.



### 3.9 Digestion Procedure for Fish Samples

5 g of dry ground whole fish sub-sample was measured into pre-cleaned digestion vessels (Teflon container). 6 ml of 65% $HNO_3$ and 1.0 ml of 30% $H_2O_2$ were added (in a fume chamber) to each sample in the digestion vessels and allowed to stay (for 5 minutes) to complete the reaction process. This was then placed in an ETHOS 900 micro-wave labstation oven using the following step program of treatment: 250 W for 1 minute during the 1st step, 0 W for 1 minute during the 2nd step, 250 W for 5 minutes during the 3rd step, 400 W for 5 minutes during the 4th step and 650 W for 5 minutes during the final step. It was then removed from the oven and allowed to cool for two hours to room temperature. All samples were digested in duplicate.

### 3.10 Digestion Procedure for Sediment Samples

About 1.5 g of dried sediment sub-sample was measured into a pre-cleaned 30 ml Teflon container and 1 ml of 65% $HNO_3$, 3.0 ml of 35% HCl and 0.25 ml of 40% HF were added (in a fume chamber) to the digestion flask, capped, well-sealed and allowed to stay for 5 minutes. This was then placed in an ETHOS 900 micro-wave labstation oven using the following step program of treatment: 250 W for 1 minute during the 1st step, 0 W for 1 minute during the 2nd step, 250 W for 10 minutes during the 3rd step and 450 W for 5 minutes during the final step. It was then removed from the oven and allowed to cool for two hours to normal room temperature. The digests were then transferred into a pre-cleaned 25ml volumetric flask and topped-up with double-distilled water to 20 ml mark, sealed and stored for trace metal analysis.

### 3.11 Analytical Procedure



Heavy metals (Pb, Cu, Zn, and Cd) were determined by Atomic Absorption Spectrometry (AAS). Flame atomic absorption measurements were made using AA240FS Fast Sequential Atomic Absorption Spectrometer at the following the working conditions as shown in Table 3.

Table 3: Working conditions for the analysis of heavy metals by Atomic Absorption Spectrophotometer (AAS)

| Metals | Wavelength (nm) | Silt width (nm) | Lamp current (mA) | Gas | Support | Detection limit |
|---|---|---|---|---|---|---|
| Cd | 326.1 | 0.5 | 4 | Acetylene | Air | 0.002 |
| Zn | 213.9 | 1.0 | 5 | Acetylene | Air | 0.001 |
| Cu | 327.4 | 0.2 | 4 | Acetylene | Air | 0.003 |
| Pb | 205.3 | 0.5 | 5 | Acetylene | Air | 0.010 |

Quantification of trace metal concentrations was based upon calibration curves obtained from varying concentrations of standard solution, Spectrascan (TEKNILAB AB, Sweden) of respective metals. The stock solutions were used to calculate the required volumes for concentrations of 2, 5, and 10 ppm in 100 ml using the formular:

$$C_1V_1 = C_2V2,$$

where $C_1$ is the standard concentration of 1000 ppm, $V_1$ is the required volume to be calculated, $C_2$ is the different concentrations of 2, 5 and 10 ppm, $V_2$ is the 100 ml volumetric flask used.

After calculating the required volumes for each metal, the volumes were then used to set up a standard linear graph which was used to determine the concentration of metal in the samples.

### 3.12 Quality Assurance



In order to check the purity of the chemical used, a number of chemical blanks were run. The quality of the analytical method was checked by the analysis of Standard Reference Materials (SRMs1646a). Percentage recoveries (Table 5) from the SRMs1646a were calculated based on the formula:

$$\%\ Recovery = \frac{Measured\ Value}{Expected\ Value} \times 100\%$$

Calibration of the instrument was repeated after every ten samples during operation.



### 3.13 Statistical Analysis

The physico-chemical parameters (Cu, Zn, Cd, Pb, EC, pH and temperature) for water were analyzed using Microsoft excel 2007 program to determine mean concentration, plot error bar graphs with standard deviations to show the distribution of the metals in the sediment and fish as well as show the trend of metals in the water column at various sites for each month.

The relationship between the heavy metals and physical parameters of the surface water and sediment of the Fosu Lagoon was determined using Pearson Product Moment Correlation Coefficient. This was made possible with the aid of the Statistical Package for Service Solutions (SPSS 16.0).

In order to determine the level of contamination with respect to heavy metals in the sediment, the concentrations of the heavy metals were used to calculate the Contamination Factor (CF). The Contamination Factor (CF) gives an indication of the level of contamination, and is computed for the sediments by using the measured concentrations of the heavy metals and their corresponding values in the world average shale reported by Turekian and Wedepohl, (1961). It is computed using the formula below:

$$CF = \frac{C_{metals}}{C_{background\ values}}$$

where CF= Contamination Factor, $C_{metal}$ = metal concentration in polluted sediments; $C_{background\ value}$ = background value of that metal.

The pollution level of the heavy metals was calculated by a method based on Pollution Load Index (PLI), as was used by Tomlinson *et al.* (1980), Ray *et al.* (2005) and Adomako *et al.* (2006). The formula is as stated below:

$$PLI = \sqrt[n]{(CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)}$$

where PLI=Pollution Load Index, n = number of metals, $CF_1$= Contamination Factor Cd, Pb, Zn and Cu respectively.

### 3.14 Available Standards and Quality Guidelines

To evaluate any likely toxicity resulting from the measured heavy metal contaminants in Fosu lagoon, an arbitrary choice of known international, national or provincial standards were chosen to verify compliance. The data obtained in this current investigation were compared to the Interim Canadian Sediment Quality Guidelines (ISQDs) established by the Canadian Council of Ministers of the Environment (CCME) for the protection of aquatic life exposed to bed sediments and that of water compared with the British Columbia guidelines for the protection of marine and estuarine life. These guidelines were based on the probable effect levels (PELs) - i.e., concentration above which deleterious effects to organisms have been determined to occur and lowest effect levels (LEL) of concentrations, which indicate a level of sediment/water contamination at which majority of aquatic organisms (including benthic ones) are unaffected.

Metals concentrations in black chin tilapia (S. *melanotheron*) were compared with the Provisionally Maximum Tolerable Daily Intake (PMTDI) and Provisional Tolerable Weekly Intake (PTWI) set by the Food and Agriculture Organization/World Health Organization (FAO/WHO) Joint Expert Committee on Food Additives (JECFA) in 1982 and 1993 respectively since the consumption of contaminated fish can be a major source of exposure to humans (Adams *et al*., 1992).

Table 4: Available quality standards/guidelines

| Heavy metals | Cu | Zn | Cd | Pb |
|---|---|---|---|---|
| ISQD's for protection of aquatic life exposed to bed sediment, mg/kg (CCME, 1996) | 18.70 | 124.0 | 0.70 | 30.20 |
| British Columbia guidelines for the protection of marine and estuarine life, μg/l | 3.00 | 10.00 | 0.12 | 140.00 |
| Provisionally Maximum Tolerable Daily Intake (PMTDI), mg/kg (JECFA , 1982) | 0.500 | 1.00 | - | - |
| Provisionally Tolerable Weekly Intake (PTWI), mg/kg (JECFA, 1993) | 2.000 | 15.00 | 0.007 | 0.025 |

## CHAPTER FOUR

## RESULTS AND DISCUSSION

### 4.1 Validation of Analytical Method

Table 5 indicates the validation of the AA240FS Fast Sequential Atomic Absorption Spectrometer. There was a high level of recovery for metals (Table 5), suggesting that digestion process released the organic bound metals from the samples. A high level of recovery places greater confidence in the results, as concentrations are likely to be close to actual whole fish, water and sediment concentrations. More than 100% of each of the metals (Cu, Cd and Pb) in the Standard Reference Material (SRM1646a) with the exception of Zn was recovered suggesting a small amount of contamination present. The above 100% recovery is, however, not unusual as similar results were obtained by Tarley *et al*. (2001).

Table 5: Percentage recoveries for the SRM 1646a used to verify the accuracy of the AAS used

| Heavy Metals | Expected value | Measured value | % Recovery |
|---|---|---|---|
| Zn | 48.9 | 36.0 | 73.6 |
| Cu | 10.01 | 11.1 | 110.8 |
| Cd | 0.148 | 0.173 | 116.9 |
| Pb | 11.7 | 17.0 | 145.0 |

### 4.2 Physico-chemical Parameters of Surface Water

There are no formal standards in Ghana for both inland and coastal water and sediment quality. However, in order to evaluate the likely toxicity resulting from the measured heavy metal contaminants in the lagoon, it is informative to verify their compliance with known international, national or provincial standards. As an arbitrary choice, the data obtained in this current investigation are compared to the Canadian Environmental Quality Guidelines for the protection of marine and estuarine life [Canadian Council of Ministers of the Environment (CCME), 1996].

### 4.2.1 pH

The mean concentrations of heavy metals and other physical properties determined for the surface water of Fosu Lagoon are as shown in Table 6. Generally the water was alkaline (pH of 8.9–9.5). The pH values recorded at all the sampling points exceeded the Canadian Environmental Quality Guidelines of 7.0–8.7 for the protection of marine and estuarine life (CCME, 1996).



Table 6: Mean pH, temperature (Temp.) and electric conductivity (EC) in surface water at various sampling sites

| Sampling Sites | pH | Temp / $^oC$ | EC / µS/cm |
|---|---|---|---|
| SP2 | 9.4 | 31.9 | 6075 |
| SP3 | 9.5 | 32.2 | 5958 |
| SP1 | 9.4 | 31.8 | 6181 |
| SP4 | 9.4 | 31.9 | 5656 |
| SP5 | 8.9 | 31.3 | 5020 |

### 4.2.2 Electric Conductivity

Electric conductivity (EC), which is a measure of the total dissolved solids and ionized species in water and a good indicator of major ions and inorganic pollution, ranged from 5,020 μS/cm to 6,181μS/cm (Table 6). These values exceeded the Canadian Environmental Quality Guidelines of 1000 μS/cm for the protection of marine and estuarine life (CCME, 1996). The high EC observed in the surface water of Fosu Lagoon might be due to several factors. For example, it may be due to high ionic concentration resulting from anthropogenic activities or the underlying geology of the catchment area, or even sea spray.



### 4.2.3 Temperature

The water temperature measured ranged from 32.2°C at SP3 to 31.3°C at SP5 (Table 6). This could be attributed to the time of sampling since samples were collected around 10:00 am–12: 00 pm. By that time several anthropogenic activities were taking place both on and around the lagoon, hence resulting in the increase of the surface water temperature.

