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DISTRIBUTION OF HEAVY METALS IN THE FOSU LAGOON (CAPE COAST)

A Thesis submitted to the Department of Environmental Science, Kwame Nkrumah University of Science and Technology, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE (ENVIRONMENTAL SCIENCE) College of Science



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DECLARATION

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



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ABSTRACT

Mining and industrial processing are among the main sources of heavy metals contamination in the environment. Heavy metals concentration may accumulate to toxic level which can cause a potential risk to human health. Continuous discharge of industrial and residential waste water into the Fosu lagoon is a potential source of environmental pollution. Water, sediment and fish samples from the lagoon were used to assess the extent of heavy metals concentration in the lagoon. Heavy metal concentrations in the samples were measured using the Perkin-Elmer Atomic Absorption spectrophotometer. Some physicochemical parameters were also measured to know the level of the water quality. Twelve samples of water and sediment were collected from the lagoon at six different points to represents the wet and dry seasons. Results obtained for water samples were compared with USEPA National Recommended Water Quality Criteria. Geoaccumulation index was used to determine the extent of heavy metal pollution in the sediment samples whiles the heavy metal concentrations in fish samples were compared with US Food and Nutrition Board daily recommended intake levels. Pearson's correlation was also used to determine how correlated the metals are to each other and their possible sources. The results obtained revealed that heavy metals concentrations were significantly higher during the dry season for both water and sediment samples but nutrients concentration in water samples were higher in the wet season. pH values for water and sediments revealed that the lagoon is neutral during the wet season but basic in the dry season. Only lead and cadmium were recorded in water samples for the wet season with lead concentration exceeding the USEPA threshold level of 3.0 mg/kg. The sediment samples contained high concentration of metals. Fe, Mn, Zn and Pb recorded mean concentrations of 1275.25 mg/kg, 236.72mg/kg, 22.72 mg/kg and 14.22 mg/kg for the dry season respectively. Geoaccumulation indices showed that the lagoon sediments were

highly contaminated with iron, manganese, zinc and lead. Metal concentrations in fish samples were also detected and again, iron, manganese, zinc and lead recorded high concentrations. Examination of health of the fish by Fulton's formula showed that all fish samples were in good condition. However, the presence of lead and cadmium in the fish samples is a health threat since these two metals are of no nutritional value and also have the tendency to bio accumulates in the fish and also be biomagnified along the food chain.



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CHAPTER ONE

INTRODUCTION

1.1 Background

Many of the sediments in our rivers, lakes and oceans have been contaminated by pollutants. Some of these pollutants are directly discharged by industrial plants and municipal sewage treatment plants, others come from polluted runoff in urban and agricultural areas and some are the results of historical contamination (Abida, 2009). The problem of heavy metal pollution is attracting the attention of people around the world, due to its negative effects on the environment and on human health (Abida, 2009). With increased urbanization and industrialization, there has been rapid increase in the generation of municipal waste water (sewage water and industrial effluents), which in turn has intensified environmental pollution. Proper disposal of industrial effluents and municipal wastes is therefore a major problem for big cities. Major sources of contamination in surface water can be traced to industrial discharges, domestic waste disposal and application of agrochemicals on farmlands (Kennicutt et al; 1992). Pollutants like heavy metals, after entering into aquatic environment accumulate in tissues and organs of aquatic organisms. The amount of absorption and assembling depends on ecological, physical, chemical and biological conditions and also the kind of element and physiology of the organisms (Jaffa et al; 1998). These metals after their assimulation by the aquatic organisms enter into the food chain and are finally consumed by humans (Agbozu et al; 2007). Effects of these metas on consumers depend on the concentration, physiochemical properties, chemical bonds and their distribution in body (Gharib et al; 2003). Aquatic ecosystems are very vulnerable since they are

the final recipients of several pollutants including metals (Udosen, 2006). Notably aquatic ecosystems are often polluted with anomalously high levels of toxicants (organic and inorganic substances), which find their way into the aquatic systems with wastewater and effluents generated from industrial enterprises. Pollutants such as heavy metals accumulation in aquatic ecosystems is either in aquatic organisms or in the sediment (Udosen, 2006).

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Contaminated sediments can threaten creatures in the benthic environment, exposing worms, crustaceans and insects to hazardous concentrations of toxic chemicals. Some polluted sediment can kill benthic organisms, thereby reducing the food available to larger animals such as fish (Pan and Brugam, 1997). Human activities have increased the concentration of metals in many of the natural water systems which have raised concerns regarding metal bioaccumulation and human health hazards (Pan and Brugam, 1997). Pollutants in aquatic ecosystems precipitate on sediments surface and form as deposited pollutants. Sediment is well known as an important sink and a source for metal contaminant (Li and Thornton, 2001). Sediments naturally consist of a complex mixture of organic and inorganic components like clays, silicates, carbonate, sulphide, minerals and bacteria. Contaminated sediments do not always remain at the bottom of a water body. Anything that stirs up the water, such as dredging, can resuspend sediments. Resuspension may mean that all of the animals in the water and not just the bottom-dwelling organisms will be directly exposed to toxic contaminants (Pan and Brugam, 1997).

Consumption of fish is the main route through which aquatic pollutants and that heavy metals in this context, enter into the food chain and finally into the human system (APHA, 1981). In recent

years, there has been an increasing interest in the utilization of fishes as bioindicators, of the integrity of aquatic environmental systems (Fausch *et al*; 1990). The good response of fish to environmental change makes it suitable for use as an environmental pollution indicator. Fish is a good bioindicator because it is easy to obtain in large quantities, has the potential to accumulate metals, optimum size for analysis and also is easy to be sampled (Batvari *et al*; 2007). Heavy metals intake by fish in polluted aquatic environment depends on ecological requirements, metabolisms and other factors such as salinity. Several studies have indicated enhanced levels of both non-essential and essential heavy metal load in muscle and liver tissues of fishes (Ekpo and Ibok, 1999). Depending on the level of exposure, this can cause both acute and chronic effects to humans (Dogan and Yilmaz, 2007; Fidan *et al*; 2007).

1.2 Problem Statement

Ghana, being a developing country is faced with pollution challenges and one of the major pollution problems is polluting of water bodies (EPA, Ghana, 2006). About two years ago the Environmental Protection Agency of Ghana advised that all fishing and swimming activities in the Fosu Lagoon be stopped due to it highly polluted nature. The Fosu Lagoon is now the third most polluted lagoon in Ghana, aside the Korle lagoon in Accra and the Chemu lagoon in Tema (EPA, Ghana, 2008). It was also recently added to the list of water bodies with dead zones in the world. Formerly, the Fosu lagoon served as a tourist attraction in Cape Coast, but this attraction is dying out due to the polluted nature of the water. Apart from this, fish caught from the lagoon also serves as a source of livelihood and food for the inhabitants.

Little literature about heavy metal pollution in the Fosu Lagoon is available. Almost all the research works about heavy metal pollutants in the environment are performed in the mining areas of Ghana (Nyarko *et al*; 2006). However, some of these metal pollutants can travel long distances through the air and other means to places far from where they were released. A good example of such pollutants is methyl mercury, due to it high volatility. The 100% bioavailable methyl mercury comes into contact with deep waters and transfers in the marine food chain. A positive correlation between mercury level in sediments, in algae and in benthic organisms has been proved (Brambati, 1996). Most of the research works on the Fosu Lagoon focuses on the water quality and the few ones that consider the presence of heavy metals also base their analysis by considering only sediment samples of the lagoon (Nyarko *et al*; 2006). However, the black chin tilapia in the lagoon can also be used as bioindicators to check for the presence of heavy

metals.

1.3 OBJECTIVES

The main objective of this study is to assess the heavy metal contamination of the Fosu Lagoon.

The specific objectives of this research are:

- To determine the concentration of heavy metals in water, sediment and fish samples from the lagoon.
- To compare the concentrations at which these metals occur with permissible levels of heavy metals in surface water prescribed by USEPA
- ✤ To statistically analyse the existence of any relationship between the metals and the extent of pollution.

1.4 JUSTIFICATION

The Fosu lagoon came into the spot light about two years ago as a result of it heavily polluted nature. The EPA then took some temporal measures as a way of salvaging the lagoon from it polluted nature. However, the source of these pollutants such as the various garages cited close to the lagoon and the drainages from the surrounding residential settlements that lead into the lagoon are still there and can introduce some pollutants including heavy metals into the lagoon. There is therefore the need to assess the extent of heavy metal pollution in the lagoon and the fish which is heavily consumed by the inhabitants of Cape Coast and it environs. This can also provide clues on how to solve the metal pollution problems in the lagoon.



CHAPTER TWO

LITERATURE REVIEW

2.1 The Fosu Lagoon

The Fosu Lagoon is located in Cape Coast, the capital city of the Central Region in Ghana. The geographical coordinates of the lagoon are 5^{0} 7'N and 1^{0} 16'W. The lagoon is a shallow body of water which is separated from the sea by a sand bar which is usually broken by heavy rains or manually as part of the rituals during the Fetu festival in Cape Coast (Armah, 1991). Lagoons in Ghana are important resource as they provide benefits and values to coastal populations (Gordon, 1996). However, due to industrialization and increasing population, most of Ghana's coastal lagoons are heavily polluted. Ghana's coastal zones represent about 6.5% of the total land area in the country, yet it houses about 25% of the nation's population (EPA Ghana, 1996).

The Fosu Lagoon is an important resource to the people of Cape Coast because it provides both economic and cultural benefits to the people. The enormous amount of fish that live in the lagoon provides the fishermen with some income as well as the people with food. The lagoon also forms part of the Fetu festival celebrated by the people of Cape Coast. Two months to the commencement of the festival, all fishing activities in the lagoon is banned and just before the festival is started, this ban is lifted after which the first net is cast by the Paramount Chief to mark the beginning of the festival. Apart from these, the lagoon also serves as a tourist attraction which benefits the country as a whole (Armah, 1991).

In March 2008 the Environmental Protection Agency, Ghana, advised that all activities in the Fosu Lagoon be put to a halt, due to the highly polluted nature of the lagoon. According to the EPA, test performed on the lagoon water revealed that the water was highly polluted with most of the commonly known cations and anions measured. All physiochemical and bacteriological parameters measured were highly above the World Health Organizations guidelines for swimming and fishing. Also the total coliforms recorded from the samples showed that the lagoon also contained a high amount of faecal matter, The EPA in an attempt to salvage the lagoon advised that portions of the sand bar that separates the lagoon from the sea should be wined to allow the sea to flow into the lagoon and dilute the lagoon water. However, this exercise was highly criticized by the fishermen who claimed that the sea water will kill the fishes in the lagoon and also cause the lagoon to dry up.

2.2 General Characteristics of Heavy Metals

Heavy metals have been defined differently by many sectors of academia. Many different definitions have been proposed – some based on density, some on atomic weight, and some on chemical properties or toxicity (Duffus, 2002). One source defines heavy metals as common transition metals such as copper, lead and zinc (Sanchez, 2008). "Heavy metals" are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. Heavy metals are not biodegradable and thus are harmful to plants, aquatic animals and human health at certain levels of exposure (Mustafa and Nilgun, 2006). However, in small quantities, certain heavy metals are nutritionally essential for a healthy life. They are referred to as trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are commonly

found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products (IOSAHIC, 1999).

