## KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

## COLLEGE OF SCIENCE

## DEPARTMENT OF THEORETICAL AND APPLIED BIOLOGY

## ASSESSMENT OF THE POLLUTION STATUS OF BUTUAH LAGOON IN THE SEKONDI-TAKORADI METROPOLIS, WESTERN REGION, GHANA



## JULY, 2012

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A THESIS SUBMITTED TO THE DEPARTMENT OF THEORETICAL AND APPLIED BIOLOGY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE (MSc) IN ENVIRONMENTAL SCIENCE

BY

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JULY, 2012

## DECLARATION

"I declare that I have wholly undertaken this study reported herein under the supervision of Dr. Ebenezer J. D. Belford and that except portions where references have been duly cited, this dissertation is the outcome of my research."



### ABSTRACT

The water quality of Butuah Lagoon was monitored together with the concentrations of seven heavy metals (As, Cu, Pb, Zn, Fe, Cd and Hg) determined in the sediments, muscles of Tilapia fish and lagoon water using Atomic Absorption Spectrophotometer (AAS 220 Model) except Hg which was determined using the Automatic Mercury Analyzer (HG 6000 Model). The same parameters were determined in an effluent discharging into the lagoon from an Industrial Complex. The results indicated that the concentrations of heavy metals in the effluent samples were generally below the recommended standards. The effluent discharged into the lagoon was not a major source of pollution indicating that there are other major sources of pollutants discharging into the lagoon. When compared with ISQG (2002), heavy metal concentrations of sediments from Butuah Lagoon recorded higher values except for Hg which was below the permissible limits. The highest levels of pollutants were found in the sediment followed by fish and the least being recorded in water. The concentrations of As, Cu, Pb, Zn, Fe, Cd and Hg in sediments were 94.1%, 92.7%, 88.1%, 81.3%, 95.4%, 92.7% and 27.4% higher than those obtained in muscles of fish. Similarly, the concentrations of As, Cu, Pb, Zn, Fe, Cd and Hg in sediments were 100%, 99.9%, 99.4%, 99.8%, 100%, 99.3% and 100% higher respectively than in water samples from the same lagoon. The range of heavy metal concentrations in fish during the sampling period was 1.93 mg/kg to 8.13 mg/kg for As, 0.08 mg/kg to 8.00 mg/kg for Cu, 1.00 mg/kg to 13.43 mg/kg for Pb, 15.20 mg/kg to 37.67 mg/kg for Zn, 33.17 mg/kg to 210.06 mg/kg for Fe, 0.00 to 0.97 mg/kg for Cd to 0.008 mg/kg to 0.014 mg/kg for Hg. In terms of location the midstream was more polluted than downstream which was more polluted than upstream. Monthly levels of pollutants determined over four months indicated that the concentrations decrease with the onset of the wet season. The use of Butuah Lagoon as source of fish (Tilapia) supply should be discouraged.



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Declarationiii		
Abstrac	tiv	
Acknow List of T List of F List of F List Abb	ledgement v   Tables x   Figures xi   Plates xi   previations xii	
CHAI	PTER ONE	
1.0	INTRODUCTION	
1.1	Background1	
1.2	Problem Statement and Justification	
1.3	Main Objective	
1.4	Specific Objectives	
CHAI	PTER TWO	
2.0	LITERATURE REVIEW	
2.1	Environmental Pollution	
2.1.1	Sources of Environmental Pollution	
2.1.2	Transformation of environmental pollutants	
2.1.3	Factors Affecting Accumulation of Pollutants7	
2.2	Heavy Metals	
2.2.1	Lead	
2.2.2	Mercury	
2.2.3	Zinc and Cadmium	
2.2.4	Toxicity of Cadmium	
2.2.5	Arsenic11	
2.2.6	Copper	
2.2.7	Iron 12	
2.3	Sources of Heavy Metal Pollution in Aquatic Ecosystems	
2.4	Standards of Water Quality	
2.4.1	Alkalinity	

## **TABLE OF CONTENTS**

2.4.2	Chemical Oxygen Demand and Biological Oxygen Demand	. 14	
2.4.3	Chloride	. 15	
2.4.4	Conductivity		
2.4.5	Temperature		
2.4.6	pH	. 17	
2.4.7	Phosphates	. 18	
2.4.8	Sulphates	. 19	
2.4.9	Total Suspended Solids	. 20	
2.4.10	Nitrates	. 20	
2.4.11	Oil and Grease	. 21	
2.5	Food Chain	. 21	
2.5.1	Bioacummulation within the Aquatic Food Chain	. 21	
2.5.2	Biomagnification along the Aquatic Food Chain	. 22	
2.6	Estuaries and Lagoons	. 22	
2.7	Sediments	. 23	
2.8	Monitoring Of Aquatic Ecosystems.	. 24	
2.8.1	Biomonitoring	. 24	
2.8.2	Limitations of Biomonitoring	. 25	
2.9	Oreochromis niloticus	. 25	
2.9.1	Habitat and Biology	. 26	
CHAP	TER THREE	. 27	
3.0	MATERIALS AND METHODS	. 27	
3.1	Study Area	. 27	
3.2	Sampling sites	. 27	
3.3	Sampling	. 29	
3.4	Physicochemical Water Analysis	. 30	
3.4.1	Determination of Alkalinity and Chloride	. 30	
3.4.2	Determination of BOD and COD	. 31	
3.4.3	Wagtech Nitratest	. 32	
3.4.4	Oil and Grease Determination (Partition- Gravimetric Method)	. 33	
3.4.5	Total Suspended Solids (TSS)	. 33	

3.5 L	aboratory analysis of samples	34		
3.5.1	Digestion of Samples	34		
3.5.2	Determination of Lead, Cadmium, Copper, Arsenic, Iron and Zinc			
3.5.3	Determination of Total Mercury			
3.6 D	3.6 Data Analysis			
CHAPT	ER FOUR	38		
4.0 R	ESULTS	38		
4.1 P	hysicochemical Parameters of Butuah Lagoon	38		
4.1.1	Physicochemical Parameters of Effluent	42		
4.2 L	evels of Heavy Metals in Sediments, Fish, Water and Effluent	46		
4.2.1	Levels of Heavy Metals in Sediments	46		
4.2.1.1	Arsenic	47		
4.2.1.2	Copper	47		
4.2.1.3	Lead	49		
4.2.1.4	Zinc	49		
4.2.1.5	Iron	49		
4.2.1.6	Cadmium	50		
4.2.1.7	Mercury	50		
4.2.2	Monthly Variation of Heavy Metal Concentrations in Sediments	51		
4.2.3	Heavy Metals in Muscles of Fish	54		
4.2.3.1	Arsenic	55		
4.2.3.2	Copper	55		
4.2.3.3	Lead	57		
4.2.3.4	Zinc	57		
4.2.3.5	Iron	57		
4.2.3.6	Cadmium	58		
4.2.3.7	Mercury	58		
4.2.4	Monthly Variation of Heavy Metal Concentrations in Muscles of fish	59		
4.2.5	Heavy Metals in Butuah Lagoon and Effluent	62		
4.2.5.1	Copper	62		
4.2.5.2	Lead	62		

4.2.5.3	3 Zinc	3
4.2.5.4	4 Iron 6	4
4.2.5.5	5 Cadmium	4
4.3	Bioaccumulation Ratio in fish in relation to sediments	7
CHAP	TER FIVE	9
5.0	DISCUSSION	9
5.1	Physicochemical Properties of Butuah Lagoon and Effluent	9
5.2	Heavy Metals in Sediments of Butuah Lagoon7	1
5.3	Heavy Metals in Muscles of Fish7	3
5.4	Heavy Metals in Butuah Lagoon and Effluent 7	4
5.5	Monthly Variation of Heavy Metal Concentrations in Sediments, Fish and Water	4
5.6	Bioaccumulation in fish	5
CHAPTER SIX		
6.0	CONCLUSIONS AND RECOMMENDATIONS	7
6.1	Conclusion	7
6.2	Recommendation	7
REFERENCES		
APPE	NDICES	7
	STR. SECTO	



## LIST OF TABLES

Table 1. Description of sampling points	. 29
Table 2. Mean values of physicochemical parameters along Butuah Lagoon	.39
Table 3. Mean values of physicochemical parameters of effluent	44
Table 4. Mean concentration (mg/kg) of heavy metals in sediments from Butuah   Lagoon	48
Table 5. Mean concentration (mg/ kg) of heavy metals in muscles of fish from Butuah   Lagoon	. 56
Table 6. Mean concentration (mg/ L) of heavy metals in Butuah lagoon and effluent	. 63
Table 7. Bioaccumulation ratio in fish in relation to sediments of Butuah Lagoon	. 68



## LIST OF FIGURES

Figure 1. Map of Butuah Lagoon showing sampling points	.28
Figure 2. Variations in As, Cu, Pb and Zn in sediments from Butuah Lagoon	52
Figure 3. Variations in Fe, Cd and Hg in sediments from Butuah Lagoon	.54
Figure 4. Variations in As, Cu, Pb and Zn in fish from Butuah Lagoon	.60
Figure 5. Variations in Fe, Cd and Hg in fish from Butuah Lagoon	61
Figure 6. Variations in Cu, Pb, Zn, Fe and Zn in Butuah Lagoon and Effluent	65

## LIST OF PLATES

Plate 1. The Atomic Absorption Spectrophotometer (AAS 220 M0del)......35



## LIST OF ABBREVIATIONS AND UNITS

ALKALAlkalinityANOVAAnalysis of VarianceAOACAssociation of Official Analytical ChemistsAsArsenicBODBiological Oxygen DemandCaCO3Calcium CarbonateCdCadmiumCHLORChlorideCH4MethaneCONDConductivityCODCarbon Oxygen DemandCO2Carbon Oxygen DemandCO2Carbon DioxideCuCopper° CDegree CelsiusDDEDichlorodiphenyldichloroethyleneDecDecemberDDTDichlorodiphenyltrichloroethaneDNADeoxyribonucleic acidEPAFebruaryFeIronFebGramggramH_SSO4Hydrogen sulphideHCLIO4Hydrogen carbonateHNO3Hydrogen nitrate
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HCO3Hydrogen carbonateHNO3Hydrogen nitrate
HNO <sub>3</sub> Hydrogen nitrate
5
Hg Mercury
ISOG Interim Sediment Quality Guidelines
Jan January
K <sub>2</sub> CrO <sub>4</sub> Potassium dichromate
Kg Kilogram
LSD Least Significant Difference
Mar March
mg/ kg Milligram per kilogram
mg/ L Milligram per litre
mg Milligram
ml Millilitre
mm Millimetre
N Nitrogen
nm Nanometre
ND Not detected
N <sub>2</sub> Nitrogen gas

NO <sub>3</sub>	Nitrate
$NO_2$	Nitrite
$O_2$	Oxygen
Oil&G	Oil and Grease
$PO_4$	Phosphate
Pb	Lead
RNA	Ribonucleic acid
SnCl <sub>2</sub> .2H <sub>2</sub> O	Stannous Chloride
SPSS	Statistical Package for Social Scientist
TEMP	Temperature
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
US EPA	United States Environmental Protection Agency
UNEP GEMS	United Nations Environment Programme Global
	Environmental Monitoring System
v/v	Volume per volume
WHO	World Health Organisation
Zn	Zinc

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### **CHAPTER ONE**

## **1.0 INTRODUCTION**

#### **1.1 Background**

Anthropogenic activities of which industrialization forms a part undoubtedly has brought about many important benefits across the world. However, the negative impacts of industries to the environment particularly the aquatic ecosystem cannot be underestimated. The growing rate of anthropogenic waste input into aquatic systems leads to bioaccumulation of heavy metals in biota and their levels in economically important fin fish and shell fishes have become a matter of great concern (Kamaruzzaman *et al.*, 2010). The pollution burden of many lakes and rivers, together with certain areas of the marine environment, are a serious cause for environmental concern. The general effect of pollution on aquatic ecosystems is one of impoverishment with a sharp decline in species richness (Jackson and Jackson, 1996). Most heavy metals find their way into water bodies via, chemical weathering of rocks and soil, agricultural runoffs, industrial waste discharge, mining, batteries, lead based paints and gasoline and improper discharge into water ways (Anim *et al.*, 2010).

Due to the deleterious effect of metals on aquatic ecosystems, it is necessary to monitor their bioaccumulation in key edible species, because this will give an indication of the temporal and spatial extent of the process, as well as an assessment of the potential impact on organism's health (Fernandes *et al.*, 2007). Environmental conditions such as oxygen concentration, temperature, hardness, salinity and presence of other metals may also affect metals toxicity to the fish. Hypoxic conditions like temperature increase and acidification usually renders the fish more susceptible to intoxificant (Witeska and Jezierska, 2003). Many important functions and benefits

can be attributed to the Butuah Lagoon and this will be perpetuated if proper attention is devoted to its management. Wetlands serve both direct and indirect functions. Direct functions include fishing, fuel wood, wild foods, medicinal plants, agriculture, pasture, transport, recreation (green corridors) etc. The indirect or ecosystem functions include; maintenance of water quality (Okurut *et al.*, 2000; Cunningham and Cunningham, 2002) and flow, water storage, water recharge, flood control, reproduction area for fish, climate control and shore stability. Other functions include cultural, biodiversity of flora and fauna, aesthetic, heritage bequest values and nesting site for birds. Edem *et al.*, (2008) reported that compared with other types of aquatic pollution, heavy metal pollution is less visible but its effects on the ecosystem and humans are intensive and very extensive. The numerous reasons stated above on wetlands of which Butuah Lagoon is an example and the increased anthropogenic activities going on around the lagoon makes it very imperative for research to be conducted to ascertain the state of the lagoon.

## **1.2 Problem Statement and Justification**

Butuah lagoon, as an example of wetland, supports a wide variety of life forms, including bacteria, fungi, protozoa, bottom-dwelling organisms (such as insect larvae, snails, and worms), plankton, large plants (such as grasses and mangroves), fish, amphibians, reptiles and birds. The inhabitants also derive benefits including fish for consumption, swimming, aesthetic view, recreation and water for farming and other purposes, from the lagoon (Ansong, 2007).

Despite these important functions of the lagoon, about 33,276 sq meters of land around it has been identified as been used for industrial purposes (Coastal Resource Center-Ghana/Friends of the Nation, 2010). The presence of these industries and settlements around the lagoon makes it very vulnerable to a variety of pollutants which will ultimately affect the integrity of the lagoon. Ansong (2007) in a study revealed that construction, disposal of garbage and industrial activities were happening around the lagoon, and these threaten the existence of the lagoon. It is in no doubt that these will have varied consequences on the state and existence of the lagoon. For example there has been a report of reduction in fish catch (Coastal Resource Center-Ghana/Friends of the Nation, 2010). Saxena et al. (2009) reported that occurrence of aquatic pollutants (such as heavy metals) has been correlated to alterations in the fish immune system and the incidence of infectious diseases and that even very low sub lethal doses of certain heavy metals can have profound effects upon the structure and/or functions of the immune system that could be almost as harmful as direct toxic doses and went further to say that pollution of water with heavy metals may adversely affect the immune system of fish leading to decreased production, increased susceptibility to diseases and mortality. Reports made by Ruelas-Inzunza and Paez-Osuna (2000) indicated that direct analysis of pollutants does not provide information about their effect on the ecosystem and that the use of biomonitors is a highly recommended option because biomonitors respond specifically to bioavailable pollutant loads.

There is therefore the need for studies to be conducted to assess the state of the Lagoon particularly the level of heavy metals as well as other physicochemical water properties. The consumption of fish contaminated with heavy metals beyond tolerable limits could have adverse effects on the people. This study will ascertain the levels of heavy metals in the Butuah lagoon by measuring their concentrations in muscles of fish, water and sediments as well as other physicochemical water analysis to provide information to create awareness to individuals and industries operating around the lagoon. Similarly, heavy metals together with some physicochemical parameters will be ascertained in effluent samples.

## 1.3 Main Objective

This study seeks to investigate the pollution status of Butuah Lagoon in the Western Region of Ghana using water, fish and sediment samples.

## **1.4 Specific Objectives**

The specific objectives are;

 To determine the concentrations of lead, cadmium, copper, mercury, arsenic, iron and zinc in muscles of tilapia fish (*Oreochromis niloticus*), water and sediments of Butuah Lagoon.

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- To determine the levels of some physicochemical parameters (pH, Temperature, COD, BOD, TDS, TSS, Turbidity, Conductivity, Alkalinity, Chloride, Nitrate, Phosphates, and Oil and Grease of Butuah Lagoon
- 3. To determine the levels of heavy metals in the main drain discharging into Butuah Lagoon.
- To determine the levels of some physicochemical parameters (pH, Temperature, COD, BOD, TDS, TSS, Turbidity, Conductivity, Alkalinity, Chloride, Nitrate, Phosphates, and Oil and Grease of the main drain discharging into Butuah Lagoon.