### 4.2.4 Heavy Metals in Surface Water

Figure 2 shows the graph of heavy metal concentrations recorded in the surface water at various sampling points of the lagoon.

#### *4.2.4.1 Lead*

Lead was not detected in any of the water samples collected at the various sampling points, since their concentrations (if any) were below the detection limit of the analytical method used. The absence of Pb in the surface water may be attributed to several factors like: the form of lead compound present (organic and inorganic forms) and pH. Inorganic lead compounds (sulphide, carbonate and sulphate minerals) for example, have low solubilities in natural water especially when pH is basic as pertained in the study area.

*4.2.4.2 Copper*

Copper was detected in all the samples collected, with mean values higher than the British Columbia guidelines for the protection of marine and estuarine life value of 3 µg/l (Table 4). The highest mean value of Cu was recorded at SP4 with a value of 0.155 mg/l and the lowest value of 0.013 mg/l at SP2. The high levels of Cu in all the surface water samples may be attributed to the discharge of untreated mixed effluent from surrounding household, institutions and recreational centre.

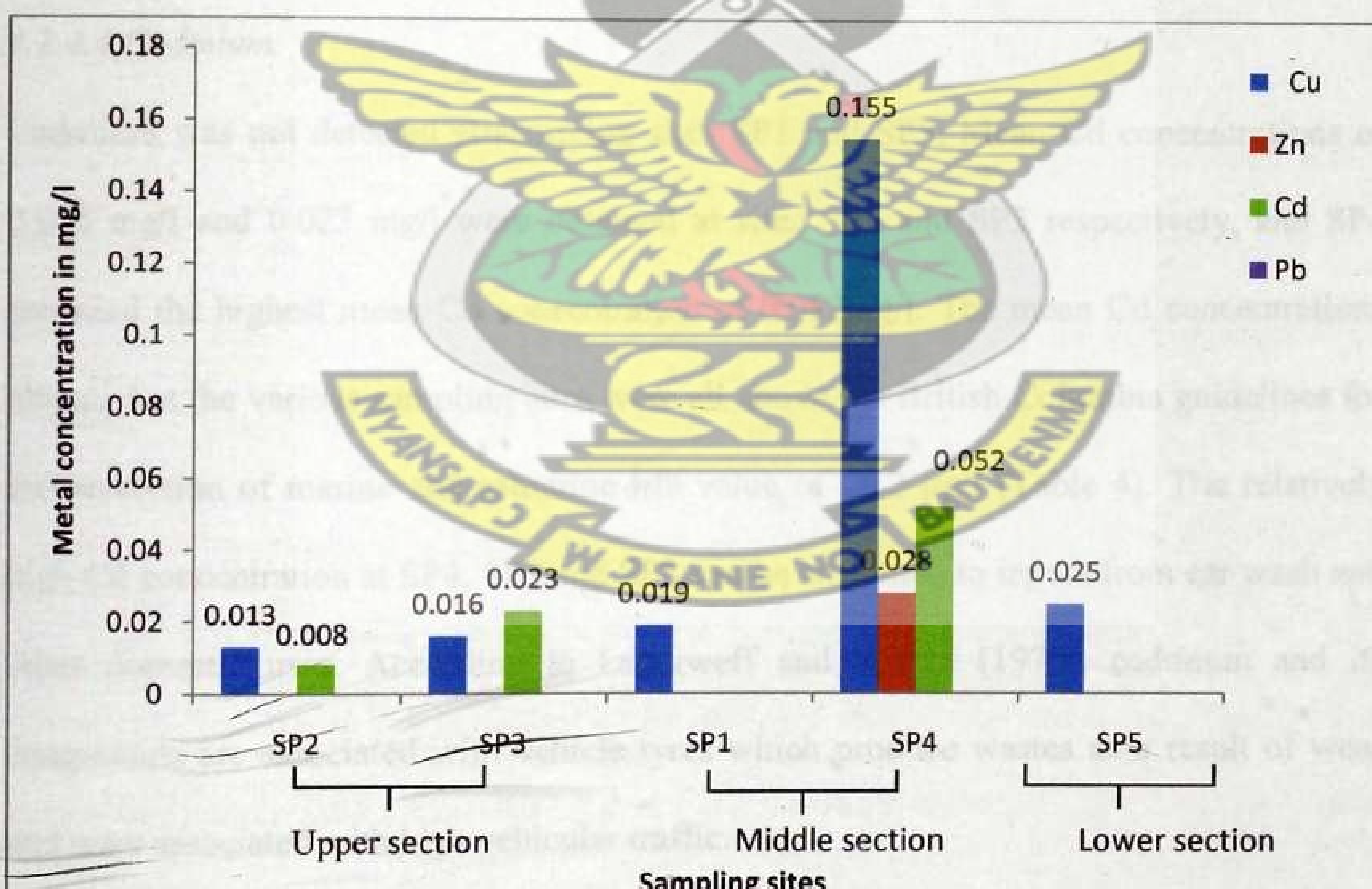


Figure 2 Graph of metal concentration in surface water

Furthermore, the high levels of Cu may be due to, especially the use of copper sulfate [as used in fungicides, pesticides, algaecides, nutritional supplements in animal feeds (e.g. Pigs)] and fertilizers or the use of Cu antifouling paints by the fishermen, or even as a result of high natural levels.

*4.2.4.3 Zinc*

Zinc was not detected in all the samples with the exception of SP4 which recorded a mean Zn concentration of 0.028 mg/l which was about three times higher than the British Columbia guidelines for the protection of marine and estuarine life value of 10 μg/l (Table 4). This site is adjacent to domestic settlement where mixed effluents which include Zn (e.g. dungs, poultry droppings, fertilizer, kitchen and bathroom waste, etc) are discharged into the lagoon without any treatment.

*4.2.4.4 Cadmium*

Cadmium was not detected at sampling sites SP1 and SP5. Mean Cd concentrations of 0.008 mg/l and 0.023 mg/l were obtained at sites SP2 and SP3 respectively, and SP4 recorded the highest mean Cd concentration of 0.052mg/l. The mean Cd concentrations obtained at the various sampling sites were all above the British Columbia guidelines for the protection of marine and estuarine life value of 0.12 μg/l (Table 4). The relatively high Cd concentration at SP4, SP2 and SP3 can be attributed to inputs from car wash and other domestic uses. According to Lagerweff and Specht (1970), cadmium and its compounds are associated with vehicle tyres which produce wastes as a result of wear and tears associated with high vehicular traffic.

From figure 4, SP4 recorded higher concentrations than all the other points. This may be due to several human related factors like: discharge of untreated liquid waste, open defecation, leaching from solid waste, etc.

Generally, Cu, Zn and Cd concentrations in the surface water of Fosu Lagoon exceeded the British Columbia guidelines for the protection of marine and estuarine life values of 3.0 mg/l, 10.0 mg/l and 0.12 mg/l respectively. The high heavy metals concentrations in the water column may have several detrimental effects such as: decreased growth in fishes (Hansen *et al.*, 2002b), changes in fish behavior, including olfactory responses, agonistic responses, avoidance and attraction and changes in swimming ability or swimming speed (Beaumont *et al.*, 1995) or even delayed hatching Meteyer *et al.* (1988) on aquatic life.

Pearson product-moment correlation test did not show any significant relationship between the mean metal concentrations (Cu, Zn and Cd) and the physical parameters (pH, EC and temp.) as shown in Table 7. Similar results were obtained by Adomako *et al.* (2006) in a study of the Subin River, Kumasi, Ghana.

However, very strong positive correlation exist between Cu and Zn with a positive correlation of 0.997 at a significant level of 0.01; followed by Cd–Zn with 0.903 and Cd–Cu with 0.844, all at a significant levels of 0.05. The strong metal inter-relationship means that those metals were introduced into the water column of the Lagoon from a common source.

Table 7: Pearson product-moment correlation coefficients between the metals, pH, EC and temperature in surface water from study area

| | Cu | Zn | Cd | pH | EC | temp |
|---|---|---|---|---|---|---|
| Cu | 1 | | | | | |
| Zn | 0.997** | 1 | | | | |
| Cd | 0.884* | 0.903* | 1 | | | |
| pH | 0.125 | 0.187 | 0.427 | 1 | | |
| EC | -0.205 | -0.146 | 0.004 | 0.890* | 1 | |
| temp | 0.077 | 0.137 | 0.472 | 0.954* | 0.767 | 1 |

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).



### 4.3 Monthly Metal Concentration Pattern in Surface Water

Graphs of metal concentration patterns were plotted for only Cu as values for the other metals (Zn, Cd and Pb) were below detection limit for some sampling months.

#### 4.3.1 Copper

Pattern of Cu concentrations at SP2, SP3, SP1, SP4 and SP5 from the month of October 2008-February 2009 are as shown in figure 3, 4, 5, 6 and 7 respectively. Copper concentration at SP2 increased from <0.003 mg/l (taken as zero) in the month of October 2008 to 0.044 mg/l in January 2009 and then decreased to 0.02 mg/l in the month of February (figure 3). This irregular pattern of Cu concentration at SP2 may be as a result of high Cu-laden inputs during some months. For example, surface run-off from nearby farms during the minor rainy season (October, November and December) and evaporation during the harmattan (January and February). At SP3 Cu concentration decreased from 0.028 mg/l in October, 2008 to <0.003 mg/l in December, January and February (figure 4). The decreasing trend of Cu concentration at SP3 can be attributed to surface run-off from nearby palm kernel extractors and mechanical shops during the minor rainy season and low Cu input during the harmattan.