2.3 Sources of Heavy Metals

Metals form part of the earth crust and are generally made available in the environment by processes such as chemical weathering of minerals and soil leaching (Biney *et al*; 1994). The anthropogenic sources are associated mainly with industrial and domestic effluents, urban storm, water runoff, landfill leachate and mining of coal and ore (Zarazua *et al*; 2006). Heavy metals are among the most common environmental pollutants, and their occurrence in waters and biota indicate the presence of natural or anthropogenic sources. All heavy metals exist in surface waters in colloidal, particulate or dissolved phases (Osmond *et al*; 1995). Rivers are a dominant pathway for metal transport and this may cause trace metals to become significant pollutants in many small riverine systems (Miller *et al*; 2003). During their transport, the trace metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena and this affects their reactions and bioavailability (Dassenakis *et al*; 2006).

2.4 Heavy Metals Toxicity

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Virtually all metals can produce toxicity when ingested in sufficient quantities, but there are several of them which are especially important because they produce toxicity at low concentrations (Hoekman, 2008). Heavy metals may enter the human body through food, water,

air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, industrial, or residential settings. Industrial exposure accounts for a common route of exposure for adults. Ingestion is the most common route of exposure in children (Roberts, 1999). Children may develop toxic levels from the normal hand-to-mouth activity of small children who come in contact with contaminated soil or by actually eating objects that are not food (Dupler, 2001). Less common routes of exposure are during a radiological procedure, from inappropriate dosing or monitoring during intravenous (parenteral) nutrition, from a broken thermometer (Smith *et al*; 1997), or from a suicide or homicide attempt (Lupton *et al*; 1985). In general, heavy metals produce their toxicity in organisms by forming complexes or "ligands" with organic compounds (Soghoian, 2008; Hoekman, 2008). These modified biological molecules lose their ability to function properly, and result in malfunction or death of the affected cells. Some heavy metals may form complexes with other materials in living organisms. These complexes may inactivate some important enzymes, systems and certain protein structures (Hoekman, 2008).

2.5 CHARACTERISTICS OF SELECTED METALS IN THIS STUDY

2.5.1 Manganese

Manganese is a hard metal and is very brittle. Manganese is reactive when pure, and as a powder it will burn in oxygen (Stokinger, 1981). Manganese occurs principally as pyrolusite (MnO_2), and to a lesser extent as rhodochrosite ($MnCO_3$). Manganese (Mn) is an essential element that is found in living systems most often in the +2 oxidation state (Keen *et al*; 1988; Stokinger, 1981).

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It is an essential trace element but can bring forth a variety of serious toxic responses upon prolonged exposure to elevated concentrations. Normal nutritional requirements of Mn are satisfied through the diet, which is the normal source of the element, with minor contributions from water and air (US EPA, 1984). Toxic exposures occur largely due to particulate material in the air from mining and manufacturing activities (Francis and Forsyth, 2005). This heavy metal is frequently associated with iron deposits (Hoekman, 2008).

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Manganese effects occur mainly in the respiratory tract and in the brains. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage. A syndrome that is caused by manganese has symptoms such as schizophrenia, dullness, weak muscles, headaches and insomnia (ATSDR, 1991). Chronic Manganese poisoning may result from prolonged inhalation of dust and fume. The central nervous system is the chief site of damage from the disease, which may result in permanent disability and can also cause impotency in men (Francis and Forsyth, 2005).

Manganese is an essential component of over thirty-six enzymes that are used for the carbohydrate, protein and fat metabolism (Stokinger, 1981). For some animals the lethal dose is quite low, which means they have little chance to survive even smaller doses of manganese when these exceed the essential dose. Manganese substances can cause lung, liver and vascular disturbances, declines in blood pressure, failure in development of animal foetuses and brain damage.

2.5.2 Lead

Lead is a bluish-white lustrous metal and a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to air. Lead occurs naturally in the environment. However, most lead concentrations that are found in the environment are a result of human activities (ATSDR, 1989). The burning of leaded fuels in automobiles is an example of such activities. Lead accounts for most of the cases of pediatric heavy metal poisoning (Roberts 1999). Every year, industry produces about 2.5 million tons of lead throughout the world. Most of this lead is used for batteries. The remainder is used for cable coverings, plumbing and ammunition. Other uses are as paint pigments and in PVC plastics, x-ray shielding, crystal glass production, and pesticides (ATSDR, 1991).

Lead is one of the metals that have the most damaging effects on human health (Greenberg *et al*; 1992). It can enter the human body through uptake of food, water and air. Lead is a toxicant that accumulates in the skeleton and accounts for most cases of pediatric heavy metal poisoning (Roberts, 1999). Even at low levels, lead may cause a range of health effects including behavioural problems and learning disabilities. Other target organs are the brain, blood, kidneys, and thyroid gland (ATSDR, 1989). Lead affects the central and peripheral nervous systems, eventually causing neurological and behavioural disorders in patients (WSH, 2005). Lead has been found to be carcinogenic and also a potential enzyme inhibitor (Greenberg, *et al*; 1992), which interferes with fertility and causes renal damage. Children below 6 years of age and pregnant women are most susceptible to the adverse health effects of lead (Klaassen, 1996). Children absorb 4–5 times as much lead as adults, whilst its biological half-life is also considerably longer in children than in adults, (WSH, 2010).

2.5.3 Cadmium

Cadmium is a byproduct of the mining and smelting of lead and zinc. It is used in nickelcadmium batteries, PVC plastics, and paint pigments. It can be found in soils because insecticides, fungicides, sludge, and commercial fertilizers that contain cadmium are used in agriculture (Young, 2005).

Exposure to cadmium and its compounds may occur in both occupational and environmental settings, the latter primarily via the diet and drinking water (ATSDR, 1989). Acute oral exposure to 20-30 g of Cd has caused fatalities in humans. Exposure to lower amounts may cause gastrointestinal irritation, vomiting, abdominal pain, and diarrhea (Young, 2005b). Long term exposure to cadmium primarily affects the kidneys, resulting in tubular proteinosis (Goyer, 1991). The 1-minute and 10-minute lethal concentration of cadmium for humans has been estimated to be about 2,500 and 250 mg/m³, respectively (RIAS, 2005). An 8-hour time-weighted-average (TWA) exposure level of 5 mg/m³ has been estimated for lethal effects of inhalation exposure to cadmium, and exposure to 1 mg/m³ is considered to be immediately dangerous to human health (Friberg *et al*; 1974). Renal toxicity (tubular proteinosis) may also result from inhalation exposure to cadmium (Goyer, 1991). Inhalation of cadmium fumes or dust may result in a wide range of effects, including a metallic taste, headache, dyspnea, chest pains, cough with foamy or bloody sputum, and muscular weakness (Young, 2005b). Severe exposure may result in pulmonary edema and death (USAF, 1990).

Cadmium strongly adsorbs to organic matter in soils. When cadmium is present in soils it can be extremely dangerous, its uptake through food will increase (USAF, 1990). Soils that are acidified enhance the cadmium uptake by plants. In aquatic ecosystems cadmium can bio accumulate in mussels, oysters, shrimps, lobsters and fish. The susceptibility to cadmium can vary greatly between aquatic organisms. Salt-water organisms are known to be more resistant to cadmium poisoning than freshwater organisms (Klaassen, 1996). Animals eating or drinking cadmium sometimes get high blood-pressures, liver disease and nerve or brain damage (Goyer, 1991).

2.5.4 Copper

Copper is malleable, ductile, and an extremely good conductor of both heat and electricity. It is used for electrical equipment, construction; such as roofing and plumbing; industrial machinery, such as heat exchangers. Most copper (Cu) compounds found in air, soil and water are strongly attached to dust or embedded in minerals (MDH, 2006). One may be exposed to Cu by breathing air, eating food, or drinking water containing Cu as well as through skin contact with coppercontaining substances (MDH, 2006).

Copper is an essential element for living organisms, including humans, and small amounts is necessary in diets to ensure good health (Vitosh *et al*; 1994; MDH, 2006). However, too much Cu can cause adverse health effects in humans, including vomiting, diarrhea, stomach cramps, nausea, irritation of skin, eyes and respiratory tract (Kegley *et al*; 2009; MDH, 2006). Copper has also been associated with liver damage and kidney disease (MDH, 2006).

2.5.5 Iron

Iron, is the most abundant element in the Earth's crust (Aisen *et.al*; 2001). Iron can exhibit two oxidation states; ferrous (Fe²⁺), and ferric (Fe³⁺). Ferrous iron reacts with molecular oxygen via Fenton chemistry and generates toxic hydroxide radicals; these hydroxide radicals cause extensive cell damage by attacking proteins, nucleic acids, lipids and carbohydrates (Hentze *et al*; 2004). On the other hand, ferric iron is virtually insoluble in aqueous solution (Aisen, and Listowsky, 1980). Despite its toxicity, iron is essential to several life processes including the synthesis of DNA, the respiratory electron transport chain, as well as oxygen storage and transport. Cellular iron deficiency arrests cell growth and leads to cell death (Hentze *et al*; 2004).

Iron may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues (Braun and Killmann, 1999). Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis, which is observable as an x-ray change (Archibald, 1983). No physical impairment of lung function has been associated with siderosis. Inhalation of excessive concentrations of iron oxide may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens (Hentze *et al*; 2004).

2.5.6 Zinc

Zinc is a fairly reactive metal that will combine with oxygen and other non-metals, and will react with dilute acids to release hydrogen. Common anthropogenic sources of zinc are usually smelting, mining, metallurgy, electro-galvanising, pesticides, various alloys (Forstner and Prosi, 1979). Zinc is an essential mineral that is naturally present in some foods and is also available as a dietary supplement. Zinc is also found in many cold lozenges and some over-the-counter drugs sold as cold remedies (Sandstead, 1994).

Zinc is involved in numerous aspects of cellular metabolism. It is required for the catalytic activity of approximately 100 enzymes (Sandstead, 1994) and it plays a role in immune function, protein synthesis, wound healing, DNA synthesis and cell division (Solomons, 19983). Zinc also supports normal growth and development during pregnancy, childhood, and adolescence and is required for proper sense of taste and smell. A daily intake of zinc is required to maintain a steady state because the body has no specialized zinc storage system (Rink and Gabriel, 2000).

Zinc toxicity can occur in both acute and chronic forms. Acute adverse effects of high zinc intake include nausea, vomiting, loss of appetite, abdominal cramps, diarrhea, and headaches (Food and Nutrition Board, 2001). One case report cited severe nausea and vomiting within 30 minutes of ingesting 4 g of zinc gluconate (570 mg elemental zinc) (Lewis and Kokan, 1998). Intakes of 150–450 mg of zinc per day have been associated with such chronic effects as low copper status, altered iron function, reduced immune function, and reduced levels of high-density lipoproteins (Hooper *et al*; 1980). Reductions in a copper-containing enzyme, a marker of copper status, have been reported with even moderately high zinc intakes of approximately 60 mg/day for up to 10 weeks. The doses of zinc used in studies (80 mg per day of zinc in the form of zinc oxide for 6.3 years, on average) have been associated with a significant increase in hospitalizations for genitourinary causes, raising the possibility that chronically high intakes of zinc adversely affect some aspects of urinary physiology (Johnson *et al*; 2007).