### **CHAPTER TWO**

### 2.0 LITERATURE REVIEW

## 2.1 Environmental Pollution

Pollution is defined as the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structure or amenity, or interference with legitimate uses of the environment (Holdgate, 1979). Much pollution is chronic (or steady state), that is, the water course receives discharge continuously or regularly. Given the right legal framework and resources, such pollution can be reduced so that its impact on the aquatic ecosystem is acceptable. In much of the developed world, marked improvements in water quality have taken place over the last three decades. A greater problem now is that of episodic (or intermittent) pollution, which is unpredictable in both space and time. Episodic pollution is of special concern to water managers, for a single event can destroy years of careful, patient work in reducing the impact of pollution from known discharges. Many freshwater resources are contaminated through human activities.

## 2.1.1 Sources of Environmental Pollution

Pollutants may be derived from point sources, often discharges known to the authorities and readily amenable to abatement provided resources are available (Mason, 1996). Point sources, as their name suggests, are sources from which pollutants are released at one readily identifiable spot and are often easier to identify as potential pollution problems. They are also easier to monitor systematically (Montgomery, 2000). Examples of point sources are discharges of effluent from sewage treatment works or of wastes from factories.

Alternatively, sources of pollution may be diffuse, entering watercourses from run-off and land drainage. Nonpoint sources of water pollution are scattered or diffuse, having no specific location where they discharge into a particular body of water. They are much harder to monitor and regulate than point sources because their sources are hard to identify. Perhaps the ultimate in diffuse, nonpoint pollution is atmospheric deposition of contaminants carried by air currents and precipitated into watersheds or directly onto surface waters as rain, snow or dry particles (Cunningham and Cunningham, 2002). Fertilizers and pesticides applied to crops, and acid precipitation, provide examples of diffuse pollution. Only rarely, is a single pollutant present in a water course. Normally an effluent will consist of a variety of potentially harmful substances and the effects of these will often be difficult or impossible to disentangle. Pollutants occurring together may act completely independently on a target, and the one exerting the greatest effect would then be the most important. The effects of pollutants might also be additive, antagonistic or synergistic (Mason, 1996). The release of large quantities of oxygen demanding wastes into watercourses often has disastrous effects on the indigenous flora and fauna. The primary source of organic waste released into fresh water is sewage effluent. Other sources include run-off from urban areas and farms, and some industrial effluents (Jackson and Jackson, 1996).

## 2.1.2 Transformation of environmental pollutants

Many of the compounds released into watercourses are subject to transformations within the environment, and this may render them more toxic. Mercury can be taken as an example, and some of its transformations are conversion from inorganic mercury (Hg  $2^+$ ) to methyl (CH<sub>3</sub>Hg<sup>+</sup>) and dimethyl mercury in aquatic environments due to the activities of bacteria and fungi. The methylation process may occur under anaerobic (e.g. by *Clostridium*) or aerobic (e.g. by

*Pseudomonas, Neurospora*) conditions. Several non-biological transformations of mercury also occur, depending on the environmental conditions. Pesticides also undergo transformations in the environment, but these tend to be minor. For instance, aldrin is converted to dieldrin and DDT to DDE, but these products are still highly toxic (Mason, 1996).

## 2.1.3 Factors Affecting Accumulation of Pollutants

The rate of accumulation of pollutants will depend on factors both external and internal to the organism. The concentration of the pollutant in water is clearly important, and many species carry higher loadings of pollutants when living in contaminated waters. For example, metal concentrations in algae and bryophytes are significantly correlated with concentrations in water. There appear to be no consistent correlations, however, between environmental levels of metals, other than mercury, and concentrations in invertebrates and fish (van Hattum et al., 1991). Temperature influences the absorption, detoxification and excretion rates of pollutants (Green et al., 1988), but not necessarily to the same extent, so that the overall bioconcentration may vary with temperature. Internal factors that influence bioconcentration include physiological condition. Fish with higher metabolic rates also accumulate contaminants faster and, because feeding results in a higher metabolism, a greater uptake of pollutants across the gills may occur in feeding as opposed to starved fish, as has been shown for cadmium uptake in the loach (Douben, 1989). Age, sex and the presence of competing pollutants in the water may also influence accumulation rates. The mercury concentration in fish is inversely related to the pH or alkalinity of lake water (Spry and Wiener, 1991). This is due, at least in part, to the microbial production of methyl mercury, itself inversely correlated with pH at the sediment- water interface (Mason, 1996).

## 2.2 Heavy Metals

Metals such as lead, nickel, cadmium, zinc, copper and mercury, arising from many industrial processes and some agricultural uses are among the major types of toxic pollutants in aquatic ecosystems. The term "heavy metal" is somewhat imprecise, but includes most metals with an atomic number greater than 20, and excludes alkali metals, alkaline earths, lanthanides and actinides (Mason, 1996).

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### 2.2.1 Lead

The two major uses of Lead are in lead-acid storage batteries, particularly for motor vehicles, and as lead alkyl compounds added to petrol. Petrol engines give higher-power outputs and use fuel more efficiently when operated at higher compression ratios. Smooth running can only be achieved under these conditions by using petrol containing more branched chain or aromatic hydrocarbons or by the cheaper expedient of adding lead alkyl compounds (O'Neill, 1993). Lead can cause hypertension, one of the factors influencing heart disease, and it has been suggested that the lower levels of heart diseases in hard-water areas may be due to lower levels of lead in the water supply. Lead is a cumulative poison. About 90% of the lead retained in the body enters the bones, from which it can be remobilized. It binds strongly to a large number of molecules, such as amino acids, haemoglobin, many enzymes, RNA and DNA; it thus disrupts many metabolic pathways. The effects of lead toxicity are very wide ranging and include impaired blood synthesis, hypertension, hyper-activity and brain damage. The widespread distribution of lead from motor-vehicle exhaust increases atmospheric levels by factors of 20 (much more in urban areas). The analysis of lead is difficult. In natural waters lead levels are at the microgram per cubic decimetre level (O'Neill, 1993).

### 2.2.2 Mercury

Mercury is much less common than lead in the earth's crust and consequently the geochemical cycle has smaller fluxes. Mercury is the only metal that is liquid at normal temperatures, being 15.5 times denser than water. Because of mercury's association with lead-zinc-silver ores, the presence of high levels of mercury vapour in the atmosphere, or in the air trapped in soil, can be used to indicate the presence of these ore bodies (O'Neill, 1993).

The most important difference between the lead and mercury cycles is the importance of methylation reactions. In its natural cycle lead remains in the +2 state and little natural methylation occurs. Mercury exists in the 0, +1 and +2 oxidation states, and methylation is an important feature of its cycle, particularly with regard to its uptake by fish and humans. Methylmercury is the major mercury species found in fish and about 90% of the  $CH_3Hg^+$  eaten is absorbed by humans. The methylation of mercury is especially important in rivers and lakes that have a low pH either continuously or intermittently. Methylmercury makes up 60-90% of the mercury in fish because the degree of absorption is high and the rate of elimination is usually very low. There have been a number of tragic episodes of organo-mercury poisonings in Japan, Guatemala, Iraq and Pakistan; these awakened interest in mercury as an environmental pollutant (O'Neill, 1993).

The target organ of methylmercury in humans is the brain, where it disrupts the blood-brain barrier, upsetting the metabolism of the nervous system. In addition, mercury forms very strong bonds with sulphur groups in proteins and enzymes, disrupting various enzymatic systems and synthetic mechanisms (O'Neil, 1993). Mercury most likely reaches isolated lakes via air transport. Mercury, like Lead, provokes most concern because it is toxic to the nervous system and the foetus and small child are the ones most sensitive to its adverse effects (Hill, 1997). There are very sensitive methods available that will detect mercury at levels in the microgram per kilogram range, but the high volatility of many mercury species causes difficulties. Samples must be collected in a manner that will avoid contamination, and the sample must be representative of the mass being investigated and the sample must be stored and then converted into a form suitable for analysis (O'Neill, 1993).

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## 2.2.3 Zinc and Cadmium

Zinc is an essential element, but cadmium has no known useful biological function in humans. The cycles of zinc and cadmium are very closely inter-related because natural zinc minerals and most anthropogenic fluxes contain small amounts of cadmium. Zinc, cadmium and mercury are in the same group in the periodic table because they all have similar arrangements of electrons in the outermost shells. However, the inner electron structure of mercury differs from that of zinc and cadmium, and therefore its chemical properties also differ; the properties of zinc and cadmium, though are very similar. The hydrated zinc ion  $(Zn^{2+} aq)$  is relatively more stable than the hydrated cadmium ion ( $Cd^{2+}$  aq). As a consequence, when there is competition between zinc and cadmium to bind to sites in insoluble species, cadmium tends to bind more strongly than zinc, especially if a metal-sulphur bond is formed. Cadmium therefore displaces zinc from many of the zinc –containing enzymes. Zinc deficiency in humans leads to dwarfism, reduced rates of blood clotting and wound healing, skin abnormalities. The mobilization of zinc and cadmium by human activities out-weighs natural cycling processes. The increased quantities of cadmium mobilized are partly related to demand for cadmium itself but also to increased use of zinc and phosphate fertilizers. Cadmium is used in electroplating (in which it forms a bright corrosionresistant finish), in plastic stabilizers, in pigments, in solder, and in nickel-cadmium batteries. Zinc is used to prevent corrosion (by galvanizing), in alloys, in paints, in dyes and in tyres (O'Neill, 1993).

## 2.2.4 Toxicity of Cadmium

The toxic effects of cadmium received widespread attention as a result of some Japanese developing Itai-Itai byo ('ouch ouch' disease). The name came from the severe pain developed by the sufferers as lumbago-type pains progressed to become severe bone damage with multiple fractures of the softened bones. Death was attributed to kidney failure (O'Neill, 1993). Cadmium bioaccumulates in the kidney and the amount of cadmium stored in this organ increases with age. Because Cadmium affects calcium metabolism, bone degeneration has also been observed. Cadmium can also accumulate to high levels in the liver (Hill, 1997). An example of homeostasis in animals and the control of excess metals is the formation of metallothionein proteins containing –SH groups which bind certain metals, such as Cd and Zn and enable them to be excreted without causing biochemical dysfunction (Alloway and Ayres, 1993).

### 2.2.5 Arsenic

Before the advent of synthetic organic pesticides, arsenic was used as a weed killer and rat poison. Along with chromium and copper, it is still a wood preservative in pressure- treated wood (Hill, 1997). It is also present in many sulphide ores of metals and is therefore emitted from metal smelters as an atmospheric pollutant (Alloway and Ayres, 1993). The toxicological importance of Arsenic is partly due to its chemical similarity with Phosphorus which means that Arsenic can disrupt metabolic pathways involving Phosphorous. Both acute and chronic toxicity are recognized and the continual inhalation of airbone forms of Arsenic is known to be carcinogenic (Alloway and Ayres, 1993).

### 2.2.6 Copper

A micronutrient which can be deficient in some soils causing severe loss of yield in several crops, especially cereals. Copper pollution can arise from cupper mining and smelting, brass manufacture, electroplating and excessive use of copper- based agrochemicals. Copper sulphate is used widely as an algicide in ornamental ponds and even in water supply reservoirs which are affected by blooms of toxic blue-green algae. Copper is used widely in houses for piping water although the concentrations in the drinking water is higher in soft water, this is not considered to be a hazard so long as the pH is within the normal limits (pH 6.5 - 8.5) (Alloway and Ayres,

1993).

#### 2.2.7 Iron

Iron, one of the most abundant metals on earth, is essential to most life forms and to normal human physiology. Iron is an integral part of many proteins and enzymes that maintain good health according to the American Institute of Medicine. In humans, iron is an essential component of proteins involved in oxygen transport (Dallman, 1986). It is also essential for the regulation of cell growth and differentiation (Bothwell, 1979, Andrews, 1986). A deficiency of iron limits oxygen delivery to cells, resulting in fatigue, poor work performance, and decreased immunity (Bhaskaram, 2001). On the other hand, excess amounts of iron in man can result in toxicity and even death (Corbett, 1995).

## 2.3 Sources of Heavy Metal Pollution in Aquatic Ecosystems

Domestic, industrial and agricultural users produce large quantities of waste products, and waterways provide a cheap and effective way of disposing of many of these. During dry weather, the flow of some rivers consists almost entirely of effluents (Mason, 1996). Environmental pollution by heavy metals became widely recognized with the Minmata disaster in Japan in the early 1950s (Mason, 1996). It has been suggested that over one billion human beings are currently exposed to elevated concentrations of toxic metals and metalloids in the environment and several million people may be suffering from subclinical metal poisoning. Some potentially toxic compounds, such as heavy metals, are continually released into the aquatic environment from natural processes such as volcanic activity and weathering of rocks and a number (e.g. copper, zinc) are essential, in small amounts, to life. Industrial processes have greatly increased the mobilization of many metals (Mason, 1996).

### 2.4 Standards of Water Quality

There are many sources of water quality criteria and standards - they may originate in the Member States of the European Union, or may be adopted by the Council or Parliament of the EU, or by individual countries, or they may be issued by international bodies. Further, these various levels specified will take cognisance of the differing uses for which water quality must be maintained. The requirements, as regards suitability, of water for industrial use, for drinking, for boilers and so on, may differ widely and each may be quite demanding. Environmental factors may modify the acute toxic effect of pollutants. The toxic effect of pollutants varies with the quality of water, pH and hardness being especially important. The chemical speciation of some metals is markedly affected by pH. Generally the ionic form of the metal is most toxic.

### 2.4.1 Alkalinity

Alkalinity of water is generally due to the presence of bicarbonates formed in reactions in the soils through which the water percolates. It is a measure of the capacity of the water to neutralise acids and it reflects its so-called *buffer capacity* (its inherent resistance to pH change). Poorlybuffered water will have a low or very low alkalinity and will be susceptible to pH reduction by atmospheric, acid deposition (Chapman, 1996). At times, however, river alkalinity values of up to 400 mg/l CaCO3 may be found; they are without significance in the context of the quality of the water. There is little known sanitary significance attaching to alkalinity (even up to 400 mg/l CaCO3), though unpalatability may result in highly alkaline waters. Alkalinity is involved in the consequential effects of eutrophication [over-enrichment] of waters (Ireland EPA, 2001).

## 2.4.2 Chemical Oxygen Demand and Biological Oxygen Demand

The chemical oxygen demand (COD) is a measure of the oxygen equivalent of the organic matter in a water sample that is susceptible to oxidation by a strong chemical oxidant, such as dichromate. The COD is widely used as a measure of the susceptibility to oxidation of the organic and inorganic materials present in water bodies and in the effluents from sewage and industrial plants. The test for COD is non-specific, in that it does not identify the oxidisable material or differentiate between the organic and inorganic material present. Similarly, it does not indicate the total organic carbon present since some organic compounds are not oxidised by the dichromate method whereas some inorganic compounds are oxidised. Nevertheless, COD is a useful, rapidly measured, variable for many industrial wastes and has been in use for several decades. The concentrations of COD observed in surface waters range from 20 mg/L  $O_2$  or less

in unpolluted waters to greater than 200 mg/L  $O_2$  in waters receiving effluents. Industrial wastewaters may have COD values ranging from 100 mg/L  $O_2$  to 60,000 mg/L  $O_2$ .

The biochemical oxygen demand (BOD) is an approximate measure of the amount of biochemically degradable organic matter present in a water sample. It is defined by the amount of oxygen required for the aerobic micro-organisms present in the sample to oxidise the organic matter to a stable inorganic form. The method is subject to various complicating factors such as the oxygen demand resulting from the respiration of algae in the sample and the possible oxidation of ammonia (if nitrifying bacteria are also present). The presence of toxic substances in a sample may affect microbial activity leading to a reduction in the measured BOD. BOD measurements are usually lower than COD measurements. Unpolluted waters typically have BOD values of 2 mg/L  $O_3$  or less, whereas those receiving wastewaters may have values up to 10 mg/L  $O_2$  or more, particularly near to the point of wastewater discharge. Raw sewage has a BOD of about 600 mg/L  $O_2$ , whereas treated sewage effluents have BOD values ranging from 20 to 100 mg/L  $O_2$  depending on the level of treatment applied. Industrial wastes may have BOD values up to 25,000 mg/L  $O_2$  (Chapman, 1996).

## 2.4.3 Chloride

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Most chlorine occurs as chloride (Cl<sup>-</sup>) in solution. It enters surface waters with the atmospheric deposition of oceanic aerosols, with the weathering of some sedimentary rocks (mostly rock salt deposits) and from industrial and sewage effluents, and agricultural and road run-off. The salting of roads during winter periods can contribute significantly to chloride increases in groundwater. High concentrations of chloride can make waters unpalatable and, therefore, unfit for drinking or livestock watering. In pristine freshwaters chloride concentrations are usually lower than 10

mg/L and sometimes less than 2 mg/L. Higher concentrations can occur near sewage and other waste outlets, irrigation drains, salt water intrusions, in arid areas and in wet coastal areas. As chloride is frequently associated with sewage, it is often incorporated into assessments as an indication of possible faecal contamination or as a measure of the extent of the dispersion of sewage discharges in water bodies (Chapman, 1996).

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## 2.4.4 Conductivity

Conductivity, or specific conductance, is a measure of the ability of water to conduct an electric current. It is sensitive to variations in dissolved solids, mostly mineral salts. The degree to which these dissociate into ions, the amount of electrical charge on each ion, ion mobility and the temperature of the solution all have an influence on conductivity. Conductivity is expressed as microsiemens per centimetre ( $\mu$ S/cm). The conductivity of most freshwaters ranges from 10 to 1,000  $\mu$ S/cm but may exceed 1,000  $\mu$ S/cm, especially in polluted waters, or those receiving large quantities of land run-off. In addition to being a rough indicator of mineral content when other methods cannot easily be used, conductivity can be measured to establish a pollution zone, e.g. around an effluent discharge, or the extent of influence of run-off waters (Chapman, 1996).