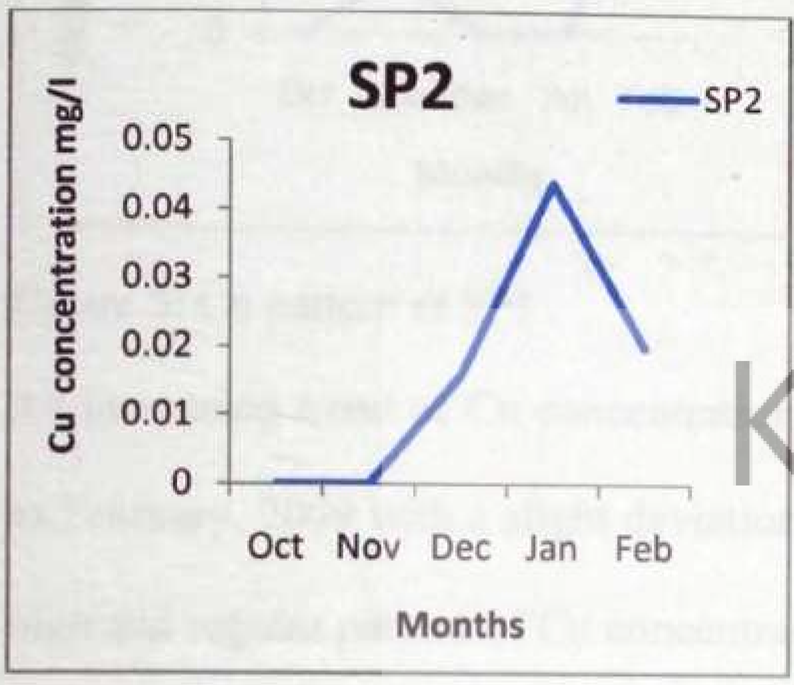


Figure 3: Cu pattern at SP2

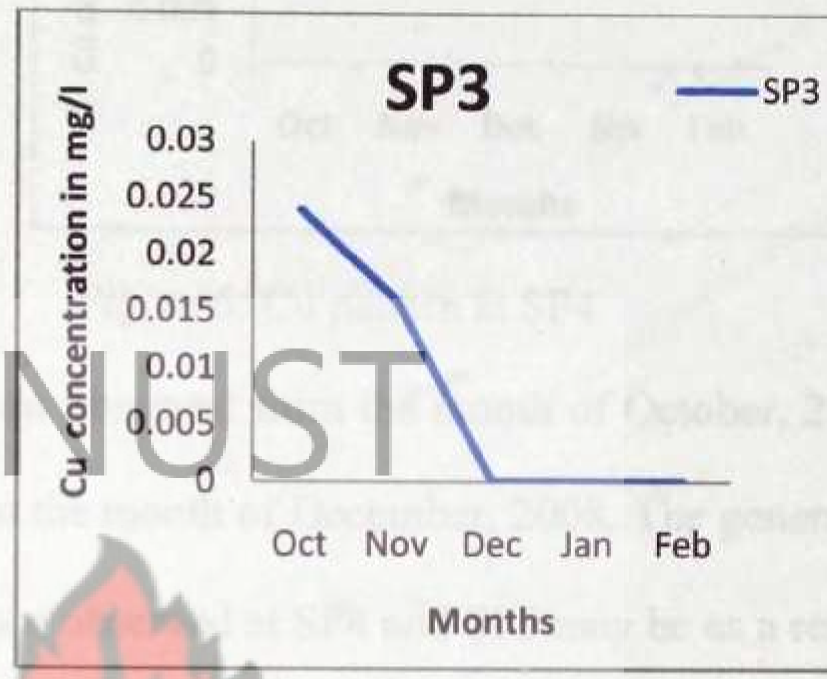


Figure 4: Cu pattern at SP3

No regular pattern of Cu concentration was observed at SP1 (figure. 5). The occurrence of irregular pattern of Cu concentration observed at SP1 can be attributed to several factors including: high rate of evaporation which reduces the volume of water required to dissolve the metal, low Cu-laden input, surface run-off, etc. Copper concentration at SP4 and SP5 followed a similar pattern as shown in figure 6 and 7 respectively.

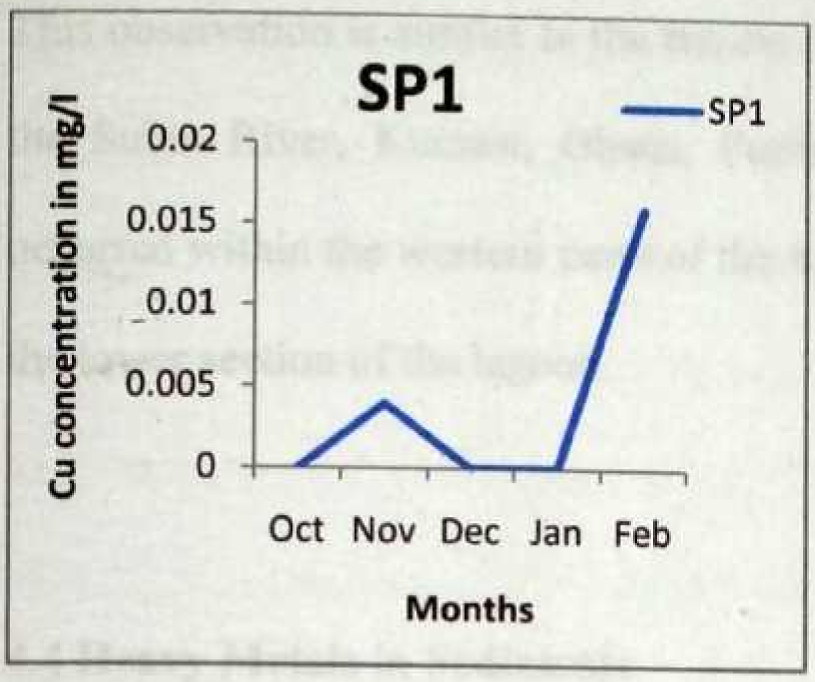


Figure 5: Cu pattern at SP1

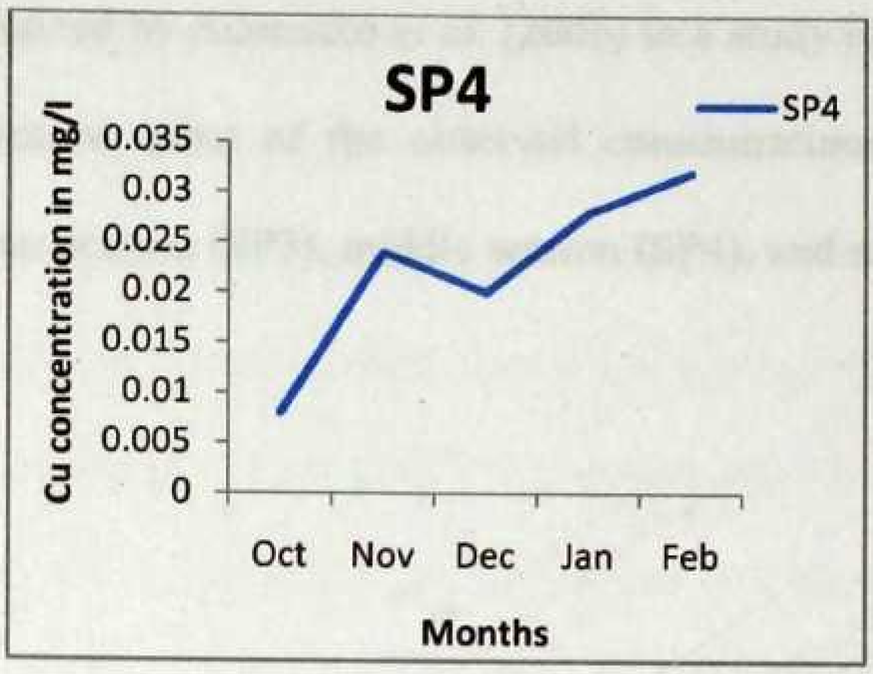


Figure 6: Cu pattern at SP4



An increasing trend of Cu concentration was observed from the month of October, 2008 to February, 2009 with a slight deviation in the month of December, 2008. The generally high and regular pattern of Cu concentrations observed at SP4 and SP5 may be as a result of the nearness of these two sampling points, high atmospheric, industrial and domestic input of Cu-laden materials from urban drains, refuse damps, among others.

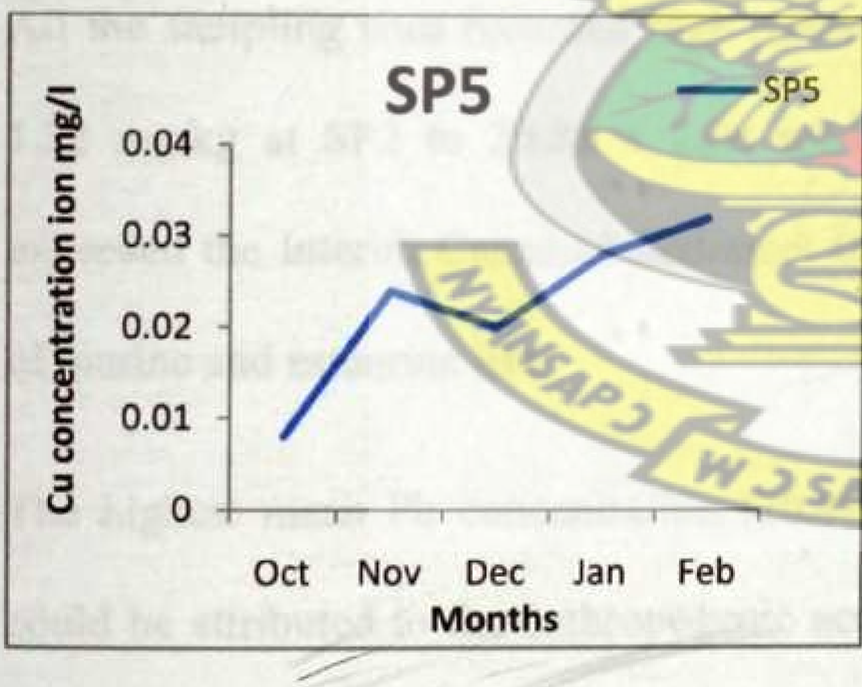


Figure 7: Cu pattern at SP5

Generally, the patterns of heavy metals concentration in the surface water of Fosu lagoon during the study were high during the harmattan and low during the minor rainy season.

This observation is similar to the results obtained by Adomako *et al.* (2006) in a study of the Subin River, Kumasi, Ghana. Furthermore, most of the observed concentrations occurred within the western parts of the upper section (SP3), middle section (SP4), and at the lower section of the lagoon.

### 4.4 Heavy Metals in Sediments

The mean heavy metal (± standard deviation) concentrations examined in the bottom sediment of the Fosu lagoon is presented in Table 11 (Appendix 1).



Figure 8 shows the distribution of heavy metals in the bottom sediment of the Fosu Lagoon and the Interim Canadian Sediment Quality Guidelines (ISQDs) for the protection of marine and estuarine life.

#### 4.4.1 Lead

All the sampling sites recorded high mean concentrations of Pb, ranging from 15.18 ± 1.22 mg/kg at SP2 to 20.88 ± 2.04 mg/kg at SP5. However, none of these values exceeded the Interim Canadian Sediment Quality Guidelines (ISQDs) for the protection of marine and estuarine life.