2.5.7 Nickel

Nickel is relatively widespread in the environment (Doig and Liber, 2006). Although it can exist in several different oxidation states, the prevalent oxidation state under environmental conditions is Ni²⁺ (Cempel and Nikel, 2006). Expressly, Ni²⁺ is among the prominent metal pollutants such as Pb(II), Hg(II), and Cd(II) that exert toxic and lethal effects (ATSDR, 2005). Compared to most metal pollutants though, Ni is less toxic and more soluble. Nickel is a transition metal that shows a wide range of both redox behavior and complex formation. Both allergic and carcinogenic effects of Ni have been well documented (Cempel and Nikel, 2006) The USEPA water quality criteria maximum concentration, (CMC) and critical continuous concentration, (CCC) for Ni in freshwaters are 470 and 52 μ g/L, respectively (USEPA, 2008).

Humans may be exposed to nickel by breathing air, drinking contaminated water, eating food or smoking cigarettes. Skin contact with nickel-contaminated soil or water may also result in nickel exposure. In small quantities nickel is essential, but when the uptake is too high it can be a danger to human health (W.H.O., 2005). Nickel and certain nickel compounds have been listed by the National Toxicology Program (NTP) as being reasonably anticipated to be carcinogens (ATSDR, 2005). The International Agency for Research on Cancer (IARC) has listed some nickel compounds as group 1 (there is sufficient evidence for carcinogenicity in humans) and other nickel compounds as group 2B (agents which are possibly carcinogenic to humans). Foodstuffs naturally contain small amounts of nickel. Chocolate and fats are known to contain severely high quantities. Nickel uptake will boost when people eat large quantities of vegetables from polluted soils. Plants are known to accumulate nickel and as a result the nickel uptake from vegetables will be eminent (ATSDR, 2005). Smokers have a higher nickel uptake through their lungs.

2.5.8 Chromium

Chromium is a lustrous, brittle, hard metal. Due to it wide industrial use, it is considered as a serious environmental pollutants (Shanker *et al.*, 2004). Chromium is unstable in oxygen, it immediately produces a thin oxide layer that is impermeable to oxygen and protects the metal below. The stable forms of Cr are the trivalent Cr(III) and the hexavalent Cr(VI) species, although there are various other valence states which are unstable and shortlived in biological systems. Cr(VI) is considered the most toxic form of Cr, which usually occurs associated with oxygen as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) oxyanions. Cr(III) is less mobile, less toxic and is mainly found bound to organic matter in soil (Becquer et al., 2003).

Chromium is found in all phases of the environment, including air, water and soil. Cr concentration varies widely in the atmosphere, from background concentrations of 5.0×10^{-6} –1.2 x $10^{-3} \mu g/m^3$ in air samples from remote areas such as Antarctica and Greenland to 0.015– $0.03 \mu g/m^3$ in air samples collected over urban areas (Nriagu, 1988). Cr and its compounds have several industrial uses. They are extensively employed in leather processing and finishing (Nriagu, 1988), in the production of refractory steel, drilling muds, electroplating cleaning agents, catalytic manufacture and in the production of chromic acid and specialty chemicals (Shanker et al., 2004). Chromium (III) is an essential nutrient that helps the body use sugar, protein, and fat (Cervantes et al., 2001). Cr (III) is a very stable oxidation state for chromium. In this state, the chrome is labile and kinetically very slow to react or form complexes. It is not a strong oxidiser and the human's natural body acidity is enough for the chrome to keep to this Cr (III) state (Cervantes *et al*; 2001).

Breathing high levels of chromium (VI) can cause irritation to the nose, such as runny nose, nosebleeds, and ulcers and holes in the nasal septum. Ingesting large amounts of chromium (VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death (Gargas, et al; 1994). Skin contact with certain chromium (VI) compounds can cause skin ulcers (Baranowska-Dutkiewicz, 1981). Some people are extremely sensitive to chromium (VI) or chromium (III). Allergic reactions consisting of severe redness and swelling of the skin have been noted. Cr (VI) is less stable when compared to Cr(III) but Cr (VI) is a very strong oxidizing agent. The main reason why Cr (VI) is so toxic is that one of the reduction products of Cr (VI) is Cr (V). Chrome (V) is a known carcinogen and can accumulate in tissues to form cancerous growths (Cohen *et al*; 1993). In the body, the activity and action of enzymes on Cr (VI) will promote the formation of small quantities of Cr (V). However, as the size of this is normally too large to be adopted by a tissue, the Cr (V) will pass out. The only place where the Cr (V) is likely to lodge is in some of the fine capillaries in the kidneys, intestines or lungs (Gargas *et al*; 1994).

2.6 Nature of the Black Chin Tilapia (*Sarotherodon Melanotheron*)

The black chin tilapia, also known scientifically as *Sarotherodon melanotheron* is the commonest species of fish found in the Fosu lagoon. It is known locally by the Fante's as "Mpatoa", and forms about 95% of the fishes caught from the lagoon (EPA Ghana, 2006).

The species is West African in origin and inhabits brackish estuaries and lagoons from Senegal to Zaire (Trewavas, 1983). It is orange or gold dorsally and light blue ventrally. Patches of black in variable patterns are sometimes present. Males can sometimes exhibits an overall darkened body coloration as shown in appendix A. The mouth is small and the underside of the head (chin)

of adult males is black, hence the name black chin (Trewavas, 1983). A fully grown black chin can measure up to 25 cm in length. The species is primarily estuarine but is also found in fresh water and marine habitats (Jennings and Williams, 1992). Outside of its native range, black chin tilapia has been introduced to several countries across Asia, North America, and Europe (Wohlfarth and Hulata 1983). The species are known to be in abundance in their habitats. Spawning activities occur all year round but this declines during the raining season. The females prepare the nest for breeding and protect it whiles the males brood the fingerlings in their mouth. Black chin tilapias are known to reach sexual maturity at a very small body size (Jennings and Williams, 1992). Black chin tilapia exhibit 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 or fouling submerged hard surfaces (Hensley and Courtenay 1980; Diouf, 1996). The many small teeth, with their spoon-shaped crowns, are wellsuited to such a diet (Trewevas, 1983).

2.7 The Health Factor (K) for Fish

In 1902, Fulton proposed the use of a mathematical formula that would quantify the condition of fish:

$K = 100W/L^{3}$

where:

K: is the Condition Factor or Coefficient of Condition; often simply referred to as the "K factor".W: is the weight of the fish in grams (g).

L: is the fork length (measured from the tip of the snout to the mid-portion of the caudal fin) of the fish in centimeters.

The value of K is influenced by age of fish, sex, season, stage of maturation, fullness of gut, type of food consumed, amount of fat reserve and degree of muscular development. With females, the K value will decrease rapidly when the eggs are shed. The K value can also be used in determining the stocking rate of trout in particular water. If the K value reaches an unacceptably low level in water which is totally or partly dependent on stocking, the stocking rate can be reduced accordingly until the K value improves and reaches an acceptable level. The K value is necessary because it helps researchers to know the health condition of the fish samples they are working with. That is, it gives an idea as to whether the fishes in a particular environment are being stressed as a result of some pollutants before the research work is even done. Table 2.1 shows the condition of fishes using the K values.



K Values	Health Condition
1.60	Excellent condition
1.40	A good, well proportioned fish
1.20	A fair fish
1.00	A poor fish, long and thin
0.80	Extremely poor fish

Table 2.1 K values and the corresponding health condition

2.8 Pollution Monitors Used in This Study

2.8.1 Water

Water samples are normally used in almost all pollution research on water bodies to quantify the various pollutants in such waters especially heavy metal studies. For instance, using water samples Aksoy *et al*; (2005) demonstrated high concentrations of heavy metals in waters of Sultan Marsh and its environs in Turkey. Through water sample analysis, Awofolu *et al*; (2005) reported the occurrence of toxic metals in Tyme River in South Africa. Aksoy *et al*; (2005) and Liua *et al*; (2002) reported that through atmospheric pollution, effluent discharges (from both domestic and industrial sources), use of agricultural chemicals, eroded soils, and domestic and industrial waste, water bodies have been the recipient of toxic substances including heavy metals.

2.8.2 Sediment

Heavy metals discharge into a river system by natural or anthropogenic sources are distributed between the aqueous phase and bed sediments (Sin *et al*; 2001). Sediment can provide a deeper insight into the long term pollution state of a water body (Awofolu *et al*; 2005). The analysis of river sediments is a useful method to study the metal pollution in an area (Sin *et al*; 2001).



2.8.3 Fish

In recent years, there has been an increasing interest in the utilization of fishes as bioindicators of the integrity of aquatic environmental systems (Fausch *et al*; 1990). The good response of fish to environmental change makes it suitable for use as an environmental pollution indicator. Fish is a good bioindicator because it is easy to obtain in large quantities, has the potential to accumulate metals, optimum size for analysis and also is easy to be sampled (Batvari *et al*; 2007).



CHAPTER THREE

METHODOLOGY

3.1 Sampling Area

The Fosu Lagoon is located in the Cape Coast municipality. The Municipality occupies an area of 122 Km² and is dominated by batholith and is generally undulating with steep slopes. There are valleys of various streams between the hills, with Kakum being the largest stream. The small streams end in wetlands, the largest of which drains into the Fosu Lagoon at Bakano, a suburb of Cape Coast. The soils of the municipality are generally lateritic and are derived from the weathered granite and schist. The soil profile shows a topsoil of about 0.33 m. In the valleys and swampy areas, fine sandy deposits occur extensively (Armah and Amlalo, 1998). The District has double maxima rainfall totalling between 750 mm and 1000 mm. The major rainy season occurs between May to July and the minor around September to October. Cape Coast is a humid area with mean monthly relative humidity varying between 75% and 85%. The sea breeze has a moderating effect on the local climate. The present vegetation of the municipality consists of shrubs of about 1.5 m high, grasses and a few scattered trees. The major economic activity in the southern coast is fishing (Bannerman *et al*; 2001).

The geographical coordinates of the Fosu lagoon are 5^0 7'N and 1^0 16'W. The main economic activity that goes on in the lagoon is fishing. The commonest and most abundant fish in the lagoon is the black chin tilapia. Some economic activities also go on at sites very close to the banks of the lagoon. The commonest are the various automobile garages at Siwdu and some

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palm kernel oil producers at the Adisadel village. Apart from these, there are lots of residential settlements which are also close to the lagoon. Wastes from all these human activities flow directly into the lagoon without any prior treatment. Due to the polluted nature of the lagoon, the Fosu lagoon is now one of the water bodies with "Dead zones" in the world (UNEP, 2006).

3.2 Sampling Locations

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Samples were collected from twelve different points in the lagoon to represent both the wet and dry seasons, six for each season. Wet season samples were collected in the month of September, 2010 and that of the dry season were collected in January, 2011. A map showing sampling points on the lagoon is represented in figure 1.





Fig. 1 A map showing the Fosu Lagoon and the sampling points.

Sampling points one and two were located at the area where the lagoon enters the sea called "Bakaano". Points three and four were located in the middle part of the lagoon just behind the Cape Coast stadium at "Siwdu", and lastly points five and six were located at the portion of the lagoon which is just behind the garages close to "Adisadel village". Even though samples for the wet and dry seasons were collected around the same area in the lagoon, it was not from the same points. That is, the samples for the dry season were collected a few meters away from where it was collected in the wet season. This has been shown in figure 1, with the red points representing

sampling points for the dry season. The points shown in the map above are not the exact sampling points but just to represent how sampling was done.

3.2.1 Water Sampling

The collection of water samples from the lagoon was performed wearing polyethylene glove. One litre polyethylene bottles were washed with 5% nitric acid, distilled water and then dried in an oven, before being used for collection of the water samples. At each sampling point, the bottles were rinsed three times with the lagoon water before collection of the sample. Each bottle was immersed at about 8 cm below the water surface. The collected water samples were acidified before being transported to the laboratory for analysis.