## 2.4.5 Temperature

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Temperature is important because it not only influences the metabolic activity and behaviour of organisms, which may affect their exposure to a pollutant, but it may also alter the physical and chemical state of the pollutant. In general, toxicity increases with temperature, as is the case for metals (Felts and Heath, 1984; Khangarot and Ray, 1987). There are, however, many exceptions to the increase in toxicity with temperature. The effect of temperature, and especially changes in

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temperature, on living organisms can be critical and the subject is a very wide and complex one. The temperature of surface waters is influenced by latitude, altitude, season, time of day, air circulation, cloud cover and the flow and depth of the water body. In turn, temperature affects physical, chemical and biological processes in water bodies and, therefore, the concentration of many variables. As water temperature increases, the rate of chemical reactions generally increases together with the evaporation and volatilisation of substances from the water. Increased temperature also decreases the solubility of gases in water, such as O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and others. The metabolic rate of aquatic organisms is also related to temperature, and in warm waters, respiration rates increase leading to increased oxygen consumption and increased decomposition of organic matter. Growth rates also increase (this is most noticeable for bacteria and phytoplankton which double their populations in very short time periods) leading to increased water turbidity, macrophyte growth and algal blooms, when nutrient conditions are suitable. Surface waters are usually within the temperature range 0° C to 30° C, although "hot springs" may reach 40° C or more. These temperatures fluctuate seasonally with minima occurring during winter or wet periods, and maxima in the summer or dry seasons, particularly in shallow waters. Abnormally high temperatures in surface water can arise from thermal discharges, usually from power plants, metal foundries and sewage treatment plants (Chapman, 1996).

## 2.4.6 pH

By definition pH is the negative logarithm of the hydrogen ion concentration of a solution and it is thus a measure of whether the liquid is acid or alkaline. The pH scale (derived from the ionisation constant of water) ranges from 0 (very acid) to 14 (very alkaline). The range of natural pH in fresh waters extends from around 4.5, for acid, peaty upland waters, to over 10.0 in waters where there is intense photosynthetic activity by algae. However, the most frequently

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encountered range is 6.5-8.0. In waters with low dissolved solids, which consequently have a low buffering capacity (i.e. low internal resistance to pH change), changes in pH induced by external causes may be quite dramatic. The effect of pH on fish is also an important consideration and values which depart increasingly from the normally found levels will have a more and more marked effect on fish, leading ultimately to mortality. The range of pH suitable for fisheries is considered to be 5.0-9.0, though 6.5-8.5 is preferable (Ireland EPA, 2001). Two contrasting responses of an organism to metal toxicity with a decrease in pH have described;

- If there is little change in speciation and metal binding is weak at the biological surface, a decrease in pH will decrease toxicity due to competition for binding sites from hydrogen ions.
- 2. Where there is a marked effect on speciation and strong binding of the metal at the biological surface the dominant effect of a decrease in pH will be to increase metal availability

### 2.4.7 Phosphates

Phosphorus occurs widely in nature in plants, in micro-organisms, in animal wastes and so on. It is widely used as an agricultural fertiliser and as a major constituent of detergents, particularly those for domestic use. Run-off and sewage discharges are thus important contributors of phosphorus to surface waters. The significance of phosphorus is principally in regard to the phenomenon of eutrophication (over-enrichment) of lakes and, to a lesser extent, rivers. Phosphorus gaining access to such water bodies, along with nitrogen as nitrate, promotes the growth of algae and other plants leading to blooms, littoral slimes, diurnal dissolved oxygen variations of great magnitude and related problems (Ireland EPA, 2001). Natural sources of phosphorus are mainly the weathering of phosphorus-bearing rocks and the decomposition of organic matter. Domestic waste-waters (particularly those containing detergents), industrial effluents and fertiliser run-off contribute to elevated levels in surface waters. Phosphorus associated with organic and mineral constituents of sediments in water bodies can also be mobilised by bacteria and released to the water column. Phosphorus is rarely found in high concentrations in freshwaters as it is actively taken up by plants. As a result there can be considerable seasonal fluctuations in concentrations in surface waters. In most natural surface waters, phosphorus ranges from 0.005 to 0.020 mg/ L PO<sub>4</sub> P. Concentrations as low as 0.001 mg/ L PO<sub>4</sub> P may be found in some pristine waters and as high as 200 mg/ L PO<sub>4</sub> P in some enclosed saline waters (Chapman, 1996).

## 2.4.8 Sulphates

Sulphate is naturally present in surface waters as  $SO4^{22}$ . It arises from the atmospheric deposition of oceanic aerosols and the leaching of sulphur compounds, either sulphate minerals such as gypsum or sulphide minerals such as pyrite, from sedimentary rocks. It is the stable, oxidised form of sulphur and is readily soluble in water (with the exception of lead, barium and strontium sulphates which precipitate). Industrial discharges and atmospheric precipitation can also add significant amounts of sulphate to surface waters. Sulphate can be used as an oxygen source by bacteria which convert it to hydrogen sulphide (H<sub>2</sub>S, HS<sup>-</sup>) under anaerobic conditions. Sulphate concentrations in natural waters are usually between 2 and 80 mg/L, although they may exceed 1,000 mg/L near industrial discharges or in arid regions where sulphate minerals, such as gypsum, are present. High concentrations (> 400 mg/L) may make water unpleasant to drink (Chapman, 1996).

## 2.4.9 Total Suspended Solids

The significance of suspended solids in water is great, on a number of grounds. The solids may in fact consist of algal growths and hence be indicative of severely eutrophic conditions; they may indicate the discharge of washings from sandpits, quarries or mines; they will reduce light penetration in surface waters and interfere with aquatic plant life; they will seriously damage fishery waters and may affect fish life; they may form deposits on the bed of rivers and lakes which will in turn give rise to septic and offensive conditions; and they may indicate the presence of unsatisfactory sewage effluent discharges (Ireland EPA, 2001).

## 2.4.10 Nitrates

The nitrate ion (NO<sub>3</sub>) is the common form of combined nitrogen found in natural waters. It may be biochemically reduced to nitrite (NO<sub>2</sub>) by denitrification processes, usually under anaerobic conditions. The nitrite ion is rapidly oxidised to nitrate. Natural sources of nitrate to surface waters include igneous rocks, land drainage and plant and animal debris. Nitrate is an essential nutrient for aquatic plants and seasonal fluctuations can be caused by plant growth and decay. Natural concentrations, which seldom exceed 0.1 mg/ L, NO<sub>3</sub> N, may be enhanced by municipal and industrial waste-waters, including leachates from waste disposal sites and sanitary landfills. In rural and suburban areas, the use of inorganic nitrate fertilisers can be a significant source. When influenced by human activities, surface waters can have nitrate concentrations up to 5 mg/L NO<sub>3</sub> N, but often less than 1 mg/L NO<sub>3</sub> N. Concentrations in excess of 5 mg/L NO<sub>3</sub> N usually indicate pollution by human or animal waste, or fertiliser run-off. In cases of extreme pollution, concentrations may reach 200 mg/L NO<sub>3</sub> N. In lakes, concentrations of nitrate in excess of 0.2 mg/L NO<sub>3</sub> N tend to stimulate algal growth and indicate possible eutrophic conditions (Chapman, 1996).

## 2.4.11 Oil and Grease

Oil and grease can affect aquatic organisms in a number of ways. They can kill directly through coating and asphyxiation, contact poisoning, or through exposure to water-soluble components. Oil and grease can have population effects through the destruction of more sensitive juvenile life-stages or through the reduction of prey species. Oil is also capable of causing sub-lethal and stress effects, carcinogenic and mutagenic effects, and can affect the behaviour of individual organisms (UNEP GEMS/ Water Programme, 2006).

## 2.5 Food Chain

In a general way it can be said that usually a body of water maintains a certain standing crop of organisms composed primarily of five large groups, viz; phytoplankton, bottom flora, bottom fauna, zooplankton and fishes. This series composes a nutritional chain in which the first two constitute a producing class and the other three are the consumers. Taken as a whole, these organisms are an expression of the productivity of the water concerned. In such a dependency chain, as maintained in nature, it is highly important that the ability of the supporting classes to maintain the dependent groups be known if productivity is to be understood (Welch, 1952).

## 2.5.1 Bioacummulation within the Aquatic Food Chain

Bioaccumulation refers to the uptake of pollutants from water and is independent of trophic level. Bioaccumulation occurs with many toxic pollutants, very high levels being accumulated in organisms from very low levels in water (Mason, 1996). Cells have mechanisms for bioaccumulation, the selective absorption and storage of a great variety of molecules. This allows them to acquire nutrients and essential minerals, but at the same time, can also result in the absorption and build-up of harmful substances. Toxins that are rather dilute in the environment can reach dangerous levels inside cells and tissues through this process (Cunningham and Cunningham, 2002).

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## **2.5.2 Biomagnification along the Aquatic Food Chain**

With biomagnifications there are progressively greater amounts of contaminant along the food chain, carnivores containing greater concentrations than herbivores, which contain more than plants. Organochlorine pesticides have been shown to biomagnify along the food chain, but biomagnification is the exception for metals (Mance, 1987). Biological magnification is most apt to occur in aquatic food chains; there are more trophic levels in aquatic food chains than there are in terrestrial food chains (Mader, 1990). Phytoplankton and bacteria in aquatic ecosystems, for instance, take up heavy metals or toxic organic molecules from water or sediments. Their predators- zooplankton and small fish collect and retain the toxins from many prey organisms, building up higher toxin concentrations. The top carnivores in the food chain- game fish, fisheating birds, and humans can accumulate such high toxin levels that they suffer adverse health effects (Cunningham and Cunningham, 2002).

## 2.6 Estuaries and Lagoons

Near the shores of the oceans are many bodies of water either continuously, intermittently, or not connected with the ocean. Estuaries are where freshwater and salt water meet and mix. The most generally accepted definition is a semi-enclosed body of water that has a free connection with the

open sea and within which seawater is measurably diluted with fresh water derived from land drainage (Royce, 1984). Lagoons are coastal bodies of either freshwater or salt water that may have an intermittent connection with the ocean but that usually have a stable salinity and little or no tidal exchange. They may be fresh if elevated slightly above the ocean. Lagoons are usually small and shallow and can be considered another variety of lake (Royce, 1984).

## 2.7 Sediments

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Sediment is the collective name for loose, solid particles that originate from weathering and erosion of pre-existing rocks and chemical precipitation from solution, including secretion by organisms in water. Sediments are said to be unconsolidated, which means that the grains are separate, or unattached to one another (Plummer et al., 2001). Some cases of high suspendedsediment load in water occur naturally. In many agricultural areas, sediment pollution of lakes and streams is the most serious water quality problem. Sediment pollution not only causes water to be murky and unpleasant to look at, swim in, or drink, it reduces the light available to underwater plants, and blankets food sup-populations and the nests of fish, thus reducing fish and shellfish populations (Montgomery, 2000). Sediment particles are classified and defined according to the size of individual fragments. These could be gravel, sand, silt or clay (Plummer et al., 1996). It has been recognized that aquatic sediments absorb persistent and toxic chemicals to levels many times higher than the water column concentration (Linnik and Zubenko, 2000). Depending on the river morphology and hydrological conditions, suspended particles with associated contaminants can settle along the watercourse and become part of the bottom sediments, often for many kilometers downstream from the chemical sources (Ciszewski, 1997).
# 2.8 Monitoring Of Aquatic Ecosystems

Aquatic ecosystem monitoring activities encompass a range of water quality, sediment quality and aquatic biota assessments. Among other considerations, the design assumes a current knowledge of sources and types of contaminants and an understanding of the interactions between climate, hydrology and watershed processes (Alberta Environment, 2006). De Zwart (1995) reported that clearly environmental monitoring must have a purpose and a function in the process of risk management and pollution control and in general a number of purposes for monitoring can be discerned:

- The **signal or alarm function** for the detection of suddenly occurring (adverse) changes in the environment. Preferably the monitoring system should be designed to immediately enable the tracing of causes;
- The **control functions** for a verification on the effectivity of pollution control strategies and a check on compliance;
- The trend (recognition) function based on time series analysis of concentrations and loads to enable the prediction of future developments;
- The **instrument function** to help in the recognition and clarification of underlying processes by operational investigations (surveys).

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#### 2.8.1 Biomonitoring

Different interpretations of what is considered to be a biological variable or biological observation caused a lot of confusion about which activities belong to biomonitoring. In the medical world, biomonitoring is solely defined as the concentration measurement of pollutants inside the human body. Naturalists generally also include measurements of the direct effects of

disturbances on physiological processes in organisms. Measurements on the responses on a higher level of biological integration (populations, communities and ecosystems) naturalists classify as inventories. Finally, according to environmentalists, all varieties of biologically oriented measurements, as long as they are performed with the objective of protecting, preserving and correcting the biological integrity of natural systems, fall under the reign of biomonitoring (De Zwart, 1995).

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## 2.8.2 Limitations of Biomonitoring

A disadvantage of biological effect measurements is that sometimes it is very difficult to relate the observed effects to specific aspects of pollution. In view of the present chemical oriented pollution abatement policies and to reveal chemical specific problems, it is clear that biological effect analysis will never totally replace chemical analysis. However, in some situations the number of standard chemical analysis can be reduced, by allowing bioeffects to trigger chemical analysis (integrated monitoring), thus buying time for more elaborate analytical procedures (De Zwart, 1995). Results of biomonitoring studies are often equivocal because of the lack of adequate controls, non-random assignment of treatments, and lack of replication (Hurlbert, 1984).

#### 2.9 Oreochromis niloticus

*Oreochromis niloticus* (Nile tilapia) is a highly invasive fish that plagues a variety of ecosystems, particularly those located in the tropics. *Oreochromis niloticus*' effective mouthbrooding reproductive strategy allows it to increase in numbers at a rate which, not only crowds native species, but pollutes and unbalances the water column. It is a frequently farmed

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aquatic species, due to its relative ease of culture and rapid reproduction rates. Most infestations are a result of aquaculture.

### 2.9.1 Habitat and Biology

Nile tilapia is a tropical species that prefers to live in shallow water. The lower and upper lethal temperatures for Nile tilapia are 11-12 °C and 42 °C, respectively, while the preferred temperature ranges from 31 to 36 °C. It is an omnivorous grazer that feeds on phytoplankton, periphyton, aquatic plants, small invertebrates, benthic fauna, detritus and bacterial films associated with detritus. Nile tilapia can filter feed by entrapping suspended particles, including phytoplankton and bacteria, on mucous in the buccal cavity, although its main source of nutrition is obtained by surface grazing on periphyton mats. The breeding process starts when the male establishes a territory, digs a craterlike spawning nest and guards his territory. The ripe female spawns in the nest, and immediately after fertilization by the male, collects the eggs into her mouth and moves off. The female incubates the eggs in her mouth and broods the fry after hatching until the yolk sac is absorbed. Incubating and brooding is accomplished in 1 to 2 weeks, depending on temperature. After fry are released, they may swim back into her mouth if danger threatens. Being a maternal mouth brooder, the number of eggs per spawn is small in comparison with most other pond fishes. The male remains in his territory, guarding the nest, and is able to fertilize eggs from a succession of females. If there is no cold period, during which spawning is suppressed, the female may spawn continuously. While the female is brooding, she eats little or nothing. Nile tilapia can live longer than 10 years and reach a weight exceeding 5 kg (FAO, 2006).

#### **CHAPTER THREE**

### 3.0 MATERIALS AND METHODS

#### 3.1 Study Area

The study was carried out on the Butuah Lagoon which is located close to New Takoradi, a suburb of Sekondi-Takoradi, Ghana. It is the classically closed lagoon type that is cut from the sea for a greater part of the year but opened for a relatively short period of time during the rainy season (Coastal Resource Center-Ghana/Friends of the Nation, 2010).

Generally, the Sekondi-Takoradi Metropolis does not experience severe weather conditions. The climate of the metropolis is equatorial, with an average annual temperature of about 22°C. Rainfall is bi-modal, with the major season occurring between March and July and the minor season occurring between August and November. The mean annual rainfall is about 1,380 mm, covering an average of 122 rainy days (www.mofa.gov.gh/site/).

The lagoon is surrounded by a number of industries; the major ones include Ghana Oil Limited (GOIL) Depot, Ghana Primewood Products Limited, Ghana Household Utility Manufacturing Company (GHUMCO), West African Mills Company Limited (WAMCO), Takoradi Polytechnic and Western Castings Limited. There are also hotels as well as artisanal and farming activities going on around the lagoon, and a waste dump site very close to the bank of the lagoon which sometimes over flows into the lagoon contributing to the level of pollution of the lagoon.

#### **3.2** Sampling sites

The sampling points are within latitude 04.90500° N, 001.74870° W (Downstream), Latitude 04.91176° N, 001.75003° W (Midstream) and Latitude 04.91522° N, 001.75355° W (Upstream)

(Fig. 1). Samples were also collected from a drain discharging effluent from industries into the Butuah Lagoon (Latitude 04.91340° N, 001.75355° W).