The highest mean Pb concentration (20.88 ± 2.04 mg/kg) was observed at SP5. This could be attributed to the anthropogenic activities near that site, atmospheric deposition of combustible fuel and surface run-off from the nearby road. Furthermore, a large and filthy urban drain from nearby petroleum fuelling station empties into the lagoon, which might have resulted in large Pb input from unleaded Petrol (Plate 1a). The second highest Pb concentration was observed at SP3 (17.98 ± 2.75 mg/kg). This site is close to mechanical/automobile repair shops where industrial activities include car fitting, welding, painting, etc are carried out. However, improper disposal of all kinds of waste (Plate 1b) from these activities into the lagoon is the norm in the locality. For example, disposal of waste from Pb-acid storage batteries, Pb-containing alloys, lubricating-oil additives and small electric motors, etc. are all possible sources of Pb in the lagoon. The third highest concentration was observed at SP1 (17.58 ± 0.91 mg/kg), which is within the middle section but on the south-western part of the lagoon. This site is located adjacent to an educational and health institution as well as a recreational centre. Effluents (e.g. Pb containing drugs and chemicals) from the laboratories of these institutions empty into the lagoon without any treatment and could be a possible cause of elevated Pb concentration observed.

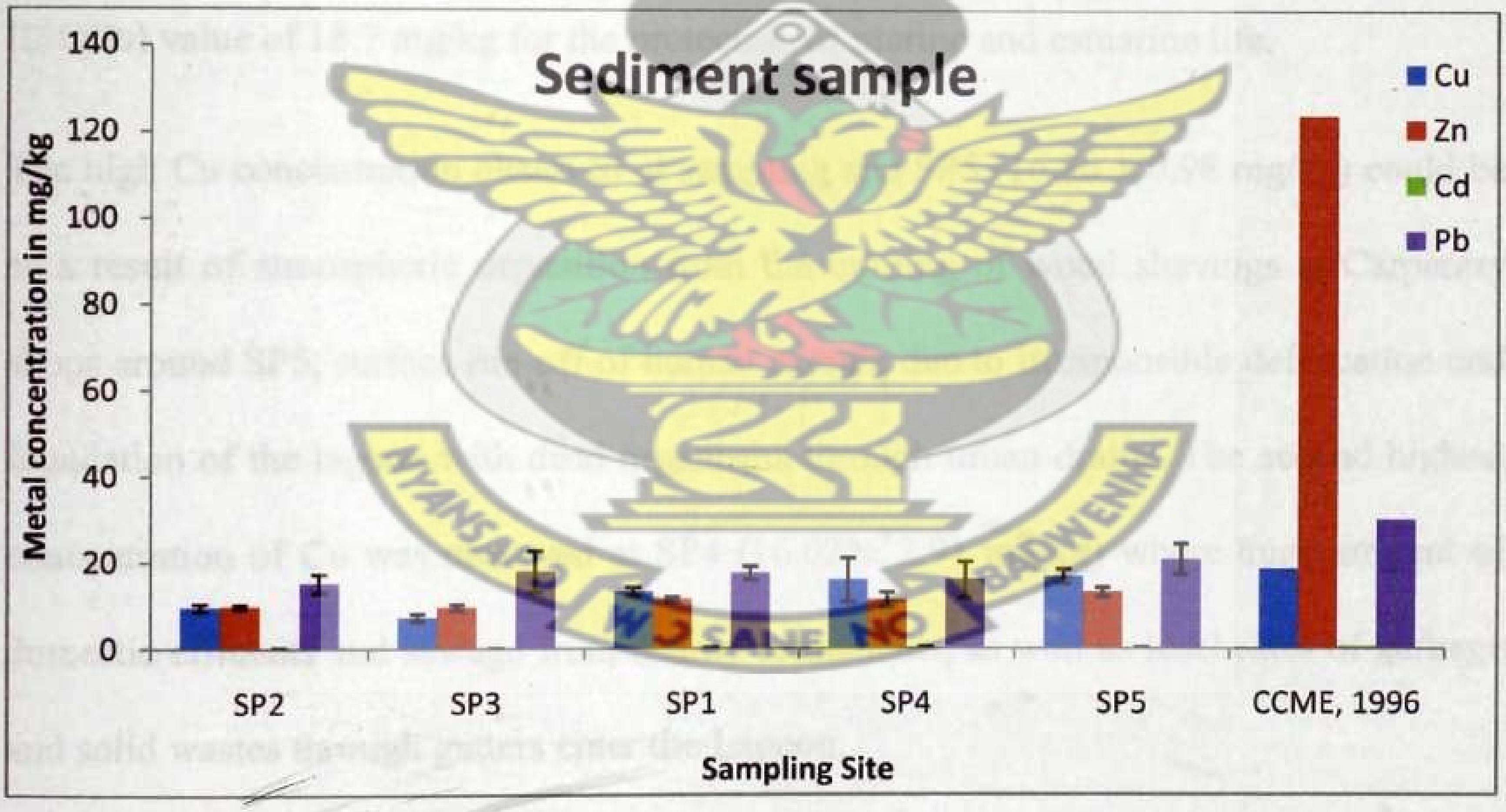


Figure 8: Mean concentration of metals (±SD) in bottom sediments of Fosu Lagoon

The fourth (16.08 ± 2.43 mg/kg) and fifth (15.18 ± 1.22 mg/kg) highest concentrations were observed at SP4 (within middle section) and SP2 (within upper section), respectively. These portions of the lagoon, especially SP4, receive huge amount of domestic effluents, leacheates of garbage and solid wastes through gutters. The elevated Pb concentrations at SP2 could be attributed to surface run-off from farms and burnt areas (during the study period) as well as atmospheric deposition of windblown dust from farm lands.

#### 4.4.2 Copper

Mean concentration of Cu ranged from a highest value of 16.8 ± 0.98 mg/kg at SP5 (within lower section) to the lowest mean value of 7.32 ± 0.50 mg/kg at SP3 (upper section). These values were all below the Interim Canadian Sediment Quality Guidelines (ISQDs) value of 18.7 mg/kg for the protection of marine and estuarine life.

The high Cu concentration observed at sampling site SP5 (16.80 ± 0.98 mg/kg) could be as a result of atmospheric deposition from the burning of wood shavings at Carpentry shops around SP5, surface run-off of human excreta due to irresponsible defaecation and inundation of the lagoon with dead organisms through urban drains. The second highest concentration of Cu was observed at SP4 (16.02 ± 2.91 mg/kg) where huge amount of domestic effluents and sewage from nearby settlements, as well as leacheates of garbage and solid wastes through gutters enter the Lagoon.

SP1 (middle section) recorded the third highest mean Cu concentration of (13.30 ± 0.58 mg/kg).This could be attributed to agricultural run-off of Cu compounds, especially copper sulfate, used as fungicides, pesticides and fertilizers. The other sites SP2 (9.71 ±

0.47 mg/kg) and SP3 (7.32 ± 0.50 mg/kg) had relatively lower concentrations of Cu input.

### 4.4.3 Zinc

The concentration pattern displayed by Zn was similar to that of Cu. The highest (13.19 ± 0.63 mg/kg) and lowest (9.69 ± 0.40 mg/kg) mean concentrations of Zn were recorded at SP5 and SP3, respectively. These values were all below the Interim Canadian Sediment Quality Guidelines (ISQDs) value for the protection of marine and estuarine life.

Previous work by Gilbert *et al.* (2006) showed the highest Zn concentration in the sediment of the Fosu Lagoon at a sampling point which corresponds to SP1 of this study (i.e. the point site behind a recreational area and St. Augustine's Senior High School), where untreated laboratory waste from the institution as well as that from the District Teaching Hospital are discharged directly into the Lagoon. However, in this study, the highest Zn concentration was observed at site SP5 which has a lot of decaying organic matter input from the urban drain (Plate 1a) which could be a major source of Zn input into the lagoon. The high Zn concentration could also be attributed to the atmospheric deposition of products of fuel combustion, waste incineration and the geology of the underlying rock. The other sites recorded relatively lower concentrations with small variations from site to site.

### 4.4.4 Cadmium

Cadmium recorded the least of all the metals mean concentrations measured in the sediment with values ranging from a highest of 0.29 ± 0.06 mg/kg at sampling site SP1 to a lowest of 0.10 ± 0.06 mg/kg at SP3. These values were all below the Interim Canadian Sediment Quality Guidelines (ISQDs) value for the protection of marine and estuarine life.

The highest Cd concentration observed at SP1 (0.29 ± 0.06 mg/kg) could be attributed to the proximity of this area to St. Augustine's Senior High School and the District Teaching Hospital, where effluents from these institutions are discharged directly into the lagoon without any treatment. The hospital could be adding a constant source of Cd all year-round into the lagoon, perhaps from the laboratory or the general medical practices, as was suggested by Gilbert *et al*. (2006).



The second and third highest Cd mean concentrations were observed at SP4 (0.28 ± 0.13 mg/kg) and SP5 (0.25 ± 0.09 mg/kg), respectively. These sites are at the southern section of the lagoon, which receives huge amount of domestic effluents and sewage from nearby settlements, as well as leacheates of garbage and solid wastes dump from gutters that drain directly into the lagoon (Plate 1a). The relatively high prevalence of Cd distribution in these two sites seems to be mainly attributable to leaching of discarded metals that might contain Cd from garbage and solid waste dumped into the lagoon.

Atmospheric deposition from garbage incineration, volatile petroleum products from the nearby fuel filling station, and fumes from vehicles as well as particles from wear and tear of metallic parts, and brake pads of vehicles might have also contributed to Cd enrichment in sediments.

The fourth highest Cd concentration was observed at SP2 (0.23 ± 0.03 mg/kg) which is close to SP1 where the highest Cd mean concentration was recorded. At this site, domestic waste discharge from the Adisadel Estates, burnt bushes (as at the time of the study), and agricultural run-off from nearby farms into the lagoon might have caused the elevated Cd concentration at the site.

The lowest Cd concentration was observed at SP3 (0.10 ± 0.06 mg/kg) which is a site adjacent to the mechanical/auto repair shops. This finding is not in conformity with that of Gilbert *et al.* (2006), who observed a mean Cd concentration of 0.46 ± 0.04 mg/kg at this area when they performed analysis on 90-$\mu m$ fraction of the sediment. The reduced Cd concentration observed in this study could be attributed to the grain size (< *0.5mm*) of the sediment analysed, or reduced anthropogenic Cd input, even though surrounding activities still exist.