3.2.2 Sediment Sampling

Sediment samples were collected with a plastic scooper. The scooper was used to scoop soil sample from the lagoon bed and placed in polyethylene bags that had previously been cleaned with 5% nitric acid, distilled water and oven dried, before being transported to the laboratory. At the laboratory, the sediment samples were air dried at room temperature in an open dust free environment for three days. Organic debris and other unwanted materials were handpicked from the samples. The dried sediment samples were ground and sieved using 2mm sieve. Samples were then transferred into polyethylene bags and stored until day of analysis.
3.2.3 Fish Sampling

Fish samples were bought from the fishermen who fish from the lagoon. The main fish caught from the lagoon is the black chin tilapia *Sarotherodon melanotheron*. The fish samples were washed and their length (fork length) and weight measured. Fish samples were kept frozen in an ice chest and transported to the laboratory where it was kept frozen in a deep freezer until day of analysis.

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3.3 Laboratory Procedures

All laboratory analysis was performed at the Eco-Lab of the University of Ghana. With the water and sediment samples, some physicochemical parameters were measured in addition to the heavy metal analysis. The Perkin-Elmer flame atomic absorption spectrophotometer (AAS) was used to measure the heavy metals in the samples. All chemicals used in the laboratory analysis are listed below:

- ✤ 97% H₂SO₄ (BDH)
- ✤ 99.7% Ascorbic Acid (BDH)
- ✤ 69 79% HNO₃ (BDH)
- ✤ 60% HClO₃ (BDH)
- ✤ NH₃ (Reagent grade)
- Sodiumhexametaphosphate (MW: 611.79)

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3.3.1 Analysis of Water Samples

All physicochemical parameters were measured within 32 hours after samples were taken. pH and conductivity were measured on site using Metrohm 691 pH meter and Metrohm E587 conductometer respectively. Concentrations of chloride and nitrate were measured using the All Solid State Ion Selective Electrodes. This was done by first measuring 50 ml each of water samples into 100 ml beakers. The electrode of the parameter to be measured (eg. Chloride electrode) together with its reference electrode, were inserted into the water sample. The measured figures were then displayed on a screen and recorded. The meter was calibrated with distilled water and standard solution of the parameter to be measured prior to measurement. With the phosphate measurement, phosphorous was first measured and the value obtained was used to generate the phosphate level. The Lamder 45 uv/vis Spectrometer (λ = 890.4 Hz) was used to measure this. First 10 ml of the water was measured into a 50 ml volumetric flask. Two drops of phenolphthalein was then added followed by a drop of ammonia. Lastly, 5 ml of 99.7% ascorbic acid was added to generate the colour and the volume of the water topped to the 50 ml mark. The flask was then placed in the compartment box of the Lamder spectrometer for the measurement of phosphorous after the machine had been calibrated with distilled water and standard solutions.

Heavy metal content in the water samples were measured with the Analyst 400 Perkin-Elmer atomic absorption spectrophotometer according to the method prescribed by Serfor-Armah, *et al*; (2006). The water sample was first filtered with Whatman No. 0.45 filter paper, after which 50ml of the filtrate was acidified with 50% nitric acid to give a pH of 1. The AAS was calibrated with standard solutions and de-ionized water before heavy metal concentrations in water samples were measured.

3.3.2 Chemical Analysis of Sediment Samples

In measuring heavy metal content in sediment samples, samples were first digested by weighing 1 g each into digestion tubes. 25 ml of ternary mixture (500 ml HNO_3 , 20 ml $HClO_4$ and 50 ml H_2SO_4) was then added to the samples in the digestion tubes and the mixture was heated in a digestion block inside a fume chamber. The mixture was heated gently initially and then strongly until all the yellow fumes turned white. The mixture was then filtered into 50 ml volumetric flask using Whatman No. 0.45 filter paper. The volume was then made up to the mark by topping it up with distilled water. The AAS was calibrated with standard solutions of the respective metals and de-ionized water before it was used to measure the levels of heavy metals in the digested samples.

pH and conductivity of the soil samples were determined by measuring 10 g of the sediment samples into 20 ml of distilled water and stirring for 15 minutes after which measurement were made with the pH meter and conductometer.

Particle size analysis of the sediment samples were performed using the Bouyoucos Hydrometer. Fourty grams (40 g) of sediment sample were weighed into a clean plastic bottle and 100 ml of 5% Calgon solution (sodium hexametaphosphate) was added to the weighed sample. The mixture was placed on a mechanical shaker and shaken for one hour. The suspension was then transferred into a 1000 ml measuring cylinder by washing with distilled water from a washbottle, bringing the final volume to 1000 ml and cooled to room temperature. The temperature of the suspension was measured when it became constant and a plunger was then inserted into it, moving it up and down to mix the content thoroughly. A stop watch was started immediately and the hydrometer was simultaneously lowered gently into the suspension. The hydrometer was read after five minutes. A second reading was taken four hours later. The suspension was then poured into a 47 micron sieve and the affluent discarded. The residue on the sieve was agitated by running tap water from a tube onto it. When the washing was clear, the sand particles was transferred into a beaker and dried in an oven at 105°C overnight. The particles were then weighed to get the weight of sand (WS). Another 40 g of sample was weighed into a moisture can and dried in an oven at 105 °C overnight. After drying, sample was re-weighed to get the dry weight (i.e. dry weight of sediment sample, DW).

The weight of the sand was obtained by weighing the oven dry fraction collected on the sieve. The reading taken after five minutes with hydrometer was the weight of silt and clay fraction (WSC) in the sample and the one taken after four hours was the weight of clay (WC). Hence, the silt fraction can be calculated from the difference.

i.e. weight of silt (WSI) = WSC - WC

1. % Sand =
$$\frac{WS}{40} \times 100$$

2. % Silt = $\frac{WSI}{DW} \times 100$
3. % Clay = $\frac{WC}{DW} \times 100$

Where WSI and WC are weights of silt and clay respectively.

3.3.3 Work Done on Fish Samples

The length and weight of the fish samples were measured prior to preservation. The physical characteristics of the sampled fish species were assessed. The ratio between the fish whole body weight to body length (head to tail) was calculated to identify fishes with anomalously high or low ratios. The overall health of fish species in the lagoon were assessed using the method developed by Williams (2000). A health factor (K) was calculated using the equation:

$K = 100W/L^3$

Where, W = body weight in grams; L = body length (fork length) in cm.

The fish samples were washed with distilled water and dried in a hot air oven at 105^oC for 48 hours. The wet digestion method was used in digestion of fish tissues. The dried muscles of the fish were removed with steel blade and plastic forceps and grounded into powder. 2 g of these were digested with 25 ml of a mixture of 500 ml concentrated nitric acid and 20 ml perchloric acid in digestion tubes inside a fume chamber. The sample mixture was then filtered and the filtrate was analyzed for heavy metals using the AAS. The AAS was calibrated with standard solutions and de-ionised water before measurement was made. Ten fish samples were used in all.

The concentration of the target metals in fish samples were compared with the standards of the U.S. Food and Nutrition Board with regards to the daily recommended intake as shown Table 3.1 below.

Table 3.1 Recommended Daily Intakes of Heavy Metals



*- of no nutritional value

3.4 Statistical Procedures

Various interrelationships among elemental concentrations in water and sediment samples obtained at individual sampling points and between different elements were analysed using Microsoft Excel 2007 software. Metal concentrations in water and sediment samples were analysed using Pearson's correlation coefficients. The element-element and water-sediment correlation coefficients that were derived determined the extent to which concentrations of metals in sediments and water samples and between elements in both water and sediment samples interrelated with each other.

3.5 Pollution Indices

Commonly used methods in analyzing pollution intensity in the environments are the Contamination Factor (CF), and the Geoaccumulation Index (Igeo) (Tomlinson *et al*; 1980). Indices make it possible for the quality of the environment to be quantified and easily understood by non-specialists (Tomilson et al; 1980). Additionally, indices are useful for making comparisons on the pollution status of different areas of the environment. Concentrations of metals in water samples were compared with acceptable limits for water quality (guidelines) offered by the US Environmental Protection Agency National Recommended Water Quality Criteria (USEPA, 2010). These are presented in Table 3.2.

Table 3.2 USEPA recommended criteria for surface water

CEE	N A A
Element	Criteria (ppm)
Iron (Fe)	*
Lead (Pb)	0.065
Chromium (Cr)	0.57
Nickel (Ni)	0.47
Zinc (Zn)	SANE 0.12
Copper (Cu)	1.3
Managese (Mn)	*
Cadmium (Cd)	0.34

* no known standard

3.6 Geoaccumulation Index

The geoaccumulation index (I_{geo}) has been used since the late 1960s, and has been widely employed in European trace metal studies (Yaqin *et al*; 2008). Originally used for bottom sediments, it has been successfully applied to the measurement of soil pollution (Cabrera *et al*; 1999; Grzebisz *et al*; 2002; Yaqin *et al*; 2008, Okweye *et al*; 2009). The Igeo values enable the assessment of pollution by comparing current and pre-industrial concentrations, although it is not always easy to reach pre-industrial sediment layers (Yaqin *et al*; 2008). Geoaccumulation Index is calculated using the formula;

 $I_{geo} = Log_2(Cn/1.5 \times Bn)$

where Cn is the measured concentration of the element in soil or sediment, Bn is the world average shale background value and 1.5 is a constant. The constant 1.5 allows for analyses of natural fluctuations in the content of a given substance in the environment and to detect very small anthropogenic influences (Teng *et al*; 2004; Lokeshwari and Chandrappa, 2007; Yaqin *et al*; 2008). The equation indicates that the index will be affected by the content of the samples and the geochemical background values. The world average shale, Earth's crust, and the world average soil are some of the materials often used to provide background values (Turekian and Wedepohl, 1961; Karbassi *et al*; 2008; Yaqin *et al*; 2008). The world average shale concentrations of elements of interest are either directly measured in texturally equivalent uncontaminated sediments or size fractions or taken from literature (Teng *et al*; 2004). Table 3.3 shows the target metals and their corresponding background concentration values (Wehepohl, 1961, Bowen, 1979).

Elements	World Average Concentration Background Values (mg/Kg)
Iron	47200
Lead	20
Chromium	111
Nickel	50
Zinc	30
Copper	45
Manganese	850
Cadmium	0.30

The geoaccumulation index consists of 7 grades or classes (Grzebisz et al; 2002; Lokeshwari and

Table 3.3 World average shale concentrations of target metals

Chandrappa, 2007; Yaqin *et al*; 2008). Class 7 is an open class and comprises all values of the index higher than class 6. The elemental concentrations in class 7 may be hundredfold greater than the geochemical background value (Teng *et al*; 2004; Lokeshwari and Chandrappa, 2007; Yaqin *et al*; 2008). A Igeo value greater than five, falls under class 6 and implies an extreme contamination level. Values between 4 and 5 are in class 5 and imply an extreme or strongly contaminated environment. A Igeo value between 3 and 4 means an Igeo class of 4 and imply a strongly contaminated environment. Values between 2 and 3 are in class 3 and means the environment is moderately to strongly contaminated. Those that are between 1 and 2 fall in class 2 and imply a moderate level of contamination. Values between 0 and 1 are in class 1 and means moderately to uncontaminated environment. Lastly, values below zero are indication of an uncontaminated environment.