Samples were collected from four points, three (3) within the lagoon and the fourth from an effluent from the industries. Point one (downstream) was 310 meters away from point two (midstream) and point two (midstream) was 260 meters away from point three (upstream). Study points were areas of high fishing activities. The fourth sampling point was identified along a

main effluent discharge channel and samples were collected a point 70 meters away from where it joins the lagoon. Table 1 gives a description of samples and the sampling points.

Sampling location	Sample code and description
Downstream	W1 is water samples from downstream
	F1 is fish samples from downstream
	S1 is sediment samples from downstream
Midstream	W2 is water samples from midstream
	F2 is fish samples from midstream
	S2 is sediment samples from midstream
Upstream	W3 is water samples from upstream
	F3 is fish samples from upstream
(	S3 is sediment samples from upstream
Drain	WE is water samples from effluent
2	103R R BADY
	WJ SANE NO

Table 1. Description of samples and sampling sites

#### 3.3 Sampling

Sampling was conducted for a period of four months starting December, 2011 and ending in March, 2012. In-situ measurement of temperature was done using BRANNAN 76mm Immersion Thermometer. Water samples for heavy metal analysis were collected in 500-mL acid-washed low density polyethylene bottles and the samples were acidified with 50% of 5.0ml HNO<sub>3</sub> at the point of collection. Similarly, sediment samples were collected using an Ekman grab at the three

points. Sediment samples were transferred into 500-mL acid-washed polyethylene bottles (PE). Samples (water, fish and sediments) were kept in ice chests at about 4°C and transported to the Plant Pathology and Fisheries laboratory of the Faculty of Renewable Natural Resources (FRNR), KNUST for analysis.

#### 3.4 Physicochemical Water Analysis

The water samples for analysis of conductivity, turbidity, pH, total dissolved solids (TDS) and oil and grease were immediately transported in ice chests to the quality control laboratory of West African Mills Company Limited, Takoradi, Ghana. At the laboratory TDS and Conductivity were determined using the Conductivity Meter (EH CLM 381 model). Turbidity was determined using Hach Ratio Turbidimeter (Ranges NTU 2 20 200) and pH was determined using JENWAY 3505 pH Meter. Samples for analysis of COD, BOD, TSS, Phosphates, Nitrates, Alkalinity and Sulphates were transported to the Laboratory of the Minerals Commission, Takoradi, Ghana.

#### 3.4.1 Determination of Alkalinity and Chloride

Titrimetric analysis was employed in the determination of alkalinity with reference to APHA (1992). A volume of 100 ml of the sample was measured into a volumetric flask and three drops of phenolphthalein indicator was added. The sample was titrated with 0.1 N acid until a red colour appeared indicating the endpoint. The volume was recorded and alkalinity calculated:

Where pH is > 8.3 Alkalinity as mg/L CaCO<sub>3</sub> =  $\frac{(V \times N) \times 1000}{\text{sample volume, mL x 2}} \times 100$ 

Where pH is  $\leq 8.3$  Alkalinity as mg/L HCO<sub>3</sub> =  $\frac{(V \ge N) \times 1000}{\text{sample volume, mL}} \times 61$ 

V = titration volume in mL, N = normality of the acid solution, 100 = molecular mass of CaCO<sub>3</sub>, 61 = molecular mass of HCO<sub>3</sub>,

#### **CHLORIDE** (Argentometric Titration)

100 ml of the sample was measured into a volumetric flask and 1 ml  $K_2CrO_4$  was added as indicator. The sample was then titrated with AgNO<sub>3</sub> until the endpoint was reached. A blank test was carried out for quality control and chloride content determined:

Chloride mg Cl<sup>-</sup>/ L =  $\frac{(A - B) \times M \times 35.45 \times 1000}{\text{sample volume, mL}}$ 

Where A= ml titration for sample, B= ml titration for blank, M= molarity of AgNO<sub>3</sub>

#### 3.4.2 Determination of BOD and COD

#### 3.4.2.1 BOD

An airtight BOD bottle was filled with the sample till it overflowed. The sample was corked and incubated at 20° C for five days. The dissolved oxygen concentration was measured before and after the incubation. BOD was calculated from the difference between the initial and final DO.

# 3.4.2.2 COD (Open Reflux Method)

The sample, to be measured, was oxidized under reflux with a known amount of potassium dichromate in strong sulphuric acid with silver sulphate as a catalyst. Organic matter reduced part of the dichromate and the remainder was determined by titration with iron (II) ammonium sulphate or iron (II) sulphate using ferroin as indicator. Interferences from chloride were suppressed by the addition of mercuric sulphate to the reaction mixture. The chemical oxygen

demand (COD) was expressed as milligrams of oxygen absorbed from standard dichromate per litre of sample (APHA, 1992).

CALCULATION,

 $COD (mg/L) = \frac{(A - B) x M \times 8000}{sample volume, mL}$ 

Where,

A = ml FAS used for blank, B = ml FAS used for sample, M = molarity of FAS and 8000 = milliequivalent of Oxygen x 1000 ml/ L

## 3.4.3 Wagtech Nitratest

The Nitratest Tube was filled with the sample to the 20 ml mark. One level spoonful of Nitratest Powder and one Nitratest tablet was added. The screw cap was replaced and the tube was shaken for one minute. The tube was allowed to stand for about one minute and gently inverted three or four times to aid flocculation. Tube was allowed to stand for 5 minutes to ensure complete settlement. The screw cap was removed and a clean tissue was used to wipe around the top of tube. The clear solution was carefully decanted into a round test tube, filling to the 10 ml mark. One Nitricol tablet was crushed and added to the solution, then shaken for it to completely dissolve.

The mixture was allowed to stand for 10 minutes to allow full colour development. Wavelength of 570 nm on the Photometer was selected and Photometer reading was taken.

## **3.4.4** Oil and Grease Determination (Partition- Gravimetric Method)

200 ml of sample was measured into a flask and acidified with Hydrochloric acid to pH 2 and transferred into a separatory funnel. The sampling bottle was carefully rinsed with 30 ml petroleum ether and solvent washings were added to separatory funnel. The separatory funnel was shaken vigorously for 2 minutes and corked. The separating funnel was inverted and the pressure was released through the bottom. The shaking was repeated and the pressure released until there was no more pressure built up in the separatory funnel. The separatory funnel was opened and hung upright to allow solvent to separate from the water sample. The solvent layer was drained through a funnel containing solvent moistened filter paper into a clean-tarred evaporating dish when the layer separates. The extraction was repeated twice more with 30 ml solvent each.

The extracts were combined in a tarred flask and the filter paper washed with additional 20 ml solvent. The solvent was distilled from a distilling flask on a water bath at 70° C until all the water has evaporated from the flask leaving only the oil and grease.

The oil and grease content was determined;

Oil and Grease (mg/L) =  $\frac{(A - B) \times 1000}{\text{sample volume, mL}}$ 

Where A = total gain in the weight of the flask in grams, B = Solvent blank.

## 3.4.5 Total Suspended Solids (TSS)

# Procedure

50 mL of a well-mixed sample was filtered through a weighed standard glass-fiber filter paper. The residue retained on the filter was then dried in an oven at 103 to 105°C for 1 hour. It was then cooled in a dessicator and weighed. The increase in weight of the filter represents the total suspended solids.

#### Calculation

The T.S.S was computed for using the formula below:

mg total suspended solids/L =  $\frac{(A - B) \times 1000}{\text{sample volume, mL}}$ 

A = weight of filter + dried residue, mg, and B = weight of filter, mg.

## 3.5 Laboratory analysis of samples

At the laboratory, sediment samples were air-dried to a constant weight. The dried samples were grounded in ceramic mortars and gently sieved. Fish samples were washed thoroughly with distilled water to remove debris and the muscles removed using a stainless steel knife.

#### **3.5.1 Digestion of Samples**

1.0 g of the homogenized fish samples and sediment samples were weighed using Sartorius BP 6100 Analytical balance into separate 50 ml digestion tube and 10 ml diacid ( $HNO_3-HCIO_4$ ) in the ratio (9:4 vv) was added. Each mixture was heated on a hot plate until the red  $NO_2$  fumes ceased and white fumes were produced (Motsara and Roy, 2008). For the water samples, 100 ml of each were measured using a measuring cylinder and transferred into separate digestion tubes. 10 ml of 50%  $HNO_3$  was added to each of the samples and then heated on a hot plate until white fumes were produced. The digested samples were allowed to cool after which they were washed with distilled water and filtered into separate 100 ml volumetric flasks and topped up with distilled water to the 100 ml mark.

# 3.5.2 Determination of Lead, Cadmium, Copper, Arsenic, Iron and Zinc

Atomic Absorption Spectrophometer (AAS 220 model) was used in determining the total concentrations of Lead, Cadmium, Copper, Arsenic, Iron and Zinc in the previously digested samples (Plate 1).



Plate 1. The Atomic Absorption Spectrophotometer (AAS 220 Model)

The acetylene gas and compressor were fixed and compressor turned on and the liquid trap blown to rid off any liquid trapped. The Extractor was turned on and the AAS 220 power turned on (AOAC, 2006). The capillary tube and nebulizer block were cleaned with cleansing wire and opening of the burner cleaned with an alignment card. The worksheet of the AAS software on the attached computer was opened and the hollow cathode lamp inserted in the lamp holder. The lamp was turned on ray from cathode aligned to hit target area of the alignment card for optimal light throughput, and then the machine was ignited. The capillary was placed in a 10 ml graduated cylinder containing deionized water and aspiration rate measured, and set to 6 ml per minute. The analytical blank was prepared, and a series of calibration solutions of known amounts of analyte element (standards) were made. The blank and standards were atomized in turn and their responses measured. A calibration graph was plotted for each of the solutions, after which the sample solutions were atomized and measured. Metal concentrations from the sample solutions were determined from the calibration, based on the absorbance obtained for the unknown (AOAC, 2006).

# KNUST

# 3.5.3 Determination of Total Mercury

The Automatic Mercury Analyzer (Model HG 6000) at the Chemistry Department of Kwame Nkrumah University of Science and Technology (KNUST), equipped with a mercury lamp at a wavelength 253.7 nm was used for the determination of total mercury in the fish, water and sediment samples. During the determination, a known volume (5 ml) of the sample solution was introduced into a reaction vessel using a micropipette and immediately stoppered. 0.5 ml of the 10% (w/v) stannous chloride (SnCl<sub>2</sub>· 2H<sub>2</sub>O) in 1 ml HCl was added from a dispenser to aid the reduction reaction. The stannous chloride solution (10% w/v) was prepared by dissolving 10 g of the salt in 100 ml of 1m HCl. The solution was aerated with nitrogen gas at 50 ml per minute for 30 minutes to expel any elemental mercury from it. Responses were recorded on strip chart recorders as sharp peaks. The peak heights were used for the computation of the total mercury concentrations in the fish tissues, water and sediments.

# 3.6 Data Analysis

Results of the heavy metal and physicochemical water analyses were subjected to a one-way Analysis of Variance (ANOVA) to test for significant differences (p<0.05) using SPSS (Appendix 1). All graphs were plotted using the GraphPad Prism 5.03 Software.



#### **CHAPTER FOUR**

## 4.0 RESULTS

## 4.1 Physicochemical Parameters of Butuah Lagoon

The results of the physicochemical properties of Butuah Lagoon obtained during the four months sampling period are represented in Table 2. pH values were in the alkaline range between 7.49 and 8.71 with the lowest values being recorded at W3 for all months. There were significant differences in mean pH values among water samples collected from Upstream (W3) in December and January from those collected in February and March. Similarly mean pH values of water sample collected from midstream (W2) in February was significantly different from those collected in December, January and March (Table 2).

Samples collected from the upstream generally recorded the lowest Total Dissolved Solids (TDS) for all four months (Table 2). Total Dissolved Solids ranged between 140.33 and 1961 mg/L with highest concentration being recorded at W1 in December whilst the lowest concentration was recorded in March at W3. There were significant differences among TDS in samples collected from all three sites (W1, W2 and W3) for all four months (Table 2).

Total Suspended Solids (TSS) values ranged between 7.67 and 37.00 mg/L. The lowest concentration was recorded in March at W3 whilst the highest concentration was recorded at W1 in January (Table 2). There were significant differences among TSS in samples collected from upstream (W3) from those collected from midstream (W2) and downstream (W1) in all four months. TSS in samples from upstream in March was significantly different from upstream samples collected in the other three months (December, January and February) (Table 2).

PARAMETERS														
Samplin period and	ng pH	TDS	TSS	COND	TEMP	TURB	COD	BOD	<b>P0</b> <sub>4</sub>	$SO_4$	NO <sub>3</sub>	Oil&G	Chlor	Alkal
code		(mg/L)	(mg/L)	(µS/cm)	(° C)	(NTU)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Dec W1 W2 W3	8.24 <sup>bc</sup> 8.27 <sup>bc</sup> 7.49 <sup>a</sup>	1961.33 <sup>e</sup> 1903.33 <sup>b</sup> 141.67 <sup>a</sup>	35.00 <sup>cd</sup> 31.33 <sup>cd</sup> 14.67 <sup>b</sup>	3922.33 <sup>f</sup> 3805.33 <sup>bc</sup> 283.00 <sup>a</sup>	30.67 <sup>cd</sup> 31.00 <sup>d</sup> 29.33 <sup>abcd</sup>	19.33 <sup>a</sup> 22.33 <sup>abc</sup> 101.33 <sup>g</sup>	383.00 <sup>d</sup> 136.67 <sup>a</sup> 180.3 <sup>b</sup>	120.33 <sup>d</sup> 45.67 <sup>a</sup> 65.67 <sup>c</sup>	$40.32^{d}$ 29.89 <sup>a</sup> 40.19 <sup>d</sup>	$50.00^{\rm f}$ $51.33^{\rm fg}$ $29.17^{\rm a}$	$0.02^{a}$ $0.02^{a}$ $0.15^{a}$	10.67 <sup>a</sup> 13.33 <sup>a</sup> 70.00 <sup>b</sup>	7092.67 <sup>c</sup> 5646.33 <sup>b</sup> 2449.00 <sup>a</sup>	719.80 <sup>de</sup> 679.13 <sup>cd</sup> 353.80 <sup>a</sup>
Jan W1 W2 W3	8.32 <sup>bc</sup> 8.29 <sup>bc</sup> 7.60 <sup>a</sup>	1960.33 <sup>de</sup> 1904.67 <sup>b</sup> 142.33 <sup>a</sup>	37.00 <sup>d</sup> 32.67 <sup>cd</sup> 17.67 <sup>b</sup>	$3920.00^{\rm ef} \\ 3809.67^{\rm c} \\ 285.00^{\rm a}$	31.00 <sup>d</sup> 31.33 <sup>d</sup> 29.33 <sup>ab</sup>	21.00 <sup>ab</sup> 23.33 <sup>bcd</sup> 102.00 <sup>g</sup>	386.00 <sup>d</sup> 137.67 <sup>a</sup> 181.67 <sup>b</sup>	123.33 <sup>de</sup> 45.00 <sup>a</sup> 66.67 <sup>c</sup>	40.22 <sup>d</sup> 31.12 <sup>b</sup> 44.58 <sup>g</sup>	52.67 <sup>g</sup> 53.00 <sup>g</sup> 30.67 <sup>a</sup>	$0.02^{a}$ $0.03^{a}$ $0.21^{a}$	12.50 <sup>a</sup> 13.67 <sup>a</sup> 71.67 <sup>b</sup>	7097.67 <sup>cd</sup> 5649.33 <sup>b</sup> 2449.67 <sup>a</sup>	642.53 <sup>bcd</sup> 636.03 <sup>bcd</sup> 366.00 <sup>a</sup>
Feb W1 W2 W3	8.47 <sup>cd</sup> 8.71 <sup>d</sup> 8.12 <sup>b</sup>	$1956.00^{cd} \\ 1902.00^{b} \\ 140.67^{a}$	35.67 <sup>cd</sup> 30.00 <sup>c</sup> 16.33 <sup>b</sup>	3912.33 <sup>de</sup> 3803.67 <sup>bc</sup> 281.33 <sup>a</sup>	29.00 <sup>a</sup> 30.00 <sup>abcd</sup> 29.50 <sup>abc</sup>	59.50 <sup>e</sup> 25.67 <sup>cd</sup> 73.77 <sup>f</sup>	392.33° 142.33 <sup>a</sup> 192.67°	131.00 <sup>f</sup> 53.33 <sup>b</sup> 69.00 <sup>c</sup>	41.72 <sup>e</sup> 32.41 <sup>c</sup> 41.45 <sup>e</sup>	40.32 <sup>c</sup> 31.27 <sup>ab</sup> 44.57 <sup>e</sup>	$0.17^{a}$ $0.05^{a}$ $0.04^{a}$	10.33 <sup>a</sup> 11.33 <sup>a</sup> 70.33 <sup>b</sup>	7100.33 <sup>cd</sup> 5649.67 <sup>b</sup> 2447.33 <sup>a</sup>	$590.00^{bc}$ $565.00^{b}$ $353.80^{a}$
Mar W1 W2 W3	$8.29^{bc}$ $8.45^{bc}$ $8.04^{b}$	1953.00 <sup>c</sup> 1899.67 <sup>b</sup> 140.33 <sup>a</sup>	17.33 <sup>b</sup> 19.33 <sup>b</sup> 7.67 <sup>a</sup>	3906.00 <sup>d</sup> 3799.33 <sup>b</sup> 279.67 <sup>a</sup>	29.50 <sup>abc</sup> 30.33 <sup>bcd</sup> 29.67 <sup>abc</sup>	6 <mark>1.33<sup>e</sup> 26.60<sup>d</sup> 74.00<sup>f</sup></mark>	405.00 <sup>f</sup> 141.33 <sup>a</sup> 194.67 <sup>c</sup>	127.00 <sup>ef</sup> 50.67 <sup>b</sup> 68.67 <sup>c</sup>	<b>43</b> .32 <sup>f</sup> <b>32</b> .14 <sup>c</sup> 44.54 <sup>g</sup>	39.67 <sup>c</sup> 33.00 <sup>b</sup> 42.33 <sup>d</sup>	3.10 <sup>b</sup> 3.13 <sup>b</sup> 3.43 <sup>b</sup>	$11.67^{a}$ $14.00^{a}$ $68.00^{b}$	7104.67 <sup>d</sup> 5652.67 <sup>b</sup> 2448.33 <sup>a</sup>	793.00 <sup>ef</sup> 872.30 <sup>f</sup> 693.37 <sup>cd</sup>

# Table 2. Mean values of physicochemical parameters along Butuah Lagoon

Mean (in same column) with different letters in superscript differ significantly (p<0.05)

Conductivity values ranged between 279.67  $\mu$ S/cm and 3922.33  $\mu$ S/cm. The lowest concentration was recorded in March at W3 whilst the highest concentration was recorded at W1 in December (Table 2). Conductivity in samples from upstream (W3) was significantly different from midstream (W2) and downstream (W1) samples collected in all four months (Table 2).