The mean concentration of Cd, however, did not exceed the Canadian Interim Guideline value of 0.7 mg/kg for the protection of marine/estuarine sediment lives.

From figure 8, it can be observed that almost all of the highest concentrations with the exception of Cd occurred at the lower section of the lagoon. This can be attributed to the flow pattern of the lagoon, the rate of deposition of pollutants as well as low flushing effect.

The low concentrations of heavy metals in the sediment of Fosu lagoon compared to the Interim Canadian Sediment Quality Guidelines (ISQDs) (Table. 4) means that no detrimental effects associated with dermesal (bottom-associated) species is expected to occur.

The correlation matrix of the elements in the sediment of Fosu Lagoon is presented in (Table 8).The correlation between Cu and Zn was significant (0.904) at a level of 0.05.

The good interrelation between Cu and Zn suggests a common sink of these elements into the sediments, likely resulting from domestic and industrial waste discharges into the lagoon.

Table 8: Pearson correlation coefficients between metal levels in sediment

| | Cu | Zn | Cd | Pb |
|---|---|---|---|---|
| Cu | 1 | | | |
| Zn | 0.904* | 1 | | |
| Cd | 0.791 | 0.606 | 1 | |
| Pb | 0.381 | 0.714 | -0.099 | 1 |

*Correlation is significant at the 0.05 level (2-tailed).

However, there was no significant correlation between other elemental pairs, such as Cu–Cd, Cu–Pb, Zn–Pb and Zn–Cd, and Pb–Cd yielded an insignificant negative correlation.

Table 9 shows the concentrations of heavy metals at the various sampling sites, the world average shale (reported by Turekian and Wedepohl, 1961), contamination factor (CF) and pollution load index (PLI) values. The results show that with the exception of Pb at sampling site SP5, the contamination factor (CF) for the metals (Cu, Zn and Cd) were all less than one.

Table 9: Concentrations (A), Contamination Factor (CF)-B and Pollution Load Index (PLI) of metals in sediment.

| Sampling Sites | Cu | | Zn | | Cd | | Pb | | PLI |
|---|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | A | B | |
| World Average Shale | 45 | - | 95 | - | 0.3 | - | 20 | - | |
| Fosu Lagoon | | | | | | | | | |
| SP2 | 9.71 | 0.216 | 9.87 | 0.104 | 0.23 | 0.767 | 15.2 | 0.759 | 0.338 |
| SP3 | 7.32 | 0.163 | 9.68 | 0.102 | 0.10 | 0.333 | 18.0 | 0.899 | 0.266 |
| SP1 | 13.3 | 0.296 | 11.5 | 0.121 | 0.29 | 0.967 | 17.6 | 0.879 | 0.418 |
| SP4 | 16.02 | 0.356 | 11.4 | 0.119 | 0.28 | 0.933 | 16.1 | 0.804 | 0.423 |
| SP5 | 16.8 | 0.373 | 13.2 | 0.139 | 0.25 | 0.833 | 20.9 | 1.044 | 0.461 |



The PLI values for all sediments were generally low and ranged from 0.27 at SP3 to 0.46 at SP5. The highest PLI value observed at SP5 might be attributed to high solid and liquid waste input, atmospheric deposition from combustible fuel and surface run-off from adjacent road as well as the relatively low pH observed at that site.

### 4.6 Heavy Metals in Black Chin Tilapia (*S. melanotheron*)-Whole Fish

The range, mean and standard deviation of total length (TL), dry weight (DW), the concentration of heavy metals quantified in black chin tilapia (S. *melanotheron)* - whole fish on dry weight basis and mean Condition Factor ($CF_B$) are presented in Table 10. The mean values were calculated irrespective of the site where the fishes were caught.

Generally, the mean $CF_B$ values for all the sampled fishes were >1, with values ranging from 1.42–1.76, implying that all the fishes sampled were of good health.

No values were obtained for Cd and Pb in S. *melanotheron* (dry weight) as their concentrations were below the detection limit of the analytical method used. Zinc and Cu, however, recorded concentrations ranging from 18.04 ± 0.17 to 20.23 ± 1.7 mg/ kg and 4.46 ± 4.43 to 8.54 ± 5.71 mg/kg respectively.

#### 4.6.1 Zinc

The mean concentrations of Zn distribution in *S. melanotheron* of varying lengths of fishes is shown in Figure 9. Generally, with the exception of length range 9.1–10 cm (20.23 ± 1.7 mg/kg) there is a decreasing trend in Zn concentration as length increases. This observation is in agreement with what was observed by Newman and Mitz (1988) when they conducted a study of the effects of size on Zn uptake and elimination rates of *Gambusia spp*. It is, therefore, possible for *S. melanotheron* to have naturally high levels of Zn, which are internally maintained, as has been suggested by van den Broek *et al.* (2002).

The average concentration of Zn in *S. melanotheron* of Fosu Lagoon is 19.34 mg/kg. This value is about 19 times more than the PMTDI value of 1.0 mg/kg and about 1.3 times more than the PTWI intake value of 15 mg/kg set by JECFA in 1982 and 1993 respectively.

Table 10: Range of Total Length (TL), Dry Weight (DW); Concentrations of total trace metals and Condition Factor ($CF_B$) of Black Chin (*S. melanotheron*)

| TL cm | n | DW g | Cu mg/kg | Zn mg/kg | Cd mg/kg | Pb mg/kg | $CF_B$ |
|---|---|---|---|---|---|---|---|
| 6.5–8.0 | 13 | 1.24–2.60 | 2.32–18.32 | 15.92–22.96 | <0.002 | <0.010 | 1.37–2.64 |
| (7.7±0.44) | | (2.05±0.45) | (7.11±3.76) | (19.94±1.99) | | | (1.76±0.35) |
| 8.1–9.0 | 13 | 1.33–4.20 | 1.76–22.68 | 17.24–20.06 | <0.002 | <0.010 | 1.25–2.22 |
| (8.6±0.34) | | (2.57±0.66) | (8.54±5.71) | (19.33±1.04) | | | (1.62±0.3) |
| 9.2–10.0 | 12 | 2.43–3.77 | 1.44–17.48 | 17.8–22.96 | <0.002 | <0.010 | 0.67–1.88 |
| (9.7±0.32) | | (3.28±0.45) | (5.47±4.44) | (20.23±1.7) | | | (1.42±0.29) |
| 10.3–11.3 | 2 | 4.09–7.10 | 1.40–7.52 | 17.92–18.16 | <0.002 | <0.010 | 1.63–1.88 |
| (10.8±0.71) | | (5.60±2.13) | (4.46±4.33) | (18.04±0.17) | | | (1.76±0.18) |

( ) mean ± SD, *n* – class size, DW – Dry Weight, $CF_B$ – Condition Factor, TL – Total Length

There are no known records on the effect of consuming 19.34 mg/kg of Zn on humans, however consuming this amount for about eight days or 154.78 mg/kg is likely to cause: severe abdominal cramping, hypertension, end-stage biliary cirrhosis in children, diarrhoea, tenesmus, lethargy, bloody stools, nausea, vomiting, and symptoms of dryness as reported by Brown *et al.* (1964), Murphy, (1970), Knapp *et al.* (1994) and Phillips *et al.*, (1996).

It must be noted however that, the concentrations were calculated for whole fish, but not just the flesh which the PMTDI and PTWI value were based on. Therefore, the whole fish concentration would involve skeletal and gut contents, which could potentially have higher concentrations thus resulting in the overall high concentration. It has also been determined elsewhere that Zn is concentrated in the liver, kidney and digestive tract and not in muscle tissue (Hart, 1982), which could therefore be responsible for the elevated concentrations when compared to PMTDI and the PTWI.

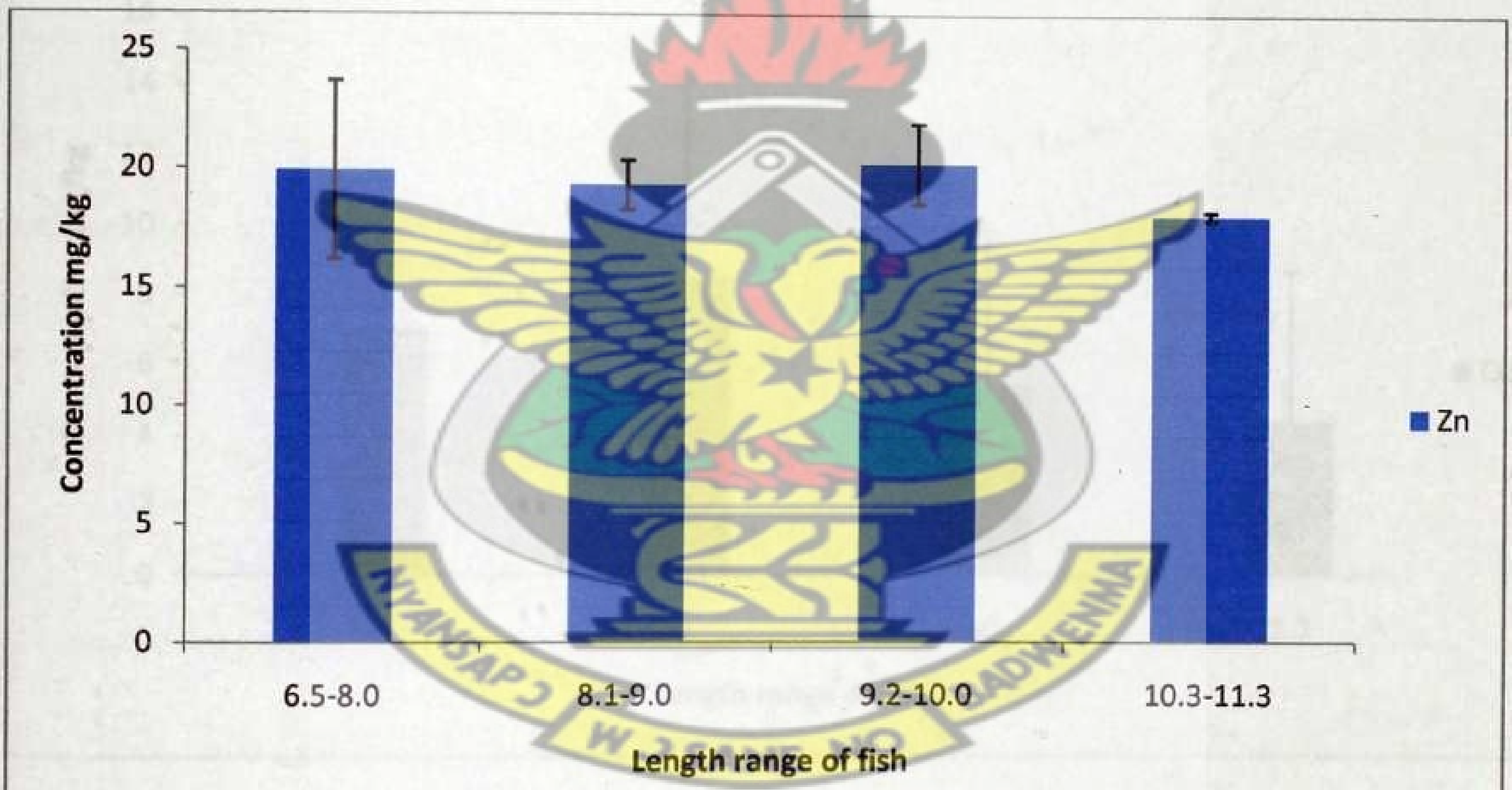


Figure 9: Mean Zn concentration distribution in Black Chin tilapia (S. *melanotheron)*-whole body on dry weight basis.