CHAPTER FOUR

RESULTS

4.1 RESULTS OF WATER SAMPLES

Generally, it was observed that heavy metals content in water samples were very low as compared to that of the sediment samples. Field results of all measurements made can be found in the appendix B and C.

Parameter	Range	Range Mean		
PH	7.43 – 8.18	7.87	0.30	
Conductivity (µS/cm)	2250 - 5500	3291.67	1166.37	
PO_4 (mg/l)	1.29 – 10.06	4.59	3.10	
NO_3^- (mg/l)	102.82 – 197.80	131.93	34.32	
NH4 ⁺ (mg/l)	2.74 - 4.97	3.51	0.82	
Cl ⁻ (mg/l)	799.18 – 2006.75	1192.06	430.17	
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 Table 4.1 Results of Physicochemical Parameters Analysed in Water Samples (wet season)

Table 4.1 shows summarized values of measurement made in the wet season. The lagoon recorded a mean pH of 7.87 during the wet season which implies the water was slightly basic. The highest pH of 8.18 was recorded at point whiles the lowest pH of 7.43 was at point 2. Conductivity values recorded for this season were much higher as compared to the World Health Organization's recommended standard of 1000 μ S/cm. The highest value of 5500 μ S/cm was

recorded at sampling point 2 whiles the lowest of 2250 μ S/cm was at point 5. With phosphate measurements, point 2 recorded the highest value of 10.06 mg/L and point 3 the lowest, 1.29 mg/L. Point 3 recorded the highest level of nitrate, 197.80 mg/L, and point 2 recorded the lowest of 102.83 mg/L. The highest value of 2006.75 mg/L for chloride was recorded at point 2 and the lowest of 799.18 mg/L was at point 5. With NH₄⁺, the highest value was recorded at point 2, (4.97 mg/L) and the least of 2.74 mg/L was recorded at point 5.

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Table 4.2 Results of Physicochemical Analysis on Water Samples (dry season)

Parameter	Range	Mean	Standard deviation (±)
РН	7.92 - 9.80	8.99	0.68
Conductivity (µS/cm)	4350 - 5200	4816.67	341.57
PO ₄ ⁻ (mg/l)	0.197 – 0.780	0.48	0.25
NO_3^- (mg/l)	16.07 – 33.83	22.19	6.38
$\mathrm{NH_4^+}(\mathrm{mg/l})$	2.30 - 3.01	2.59	0.26
Cl ⁻ (mg/l)	777.55 – <mark>949.95</mark>	895.83	68.30

As shown it table 4.2, the pH levels for the dry season samples were higher than those of the wet season. This implies the lagoon water is more basic in the dry season than in the wet season. The highest pH of 9.80 was recorded at point 3 and the lowest of 7.92 at point 5. Conductivity values for the dry season were much higher than those of the wet season even though the overall highest value was recorded in the wet season. The highest for the dry season was 5200 μ S/cm and was recorded at point 3. The lowest of 4350 μ S/cm was at point 2. The highest PO₄⁻ concentration of

0.780ppm was recorded at point 3 with the lowest of 0.197 ppm at point 1. NO_3^- concentrations for the dry season were quiet low when compared to the wet season concentrations. The highest for the dry season was recorded at point 2 (33.83 mg/L) whiles the lowest of 16.07 mg/L was recorded at point 5. Cl⁻ concentrations recorded for the dry season were low, with the highest level of 949.95 ppm at point 6 and the lowest of 777.55 ppm at point 1. NH_4^+ concentrations recorded for the dry season were almost the same as those of the wet season, with the highest concentration of 3.01 mg/L being recorded at point 1 and the lowest of 2.30 mg/L also recorded at point 5 with a mean value of 2.59 mg/L.

Matala (malaa)	Damas (ma/las)	Maan	Standard deviation (1)
Metals (mg/kg)	Range (mg/kg)	wiean	Standard deviation (\pm)
		1 1	135
Fe	BDL		1373
			ALL S
~			
Cu	BDL	>	-
		1	
Mn	BDL	200	
1,111	DDD		
Cr	BDL		-
	121 2		3
Ni	BDL	_	
	40		- ADT
Dh	1 25 6 85	5.00	1.00
10	4.23 - 0.83	5.00	1.00
	3	ANE	
Cd	0.05 - 0.7	0.30	0.25
7	DDI		
Zn	BDL	-	-

Table 4.3 Concentrations of Heavy Metals in Water Samples during the Wet Season

BDL- below detection limit

Range, mean and standard deviation of heavy metal concentration recorded during the wet sason are presented in table 4.3.With the exception of lead and cadmium, all other target metals were below detection limit at the time of sampling during the wet season. The highest concentration of lead (6.85 mg/kg) was recorded at point 2 whiles the lowest of (4.25 mg/kg) was at point 3. However, lead concentration at point 6 was below detection limit. Cadmium recorded very low concentrations with the highest value of 0.7 mg/kg recorded at point 2 and the least value of 0.05 mg/kg at points 4 and 5 as presented in appendix B.



Table 4.4 Results of Heavy Metal Concentrations in Fosu Lagoon Water Samples for the

Kin

Dry	Season
-----	--------

Metals (mg/kg)	Range (mg/kg)	Mean	Standard deviation (±)
Fe	0.50 - 1.00	0.50	0.15
Cu	0.05 - 0.55	0.15	0.20
		KAA	
Mn	0.75 – 1.15	1.00	0.15
	1000	E Lister	
Cr	BDL	T OIL	-
Ni	0.45 - 0.80	0.50	0.15
Pb	BDL		3
	121 1		2
Cd	0.60 - 2.65	1.50	0.85
	S COP	E BAP	
Zn	3.20 - 4.35	4.00	0.40
	135	ANE NO	

BDL - Concentrations were below detection limit

Range, mean and standard deviation of heavy metal concentration from the Fosu Lagoon during the dry season are presented in table 4.4. Generally, concentrations of the metals recorded in the water samples were very low. However, the dry season samples recorded much higher levels than the wet season sample. Iron concentrations at the various sampling points were very close. The highest concentration of iron in the dry season samples was recorded at point 1 (1.00 mg/kg), and the lowest at point 6 (0.50 mg/kg) as presented in table 4.4. Copper concentrations were very low, with the highest value (0.55 mg/kg) being recorded at point 4 and the lowest (0.05 mg/kg) at point 2. The highest concentration of manganese (1.15 mg/kg) was at point 6 and the lowest value of 0.75 kg/mg was at point 2. The concentrations of chromium and lead in all the samples were below detection limit. The highest concentration of nickel (0.80 mg/kg) was at point 6, whiles points 2, 3 and 4 recorded the same least values of 0.45 mg/kg. Cadmium and zinc recorded highest concentrations of 2.65 mg/kg and 4.35 mg/kg at points 6 and 3 respectively. The lowest for cadmium (0.60 mg/kg) was at point 3 whiles that of zinc (3.20 mg/kg) was at point 5.



4.2 RESULTS OF SEDIMENT SAMPLES FROM THE FOSU LAGOON

Table 4.5 Range, Mean and Standard Deviation of Some Parameters Measured in theSediment Samples from the Fosu Lagoon during the Wet Season

Parameters	Range	Mean	Standard dev. (±)
рН	6.370 - 7.330	17.05	0.36
Conductivity (µS/cm)	1100 - 3000	2066.67	771.79
Fe (mg/kg)	114.80 - 135.80	130	8.00
Cu (mg/kg)	0.30 - 0.15	1.50	1.00
Mn (mg/kg)	11.65 – 543.50	235	185
Cr (mg/kg)	0.05 - 0.15	0.10	0.05
Ni (mg/kg)	0.50 - 1.35	0.50	0.50
Pb (mg/kg)	2.70 - 18.90	8.50	5.50
Cd (mg/kg)	0.20 - 0.65	0.50	0.20
Zn (mg/kg)	28.4 - 124.35	79	37.00

Range, mean and standard deviation of heavy metal concentration as well as that of the pH and conductivity in the wet season sediment samples from the Fosu Lagoon are represented in table 4.5. As shown in the table, the mean pH of the sediment samples for the wet season was 7.05. This makes the sediment of the lagoon neutral. pH of the sediment range from 6.37 at point 2 to 7.33 at point 5 are represented in appendix C. Conductivity measurements of the sediment at this season were lower as compared to that of the water samples in the same season. The highest conductivity value for the sediment samples was 3000 μ S/cm and was recorded at sampling

point 3whiles the lowest of 1100 μ S/cm was recorded at point 6. Generally, all the heavy metal levels in the sediment samples were higher than those of the water samples. Iron recorded the highest concentration with an average of 130 mg/kg. The highest concentration of iron (135.8 mg/kg) was at point 5 and the lowest of 114.8 mg/kg at point 2. Copper recorded an average concentration of 1.50 mg/kg. Concentration of copper in the samples ranged from 0.30 – 2.95 mg/kg with the highest of 2.95 mg/kg recorded at point 6 and the lowest at point 1. Concentrations of manganese were very high with an average value of 235 mg/kg. The highest value of 543.50 mg/kg was recorded at point 6 and the lowest of 11.65 mg/kg was at point 2. Chromium and cadmium concentrations were very low with average values of 0.1 mg/kg and 0.5 mg/kg respectively. Nickel also had low concentrations with the highest value of 1.35 mg/kg recorded at point 3. Lead and zinc concentrations also recorded average values of 8.50 mg/kg and 79 mg/kg respectively. The highest concentration of lead (18.90 mg/kg) was recorded at point 2 and the lowest (2.70 mg/kg) at point 5 whiles the highest for zinc (124.35 mg/kg) was also at point 6 and the lowest (28.4 mg/kg) was at point 2.



Parameters	Range	Mean	Standard dev. (±)
pH	10.680 - 10.870	10.79	0.07
Conductivity (µS/cm)	5200 - 5500	5333.33	121.11
Fe (mg/kg)	1305.5 – 1341.50	1275.25	104.73
Cu (mg/kg)	0.65 - 1.40	1.01	0.32
Mn (mg/kg)	191.85 - 300.40	236.72	37.78
Cr (mg/kg)	0.85 – 3.40	2.24	0.83
Ni (mg/kg)	2.15 - 4.10	3.43	0.66
Pb (mg/kg)	11.85 – 15.15	14.22	1.21
Cd (mg/kg)	3.10 - 4.80	4.31	10.66
Zn (mg/kg)	11.95 – 27.05	22.78	5.56

Table 4.6 Results of Heavy Metal Concentration, pH and Conductivity of the Dry SeasonSediment Samples from the Fosu Lagoon.

Summary of results of heavy metal concentrations, PH and electrical conductivity for the dry season samples from the Fosu lagoon is represented in table 4.6 above. Mean pH for the dry season samples showed that the lagoon sediment is basic. pH ranged from 10.68 at point 1 to 10.87 at point 5 with a mean value of 10.79 during the period of sampling. Conductivity values for the dry season sediment samples were also high, with the highest value of 5500 μ S/cm recorded at sampling point 5 and the lowest value of 5200 μ S/cm at points 2 and 3 as represented in appendix C.