Temperature values were slightly higher at W2 in all four months. The values ranged from a minimum of 29.00 and a maximum of 31.33 (Table 2). Temperature in samples from downstream (W1) and midstream (W2) in January and samples from downstream (W1) and upstream (W3) in March was significantly different from downstream, midstream and upstream samples collected in December and February (Table 2).

Turbidity values ranged between 19.33 and 102.00 NTU with the lowest being recorded in December at W1 whilst the highest concentration was recorded at W3 in January (Table 2). There were significant differences among Turbidity in samples collected from all three sites (W1, W2 and W3) for all four months (Table 2).

The lowest COD was recorded in December at W2 whilst the highest concentration was recorded in March at W1. The range of values recorded for COD was between 136.67 and 405.00 mg/L (Table 2). There were significant differences among COD in samples collected from all three sites (W1, W2 and W3) for all four months (Table 2).

BOD values ranged between 45.00 and 131.00 mg/L (Table 2). The lowest BOD was recorded in January at W2 whilst the highest was recorded in February at W1. Similarly, there were significant differences among BOD in samples collected from all three sites (W1, W2 and W3) for all four months (Table 2).

The range of values recorded for Phosphates during the sampling period was from 29.89 to 44.58 mg/L. The lowest concentration was recorded in December at W2 whilst the highest was recorded in January at W3 (Table 2). There were significant differences among Phosphate in samples collected from all three sites (W1, W2 and W3) in January, February and March whereas in December there was no significant differences between Phosphate in samples collected from W1 and W3 (Table 2).

Sulphate concentration in samples ranged between 29.17 and 53.00 mg/L during the period of sampling. The lowest Sulphate concentration in the samples was recorded in December at W3 whilst the highest concentration was recorded in January at W2 (Table 2). There were significant differences among Sulphate in samples collected from all three sites (W1, W2 and W3) in December, February and March whereas in January there was no significant difference between Sulphate concentration between samples collected from W1 and W2 (Table 2).

The range of values recorded for Nitrate concentrations was between 0.02 and 3.43 mg/L. The lowest concentration was recorded in December at W1 and W2 and in January at W1 whilst the highest concentration was recorded in March at W3 (Table 2). There were no significant differences among Nitrate in samples collected from all three sites (W1, W2 and W3) for all four months (Table 2).

Oil and Grease recorded values ranging from 10.33 to 71.67 mg/L during the period of sampling. The lowest concentration of Oil and Grease was recorded in February at W1 whilst the highest concentration was recorded in January at W3 (Table 2). There were no significant differences between Oil and grease in samples collected from downstream (W1) and midstream (W2) in all four months (Table 2). The range of values of Chloride concentration was between 2447.33 and 7104.67 mg/L during the sampling period. The lowest concentration of Chloride was recorded in February at W3 whiles the highest concentration was recorded in March at W1 (Table 2). There were significant differences among Chloride in samples collected from all three sites (W1, W2 and W3) for all four months (Table 2).

Alkalinity values ranged from 353.80 to 872.30 mg/L during the period of sampling. The lowest concentration of Alkalinity recorded in samples was in December and February at W3 whiles the highest concentration was in March at W2 (Table 2). There were significant differences among Alkalinity in samples collected from all three sites (W1, W2 and W3) in December, February and March except in January where Alkalinity in samples collected from W1 and W2 had no significant differences (Table2).

# 4.1.1 Physicochemical Parameters of Effluent

The results of the physicochemical properties of an effluent discharging into Butuah lagoon obtained during the four month sampling period are represented in Table 3. pH values were in the acidic to neutral range between 6.82 and 7.00. The lowest value was recorded in March and February recording the highest. There were no significant differences between pH values recorded in December and March. However, there was a significant difference in pH values between January and February (Table 3).

TDS ranged between 84.33 in March and 86.67 mg/L in February (Table 3). There were no significant differences among TDS in samples collected during the four month sampling period (Table 3).

Total Suspended Solids recorded a range of values with a low of 1.57 mg/L in December and a high of 6.67 mg/L in March (Table 3). There were no significant differences between TSS concentrations in samples collected in January and February (Table 3). The order of concentration from the highest to the least in months was March > February > January > December (Table 3).

Conductivity values ranged from 168.67 to 173.00  $\mu$ S/cm. The lowest concentration of conductivity was recorded in March whiles the highest concentration was recorded in February (Table 3). There were no significant differences between conductivity in samples collected from December and February (Table 3).

The range of Temperature values recorded during the sampling period was from 27.00 to 27.50° C. The lowest temperature was recorded in December whiles the highest temperature was recorded in January. There were no significant differences in temperature in all four months (Table 3).

Turbidity values ranged between 6.63 and 7.67 NTU. The lowest concentration was recorded in December whiles the highest was recorded in March (Table 3). There were no significant differences between Turbidity samples collected in December and January. Similarly, Turbidity in samples collected in January and February were not significantly different (Table 3).

The range of values recorded for COD in the samples collected during the sampling period was between 199.00 and 203.33 mg/L. There were no significant differences among COD in samples collected from all four months (Table 3).

a u	PARAMETERS													
Samplir period	ng pH	TDS (mg/L)	TSS (mg/L)	COND (µS/cm)	<b>TEMP</b> (° C)	<b>TURB</b> (NTU)	COD (mg/L)	BOD (mg/L)	<b>P0</b> <sub>4</sub> (mg/L)	SO <sub>4</sub> (mg/L)	NO <sub>3</sub> (mg/L)	<b>Oil&amp;G</b> (mg/L)	<b>Chlor</b> (mg/L)	Alkal (mg/L)
						K	NI	ГЛ	-					
Dec	6.85 <sup>a</sup>	86.33 <sup>a</sup>	1.57 <sup>a</sup>	171.67 <sup>ab</sup>	27.00 <sup>a</sup>	6.63 <sup>a</sup>	201.33 <sup>a</sup>	54.33 <sup>ab</sup>	0.15 <sup>a</sup>	2.73 <sup>a</sup>	0.13 <sup>a</sup>	39.33 <sup>a</sup>	108.33 <sup>a</sup>	292.80 <sup>a</sup>
Jan	6.88a <sup>b</sup>	85.23 <sup>a</sup>	2.50 <sup>b</sup>	170.67 <sup>ab</sup>	27.50 <sup>a</sup>	6.87 <sup>a</sup>	203.33 <sup>a</sup>	56.67 <sup>b</sup>	0.29 <sup>a</sup>	2.83 <sup>a</sup>	0.11 <sup>a</sup>	43.33 <sup>a</sup>	111.00 <sup>ab</sup>	302.97 <sup>a</sup>
Feb	7.00 <sup>b</sup>	86.67 <sup>a</sup>	2.67 <sup>b</sup>	173.00 <sup>b</sup>	27.17 <sup>a</sup>	7.40 <sup>b</sup>	199.00 <sup>a</sup>	<b>5</b> 1.33 <sup>a</sup>	0.16 <sup>a</sup>	6.17 <sup>b</sup>	0.26 <sup>b</sup>	42.00 <sup>a</sup>	110.33 <sup>ab</sup>	292.80 <sup>a</sup>
Mar	6.82 <sup>a</sup>	84.33 <sup>a</sup>	6.67 <sup>c</sup>	168.67 <sup>a</sup>	27.17 <sup>a</sup>	7.67 <sup>b</sup>	202.33 <sup>a</sup>	60.67 <sup>c</sup>	1.13 <sup>b</sup>	6.63 <sup>b</sup>	0.26 <sup>b</sup>	38.67 <sup>a</sup>	113.00 <sup>b</sup>	315.17 <sup>a</sup>
Ghana EPA	6-9	1000	50	1500	3	75	250	50	3	2	50	5	250	-

# Table 3. Mean values of physicochemical parameters of effluent

Mean (in same column) with different letters in superscript differ significantly (p<0.05)



BOD values ranged from a low of 51.33 to a high of 60.67 mg/L during the sampling period. There were significant differences among BOD in samples collected during the four month sampling period (Table 3).

Phosphate values ranged from 0.15 to 1.13 mg/L during the four month sampling period. The lowest concentration of Phosphate in samples collected in December was the lowest whiles samples collected in March had the highest concentration (Table 3). There were significant differences among Phosphate in samples collected in March and all samples collected in December, January and February (Table 3).

Sulphate values ranged from 2.73 to 6.63 mg/L. The lowest concentration of sulphate in samples was recorded in December whiles the highest concentration was recorded in March. There were no significant differences between Sulphate in samples collected in December and January (Table 3). Similarly, Sulphate in samples collected in February and March were not significantly different (Table 3).

Nitrate in samples recorded during the sampling period ranged from 0.11 to 0.26 mg/L. The lowest concentration of Nitrate in samples collected in January was the lowest whiles the highest concentration of Nitrate in samples collected was in February and March (Table 3). There were no significant differences between Nitrate in samples collected from December and January. Similarly, no significant differences between Nitrate in samples collected from February and March (Table 3).

Oil and Grease recorded a range of values from 38.33 to 43.33 mg/L during the four month sampling period. The lowest concentration of Oil and Grease in samples was recorded in December whiles the highest concentration was recorded in January (Table 3). There were no

significant differences among Oil and Grease in samples collected during the four month sampling period (Table 3).

The concentration of samples collected for Chloride ranged from 108.33 to 113.00 mg/L during the sampling period. The lowest concentration of chloride was recorded in December whiles the highest concentration was recorded in March. Samples collected in January and February was significantly different from samples collected in December and March (Table 3).

Alkalinity values recorded during the sampling period ranged from 292.80 to 315.17 mg/L. The lowest Alkalinity concentration in samples was recorded in December and February whiles the highest concentration was recorded in March (Table 3). There were no significant differences among Alkalinity in samples collected for all four months (Table 3).

# 4.2 Levels of Heavy Metals in Sediments, Fish, Water and Effluent

Generally the concentrations of As, Cu, Pb, Zn, Fe, Cd and Hg in sediments from Butuah Lagoon were 94.1%, 92.7%, 88.1%, 81.3%, 95.4%, 92.7% and 27.4% higher respectively than in the muscles of fish from the same lagoon. Similarly, the concentrations of As, Cu, Pb, Zn, Fe, Cd and Hg in sediments from the lagoon were 100%, 99.9%, 99.4%, 99.8%, 100%, 99.3% and 100% higher respectively than in water samples from the same lagoon.

## 4.2.1 Levels of Heavy Metals in Sediments

Concentrations of heavy metals in sediments from Butuah Lagoon are presented in (Table 4). Among all the heavy metals analysed the levels of As recorded in sediment samples were highly above the recommended standards. The highest level of heavy metal was recorded for Fe whilst Hg and Cd recorded relatively lower values in all study points during the sampling period. The general order of concentration of heavy metals from the highest to the least during the four month sampling period was Fe > Zn > As > Pb > Cu > Cd > Hg (Table 4).

#### **4.2.1.1** Arsenic

Samples collected from upstream (S3) generally recorded the lowest concentration As for all four months (Table 4) whilst midstream (S2) recorded slightly higher values for all months except December where downstream (S1) recorded the highest value. The concentration of Arsenic ranged between 51.07 mg/kg and 120.37 mg/kg during the sampling period. There were significant differences among Arsenic in samples collected from all three sites (S1, S2 and S3) for all months except in January where there was no significant difference between samples collected from S1 and S2 (Table 4). The order of concentration from the highest to the least in the months of December, January, February and March was S1 > S2 > S3, S2 > S1 > S3, S2 > S1 > S3 respectively (Table 4).

#### 4.2.1.2 Copper

Samples collected from upstream generally recorded the lowest concentration of Copper for all months (Table 4). The concentrations of Cu ranged between 4.90 mg/kg and 65.40 mg/kg during the sampling period with the lowest being recorded in March at S3 whilst the highest was recorded in February at S2 (Table 4). There were significant differences among Copper in samples collected from all three sites (S1, S2 and S3) for all four months. The order of concentration from the highest to the least during the sampling period was S2 > S1 > S3 for all months (Table 4).

PARAMETERS											
Sampling Sample period code As		le As	Cu	Pb	Zn	Fe	Cd	Hg			
				K IV	JUST						
5	<b>S</b> 1	$120.37 \pm 0.15^{j}$	32.67±0.15 <sup>d</sup>	53.37±0.11 <sup>g</sup>	$298.60{\pm}0.10^{i}$	1624.90±0.15 <sup>c</sup>	$6.80 \pm 0.00^{d}$	0.016±0.00 <sup>c</sup>			
Dec	<b>S</b> 2	$105.50{\pm}0.20^{i}$	$57.37 \pm 0.12^{f}$	$68.57 \pm 0.06^{h}$	321.66±0.06 <sup>j</sup>	1588.00±0.15 <sup>b</sup>	$10.10{\pm}0.00^{\rm f}$	$0.017 {\pm} 0.00^{e}$			
	<b>S</b> 3	76.13±0.90 <sup>de</sup>	$6.20\pm0.10^{b}$	9.83±0.06 <sup>c</sup>	<b>93.50</b> ±0.10 <sup>e</sup>	1635.40±0.15 <sup>c</sup>	$0.13 \pm 0.06^{a}$	$0.010{\pm}0.00^{d}$			
	<b>S</b> 1	$100.07 \pm 1.12^{h}$	13.47±0.06°	$30.20\pm0.00^{f}$	$120.86\pm0.31^{\rm f}$	2020.20±1.61 <sup>h</sup>	$2.50\pm0.10^{b}$	$0.001{\pm}0.00^{a}$			
Jan	S2	101.20±0.26 <sup>h</sup>	$55.13\pm0.12^{e}$	79.93±0.06 <sup>i</sup>	$120.20\pm0.26^{f}$	2025.40±4.66 <sup>h</sup>	$5.57 \pm 0.06^{\circ}$	$0.002{\pm}0.00^{ab}$			
	<b>S</b> 3	$73.60 \pm 0.79^{d}$	6.27±0.06 <sup>b</sup>	5.23±0.15 <sup>a</sup>	12.00±0.26 <sup>a</sup>	2147.30±0.06 <sup>i</sup>	$ND^{a}$	$0.001 \pm 0.00^{a}$			
	<b>S</b> 1	$86.17 \pm 1.50^{\text{f}}$	13.83±0.35 <sup>cd</sup>	$26.07 \pm 0.31^{\circ}$	84,50±0,10 <sup>d</sup>	$1214.60\pm 2.17^{a}$	2.27±0.21 <sup>b</sup>	$ND^{a}$			
Feb	S2	$90.07{\pm}1.46^{g}$	$65.40\pm0.30^{h}$	82.13±0.15 <sup>j</sup>	239.06±0.67 <sup>h</sup>	1787.70±0.49 <sup>f</sup>	$8.00\pm0.20^{e}$	$0.020{\pm}0.00^{\rm f}$			
	<b>S</b> 3	$65.33{\pm}1.82^{b}$	5.87±0.12 <sup>b</sup>	7.93±0.25 <sup>b</sup>	17.63±0.15 <sup>b</sup>	1865.30±17.56 <sup>g</sup>	$7.73 \pm 0.25^{de}$	$0.004{\pm}0.00^{b}$			
	<b>S</b> 1	69 13+1 11 <sup>c</sup>	14 23+0 25 <sup>d</sup>	$20.97 \pm 0.31^{d}$	81 03+0 40 <sup>d</sup>	1209 00 <b>+7 31</b> ª	3 03+0 15 <sup>b</sup>	$ND^{a}$			
Mar	S2	$77.90+2.07^{e}$	$64.67 \pm 0.58^{g}$	$80.43 \pm 0.59^{i}$	$234.43+3.26^{i}$	$1680.90+4.85^{d}$	$7.03\pm0.06^{d}$	$0.020+0.01^{\text{f}}$			
	S3	$51.07 \pm 0.67^{a}$	4.90±0.13 <sup>a</sup>	7.53±0.35 <sup>b</sup>	$17.10\pm0.10^{b}$	1708.60±3.67 <sup>e</sup>	$7.03 \pm 0.06^{d}$	$0.004\pm0.01^{b}$			
ISQG (2002)		5.9	35.7	35 10 55	123.00 8.00	-	0.6	0.17			

Table 4. Mean concentration (mg/kg) of heavy metals in sediments from Butuah Lagoon

Mean (in same column) with different letters in superscript differ significantly (p<0.05)

### 4.2.1.3 Lead

Samples collected from midstream (S2) generally recorded the highest Lead concentrations for all four months (Table 4). The range of Pb values was between 5.23 mg/kg and 82.13 mg/kg with the lowest being recorded in January at S3 whilst the highest was recorded in February at S2. There were significant differences among Lead in samples collected from all three sites (S1, S2 and S3) for all four months (Table 4). The order of concentration from the highest to the least during the sampling period was S2 > S1 > S3 (Table 4).