### 4.6.2 Copper

The distribution of Cu in Black Chin tilapia fish (S. *melanotheron)* of various length ranges are shown in Figure 10. Generally, there is a decreasing trend in Cu concentration with increasing length of the fishes, with the exception of the length range 8.1–9.0 cm where a mean concentration of 8.54 ± 5.71 mg/kg was recorded. This phenomenon has been observed elsewhere by Ray *et al*. (1980) where small individuals of polychaete *Neries virnes* accumulated larger amounts of heavy metals per unit of body weight than larger individuals. Smock (1983) suggested that the decreasing metal concentration with body size might indicate that surface absorption is an important mode of accumulation.

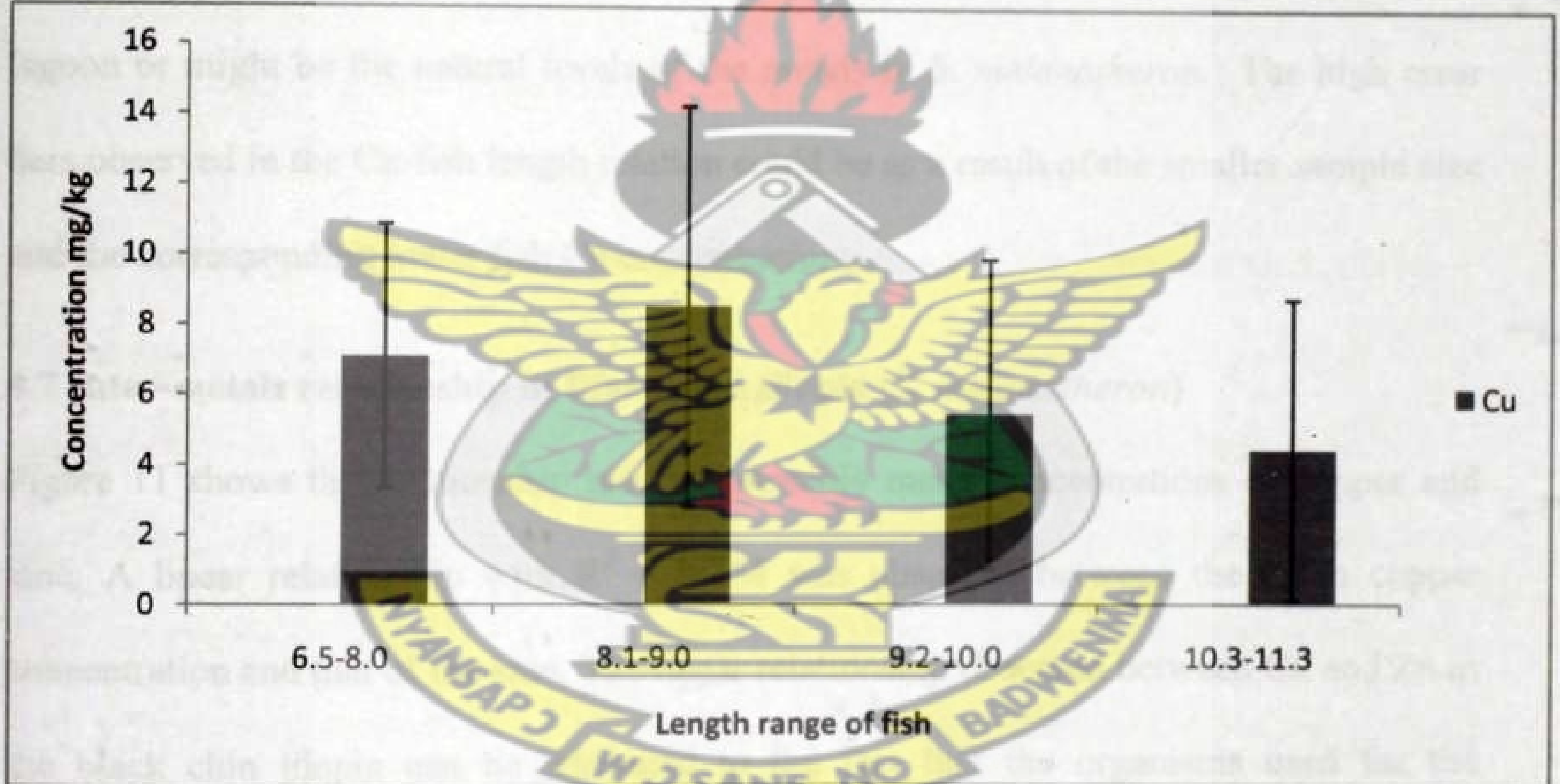


Figure 10: Mean Cu concentration distribution in Black Chin tilapia (S. *melanotheron)*-whole body on dry weight basis.

The average concentration of Cu in the fishes sampled is 6.40 mg/kg. This concentration is about 12 times the PMTDI value of 0.5 mg/kg and about 3 times the PWTI of 2 mg/kg.

Thus daily consumption of even one black chin tilapia from Fosu Lagoon is likely to result in gastrointestinal mucosal ulcerations and bleeding, acute hemolysis and hemoglobinuria, hepatic necrosis with jaundice, nephropathy with azotemia and oliguria, cardiotoxicity with hypotension, tachyeardia and tachypnea, as indicated in the literature.

Langston and Spence (1995) suggested that concentrations of metals can depend on the characteristics of the organism under study e.g. permeable surface area: volume ratio, habit and diet, as well as the chemical nature involved. Therefore, the high Cu and Zn concentrations observed in the Black Chin (S. *melanotheron)*-whole body can be attributed to the presence of elevated levels in the sediment and water column of the lagoon or might be the natural levels of the metals in S. *melanotheron.* The high error bars observed in the Cu-fish length relation could be as a result of the smaller sample size and the corresponding lower fish Cu concentrations.

**4.7 Inter-metals relationship in Black chin tilapia (*S. melanotheron*)**

Figure 11 shows the relationship between monthly mean concentrations of copper and zinc. A linear relationship with $R^2$ = 0.944 was observed between the mean copper concentration and that of the zinc. The linear relationship observed between Cu and Zn in the black chin tilapia can be attributed to the fact that the organisms used for the assessment are of the same species and thus have common source of absorption, metabolism and storage sites.

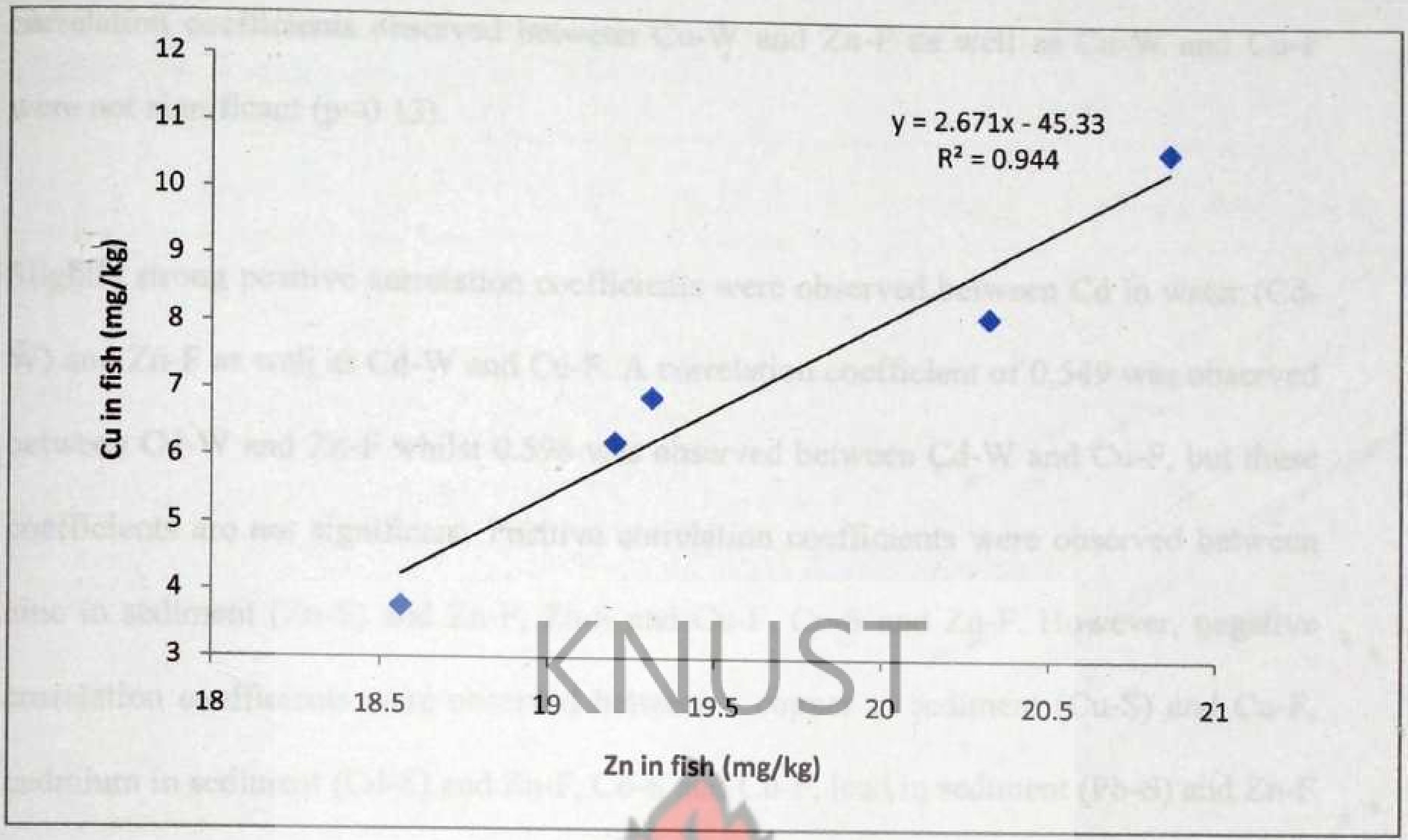


Figure 11: Copper vs. zinc relationship in black chin tilapia (*S. Melanotheron*)