Iron concentrations for the dry season samples recorded an extremely high value of 1341.50 mg/kg at point 5. Iron concentrations were very high in all the samples with an average of 1275.25 mg/kg. Copper had highest concentration of 1.40 mg/kg at point 4 and the lowest of 0.85 mg/kg at point 6 with an average value of 2.24 mg/kg. The highest concentration of manganese (300.40 mg/kg) was at point 5 and the lowest of 191.85 was at point 3. Concentrations of chromium ranged from 0.35 – 3.40 mg/kg, these were recorded at points 6 and 4 respectively. The highest concentration of nickel was 4.10 mg/kg and was at point 4 whiles the lowest of 2.15 mg/kg was recorded at point 6. Lead recorded a mean concentration of 14.22 mg/kg with the highest concentration of 15.15 mg/kg recorded at point 1 and lowest value of 11.85 kg/kg also recorded at point 6. The highest concentration of cadmium was 4.80 mg/kg and was recorded at point 4 whiles the lowest value of 3.10 mg/kg was observed at point 6. Lastly, zinc had an average concentration of 22.78 mg/kg and recorded the highest concentration of 27.05 mg/kg at point 6. The least concentration of zinc (11.95 mg/kg) was also recorded at point 3.



sample	% sand	% silt	% clay
1	60.34	1.38	29.32
2	59.2	5.83	34.98
3	62.34	6.82	30.82
4	66.88	6.62	33.11
5	68.50	5.73	25.80
6	63.30	6.70	30.00
Average	63.43	5.51	30.67

Table 4.7 Results of Soil texture Analysis of the Sediments from the Fosu lagoon

The results of percentage fractions of the components of the sediments from the Fosu lagoon is represented in table 4.7. The sediments had mean composition of 63.43% sand, 5.51% silt and 30.67% clay. The soil texture pyramid was used to interpretate the results of the sediment composition and it was concluded that the lagoon sediment is sandy clayey in nature.



4.3 Test Results for Fish Samples

Sample No.	Length (cm)	Weight (g)	Condition factor (K)
1	11.2	20.1	1.43
2	11.0	19.4	1.46
3	10.5	18.3	1.58
4	10.4	18.1	1.61
5	8.3	9.9	1.73
6	8.3	9.7	1.70
7	7.9	8.1	1.64
8	6.5	5.2	1.89
9	6.2	4.6	1.93
10	6.0	4.4	1.92

Table 4.8 Physical Characteristics of Fish Samples Obtained from the Fosu Lagoon

Comparing the K values in the Table 4.8 to that of Table 2.1, it can be concluded that all the fishes used in this exercise were in good health and under no form of stress in their habitat. It was also observed that the length of the fish was directly proportional to it weight.

 Table 4.9 Concentration of heavy metals in muscles of fish samples (mg/kg) from the Fosu

 Lagoon

Metals (mg/kg)	Range (mg/kg)	Mean (mg/kg)	Standard deviation (±)
Fe	5.50 - 18.10	9.98	4.17
Cu	0.10 - 0.35	0.22	0.08
Mn	20.95 - 32.30	27.89 C T	4.15
Cr	BDL	11051	-
Ni	0.032 - 0.55	1.16	0.32
Pb	4.00 - 10.80	6.75	2.28
Cd	1.65 - 3.20	2.75	0.47
Zn	18.25 - 23.15	20.66	1.51

BDL - below detection limit

Summary of results of heavy metal concentration in the fish samples from the Fosu lagoon is presented in table 4.9. In measuring the concentration of heavy metals in fish 10 fish samples were used. Concentration of iron in the fish samples ranged between 5.50 - 18.10 mg/kg with a mean concentration of 9.98 mg/kg and a standard deviation of 4.17. The concentration of copper in all fish samples was very low with the highest concentration of 0.35mg/kg and a minimum concentration of 0.10 mg/kg. Manganese recorded a maximum concentration of 32.30 mg/kg. Concentrations of Chromium were below detection limit for all the fish samples analysed. Nickel recorded the highest concentration of 0.55mg/kg in the fish samples and the least concentration of 0.032mg/kg. The highest concentration of lead was 10.80 mg/kg whiles the least was 4.00

mg/kg. Cadmium and zinc recorded highest concentrations of 3.20 mg/kg and 23.15 mg/kg respectively and with least values of 1.65 mg/kg and 18.25 mg/kg. Raw results of heavy metal concentrations in fish samples can be found in the appendix D.

Interactions with some fishermen and fish consumers revealed that about eleven pieces of the black chin tilapia are consumed on the average per meal per person. This represents about 138.6 g by weight of fish consumed per person. Hence, an estimate on amount of each metal consumed per meal was generated and is shown in table 4.10 below.

 Table 4.10. Average concentration of heavy metals ingested per meal (mg)

F	Metals	Levels(mg)	Z
7	Fe	15.22	R
	Cu	0.34	3
IZ	Mn	10.52	
TES	Cr	0	1
-	Ni	1.77	AN
	Pb	10.29	
	Cd	4.19	
	Zn	31.50	

4.4 Geoaccumulation Indices (Igeo) of Metals in The Sediment of The Fosu Lagoon

 I_{geo} values were used to check for the level of contamination of the sediment samples by the respective metals. Table 4.11 below shows calculated values of I_{geo} .

Metals(sediment)	Wet season	Dry season
Fe	16.321	19.614
	N. 1.1.	1
Cu	-0.059	-0.737
Mn	11.378	11.389
		1
Cr	-4.506	1.736
	ELCF	(HH
Ni	-1.099	1.202
	6 43	SON /
Pb	1.146	1.921
	unos	
Cd	-9.288	-5.878
Zn	4.985	3.189
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Table 4.11 Igeo for Sediment Samples

The table shows very high I_{geo} values of iron for both seasons, which implies the lagoon sediment is extremely contaminated with iron. However, copper shows negative values for both seasons and so is cadmium. This means sediment samples have no copper and cadmium contaminants. Manganese also shows very high I_{geo} values for both seasons and thus just like iron, the lagoon sediment is also extremely contaminated with manganese as well. Chromium shows no contamination for the wet season but moderate contamination for the dry season. Similarly, sediment samples show no contamination of nickel for the wet season but are moderately contaminated in the dry season. I_{geo} values for lead imply that the lagoon sediment is moderately contaminated with the metal. Values for zinc implies an I_{geo} class of 4 which means sediment is strongly contaminated with zinc.

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4.5 Element - Element Correlation Coefficients

The interrelationships between elements in water samples were determined using Pearson correlation coefficients. The coefficients were grouped according to the classification as shown in Table 4.12.

Table 4.12 Correlation Coefficient Classification

Ranges of Coefficients	Classification
-0.75 to -1	Very strong negative correlation
-0.5 to -0.75	Moderately strong negative correlation
-0.25 to -0.5	Moderately weak negative correlation
0 to -0.25	Very weak negative correlation
0 to 0.25	Very weak positive correlation
0.25 to 0.5	Moderately weak positive correlation
0.5 to 0.75	Moderately strong positive correlation
0.75 to 1	Very strong positive correlation

4.5.1 Correlation Coefficients of Metal in Water Samples from the Fosu Lagoon

Lead and cadmium were the only element detected in the water samples for the wet season and with correlation coefficient of 0.505, it implies these two shows moderately strong positive correlation. Correlations of elements in water for the dry season are shown Table 4.13.



Iron showed negative correlations with all the elements. Fe – Ni, and Fe – Cd were moderately weak negative correlated whiles Fe – Cu and Fe – Zn showed very weak negative correlation. With the exception of Mn, copper also showed negative correlations with all the elements with Cu - Ni and Cu - Cd showing moderately weak negatively correlated. Mn – Ni and Mn – Cd had strong positive correlation whiles the other elements had negative correlation with Mn. The

entire elements paired with Ni were negatively correlated with the exception of Cd which was strongly correlated positively with Ni. Again, Cd had a negative correlation with all the other metals.



 Table 4.14 Results of Correlation Coefficient of Metals in Wet Season Sediment Samples

 from the Fosu Lagoon

Iron showed positive correlations with all elements except chromium. Zn showed a strong positive correlation with Fe whiles Ni showed very weak positive correlation with Fe. Copper also had positive correlations with the other metals except chromium which had weakly negative correlation with copper. Cadmium with correlation value of 0.86 exhibited the strongest positive correlation with copper. Mn had moderately strong negative correlation with Cr and Ni, and had positive correlations with the rest of the metals. Mn – Fe and Mn – Zn had very strong positive

correlations with correlation coefficients of 0.78 and 0.79 respectively. With the exception of nickel which had very weakly positive correlation with chromium, all the other metals were negatively correlated to Cr. Cr – Fe had the strongest negative correlation with a correlation coefficient of -0.98. Nickel on the other hand, had positive correlations with all the metal except Mn which showed moderately strong netative correlation with Ni. Ni – Pb had the strongest positive correlation with a correlation coefficient of 0.44. Lead had positive correlations with all the metals but had moderately strong negative correlation with chromium. Pb – Fe, Pb – Cu, Pb – Cd and Pb – Zn all had moderately strong positive correlations with correlation coefficients of 0.63, 0.65, 0.75 and 0.86 respectively. Except Cr which was negatively correlated with Cd, all the other metals had strong positive correlations with Cd. Cd – Ni however, had very weak positive correlation with correlation coefficient of 0.16. Again, Zn also had strong positive correlations with all the metals except for Cr which had strong negative correlation with zinc. Zn – Fe and Zn – Pb had the strongest positive correlations with the same correlation with zinc.



4.5.2 Correlation Coefficients of Metals in Sediment Samples from the Fosu Lagoon

 Table 4.15 Results of Correlation of Metals in the Dry Season Sediment Samples from the

 Fosu Lagoon



Iron had very strong positive correlations with all the metals, with Fe – Ni having the strongest positive correlation with a correlation coefficient of 0.98. Cu – Mn had weak negative correlat with a correlation coefficient of -0.46. The strongest correlation for Cu was exhibited by Cu – Cr with a correlation coefficient of 0.82. Manganese had weak correlations with all the metals. Mn – Cd had the weakest correlation with a correlation coefficient of 0.03. Apart from Cr – Mn, chromium also had very strong positive correlations with the other metals. Again, correlations Ni, Pb, Cd and Zn all follow the same patterns as that of Cr. Zn – Pb had the highest strong positive correlation with a correlation coefficient of 0.99.

4.5.3 Correlation Coefficients of Metals in Fish Samples

 Table 4.16 Results of Correlation of Metals in Water Samples and in Fish Samples from the

 Fosu Lagoon



Iron had weak negative correlations with most of the metals. Fe – Pb had the strongest negative correlation with a correlation coefficient of -0.66. Copper had moderately weak negative correlations with Mn and Pb, and Cu – Cd had the strongest positive correlation with a coefficient of 0.76. Mn also had negative correlations with Cu, Ni and Zn, and a strong positive correlation with lead. Nickel had a strong positive correlation with lead and a strong negative correlation with manganese with correlation coefficients of 0.90 and -0.72 respectively. Lead had strong negative correlation with iron with a correlation coefficient of -0.66. Cadmium and zinc also had negative correlations with iron. Cd had a strong positive

correlations with Cu, whiles Zn had a moderately strong positive correlation with Cd with correlation coefficients of 0.76 and 0.40 respectively.