## 4.2.1.4 Zinc

Samples collected from upstream (S3) generally recorded the lowest Zinc concentrations for all four months (Table 4). A range of 12.00 mg/kg and 321.66 mg/kg was recorded for Zn during the sampling period with the lowest being recorded in January at S3 whilst the highest was recorded in December at S2 (Table 4). There were significant differences among Zinc in samples collected for all months except January where Zinc concentration in samples from S1 and S2 had no significant difference. The order of concentration from the highest to the least was S2 > S1 > S3 except in January where the order changed from S1 > S2 > S3 (Table 4).

# 4.2.1.5 Iron

The values of Iron ranged between 1209.00 mg/kg and 2147.30 mg/kg during the sampling period and the highest concentration were generally recorded in upstream samples (Table 4). The lowest concentration in samples was recorded in March at S1 whilst the highest concentration was recorded in January at S3 (Table 4). In December there was no significant difference between Iron in samples collected from S1 and S3. Similarly, in January S1 and S2 had no significant difference between them (Table 4). However, there were significant difference among

Iron in samples collected from all three sites (S1, S2 and S3) for the months of February and March (Table 4). The order of concentration from the highest to the least during the sampling months was S3 > S1 > S2 in December, S3 > S2 > S1 in January, S3 > S2 > S1 in February and S3 > S2 > S1 in March (Table 4).

# 4.2.1.6 Cadmium

Samples collected form midstream (S2) generally recorded the highest values except in March where S2 and S3 values were the same (Table 4). Cadmium recorded a range of values of 0.13 mg/kg and 10.10 mg/ kg during the sampling period with the highest being recorded in December at S2. In March there was no significant difference between Cadmium in samples collected from S2 and S3 whilst there were significant difference among Cadmium in samples collected from all three sites in the first three months (Table 4). The order of concentration from the highest to the least was the same for December and January (S2 > S1 > S3), in February the trend was S2 > S3 > S1 and in March the trend was S2 = S3 > S1 (Table 4).

#### 4.2.1.7 Mercury

Samples collected for Hg recorded lower concentrations during the sampling period. In February and March no Hg samples were detected at S1. In January there was no significant difference between Hg in samples collected from S1 and S2 whilst there were significant differences in samples collected from all three sites for the months of December, February and March (Table 4). The order of concentration from the highest to the least during the sampling months was S2 > S1 > S3 in December, S2 > S1 = S3 in January, S2 > S3 > S1 in February and S2 > S3 > S1 in March (Table4

# 4.2.2 Monthly Variation of Heavy Metal Concentrations in Sediments

The monthly variations of heavy metals concentrations in sediments from Butuah Lagoon are represented in Fig. 2 for As, Cu, Pb and Zn and Fig. 3 for Fe, Cd and Hg. For As there was a general decrease in concentration from December to March in all three sites. All values were above the ISQG (2002) recommended standard. Percentage As decrease ranged from 42.6% in S1, 26.2% in S2 and 32.9% in S3 (Fig. 2).

# KNUST

For Cu there was a monthly increase in levels from December to March in S2 and the values were all above the ISQG (2002) recommended standard. There was decrease in Cu levels from December to March in S1 whilst values for S3 were fairly constant. Monthly Cu levels in both S1 and S3 were below the ISQG (2002) recommended standard (Fig. 2). Percentage decrease ranged from 56.4% in S1 and 21.0% in S3. However, there was an increase in percentage of 12.3% in S2 (Fig. 2).

For Pb there was a monthly decrease in levels from December to March in S1 and the values were above the ISQG (2002) recommended standard in December but from January to March went below the standard. Pb levels in S2 samples increase from December to February and decreased slightly in March. The monthly Pb levels in S2 were all above the ISQG (2002) recommended standard. In S3 there was a decrease in Pb levels from December to January and the levels remained fairly constant thereafter. Monthly Pb levels were all below the ISQG (2002) recommended standard (Fig. 2). There was a percentage increase (16.5%) in S2. However, in S1 and S3 there was a decrease of 60.7% and 23.4% respectively (Fig. 2).



Fig. 2. Variations in As, Cu, Pb and Zn in sediments from Butuah Lagoon

The highest levels of Zn in all three sites (S1, S2 and S3) were recorded in December with S2 having the highest of the three. There was a sharp decrease in levels of Zn from December to January in all three sites (Fig. 2). It then increased from January to February and slightly decreased in March in S2. The concentration was above ISQG (2002) recommended standard in

December; however, in January the concentration recorded was the same as the ISQG standard and went above it thereafter.

S1 values decreased from December to March and in December the concentration was above ISQG (2002) recommended standard whilst in January the values were equal to the recommended standards. In S3 there was a decrease from December to January and remained fairly constant afterwards. All values were below the ISQG (2002) recommended standard. Percentage decrease ranged from 72.9% in S1, 27.1% in S2 and 83.7% in S3 (Fig. 2).

In all sites (S1, S2 and S3) there was initial increase in levels of Fe from December to January and decreased afterwards until March. No standards were found for Fe (Fig. 3). Percentage increase ranged from 40.2% in S1, 21.6% in S2 and 23.8% in S3 (Fig. 3).

In Cd all values were above the ISQG (2002) recommended standard except in December and January where values fell below ISQG for S3 samples. In S2 there was decrease from December to January, increased again in February and decreased once more in March. S1 values decreased from December to March and S3 values increased from December to March (Fig. 3). Percentage decrease ranged from 63.2% in S1, 30.4% in S2 and 98.3% in S3 (Fig. 3).

The trend for Hg were almost flat for all three sites (S1, S2 and S3) and were all far below the ISQG (2002) recommended standard (Fig. 3). Percentage decrease ranged from 100% in S1, 90% in S2 and S3 (Fig. 3).

WJSANE



Fig. 3. Variations in Fe, Cd and Hg in sediments from Butuah Lagoon

# 4.2.3 Heavy Metals in Muscles of Fish

The concentrations of heavy metals were determined in the muscles of fish from Butuah Lagoon and the results have been represented in (Table 5). Concentrations of heavy metals in the muscles of fish were lower as compared to the values recorded for the same metals in sediments from the lagoon. Hg and Cd concentrations were relatively lower for all samples from the study points during the sampling period.

### 4.2.3.1 Arsenic

The range of As concentrations in the muscles of fish during the sampling period was between 1.93 mg/kg and 8.13 mg/kg (Table 5). The lowest concentration was recorded in March at F1 whilst the highest concentration was recorded in December at F1 (Table 5). Apart from January where there was no significant difference between As in samples collected from F1 and F2, the remaining three months (December, February and March) recorded significant differences from all three sites (F1, F2 and F3) (Table 5). The order of concentration from the highest to the least during the sampling months was F1 > F2 > F3 in December, F2 > F1 > F3 in January, F2 > F1 > F3 in February and F2 > F3 > F1 in March (Table 5).

#### 4.2.3.2 Copper

Copper in samples recorded a range of values between 0.02 mg/kg and 8.00 mg/kg during the sampling period with the lowest being recorded in February at F1 and F2 whilst the highest was recorded in December and January at F1 and F3 respectively (Table 5). There were no significant differences among Copper in samples collected from all three sites (F1, F2 and F3) for the month of February whilst Copper in samples collected from all three sites in December, January and March differed significantly (Table 5). The order of concentration from the highest to the least during the sampling period was F1 > F2 > F3 in December, F3 > F1 > F2 in January, F3 > F2 = F1 in February and F2 > F3 > F1 in March (Table 5).

HEAVY METALS												
period	code	As	Cu	Pb	Zn	Fe	Cd	Hg				
KNUST												
Dec	F1 F2 F3	$\begin{array}{c} 8.13{\pm}0.15^{g} \\ 6.67{\pm}0.67^{f} \\ 4.97{\pm}0.15^{e} \end{array}$	$\begin{array}{c} 8.00{\pm}0.00^{\rm f} \\ 1.37{\pm}0.06^{\rm c} \\ 1.17{\pm}0.06^{\rm b} \end{array}$	$\begin{array}{c} 1.60{\pm}0.20^{bc}\\ 1.00{\pm}0.00^{a}\\ 1.17{\pm}0.15^{ab} \end{array}$	18.83±0.15 <sup>c</sup> 15.20±0.17 <sup>a</sup> 17.43±0.06 <sup>b</sup>	50.70±0.36 <sup>c</sup> 42.67±0.15 <sup>b</sup> 49.37±0.06 <sup>c</sup>	ND <sup>a</sup> ND <sup>a</sup> ND <sup>a</sup>	$\begin{array}{c} 0.002{\pm}0.00^{a}\\ 0.002{\pm}0.00^{a}\\ 0.002{\pm}0.00^{a} \end{array}$				
Jan	F1 F2 F3	$\begin{array}{c} 6.70{\pm}0.20^{f} \\ 7.03{\pm}0.15^{f} \\ 4.80{\pm}0.44^{de} \end{array}$	$\begin{array}{c} 2.00{\pm}0.00^{e} \\ 1.23{\pm}0.06^{b} \\ 8.00{\pm}0.00^{f} \end{array}$	$5.67 \pm 0.12^{f}$ 4.73 $\pm 0.06^{e}$ 8.00 $\pm 0.00^{g}$	$\begin{array}{c} 26.70{\pm}0.20^{\rm f}\\ 35.60{\pm}0.17^{\rm g}\\ 36.10{\pm}0.26^{\rm h} \end{array}$	$\begin{array}{c} 33.17{\pm}0.15^{a} \\ 48.87{\pm}0.06^{c} \\ 80.30{\pm}0.00^{f} \end{array}$	ND <sup>a</sup> ND <sup>a</sup> ND <sup>a</sup>	$\begin{array}{c} 0.001{\pm}0.00^{a}\\ 0.001{\pm}0.00^{a}\\ 0.001{\pm}0.00^{a} \end{array}$				
Feb	F1 F2 F3	$\begin{array}{c} 3.97{\pm}0.12^{c} \\ 5.13{\pm}0.12^{e} \\ 3.60{\pm}0.20^{bc} \end{array}$	$\begin{array}{c} 0.02{\pm}0.00^{a}\\ 0.02{\pm}0.00^{a}\\ 0.05{\pm}0.00^{a} \end{array}$	4.23±0.321 <sup>d</sup> 1.70±0.26 <sup>e</sup> 13.43±0.21 <sup>i</sup>	$\begin{array}{c} 20.40{\pm}0.00^{d}\\ 22.63{\pm}0.25^{e}\\ 36.90{\pm}0.36^{i} \end{array}$	$\begin{array}{c} 33.23{\pm}5.77^{a} \\ 70.47{\pm}0.25^{e} \\ 210.06{\pm}0.25^{g} \end{array}$	$\begin{array}{c} 0.80{\pm}0.00^{\rm d} \\ 0.97{\pm}0.06^{\rm e} \\ 0.90{\pm}0.00^{\rm de} \end{array}$	$\begin{array}{c} 0.008{\pm}0.00^{b} \\ 0.016{\pm}0.00^{c} \\ 0.007{\pm}0.00^{b} \end{array}$				
Mar	F1 F2 F3	$\begin{array}{c} 1.93{\pm}0.15^{a} \\ 4.20{\pm}0.20^{cd} \\ 3.20{\pm}0.20^{b} \end{array}$	$\begin{array}{c} 0.08{\pm}0.00^{a} \\ 1.50{\pm}0.02^{d} \\ 1.24{\pm}0.04^{b} \end{array}$	3.87±0.21 <sup>d</sup> 1.28±0.10 <sup>abc</sup> 9.53±0.25 <sup>h</sup>	18.23±0.25 <sup>bc</sup> 20.90±0.82 <sup>d</sup> 37.67±0.91 <sup>i</sup>	$\begin{array}{c} 67.15{\pm}1.78^{e} \\ 57.58{\pm}1.00^{d} \\ \textbf{208.90}{\pm}0.36^{g} \end{array}$	$\begin{array}{c} 0.65{\pm}0.13^{c} \\ 0.63{\pm}0.12^{c} \\ 0.45{\pm}0.05^{b} \end{array}$	$\begin{array}{c} 0.008{\pm}0.00^{b}\\ 0.014{\pm}0.00^{c}\\ 0.007{\pm}0.00^{b} \end{array}$				
FAO (1983)		-	30	0.5	30	DANE	0.5	-				

Table 5. Mean concentration (mg/kg) of heavy metals in muscles of fish from Butuah Lagoon

Mean (in same column) with different letters in superscript differ significantly (p<0.05)

#### 4.2.3.3 Lead

The concentrations of Pb recorded in samples ranged between 1.00 mg/kg to 13.43 mg/kg during the sampling period with the lowest being recorded in December at F2 whilst the highest was recorded in February at F3 (Table 5). There were significant differences among Pb in samples collected from all three sites (F1, F2 and F3) for all four months (Table 5). From December, January, February and March the order of concentration from the highest to the least was F1 > F3 > F2, F3 > F1 > F2, F3 > F1 > F2 and F3 > F1 > F2 respectively (Table 5).

#### 4.2.3.4 Zinc

The range of values recorded for Zn in fish samples during the sampling period was from 15.20 mg/kg to 37.67 mg/kg with the lowest being recorded in December at F2 whilst the highest was recorded in March at F3 (Table 5). There were significant differences among Zn in samples collected from all three sites (F1, F2 and F3) for all four months (Table 5). The order of concentration from the highest to the least during the sampling period was F1 > F3 > F2 for December, F3 > F2 > F1 for January, F3 > F2 > F1 for February and F3 > F2 > F1 for March (Table 5).

## 4.2.3.5 Iron

The concentrations of Fe recorded ranged between 33.17 mg/kg to 210.06 mg/kg during the four month sampling period with the lowest concentration being recorded in January at F1 whilst the highest was recorded in February at F3 (Table 5). There was no significant difference between Fe in samples collected from F1 and F3 in December (Table 5). In January, February and March there were significant difference among Fe in samples collected from all three sites (F1, F2 and

F3) (Table 5). In December the order of concentration from the highest to the least was F1 > F3 > F2, the order changed for January and February and it was F3 > F2 > F1 and March recorded an order of F3 > F1 > F2 (Table 5).

# 4.2.3.6 Cadmium

Cadmium was below the detectable limit during the first two months (December and January) of sampling and the highest value of 0.97 mg/kg was recorded in February at F2 (Table 5). There were significant difference among Cd in samples collected from all three sites for the months of February and March where samples were detected. In December and January the order was the same where F1 = F2 = F3. The order for February was F2 > F3 > F1 and in March the order was F1 > F2 > F3 (Table 5).

#### 4.2.3.7 Mercury

The values recorded for Hg were generally low and the range was between 0.008 mg/kg to 0.014 mg/kg during the sampling period with the highest being recorded in February at F2 (Table 5). In December and January there were no significant differences among Hg in samples collected from all three sites (F1, F2 and F3) whereas in February and March there were no significant difference between Hg in samples collected from F1 and F3 (Table 5). For December and January the order was the same where F1 = F2 = F3 and in February and March there was also an order of F2 > F1 > F3 from the highest to the least (Table 5).

## 4.2.4 Monthly Variation of Heavy Metal Concentrations in Muscles of fish

The monthly variation of heavy metals concentrations in fish samples from the Butuah Lagoon are represented in Fig. 4 for As, Cu, Pb and Zn and Fig. 5 for Fe, Cd and Hg. The concentrations of As in fish samples declined generally from December to March in all three sites (F1, F2 and F3). No standard was found for As in fish. Percentage decrease ranged from 76.3% in F1, 40.3% in F2 and 35.6% in F3 (Fig. 4).

For Cu all values from all three sites (F1, F2 and F3) were far below the recommended FAO (1983) standard. There was decrease in concentration from December to March in samples from F1 and F2. However, samples from F3 increased initially from December to January before decreasing afterwards. Percentage decrease in concentration ranged from 99.8% in F1, 98.7% in F2 and 99.4% in F3 (Fig. 4).