**4.8 Relationship between Metals in Black Chin Tilapia (*S. melanotheron*), Surface Water and/or Sediment**

Pearson correlation coefficient test between mean concentrations of metals detected in black chin tilapia (*S. melanotheron*), surface water and/or sediment for the months under study are presented in Table 11. Weak and insignificant negative correlation coefficients were observed between Zn in water (Zn-W) and Zn in fish (Zn-F) as well as Zn-W and Cu in fish (Cu-F). A correlation coefficient of –0.491 was observed between Zn-W and Zn-F whilst – 0.446 was observed between Zn-W and Cu-F. A strong negative correlation coefficient of – 0.760 was observed between Cu in water (Cu-W) and Zn-W whilst – 0.773 was observed between Cu-W and Cu-F. However, the strong negative correlation coefficients observed between Cu-W and Zn-F as well as Cu-W and Cu-F were not significant ($p<0.13$).

Slightly strong positive correlation coefficients were observed between Cd in water (Cd-W) and Zn-F as well as Cd-W and Cu-F. A correlation coefficient of 0.549 was observed between Cd-W and Zn-F whilst 0.598 was observed between Cd-W and Cu-F, but these coefficients are not significant. Positive correlation coefficients were observed between zinc in sediment (Zn-S) and Zn-F, Zn-S and Cu-F, Cu-S and Zn-F. However, negative correlation coefficients were observed between copper in sediment (Cu-S) and Cu-F, cadmium in sediment (Cd-S) and Zn-F, Cd-S and Cu-F, lead in sediment (Pb-S) and Zn-F as well as Pb-S and Cu-F. But all the correlation coefficients were not significant.

Generally, the Pearson correlation coefficients obtained (Table 11) implies that exposure of the fishes (S. *melanotheron*) to these metals (Cu and Zn) is basically from the sediment compartment of the lagoon than water column. This finding is in contradiction with what has been demonstrated elsewhere that bioaccumulation of Zn and Cu in fishes depends on the total concentration of each metal in the water column (Chen *et al*., 2000; Rashed, 2001). This outcome could be attributed to the feeding behavior (i.e. bottom-feeding) of the black chin tilapia (S. *melanotheron*).

Table 11: Correlation matrix between metals in black chin tilapia (*S. melanotheron*), surface water and/or sediment

| | Zn-F | Cu-F | Zn-W | Cu-W | Cd-W | Zn-S | Cu-S | Cd-S | Pb-S |
|---|---|---|---|---|---|---|---|---|---|
| Zn-F | 1 | | | | | | | | |
| Cu-F | 0.972 | 1 | | | | | | | |
| Zn-W | -0.491 | -0.446 | 1 | | | | | | |
| Cu-W | -0.760 | -0.773 | 0.856 | 1 | | | | | |
| Cd-W | 0.549 | 0.598 | -0.882 | -0.955 | 1 | | | | |
| Zn-S | 0.409 | 0.347 | 0.471 | 0.282 | -0.531 | 1 | | | |
| Cu-S | 0.026 | -0.124 | -0.048 | 0.295 | -0.386 | 0.466 | 1 | | |
| Cd-S | -0.525 | -0.436 | 0.278 | 0.533 | -0.371 | -0.024 | 0.390 | 1 | |
| Pb-S | -0.359 | -0.439 | -0.240 | 0.263 | -0.159 | -0.148 | 0.778 | 0.660 | 1 |

- F (fish); - W (water); - S (sediment)

# CHAPTER FIVE

# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

The surface water column was found to contain high concentrations of the measured metals (Cu, Zn and Cd) with values exceeding the British Columbia guidelines for the protection of marine and estuarine life with the exception of Pb which was below detection limit. However, the concentrations of the metals studied in the sediment compartment were all below the Interim Canadian Sediment Quality Guidelines (ISQDs) for the protection of aquatic life.



High metals concentrations were observed in sediments at the lower section of the lagoon. The trend of pollution of the lagoon was observed to follow the order of: lower section > middle section > upper section.

Generally, the concentrations of the essential heavy metals (Cu and Zn) in the fishes (S. *melanotheron)* of Fosu lagoon were found to be higher than the PMTDI and the PTWI values but the non essential metals, Cd and Pb, had values (if any) below the detection limit of the analytical method used. It can therefore be concluded that the fishes (S. *melanotheron*) in Fosu Lagoon are safe for human consumption.

## 5.2 Recommendations

1. Although, the average Pollution Load Index (PLI) <1, routine monitoring of the sediment is highly essential.
2. Further study should be conducted on other aquatic organisms in order to assess the ecological state of the Fosu lagoon.
3. Refuse along the banks of the lagoon should be cleared and further deposition discouraged.
4. Solid matter screening systems should be in-built in the urban drains systems and emptied frequently to reduce the solid matter input into the lagoon.
5. Inhabitants should be sensitized about the impact of their activities on the lagoon (esp. indiscriminate defecation along the banks of the lagoon).
6. Liquid waste treatment plants should be constructed by the surrounding educational institutions including the hospital to reduce untreated liquid waste inundation of the lagoon.

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## APPENDIX 1

Table 12: Mean metal concentrations (± SD) in sediment at various sampling sites

| Sampling Sites | Cu mg/kg | Zn mg/kg | Cd mg/kg | Pb mg/kg |
|---|---|---|---|---|
| SP1 | 13.30 ± 0.58 | 11.54 ± 0.29 | 0.29 ± 0.06 | 17.58 ± 0.91 |
| SP2 | 9.71 ± 0.47 | 9.87 ± 0.28 | 0.23 ± 0.03 | 15.18 ± 1.22 |
| SP3 | 7.32 ± 0.50 | 9.69 ± 0.40 | 0.10 ± 0.06 | 17.98 ± 2.75 |
| SP4 | 16.02 ± 2.91 | 11.35 ± 1.05 | 0.28 ± 0.13 | 16.08 ± 2.43 |
| SP5 | 16.80 ± 0.98 | 13.19 ± 0.63 | 0.25 ± 0.09 | 20.88 ± 2.04 |

SD – Standard deviation

Table 13: Total trace metal concentration in Water samples for October 2008 in mg / L

| Sampling point | Cu (DL = 0.003) | Zn (DL = 0.001) | Pb (DL = 0.010) | Cd (DL = 0.002) |
|---|---|---|---|---|
| SP1 | 0.016 | <0.001 | <0.010 | <0.002 |
| SP2 | <0.003 | <0.001 | <0.010 | <0.002 |
| SP3 | <0.003 | <0.001 | <0.010 | 0.024 |
| SP4 | 0.044 | <0.001 | <0.010 | 0.004 |
| SP5 | 0.020 | <0.001 | <0.010 | <0.002 |

DL – DETECTION LIMIT

Table 14: Total trace metal concentration in Water samples for November 2008 in mg / L

| Sampling point | Cu (DL = 0.003) | Zn (DL = 0.001) | Pb (DL = 0.010) | Cd (DL = 0.002) |
|---|---|---|---|---|
| SP1 | <0.003 | <0.001 | <0.010 | <0.002 |
| SP2 | 0.024 | <0.001 | <0.010 | <0.002 |
| SP3 | 0.016 | <0.001 | <0.010 | 0.020 |
| SP4 | <0.003 | <0.001 | <0.010 | 0.024 |
| SP5 | <0.003 | <0.001 | <0.010 | <0.002 |

DL – DETECTION LIMIT

Table 15: Total trace metal concentration in Water samples for December 2008 in mg / L

| Sampling point | Cu (DL = 0.003) | Zn (DL = 0.001) | Pb (DL = 0.010) | Cd (DL = 0.002) |
|---|---|---|---|---|
| SP1 | <0.003 | <0.001 | <0.010 | <0.002 |
| SP2 | <0.003 | <0.001 | <0.010 | 0.008 |
| SP3 | 0.004 | <0.001 | <0.010 | 0.024 |
| SP4 | <0.003 | <0.001 | <0.010 | <0.002 |
| SP5 | 0.016 | <0.001 | <0.010 | <0.002 |

DL – DETECTION LIMIT

Table 16: Total trace metal concentration in Water samples for January 2009 in mg / L

| Sampling point | Cu (DL = 0.003) | Zn (DL = 0.001) | Pb (DL = 0.010) | Cd (DL = 0.002) |
|---|---|---|---|---|
| SP1 | 0.020 | <0.001 | <0.010 | <0.002 |
| SP2 | 0.008 | <0.001 | <0.010 | <0.002 |
| SP3 | 0.024 | <0.001 | <0.010 | <0.002 |
| SP4 | 0.028 | 0.028 | <0.010 | <0.002 |
| SP5 | 0.032 | <0.001 | <0.010 | <0.002 |

DL – DETECTION LIMIT



Table 17: Total trace metal concentration in Water samples for February 2009 in mg / L

| Sampling point | Cu (DL = 0.003) | Zn (DL = 0.001) | Pb (DL = 0.010) | Cd (DL = 0.002) |
|---|---|---|---|---|
| SP1 | 0.020 | <0.001 | <0.010 | <0.002 |
| SP2 | 0.008 | <0.001 | <0.010 | <0.002 |
| SP3 | 0.024 | <0.001 | <0.010 | <0.002 |
| SP4 | 0.028 | 0.028 | <0.010 | <0.002 |
| SP5 | 0.032 | <0.001 | <0.010 | <0.002 |

DL-DETECTION LIMIT

Table 18: Total trace metal concentration in bottom sediment samples for October, 2008 in mg / kg

| Sampling point | Cu (DL = 0.003) | Zn (DL = 0.001) | Pb (DL = 0.010) | Cd (DL = 0.002) |
|---|---|---|---|---|
| SP 1 | 14.22 | 11.61 | 17.50 | 0.21 |
| SP2 | 10.02 | 10.02 | 15.80 | 0.17 |
| SP3 | 7.618 | 9.16 | 15.69 | 0.01 |
| SP4 | 21.18 | 9.16 | 9.65 | 0.21 |
| SP5 | 15.18 | 14.86 | 17.54 | 0.14 |