Table 4.17 Results of Correlation of Metals in Sediment Samples and in Fish Samples from the Fosu Lagoon



Apart from Mn and Ni, Fe had positive correlations with the rest of the metals with Fe – Cu having the strongest positive correlation with a correlation coefficient of 0.72. Copper had moderately strong negative correlation with Pb and a weak positive correlation with Ni. Mn had a moderately weak negative correlation with Fe and a strong positive correlation with zinc with correlation coefficients of -0.35 and 0.71 respectively. Except for, nickel had positive correlations with the rest of the metals. Nickel had a strong positive correlation with lead with a correlation coefficient of 0.81. Lead had a strong positive correlation with

itself and a weak negative correlation Cd. Cadmium had weak negative correlations with lead and zinc and moderately weak positive correlations with Fe and Mn with correlation coefficients of 0.42 and 0.49 respectively. Zinc had very weak negative correlations with Cu and Cd and a strong positive correlation with Mn with a coefficient of 0.71.



CHAPTER FIVE

DISCUSSION OF RESULTS

5.1 Physicochemical Parameters

The water samples showed high levels of nutrients (i.e. PO_4^- and NO_3^-) in the wet season whiles pH and conductivity were higher in the dry season. The high level of nutrients in the wet season could be as a result of runoff water that enters the lagoon. Runoff water carries residual nutrients that are applied as fertilizers in farms nearby, and also household chemicals from surrounding settlements into the lagoon. Even though these nutrients are required by some aquatic plants for growth, too much of it can be detrimental to the lagoon. This is because too much nutrients will cause rapid growth of algae (algal bloom), which in turn can cause problems such as reduction in dissolved oxygen and water level to aquatic organisms (Dubrovsky, 2010). Threshold values for nutrients in water bodies normally differ by region or area where the water body is located (US Geological survey, 2004).

pH of the lagoon ranged 7.92 – 9.80 during the dry season which is higher than those recorded in the wet season. Normally, pH of water bodies depends on the type of rock underlying the water or from where the water takes it source and also to some extent on temperature. Normal pH for surface water should fall within the range 4.5–9.0 (USEPA, 2010). With mean pH values of 7.87 and 8.99 for the wet and dry seasons respectively, it can be stated that the pH of the lagoon water is thus acceptable and poses no threat to aquatic life. Conductivity of water is a measure of positive or negative ions present in the lagoon water. Conductivity of the lagoon water had mean values of 3291.67 μ S/cm and 4816.67 μ S/cm (Tables 4.1 and 4.2) for the wet and dry seasons respectively. Higher water temperature increases the movements of ions in water and thus increases conductivity (Dubrovsky, 2010), and this can explain the high conductivity values recorded at the various points during the dry season. Comparing these high values to the World Health Organization's threshold value of 1000 μ S/cm implies that the lagoon water has more than enough ions in it and this can be as a result of the presence of pollutants in it.

Chloride ions were also very high in the lagoon water especially those recorded for the wet season. The sea is the water body with the highest amount of chloride which is normally present as sodium chloride (Evans and Fric, 2001). When there is a heavy down pour during the wet season, the sand barrier that separates the sea from the lagoon is broken, so the excess water in the lagoon can enter into the sea. However, this also allows some of the sea water to mix with the lagoon water and this can explain the high levels of chloride ions recorded for the wet season. Standard concentration of chloride ions in surface water is 600 ppm (USEPA, 2010). Comparing this to the mean chloride values of 1192,06 ppm and 895.83 ppm for the wet and dry seasons respectively means the lagoon has high levels of chloride ions. However, the fishes in the lagoon are surviving probably because according to Evans and Frick, 2001, fishes are less sensitive to effects of chloride than invertebrates.

5.2 Soil Texture

The soil texture profile performed on the lagoon sediment revealed that the soil texture of the lagoon sediment is sandy, clayey. About 65% of this is made up of sand and this is probably because of the closeness of the lagoon to the sea shore. Sandy soil does not aid in transport of pollutants due to it rough and large particle size which reduces it surface area (Ongley, 1994). The sediment consists of 30% clay with the remaining 5% being silt. The silt and clay fraction are the primary carrier of adsorbed chemicals, especially phosphorous, chlorinated chemicals and most metals which are transported into aquatic systems (Ongley, 1994). For metals adsorption, particle size is of primary importance due to the large surface area of very small particles. Metals tend to be highly attracted to ion exchange sites that are associated with clay particles and with the iron and manganese coatings that commonly occur on these small particles (US Geological survey, 2004).

5.3 Metals

Generally, metals concentration in water samples were very low when compared to those recorded in sediment samples. This was best observed in water samples for the wet season where almost all metals were below detection limit. This might be as a result of dilution of the lagoon by rain water especially during the raining season. Metals also get stored in river bed sediment after they aggregate to form large denser particles (Adomako *et al.* 2008). This can also explain why high concentrations of metals were measured in sediment samples. The high levels of metals especially iron and manganese in the lagoon sediment is worrying since this can result in the reduction in benthic biodiversity where pollutant tolerant species may probably take over the vacated niche (Okweye *et al.* 2009).

5.3.1 Iron

Concentrations of iron in lagoon water for the wet season were below detection limit for all sampling points (Appendix B). However, some significant values were recorded for the dry season samples with an average concentration of 0.5 mg/kg with a standard deviation of 0.15. Levels in the sediment samples were quiet high, especially the dry season samples. It was observed that sampling points 5 and 6 which are close to the automobile garages along the bank of lagoon recorded the highest concentration of iron for both seasons (Appendix C). This could mean that these garages are the source of the high iron concentrations in the lagoon. I_{geo} values of 16.321 and 19.614 for the wet and dry seasons respectively imply that the lagoon sediment is extremely contaminated with iron all year round.

5.3.2 Copper

Generally, copper recorded the lowest concentrations in all samples. It recorded an average of 0.15 mg/kg in water for the dry season with a standard deviation of 0.2. This is very low and poses no threat when compared to the USEPA threshold value of 65 mg/kg of copper in surface water. The main sources of copper in aquatic environment are geological weathering and corrosion of plumbing materials and infrastructure (US geological survey, 2004). Similarly, concentrations in sediment samples were also very low and ranged 0.3 - 2.95 mg/kg for the wet season and 0.65 - 1.40 mg/kg for the dry season. These low concentrations have no harmful effects on the lagoon and this is also confirmed by I_{geo} values of -0.059 and -0.737 for the wet and dry seasons respectively. These negative values imply that the lagoon sediment shows no copper contamination.

5.3.3 Manganese

Manganese recorded a concentration range of 0.75–1.15 mg/kg in water for the dry season (Table 4.4). The highest value of 1.15 mg/kg was recorded at sampling point 6 (Appendix B). However, no known threshold value exists for Mn in surface water (Table 3.2). Apart from iron which recorded the highest metal concentration in all sediment samples, manganese recorded the second highest concentrations in sediment samples. The highest values for the two seasons were 543.50 mg/kg and 300.40 mg/kg and these were recorded at sampling point 6. This could mean that the activities of the garages close to the lagoon are releasing some metal pollutants into the lagoon of which manganese is one of them. The abundance of manganese in the earth can also contribute to the high levels in the samples. Igeo values for manganese were 11.378 and 11.389 for the wet and dry seasons respectively and this put manganese in Igeo class 6, which means the lagoon sediment were extremely contaminated with Mn.

5.3.4 Chromium

The levels of chromium were below detection limit for all water samples. Only two concentrations (i.e. 0.05 mg/kg and 0.15 mg/kg) were recorded for sediment samples at sampling points 1 and 2 in the wet season (Appendix C). The dry season recorded a concentration range of 0.085 - 3.4 mg/kg. Chromium is employed in the manufacture of some cleaning agent and this when washed into water bodies can be a source of chromium pollution in water bodies (Nriagu, 1988). The high concentrations in the dry season could probably be as a result of fewer disturbances in the lagoon by heavy rains and runoffs during the dry season, which allowed the little chromium that entered the lagoon during the wet season to settle at the lagoon bed.
However, with Igeo values of -4.506 and 1.736, it can be concluded that the lagoon sediment only get moderately contaminated with chromium during the dry season.

5.3.5 Nickel

The wet season water samples had no detectable amount of nickel and thus no nickel concentrations were recorded. The dry season however had very minimal concentrations of nickel with an average concentration of 0.5 mg/kg with a standard deviation of 0.15. The USEPA standard value of nickel in surface water is 23.50 mg/kg and this means the lagoon water had harmless concentration of nickel. Similarly, the sediment samples also had very small concentrations of nickel. The wet season had an average concentration of 0.50 mg/kg with a standard deviation of 0.50 whiles the dry season had an average concentration of 3.50 mg/kg and a standard deviation of 0.50. Igeo values for nickel were -1.099 and 1.202 for the wet and dry seasons implying that the lagoon only get moderately contaminated with nickel during the dry season but shows no nickel contamination during the wet season.

5.3.6 Lead

Some significant concentrations of lead were recorded for the wet season water samples but surprisingly, none was recorded for the dry season. According to Yu (2005), leaded fuel deposited on roads by automobiles can be transported by runoffs into water bodies and cause an increase in lead in water and sediments. This can explain why the highest lead concentrations in the lagoon water occurred at points 1 and 2 (Appendix b). These two points apart from that they are close to the area where the sand bar separates the sea and the lagoon, they are also close to a

main road where a bridge passes over the lagoon. The average lead concentration in the lagoon was 5.0 mg/kg whiles the USEPA threshold concentration of lead in surface water is 3.0 mg/kg. Hence, comparing these two concentrations, it can be concluded that the lagoon water gets polluted with lead during the wet season.

The sediment samples recorded high lead concentrations, with the dry season recording the highest. Just as with the water samples, point 2 also recorded the highest lead concentration in the sediment samples for the wet season whiles points 1 and 2 recorded the highest for the dry season. This confirms that the road close to these points is actually the source of lead in the lagoon as a result of leaded fuel deposition by automobiles. However point 6 which is close to the garages recorded the second highest lead concentration for the wet season. This could mean that the activities of these garages such as recharging of automobile batteries which contains lead, also contribute some lead pollutants into the lagoon. I_{geo} values for the wet and dry seasons were 1.146 and 1.921 respectively. This put lead in I_{geo} class two which means the lagoon sediment is moderately contaminated with lead.

5.3.7 Cadmium

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Concentrations of Cd in water samples fell within the range 0.5 - 0.7 mg/kg and 0.6 - 2.65 mg/kg for the wet and dry season's respectively. The USEPA threshold value for cadmium in surface waters is 17 mg/kg. Thus the small concentration in the samples poses no threat to the lagoon. Sediment samples also had very small concentrations of cadmium with average concentrations of 0.50 mg/kg and 4.50 mg/kg for the wet and dry seasons respectively. This

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minimal concentration may be due to the conservative nature of this element in aquatic systems as shown by Karbassi et al., 2008. The small concentrations was confirmed by negative I_{geo} values of -9.288 and -5.878 which means the lagoon sediment is far from being contaminated by cadmium.

5.3.8 Zinc

Zinc concentrations in water samples for the wet season were below detection limit. However, the dry season recorded an average concentration of 4.0 mg/kg. This when compared with the USEPA recommended concentration of 6.0 mg/kg in surface water (Table 3.2) reveals that the lagoon water is free from zinc pollution.

Contrary to the low concentrations in water, zinc concentrations in sediment samples were quiet high especially, with the wet season samples. The wet season recorded an average concentration of 79 mg/kg whiles the dry season had an average concentration of 23 mg/kg. Points 5 and 6 recorded the highest zinc concentrations for both seasons. Burning of vehicle tyres has been asserted to be a significant contributor of zinc in water bodies through runoffs (O'Conner, et al., 1964). Now this is a common practice at the various automobile garages where worn out tyres are burnt close to the lagoon. This could explain why the high zinc concentrations at points 5 and 6 which are close to the garages. I_{geo} values of zinc (Table 4.11) put zinc in class 4 implying that the lagoon sediment is strongly contaminated with zinc.