The concentrations of Pb in samples from F3 increased from December to March. In F2 and F1 there was an increase from December to January after which the concentrations declined. All three sites (F1, F2 and F3) were below the recommended FAO (1983) standard. Percentage increase ranged from 71.8% in F1 and 91.3% in F3 and in F2 there was a decrease of 78.9% (Fig. 4).

The concentrations of Zn were highest in samples from F3 during the sampling period. In January both F2 and F3 recorded values which were higher when compared to the recommended FAO (1983) standard but F2 values fell below the standard from February to March. The values obtained for F1 were all below the recommended FAO (1983) standard in all months (Fig. 4). Percentage decrease in concentration ranged from 31.7% in F1, 57.3% in F2 and 53.7% in F3 (Fig. 4).
For Fe F3 samples recorded the highest concentration and this increased from December to March. F1 samples decreased from December to January and began to increase again from there and F2 samples also increased steadily from during the sampling period (Fig. 5).

The concentrations of Cd increased from December to March in all samples from all three sites (F1, F2 and F3). When compared with recommended FAO (1983) standard the samples fell above it after January through to March (Fig. 5).

The trend for mercury was generally flat for all samples from all sites and all fell far below the recommended WHO (2002) standard (Fig. 5).



Fig. 4. Variations in As, Cu, Pb and Zn in fish from Butuah Lagoon



Fig. 5. Variations in Fe, Cd and Hg in fish from Butuah Lagoon

#### 4.2.5 Heavy Metals in Butuah Lagoon and Effluent

The result of heavy metal concentrations in lagoon water and effluent is represented in Table 6. Arsenic and Mercury were not detected in water samples from the lagoon and effluent during the sampling period (Table 6).

#### 4.2.5.1 Copper

The highest concentration of Copper in samples collected during the sampling period was 0.08 mg/L and this was recorded in December at W2 (Table 6). There were no significant differences between Copper in samples collected from W1 and W2 in December and also in February, between W3 and WE in January and in February (Table 6). Similarly, in March there were no significant differences among Copper in samples collected from W1, W2 and WE. The order of concentration from the highest to the least was W2 > W1 = W3 > WE in December, W2 = W1 > W3 = WE in January, W2 = W1 > W3 = WE in February and in March the order was W1 > W2 = W3 = WE (Table 6).

#### 4.2.5.2 Lead

Lead recorded values ranging from a minimum of 0.01 mg/L in December and March at WE and a maximum of 0.45 in December at W1 (Table 6). There were significant differences among Lead in samples collected from all four sites except in February where samples collected from W1 and W2 did not differ significantly (Table 6). In December the trend of concentration was W1 > W2 > W3 > WE. The trends for January, February and March were similar and were in the order W2 > W1 > W3 > WE (Table 6).

	HEAVY METALS									
Sampling period	g Samp code	le As	Cu	Pb	Zn	Fe	Cd	Hg		
	W1	ND <sup>a</sup>	$0.07{\pm}0.00^{h}$	$0.45 \pm 0.00^{1}$	$0.001 {\pm} 0.00^{a}$	$0.20 \pm 0.00^{bc}$	$0.08{\pm}0.01^{h}$	ND <sup>a</sup>		
DEC	W2	$ND^{a}$	$0.08{\pm}0.00^{\rm h}$	$0.40 \pm 0.00^{k}$	$0.06 \pm 0.00^{\circ}$	$0.19 \pm 0.00^{b}$	$0.08{\pm}0.00^{\rm h}$	$ND^{a}$		
DLC	W3	$ND^{a}$	$0.07 \pm 0.00^{g}$	$0.25 \pm 0.00^{h}$	$0.02 \pm 0.00^{b}$	$0.74 \pm 0.00^{e}$	$0.05{\pm}0.00^{\rm f}$	$ND^{a}$		
	WE	ND <sup>a</sup>	ND <sup>a</sup>	$0.01{\pm}0.00^{a}$	$0.13{\pm}0.00^{\rm f}$	$1.77 \pm 0.00^{g}$	$0.01 \pm 0.00^{\circ}$	$ND^{a}$		
	W1	ND <sup>a</sup>	0.02±0.00 <sup>cd</sup>	$0.32 \pm 0.00^{i}$	$0.99 \pm 0.00^{m}$	$0.14{\pm}0.00^{a}$	$0.06 \pm 0.00^{g}$	ND <sup>a</sup>		
JAN	W2	$ND^{a}$	$0.02 \pm 0.00^{\circ}$	$0.33 \pm 0.00^{j}$	$0.34 \pm 0.00^{1}$	$0.24 \pm 0.00^{\circ}$	$0.06 \pm 0.00^{g}$	$ND^{a}$		
JAIN	W3	$ND^{a}$	$0.01 \pm 0.00^{b}$	$0.17 \pm 0.00^{f}$	$0.22 \pm 0.00^{h}$	$0.71 \pm 0.00^{e}$	$0.02 \pm 0.00^{d}$	$ND^{a}$		
	WE	ND <sup>a</sup>	$0.01 \pm 0.00^{b}$	0.15±0.00 <sup>de</sup>	$0.25 \pm 0.00^{i}$	$2.10\pm0.00^{j}$	$0.06 \pm 0.00^{\circ}$	$ND^{a}$		
	W1	ND <sup>a</sup>	$0.04 \pm 0.00^{f}$	$0.23 \pm 0.00^{g}$	0.15±0.00 <sup>g</sup>	1.55±0.00 <sup>g</sup>	0.01±0.00 <sup>ab</sup>	ND <sup>a</sup>		
FFB	W2	$ND^{a}$	$0.04{\pm}0.00^{\rm f}$	$0.24{\pm}0.00^{g}$	$0.11 \pm 0.00^{e}$	$0.47 {\pm} 0.00^{d}$	$0.01 \pm 0.00^{bc}$	$ND^{a}$		
I LD	W3	$ND^{a}$	0.03±0.00 <sup>e</sup>	$0.15 \pm 0.00^{de}$	$0.27 \pm 0.00^{j}$	$1.80{\pm}0.00^{hi}$	$0.01 \pm 0.00^{bc}$	$ND^{a}$		
	WE	ND <sup>a</sup>	0.03±0.00 <sup>e</sup>	$0.06 \pm 0.00^{b}$	$0.12 \pm 0.00^{f}$	$2.42\pm0.00^{k}$	$0.01 \pm 0.00^{bc}$	ND <sup>a</sup>		
	W1	ND <sup>a</sup>	0.04±0.00 <sup>e</sup>	0.14±0.00 <sup>d</sup>	0.06±0.00 <sup>c</sup>	1.44±0.17 <sup>f</sup>	$0.004{\pm}0.00^{ab}$	ND <sup>a</sup>		
MAR	W2	ND <sup>a</sup>	0.03±0.00 <sup></sup>	$0.15 \pm 0.00^{e}$	$0.09 \pm 0.00^{d}$	0.24±0.01 <sup>bc</sup>	$0.003{\pm}0.00^{a}$	$ND^{a}$		
	W3	ND <sup>a</sup>	$0.03 \pm 0.00^{d}$	0.10±0.01 <sup>c</sup>	0.30±0.02 <sup>k</sup>	$1.84{\pm}0.04^{h}$	$0.01 \pm 0.00^{\circ}$	$ND^{a}$		
	WE	ND <sup>a</sup>	0.03±0.003 <sup>e</sup>	$0.01 \pm 0.00^{a}$	$0.10 \pm 0.00^{de}$	$2.64\pm0.59^{1}$	$0.04{\pm}0.00^{e}$	$ND^{a}$		

Table 6. Mean concentration (mg/L) of heavy metals in Butuah Lagoon and effluent

Mean (in same column) with different letters in superscript differ significantly (p<0.05)

### 4.2.5.3 Zinc

The values of Zinc ranged from a minimum of 0.001 mg/L in December at W1 to a maximum of 0.99 mg/L in January at W1 (Table 6). There were significant differences among Zinc in samples collected from all four sites (W1, W2, W3 and WE) for all four months (Table 6). The order of concentration from the highest to the least was WE > W2 > W3 > W1 in December, W1 > W2 > WE > W3 in January, W3 > W1 > WE > W2 in February and in March the order was W3 > WE > W2 > W1 (Table 6).

#### 4.2.5.4 Iron

Iron recorded a minimum concentration of 0.14 mg/L in January at W1 and a maximum value of 2.64 in March at WE (Table 6). There were significant differences among Iron in samples collected from all four sites (W1, W2, W3 and WE) for all four months (Table 6). The order of concentration from the highest to the least was WE > W3 > W1 > W2 in December, WE > W3 > W2 > W1 in January, WE > W3 > W1 > W2 in February and in March the order was the same as that of February (Table 6).

#### 4.2.5.5 Cadmium

The range of values recorded for Cadmium was from a minimum of 0.003 mg/L in March at W2 and a maximum of 0.08 mg/L in December at W1 and W2 (Table 6). There were significant differences among Cadmium in samples collected from all four sites (W1, W2, W3 and WE) in March (Table 6). The order of concentration from the highest to the least during the sampling period was W1 = W2 > W3 > WE in December, W1 = W2 = WE > W3 in January, W1 = W2 = W3 = WE in February and in March the order was WE > W3 > W2 > W1 (Table 6).

#### 4.2.6 Monthly Variation of Heavy Metal Concentrations in Butuah Lagoon and Effluent

The trend of heavy metals in water samples from the Butuah Lagoon and effluent were also analysed and the results are represented in (Fig. 6). For Cu the concentrations of the samples from all sites during the sampling period were far below the recommended US EPA (1986) and the trend was almost flat for all the sites (Fig. 6). Percentage decrease in concentration ranged from 71.4% in W1, 75% in W2, 85.7% in W3 and 66.7% in WE (Fig. 6).



Fig. 6. Variations in Cu, Pb, Fe, Zn and Cd in Butuah Lagoon and Effluent

Generally the concentrations of Pb from W1, W2 and W3 declined from December to March except at site WE where there was a rise in concentration in January and declined afterwards. All

values were above the recommended US EPA (1986) standard except in February where samples from W3 fell below the recommended US EPA (1986) standard (Fig. 6). Percentage decrease in concentration ranged from 68.9% in W1, 62.5% in W2, 60.0% in W3 and 93.3% in WE (Fig. 6).

The concentrations of Zn were generally lower than the recommended US EPA (1986) standard except in February where a peak value recorded from samples from W1 coincided with the standard. For samples from W1, W2 and W3 there was an initial increase in concentration from December to January and the trend declined afterwards. However, values obtained from W3 increased steadily during the sampling period (Fig. 6). Percentage decrease in concentration ranged from 99.9% in W1, 82.4% in W2, 93.3% in W3 and 60.0% in WE (Fig. 6).

There was a general increase in concentration for samples obtained from W1, W3 and WE whilst samples from W2 increased and until in March where it decreased again. When compared with the recommended US EPA (1986) standard samples from W2 was below the standard whilst samples from WE were far above the standard. Also, samples from W1 and W3 were below the recommended US EPA (1986) standard for the months of December and January. However, in February and March the samples from the same sites (W1 and W3) fell above the recommended US EPA (1986) standard (Fig. 6).

For Cd there was a decline in concentration for all samples during the sampling period. All recorded values were above the recommended US EPA (1986) standard except in February and March where values recorded for W1 and W2 fell below the standard (Fig. 6). Percentage

decrease in concentration ranged from 95% in W1, 96.3% in W2, 80.0% in W3 and 83.3% in WE (Fig. 6).

#### 4.3 Bioaccumulation Ratio in fish in relation to sediments

Bioaccumulation factors of the various metals were calculated between concentrations in fish and sediments and the results presented in (Table 7). The bioaccumulation ratios for As ranged from a minimum of 0.03 at F1 in March and a maximum of 0.07 in December at F1 and F3 and also at F1, F2 and F3 in January (Table 7). Copper values ranged from a minimum of 0.00 at F1 and F2 in February and a maximum of 1.29 at F3 in January. The bioaccumulation ratio of 1.29 at F3 indicates hyperaccumulation in the F3 samples in February (Table 7).

For Pb the bioaccumulation ratios ranged from a minimum of 0.02 F2 both in February and March and a maximum of 3.01 at F3 in January (Table 7). The bioaccumulation ratio for Zn ranged from a minimum of 0.02 at F2 in February and a maximum of 2.20 at F3 in March (Fig. 7). Iron recorded a minimum of 0.02 at F1 and F2 in January and a maximum of 0.12 in March at F3 (Table 7). Cadmium recorded values ranging from a minimum of 0.00 in all samples (F1, F2 and F3) for January and also at F1 and F2 in December to maximum of 0.35 at F1 in February (Table 7). Mercury recorded a minimum value of 0.00 at F1 in February and March and a maximum of 1.75 also at F3 in February and March (Table 7).

HEAVY METALS									
Sampling period	g Sample code	As	Cu	Pb	Zn	Fe	Cd	Hg	
Dec	F1 F2 F3	0.07 0.06 0.07	0.25 0.02 0.19	0.06 0.05 0.19	0.03 0.02 0.12	0.03 0.03 0.03	$0.00 \\ 0.03 \\ 0.00$	0.20 0.01 0.06	
	15	0.07	0.15			0.03	0.00	0.00	
Jan	F1 F2 F3	0.07 0.07 0.07	0.10 0.02 1.29	0.22 0.30 3.01	0.19 0.06 1.53	0.02 0.02 0.04	$0.00 \\ 0.00 \\ 0.00$	1.00 0.50 1.00	
Feb	F1 F2	0.05 0.06	0.00 0.00	0.16 0.02	0.24 0.10	0.03 0.04	0.35 0.12	0.00 0.80	
100	F3	0.06	0.01	1.69	2.09	0.11	0.12	1.75	
Mar	F1 F2 F3	0.03 0.05 0.06	0.01 0.02 0.25	0.18 0.02 1.27	0.23 0.09 2.20	0.06 0.03 0.12	0.21 0.09 0.06	0.00 0.40 1.75	
		7	P			8			

Table /. Divaccumulation failo in fish in relation to scuments of Dutuan Lagoon	Table 7.	Bioaccumula	ation ratio	in fish i	in relation	to sediments	of Butuah 3	Lagoon
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#### **CHAPTER FIVE**

#### 5.0 **DISCUSSION**

#### 5.1 Physicochemical Properties of Butuah Lagoon and Effluent

Aquatic organisms live in water for part or all of their lives. For the protection of the various life forms in an aquatic ecosystem as well as human life, water must meet certain quality standards. It is in this regard that many regulatory bodies have set quality standards to ensure the continued existence of aquatic ecosystems and good human health in the wake of increased anthropogenic activities.

### 5.1.1 Physicochemical Properties of Butuah Lagoon

Chapman (1996) reported that poorly buffered water will have a low or very low alkalinity and will be susceptible to pH reduction by atmospheric, acid deposition. The pH range of 7.49 to 8.71 recorded during the sampling period fell within the recommended range of 5.0 to 9.0 set by the Ireland EPA. The neutral to basic pH range encountered could well be attributed to the high alkalinity values recorded during the sampling period. High levels of TDS which ranged from 140.33 mg/L to 1961 mg/L may have varied consequences on aquatic life in Butuah Lagoon. Study points W1 and W2 which recorded higher values of TDS could be explained by the presence of a refuse damp close to W1 leading to seepage of waste into the lagoon and the heavy presence of industries around W2.

The conductivity of most freshwaters ranges from 10 to 1000  $\mu$ S/cm but may exceed 1000  $\mu$ S/cm especially in polluted waters, or those receiving large quantities of land run-off (Chapman, 1996). The high conductivity associated with points W1 and W2 was thus explained as a result of the proximity of study point W2 to numerous industries and also the proximity of W1 to the

open sea. The range of temperature encountered during the sampling period was fairly constant. The FAO (2006), reported that the lower and upper lethal temperature for Nile tilapia are 11 to 12° C and 42° C respectively with the preferred range being 31 to 36° C. This therefore suggests that the temperature range of 29 to 31° C recorded during the sampling period thus provides favourable conditions for the tilapia species to thrive in the Butuah Lagoon. Chapman (1996) indicated that unpolluted waters typically have BOD value of 2 mg/L whereas those receiving wastewaters may have values up to 10 mg/L or more. The high values of BOD recorded at the study points may well be explained by the high input of wastewater from the industrial complex. Study point W1 recorded the highest values possibly from the numerous inputs of domestic wastewater and also the increased damping of refuse along the banks of the lagoon. Chapman (1996) observed a COD range from 20 mg/L or less in unpolluted waters to greater than 200 mg/L in waters receiving effluents. The COD values recorded fell high above the levels indicated by Chapman which suggests the lagoon is receiving effluents from varied sources. The highest values recorded at W1 could be attributed to a combination of wastes from domestic and industrial sources.

High Chloride concentrations were recorded during the study period with the highest being recorded at W1. Moving further away from study point W1 to study point W3 the chloride concentrations decreased along the line. Study point W1 experiences occasional sea water intrusion when sand which separates the lagoon and the open sea is dredged during some times in the year. The high chloride concentration at this point could be attributed to the proximity and influence of the open sea and this confirms report made by Chapman (1996) that higher concentrations of chloride can occur near sewage and other waste outlets, irrigation drains, salt water intrusions, and in areas in wet coastal areas. Sulphate concentration in natural waters is

usually between 2 and 80 mg/L, although they may exceed 1000 mg/L near industrial discharges. The US EPA (2011) recommends 250 mg/L of sulphate for standing and drinking water. The values recorded for Butuah Lagoon during the sampling period were well below the limit and fell within the concentrations in natural waters.