DL – DETECTION LIMIT

Table 19: Total trace metal concentration in bottom sediment samples for November, 2008 in mg / kg

| Sampling point | Cu (DL = 0.003) | Zn (DL = 0.001) | Pb (DL = 0.010) | Cd (DL = 0.002) |
|---|---|---|---|---|
| SP1 | 11.77 | 11.37 | 15.93 | 0.16 |
| SP2 | 8.80 | 10.12 | 13.25 | 0.30 |
| SP3 | 8.59 | 10.56 | 26.13 | 0.27 |
| SP4 | 7.47 | 9.61 | 14.93 | 0.09 |
| SP5 | 16.47 | 12.61 | 18.06 | 0.39 |

DL – DETECTION LIMIT

Table 20: Total trace metal concentration in bottom sediment samples for December, 2008 in mg / kg

| Sampling point | Cu (DL = 0.003) | Zn (DL = 0.001) | Pb (DL = 0.010) | Cd (DL = 0.002) |
|---|---|---|---|---|
| SP1 | 14.19 | 12.37 | 20.10 | 0.41 |
| SP2 | 8.99 | 10.25 | 18.53 | 0.28 |
| SP3 | 7.29 | 9.72 | 18.24 | 0.12 |
| SP4 | 17.30 | 12.98 | 17.86 | 0.07 |
| SP5 | 15.40 | 12.79 | 21.76 | 0.12 |

DL – DETECTION LIMIT



Table 21: Total trace metal concentration in bottom sediment samples for January, 2009 in mg / kg

| Sampling point | Cu (DL = 0.003) | Zn (DL = 0.001) | Pb (DL = 0.010) | Cd (DL = 0.002) |
|---|---|---|---|---|
| SP1 | 12,87 | 11.02 | 16.66 | 0.33 |
| SP2 | 10.00 | 9.04 | 13.73 | 0.21 |
| SP3 | 6.34 | 8.86 | 14.77 | 0.04 |
| SP4 | 16.55 | 12.49 | 16.98 | 0.49 |
| SP5 | 17.71 | 12.03 | 20.70 | 0.17 |

DL – DETECTION LIMIT

Table 22: Total trace metal concentration in bottom sediment samples for February, 2009 in mg / kg

| Sampling point | Cu (DL = 0.003) | Zn (DL = 0.001) | Pb (DL = 0.010) | Cd (DL = 0.002) |
|---|---|---|---|---|
| SP1 | 13.43 | 11.33 | 17.70 | 0.34 |
| SP2 | 10.76 | 9.90 | 14.57 | 0.21 |
| SP3 | 6.77 | 10.16 | 15.08 | 0.08 |
| SP4 | 17.58 | 12.51 | 20.99 | 0.56 |
| SP5 | 19.26 | 13.64 | 26.34 | 0.45 |

DL – DETECTION LIMIT

Table 23: Total trace metal concentrations in fish samples caught in October, 2008

| Sampling Points | Fish ID | L cm | WW g | DW g | Zn $mgkg^{-1}$ | Cu $mgkg^{-1}$ | Pb $mgkg^{-1}$ | Cd $mgkg^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| SP1 | 1 | 7.5 | 5.49 | 1.64 | 22.32 | 15.49 | <0.010 | <0.002 |
| | 1 | 9.5 | 11.74 | 2.43 | 22.18 | 6.22 | <0.010 | <0.002 |
| SP2 | 2 | 9.2 | 11.51 | 3.00 | 20.76 | 4.44 | <0.010 | <0.002 |
| | 2 | 10.0 | 14.02 | 3.38 | 19.20 | 7.68 | <0.010 | <0.002 |
| SP3 | 3 | 9.0 | 9.52 | 2.34 | 18.80 | 6.92 | <0.010 | <0.002 |
| | 3 | 7.6 | 6.62 | 1.86 | 20.28 | 8.92 | <0.010 | <0.002 |
| SP4 | 4 | 9.5 | 11.13 | 2.46 | 22.96 | 17.48 | <0.010 | <0.002 |
| | 4 | 8.0 | 6.40 | 1.35 | 20.40 | 18.32 | <0.010 | <0.002 |
| SP5 | ND | ND | ND | ND | ND | ND | ND | ND |

ND – No Data

Table 24: Total trace metal concentrations in fish samples caught in November, 2008

| Sampling Points | Fish ID | L cm | WW g | DW g | Zn $mgkg^{-1}$ | Cu $mgkg^{-1}$ | Pb $mgkg^{-1}$ | Cd $mgkg^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| SP1 | 1 | 8.0 | 8.35 | 1.79 | 18.40 | 6.28 | <0.010 | <0.002 |
| | 1 | 9.0 | 11.32 | 2.46 | 17.48 | 6.40 | <0.010 | <0.002 |
| SP2 | 2 | 9.2 | 12.50 | 3.32 | 21.64 | 3.92 | <0.010 | <0.002 |
| | 2 | 10.3 | 17.82 | 4.09 | 18.16 | 7.52 | <0.010 | <0.002 |
| SP3 | 3 | 8.4 | 11.32 | 2.46 | 20.60 | 22.68 | <0.010 | <0.002 |
| | 3 | 9.5 | 13.17 | 3.42 | 19.08 | 2.00 | <0.010 | <0.002 |
| SP4 | 4 | 9.5 | 14.02 | 3.58 | 19.96 | 1.84 | <0.010 | <0.002 |
| | 4 | 10.0 | 16.64 | 3.77 | 19.12 | 4.70 | <0.010 | <0.002 |
| SP5 | ND | ND | ND | ND | ND | ND | ND | ND |

ND – No Data

Table 25: Total trace metal concentrations in fish samples caught in December, 2008

| Sampling Points | Fish ID | L cm | WW g | DW g | Zn $mgkg^{-1}$ | Cu $mgkg^{-1}$ | Pb $mgkg^{-1}$ | Cd $mgkg^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| SP1 | 1 | 10.0 | 14.03 | 3.15 | 17.80 | 3.60 | <0.010 | <0.002 |
| | 1 | 8.6 | 9.13 | 1.92 | 18.68 | 5.48 | <0.010 | <0.002 |
| SP2 | 2 | 8.8 | 9.16 | 2.23 | 19.96 | 10.84 | <0.010 | <0.002 |
| | 2 | 9.6 | 16.61 | 3.60 | 21.76 | 9.08 | <0.010 | <0.002 |
| SP3 | 3 | 7.3 | 5.78 | 1.24 | 22.96 | 7.96 | <0.010 | <0.002 |
| | 3 | 8.1 | 6.67 | 1.33 | 19.40 | 9.86 | <0.010 | <0.002 |
| SP4 | 4 | 8.0 | 8.92 | 1.89 | 20.56 | 11.8 | <0.010 | <0.002 |
| | 4 | 7.6 | 7.45 | 1.67 | 21.41 | 6.8 | <0.010 | <0.002 |
| SP5 | ND | ND | ND | ND | ND | ND | ND | ND |

ND – No Data

Table 26: Total trace metal concentrations in fish samples caught in January, 2009

| Sampling Points | Fish ID | L cm | WW g | DW g | Zn $mgkg^{-1}$ | Cu $mgkg^{-1}$ | Pb $mgkg^{-1}$ | Cd $mgkg^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| SP1 | 1 | 10.0 | 13.49 | 3.60 | 18.20 | 1.44 | <0.010 | <0.002 |
| | 1 | 8.0 | 7.88 | 2.20 | 18.08 | 2.32 | <0.010 | <0.002 |
| SP2 | 2 | 10.0 | 14.73 | 3.70 | 18.68 | 3.12 | <0.010 | <0.002 |
| | 2 | 8.0 | 10.11 | 2.60 | 15.92 | 2.64 | <0.010 | <0.002 |
| SP3 | 3 | 9.0 | 9.85 | 2.40 | 19.24 | 7.16 | <0.010 | <0.002 |
| | 3 | 6.5 | 7.25 | 1.70 | 17.84 | 6.32 | <0.010 | <0.002 |
| SP4 | 4 | 8.0 | 10.79 | 2.80 | 20.24 | 2.60 | <0.010 | <0.002 |
| | 4 | 8.5 | 10.34 | 2.80 | 20.28 | 4.56 | <0.010 | <0.002 |
| SP5 | ND | ND | ND | ND | ND | ND | ND | ND |

ND – No Data

Table 27: Total trace metal concentrations in fish samples caught in February, 2009

| Sampling Points | Fish ID | L cm | WW g | DW g | Zn $mgkg^{-1}$ | Cu $mgkg^{-1}$ | Pb $mgkg^{-1}$ | Cd $mgkg^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| SP1 | 1 | 9.0 | 11.42 | 2.90 | 19.60 | 2.92 | <0.010 | <0.002 |
| | 1 | 11.3 | 27.14 | 7.10 | 17.92 | 1.40 | <0.010 | <0.002 |
| SP2 | 2 | 8.3 | 11.84 | 2.70 | 18.44 | 15.68 | <0.010 | <0.002 |
| | 2 | 9.0 | 16.18 | 4.20 | 20.48 | 1.76 | <0.010 | <0.002 |
| SP3 | 3 | 8.8 | 10.92 | 2.90 | 20.44 | 3.72 | <0.010 | <0.002 |
| | 3 | 8.0 | 8.49 | 2.30 | 20.14 | 9.60 | <0.010 | <0.002 |
| SP4 | 4 | 8.8 | 10.92 | 2.90 | 17.24 | 9.52 | <0.010 | <0.002 |
| | 4 | 8.0 | 10.42 | 2.60 | 19.36 | 5.32 | <0.010 | <0.002 |
| SP5 | ND | ND | ND | ND | ND | ND | ND | ND |

ND – No Data

APPENDIX 2



Plate 2. Collection of samples from Fosu lagoon. Plate 3. Lyophilization of fish samples

Plate 4. Determination of EC, pH or temp. Plate 5. Digestion of samples

Plate 6. S. *melanotheron* in a rubber plate

Plate 7. Teflon bombs in a microwave oven



Plate 8. Homogenization and sieving of sediment samples.

Plate 9. AA240FS Fast Sequential Atomic Absorption Spectrometer set up.