5.4 Heavy Metals in Fish

All the fishes used in this study were of good health as shown by the condition factor (K) in Table 4.8. The mean elemental concentrations measured in the fishes during the study are also presented in Table 4.9. Almost all the fish samples collected from the lagoon contained detectable amounts of the metals studied (i.e. Fe, Cu, Mn, Cr, Ni, Pb, Cd and Zn). The metals were present in varying concentrations. Cu, Ni and Cd recorded the least mean concentrations of 0.2 mg/kg, 1.15 mg/kg, and 2.25 mg/kg respectively. Chromium was below detection limit in all the samples. Mn, Zn, Fe and Pb recorded the highest concentrations in that order with mean concentrations of 27.90 mg/kg, 20.65 mg/kg, 9.95 mg/kg, and 6.75 mg/kg respectively. However, the concentrations of all the metals in the fish samples did not exceed the US Food and Nutrition Board's daily permissible limit (Table 3.1). However, since the fish only forms part of the diet, the type of food one consumes can also increase the concentration of these metals are also present in some other foodstuffs.

A comparison of Tables 4.5, 4.6 and 4.9 shows similar patterns in the concentrations of Fe, Mn, Zn and Pb. Concentrations of these metals were high in sediment samples as well as in the fish samples. This could mean that the high levels of these metals in the lagoon sediment are being absorbed by the aquatic plants and other organisms on which these fishes feed. Even though the concentrations of the metals were below harmful levels, the presence of lead and cadmium in the fishes poses health threats to it consumers since these two metals are of no nutritional value and also have the tendency to bio accumulate in consumers.

5.5 Relationships between Heavy Metals in Water and Sediment Samples

Generally, correlations between the elements in water samples were all negative except Mn, Cu and Ni which had positive correlations with each other. The negative correlations suggest that the occurrences of these elements in the lagoon water were from different sources. The different activities at different areas of the lagoon can be the reason for this result. Sediment samples however showed different correlation patterns with majority of the elements having positive correlations with each other. Chromium had strong negative correlations with the other metals, which can be an indication that its occurrence in the lagoon is from a source different from the other metals. During the dry season, the lagoon water reduces in volume as a result of evaporation and this allows for species precipitation. This can account for the strong positive correlations during the dry season, because the metals are coming from a common source which is the lagoon water.

5.6 Relationships between Heavy Metals in Fish, Water and Sediment Samples

Most of the correlation coefficients between heavy metals in fish and water samples from the lagoon were negative. This can be an indication that the heavy metal contents in the fish samples and in the water samples are from difference sources. However, Fe - Ni, Pb - Ni, Cd - Cu and Pb - Mn had strong positive correlations, which can be an indication that these metals are entering into the lagoon from the same source. Correlations between heavy metals in fish and in sediment samples were positive for most of the metals which is an indication that these metals could be entering into the lagoon from a common source. The metal pollutants that enter the lagoon settle at the lagoon bed which is the sediment. These metals may be absorbed by aquatic plants and distributed through the food chain. This can be the reason for the positive correlations

between the fish and sediment samples since they are all from a common source which is the lagoon sediment. It can therefore be concluded that the lagoon sediment acts as a source of secondary pollutants since it accumulates metal pollutants from the lagoon water and distributes it through the food chain.



CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

Samples of the lagoon water, sediments and fish were studied in this work and the results obtained confirm that the lagoon samples tested positive to most of the parameters tested. The different sampling points and seasons of sampling also gave an idea as to where and when the lagoon gets polluted with some of the pollutants.

From the analysis on the lagoon water, it can be concluded that the lagoon water receives high nutrients (PO_4^- and NO_3^-) during the wet season as a result of runoffs. The lagoon water also becomes more basic during the dry season. Heavy metals results obtained also confirmed that there are high levels of lead in the lagoon water during the wet season and this is due to lead deposit on the road close to the lagoon by automobiles. However, the concentrations of the other metals present in the water were very low and therefore posed no threats to the lagoon and aquatic life.

Analysis on sediment samples revealed that the lagoon sediment is highly basic during the dry season. It also contains varying amount of the target metals in varying quantities. The sediment samples contained very high concentrations of iron and manganese. The geoaccumulation index calculated on the levels of the metals present also confirmed that the lagoon sediment is extremely contaminated with iron and manganese and also strongly contaminated with zinc and

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lead. The results patterns also confirm that the sources of most of these metal pollutants in the lagoon are from the industrial end of the lagoon especially the automobile garages close to the lagoon. This is because samples from those areas contained very high levels of the various metals.

Results on fish samples revealed that even though the lagoon water and sediment contains various pollutants, this does not affects the health of the fishes that lives in the lagoon. This was confirmed by the condition factor (K-values) calculated for each of the fish samples. Thus, the fishes in the lagoon are not stressed by these pollutants. It can also be concluded that because iron, manganese, zinc and lead are present in the lagoon at higher levels, they are able to enter into the food chain and thus have a potential to bio accumulate. However, further analysis confirmed that the levels of these metals in the fish do not exceed the U.S. Food and Nutrition Board's daily recommended intake and thus, fish from the lagoon is safe to eat. It is however advisable to control the rate of intake since it contains low levels of lead and cadmium which are of no nutritional value and therefore have the tendency to bio accumulates.

6.2 RECOMMENDATIONS

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- The numerous garages at Siwdu and the palm kernel extractors at Adisadel village should be resettled by city authorities.
- Further investigations should be conducted to find out the presence of other metals like mercury and arsenic.

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APPENDIX A PLATES USED



APPENDIX B

TABULATED RESULTS FOR WATER SAMPLES

Average values for Physiochemical Parameters in Water Samples (Wet season)

Sampling	PH	Conductivity	PO ₄ ⁻	NO ₃ ⁻	Cl [·] (mg/l)	$\mathbf{NH_4}^+$
point		(µS/cm)	(mg/l)	(mg/l)		(mg/l)
1	7.6	3500	5.689	102.82	1290.57	3.97
2	7.43	5500	10.062	107.78	2006.75	4.97
3	8.15	3000	1.298	197.80	1061.21	3.18
4	8.18	3000	2.209	131.97	1044.60	3.21
5	7.89	2250	4.281	130.13	799.18	2.74
6	7.98	2500	4.004	121.06	950.04	3.00



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Sampling	РН	Conductivity	PO ₄ (mg/l)	NO ₃	Cl ⁻ (mg/l)	NH_4^+
point		(µS/cm)		(mg/l)		(mg/l)
1	8.75	4500	0.197	24.48	777.55	3.01
2	9.65	4350	0.250	33.83	849.81	2.77
3	9.80	5200	0.780	21.01	925.48	2.57
4	8.95	5000	0.367	20.01	926.99	2.50
5	7.92	4750	0.760	16.07	945.20	2.30
6	8.84	5100	0.539	17.75	949.95	2.41

Average values for Physiochemical Parameters in Water Samples (Dry season)

Concentrations of heavy metals for the wet season (mg/kg)

Points	Fe	Cu	Mn	Cr	Ni	Pb	Cd	Zn
1	BDL	BDL	BDL	BDL	BDL	5.50	0.60	BDL
2	BDL	BDL	BDL	BDL	BDL	6.85	0.70	BDL
3	BDL	BDL	BDL	BDL	BDL	4.25	0.30	BDL
4	BDL	BDL	BDL	BDL	BDL	4.70	0.05	BDL
5	BDL	BDL	BDL	BDL	BDL	4.70	0.05	BDL
6	BDL	BDL	BDL	BDL	BDL	BDL	0.20	BDL

BDS- below detection limit

Companyturations	of because	metals for	the draw	~~~~~	(
Concentrations	of neavy	metals for	the ary	season	(mg/kg)

Points	Fe	Cu	Mn	Cr	Ni	Pb	Cd	Zn
1	1.00	0.15	0.90	BDL	0.50	BDL	0.85	3.95
2	0.60	0.05	0.75	BDL	0.45	BDL	0.85	4.05
3	0.60	0.05	0.85	BDL	0.45	BDL	0.60	4.35
4	0.60	0.55	0.90	BDL	0.45	BDL	0.95	3.65
5	0.65	0.05	0.90	BDL	0.60	BDL	2.30	3.20
6	0.50	0.10	1.15	BDL	0.80	BDL	2.65	4.00

BDL- below detection limit



APPENDIX C

TABULATED RESULTS FOR SEDIMENT SAMPLES

Physiochemical parameters (wet season)

Sampling points	Conductance (µS/cm)	рН
1	2400 0 0	6.94
2	1150	6.37
3	3000	7.23
4	2500	7.31
5	2250	7.33
6	1100	7.10

Physiochemical parameters (dry season)

Sampling points	Conductance (µS/cm)	рН
1 7540	5400	10.68
2	5200 SANE NO	10.78
3	5200	10.75
4	5400	10.77
5	5500	10.87
6	5300	10.86

Points	Fe	Cu	Mn	Cr	Ni	Pb	Cd	Zn
1	129.05	1.25	84.35	0.06	1.20	5.25	0.30	55.30
2	114.80	1.50	11.65	0.15	0.55	18.90	0.20	28.40
3	134.45	0.31	281.00	BDL	0.50	8.45	0.20	99.40
4	131.35	1.65	221.0	BDL	0.60	5.75	0.45	58.40
5	135.80	1.90	267.50	BDL	BDS	2.70	0.55	109.10
6	135.05	2.95	543.50	BDL	1.35	8.70	0.65	124.35

Heavy Metal Concentrations for the wet season (mg/kg)

BDL- below detection limit



Heavy Metal Concentration for the dry season (mg/kg)

Points	Fe	Cu	Mn	Cr	Ni	Pb	Cd	Zn
				- 44	-			
1	1310.00	1.00	244.00	2.40	3.55	15.15	4.40	24.15
2	1314.50	0.85	247.10	2.25	3.65	15.00	4.80	23.40
3	1063.00	1.40	191.85	2.50	3.65	14.40	4.70	27.05
4	1305.50	1.40	229.45	3.40	4.10	14.25	4.80	26.85
5	1341.50	0.75	300.40	2.05	3.45	14.65	4.05	23.25
6	1317.00	0.65	207.50	0.85	2.15	11.85	3.10	11.95

APPENDIX D

Sample	Fe	Cu	Mn	Cr	Ni	Pb	Cd	Zn
1	5.55	0.30	31.25	BDL	1.35	4.00	2.15	20.50
2	5.50	0.35	31.20	BDL	1.25	4.90	2.05	20.55
3	6.00	0.20	32.30	BDL	1.15	5.90	2.05	21.00
4	12.75	0.15	27.20	BDL	1.35	6.15	3.20	21.85
5	18.10	0.20	22.25	BDL	1.60	7.70	2.80	23.15
6	11.10	0.25	30.55	BDL	0.55	10.80	2.40	20.75
7	9.25	0.30	29.45	BDL	1.10	8.90	2.55	19.85
8	13.85	0.10	30.15	BDL	0.75	4.95	1.80	22.10
9	6.80	BDL	20.95	BDL	1.00	9.25	2.00	18.25
10	10.90	0.15	23.60	BDL	1.45	4.90	1.65	18.60

Heavy Metal Concentrations in Fish Samples

BDL: Below Detection Limit

9,000

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SANE

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