Phosphorus gaining access to water bodies along with nitrogen as nitrate, promotes the growth of algae and other plants leading to blooms, littoral slimes, diurnal dissolved oxygen variations of great magnitude and related problems (Ireland EPA, 2001). The natural background level of phosphorous in waters usually ranges from 0.005 to 10 mg/L (WRC, 2003). The values recorded during the sampling period suggest high inputs from domestic sources. The presence of farms around study points W1 and W3 could account for the higher levels recorded at these points. Oil and Grease recorded the highest values at point W3 and this is explained as a result of the closeness of this area to the car repair artisans operating there and suggests improper management and disposal of waste.

### 5.1.2 Physicochemical Properties of Effluent

When compared to Ghana EPA (2011) standards (Appendix 2), the physicochemical parameters of the effluent samples were generally within the acceptable limits apart from Oil and Grease and BOD which recorded higher values during the sampling period which suggests improper management of oily waste from the industrial complex.

### 5.2 Heavy Metals in Sediments of Butuah Lagoon

Sediment pollution not only causes water to be murky and unpleasant to look at, swim in, or drink, it reduces the light available to underwater plants, and blankets food sup-populations and

the nests of fish, thus reducing fish and shellfish populations (Montgomery, 2000). This study revealed higher concentrations of heavy metals in the sediment samples than of the water samples from Butuah Lagoon. This finding corroborates with observation made by Linnik and Zubenko (2000), that aquatic sediments absorb persistent and toxic chemicals to levels many times higher than the water column concentration.

The results from the study indicated that in most cases samples from S2 were polluted, followed by S1 with S3 being the least. Anim *et al.* (2010) reported that most heavy metals find their way into water bodies via, chemical weathering of rocks and soil, agricultural runoffs, industrial waste discharge, mining, batteries, lead based paints and gasoline and improper discharge into water ways. The high levels of heavy metals recorded in the midstream area of the lagoon can be attributed to high input of industrial waste from the surrounding industries. The result also suggests that the high inputs of untreated wastes are been discharged through unauthorized points by industries into the lagoon, since the effluent that is discharged from the Industrial Complex Channel recorded lower values of physicochemical parameters and low levels of heavy metals. Ansong (2007) reported that there are networks of drains, some of which are not easily identified discharging waste from the industrial complex into the lagoon.

Point S1 recorded values next to S2 even though this point is relatively far from industries. The increased concentrations here could be attributed to domestic waste discharge into the lagoon from the surrounding community because Mason (1996) reported that domestic, industrial and agricultural users produce large quantities of waste products, and waterways provide a cheap and effective way of disposing of many of these. Again, the increased concentrations at S1 could be attributed to the transportation of these toxic chemicals downstream. Ciszewski (1997) reported

that depending on the river morphology and hydrological conditions, suspended particles with associated contaminants can settle along the watercourse and become part of the bottom sediments, often for many kilometres downstream from the chemical sources. The relatively less pollution at point S3 could be attributed to the fact that the area has less anthropogenic activities occurring there. Iron concentrations in the sediments were relatively high, but this could be due to natural processes instead of anthropogenic activities as iron occurs abundantly in the natural environment and may come from background levels in the sediments.

#### 5.3 Heavy Metals in Muscles of Fish

Increased or decreased pH as well as other environmental factors could have varied consequences on heavy metal availability to fish. From the results of the study, pH values ranged from 7.69 and 8.71 and these values fell within the neutral to alkaline range indicating increasing pH. Jezierskka and Witeska (2006) reported that water acidification affects bioaccumulation of metals by fish in an indirect way, by changing solubility of metal compounds, or directly due to damage of epethelia which become more permeable to metals. The relatively low concentrations of heavy metals in the muscles of fish could thus be as a result of the high pH in the lagoon which caused reduced solubility and low availability of the metal to the fish tissue. Again, this could be explained by the fact that there is preference for other binding sites to muscles. Uysal and Emre (2010) observed that the lowest levels of Cu, Zn, Mangan, Fe and Mg were recorded in fish muscles whereas the gills recorded relatively higher values. Similar report was made by Fernandes *et al.* (2006) where Zn and Cu concentrations were higher in the liver and gills than in the muscles.

Irrespective of the relatively low concentrations of heavy metals recorded at the time of sampling it is worth noting that some of these metals exceeded recommended levels and there is a cause for concern due to the combined effects these metals could have on aquatic organisms and the potential to magnify along the food chain. Rajamanickam and Muthuswamy (2008) in their experiment observed that the effects of sublethal concentration of combined heavy metals for 32 days proved to be toxic to common carp (*Cyprinus carpriol*).

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#### 5.4 Heavy Metals in Butuah Lagoon and Effluent

When samples from Butuah lagoon was compared with the US EPA (1986) water quality standards Pb exceeded the 0.05 mg/L limit in February and in March at W1 and W3. The increased concentrations could be explained by the proximity of these points to motor vehicle artisans in the area because O'Neill (1993) reported that the major source of Pb are in lead- acid storage batteries particularly for motor vehicles, and lead alkyl compounds added to petrol. The concentrations of Cd also exceeded the limits set by the US EPA in December and in January and this calls for concern. O'Neill (1993) observed that the increased quantities of cadmium mobilized are partly related to demand for cadmium itself but also to increased use of zinc and phosphate fertilizers. The increased concentrations could therefore be as a result of the probable use of phosphate fertilizer around the lagoon. The study showed that effluent samples from the industrial complex had heavy metal concentrations well within the recommended Ghana EPA (2011) standards.

#### 5.5 Monthly Variation of Heavy Metal Concentrations in Sediments, Fish and Water

The trend of heavy metals studied for the four month sampling period were not of a regular pattern as they increased and decreased along the sampling months. The levels of metals present may be dependent on the environmental conditions of the lagoon as well as the anthropogenic inputs into the lagoon. March coincided with the start of the rainy season in the sampling area and the generally low metal concentrations during this period could be explained from low bioavailability arising from dilution, associated with heavy rains during the rainy season. Similar observation was made by Obasohan and Eguavoen (2008) where heavy metal concentrations in water and fish from Ogba River were significantly higher in the dry season than the rainy season. Also, the fluctuations in heavy metal levels during the sampling may be attributed to the varying levels of domestic and industrial waste input into the lagoon.

#### 5.6 Bioaccumulation in fish

The heavy metal concentrations in the muscles of fish varied during the sampling. The bioaccumulation of Cd was the least as it recorded lower mean values in the month of December, January and March. Cadmium can however; bioaccumulate in the kidney and the amount of cadmium stored in this organ increases with age and can also accumulate to high levels in the liver (Hill, 1997).

The low bioaccumulation ratios recorded for the heavy metals in the fish muscles could be attributed to the preference of the metals for other binding sites with the liver and the kidney being the most important targets. Ishaq *et al* (2011), indicated that *Tilapia zilli* gills contained the highest concentration of all heavy metals (Cr, Zn, Cu, Fe, Mn, Cd, Pb) while the muscle tissues appeared to be the least preferred site for bioaccumulation of the metals. Their order of bioaccumulation from the highest to the least was gills > intestine > muscle tissue. This order gives a clear indication of the preference of heavy metals to other organs in the fish samples and

this may account for the low bioaccumulation factors observed during the four month sampling period. The bioaccumulation factors for Cu, Pb, Zn and Hg generally were higher at F3 in January, February and March and this call for proper attention and management as the potential to magnify exists along the food chain.



#### CHAPTER SIX

#### 6.0 CONCLUSIONS AND RECOMMENDATIONS

#### 6.1 Conclusion

This research sought to assess the pollution status of Butuah Lagoon using different media within the ecosystem. The results obtained indicated that sediments from the lagoon were highly polluted, followed by fish and water being the least. The potential for the heavy metals to magnify along the food chain calls for serious concern due to the implications on human health since heavy metals are known to cause damage to major organs in humans such as the kidney, heart, liver, brain upon chronic exposure.

The recorded high values of physicochemical parameters in Butuah when compared to appropriate water quality standards reflect the generally poor water quality of the lagoon. The mean values recorded for heavy metals and the other physicochemical parameters along Butuah Lagoon during the sampling indicated a general trend of pollution going on more at midstream and down-stream which suggests anthropogenic inputs from industries and households which are highly concentrated around these parts of the lagoon.

The high levels of pollutants recorded in the samples from the lagoon are indicative of untreated waste discharge through several unauthorised sources especially from the industrial community.

#### 6.2 Recommendation

Results from the study clearly showed the pollution of Butuah Lagoon which has varied consequences on the numerous users of the lagoon. It is therefore very imperative for awareness

creation on the importance of the lagoon by stakeholders such as the Ghana EPA, Water Resources Commission and Non-governmental Organisations.

Again, the Ghana EPA should embark on periodic monitoring activities of the Lagoon and also intensify checks in the industries surrounding the lagoon in order to evaluate the performance of their treatment systems so as to ensure the protection of aquatic life and humans who consume the fisheries resources.

There is the need for a comprehensive management plan for the protection of the Butuah Lagoon in consultation with all stakeholders in the Sekondi-Takoradi Metropolis and beyond so as to further stop the increased pollution going on in the lagoon in view of the possible health implications to consumers of the fishes in the lagoon.

A similar research when conducted in the lagoon and using different organs such as the kidney, gills, liver, could help better understand the pollution loads of the ecosystem leading to the development of a comprehensive management plan for the area.



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## APPENDICES

# Appendix 1.A. One Way ANOVA of Heavy metals in Sediment Samples

		Sum of Squares	Df	Mean square	F	Sig
ARSENIC	Between Groups Within Groups Total	12706.542 32.933 12739.476	11 24 35	1155.140 1.372	841.803	.000
COPPER	Between Groups Within Groups Total	20804.789 1.414 20806.203	11 24 35	1891.344 .059	3.210E4	.000
LEAD	Between Groups Within Groups Total	32543.837 1.573 32545.410	11 24 35	2958.531 .066	4.513E4	.000
ZINC	Between Groups Within Groups Total	398096.810 23.060 398119.870	11 24 35	36190.619 .961	3.767E4	.000
IRON	Between Groups Within Groups Total	2825983.519 856.233 2826839.752	11 24 35	<b>256907</b> .593 35.679	7.201E3	.000
CADMIUM	Between Groups Within Groups Total	361.343 3.160 364.503	11 24 35	32.849 .132	249.489	.000
MERCURY	Between Groups Within Groups Total	.002 .000 .002	11 24 35	.000	227.169	.000

		Sum of	Df	Mean	F	Sig
		Squares		square		
ARSENIC	Between Groups	107.946	11	9.813	128.933	.000
	Within Groups	1.827	24	.076		
	Total	109.772	35			
COPPER	Between Groups	269.476	11	24.498	2.442E4	.000
	Within Groups	.024	24	.001		
	Total	269.500	110	Т		
LEAD	Between Groups	506.476	C J	46.043	1.334E3	.000
	Within Groups	.828	24	.035		
	Total	507.304	35			
			LA.			
ZINC	Between Groups	2452.697	11	222.927	1.3743E3	.000
	Within Groups	3.983	24	.162		
	Total	2456.590	35			
IRON	Between Groups	128481.446	11	11680.131	3.695E3	.000
	Within Groups	75.857	24	3.161		
	Total	128557.303	35	353		
		FU	Jr/3	13		
CADMIUM	Between Groups	5.392	11	.490	160.413	.000
	Within Groups	.073	24	.003		
	Total	5.465	35			
		may				
MERCURY	Between Groups	.001	11	.000	55.008	.000
	Within Groups	.001	24	.000	7	
	Total	.001	35	3		
	Sec. 1			24		
	COR	2	5	and		
	1	Wasser	NO			
		SAN	EN			

# Appendix 1.B. One Way ANOVA of Heavy Metals in Fish Samples

		Sum of Squares	Df	Mean square	F	Sig
ARSENIC	Between Groups Within Groups Total	.000 .000 .000	15 32 47	.000 .000	-	-
COPPER	Between Groups Within Groups Total	.022 .000 .022	$\bigcup_{47}^{15}$	.001	481.438	.000
LEAD	Between Groups Within Groups Total	.757 .000 .757	15 32 47	.050 .000	1.086E4	.000
ZINC	Between Groups Within Groups Total	2.477 .001 2.478	15 32 47	.165 .000	5.720E3	.000
IRON	Between Groups Within Groups Total	34.750 .011 34.761	15 32 47	2.317	6.836E3	.000
CADMIUM	Between Groups Within Groups Total	.036 .000 .036	15 32 47	.002	943.960	.000
MERCURY	Between Groups Within Groups Total	.000 .000 .000	15 32 47	.000	-	-

Appendix 1.C. One Way ANOVA of Heavy Metals of Lagoon Water and Effluent

		Sum of	df	Mean	F	Sig
		Squares		square		-
pН	Between Groups	.055	3	.018	6.284	.017
	Within Groups	.023	8	.003		
	Total	.079	11			
TDS	Between Groups	10.223	3	3.408	2.255	.159
	Within Groups	12.087	8	1.511		
	Total	22.309	11			
TSS	Between Groups	46.110	3	15.370	99.161	.000
	Within Groups	1.240	8	.155		
	Total	47.350	11			
COND	Between Groups	30.000	3	10.000	3.728	.061
	Within Groups	21.460	8	2.682		
	Total	51.460	11			
TEMP	Between Groups	.396	3	.132	3.167	.085
	Within Groups	.333	8	.042		
	Total	.729	11			
TURB	Between Groups	2.029	3	.676	13.528	.002
	Within Groups	.400	8	.050		
	Total		11	· · · · ·		
COD	Between Groups	31.000	3	10.333	2.067	.183
	Within Groups	40.000	8	5.000	3	
	Total	71.000	11	173		
BOD	Between Groups	139.583	3	46.528	15.090	.001
	Within Groups	24.667	8	3.083		
	Total	164.250	11			
$PO_4$	Between Groups	1.988	3	.663	33.048	.000
	Within Groups	.160	8	.020		
	Total	2.148	11			
$SO_4$	Between Groups	39.582	3	13.194	26.477	.000
	Within Groups	3.987	8	.498		
	Total	43.569	11	ap		
NO <sub>3</sub>	Between Groups	.062	3	.021	30.141	.000
	Within Groups	.005	NE 8	.001		
	Total	.067	11			
OIL	Between Groups	43.667	3	14.556	3.881	.056
	Within Groups	30.000	8	3.750		
	Total	73.667	11			
CHLO	Between Groups	33.333	3	11.111	3.509	.069
	Within Groups	25.333	8	3.167		
	Total	58.667	11			
ALKAL	Between Groups	1017.073	3	339.024	2.877	.103
	Within Groups	942.653	8	117.832		
	Total	1959.727	11			

Appendix 1.D. One Way ANOVA of Physicochemical Parameters of Effluent

		Sum of	Df	Mean	F	Sig
		Squares		square		-
pН	Between Groups	.055	3	.018	6.284	.017
-	Within Groups	.023	8	.003		
	Total	.079	11			
TDS	Between Groups	10.223	3	3.408	2.255	.159
	Within Groups	12.087	8	1.511		
	Total	22.309	11			
TSS	Between Groups	46.110	3	15.370	99.161	.000
	Within Groups	1.240	8	.155		
	Total	47.350	11			
COND	Between Groups	30.00	3	10.000	3.728	.061
	Within Groups	21.460	8	2.682		
	Total	47.350	<u> </u>			
TEMP	Between Groups	.396	3	.132	3.167	.085
	Within Groups	.333	8	.042		
	Total	.729	11			
TURB	Between Groups	2.029	- 3	.676	13.528	.002
	Within Groups	.400	8	.050		
	Total	2.429	11	· · · · ·		
COD	Between Groups	31.000	3	10.333	2.067	.183
	Within Groups	40.00	8	5.000	1	
	Total	71.000	11	17		
BOD	Between Groups	139.583	3	46.528	15.090	.001
	Within Groups	24.667	8	3.083		
	Total	164.250	11			
PO <sub>4</sub>	Between Groups	1.988	3	.663	33.048	.000
	Within Groups	.160	8	.020		
	Total	2.148	11		-	
$SO_4$	Between Groups	39.582	3	13.194	26.477	.000
	Within Groups	3.987	8	.498		
	Total	43.569	11	ap		
NO <sub>3</sub>	Between Groups	.062	3	.021	30.141	.000
	Within Groups	.005	<b>RE</b> 8	.001		
	Total	.067	11			
OIL	Between Groups	43.667	3	14.556	3.881	.056
	Within Groups	30.000	8	3.750		
	Total	73.667	11			
CHLO	Between Groups	33.333	3	11.111	3.509	.069
	Within Groups	25.333	8	3.167		
	Total	58.667	11			
ALKAL	Between Groups	1017.073	3	339.024	2.877	.103
	Within Groups	942.653	8	117.832		
	Total	1959.727	11			

Appendix 1.E. One Way ANOVA of Physicochemical Parameters of Butuah Lagoon

Parameter	Textile	Food &	Paints &	Pharmaceuticals	Paper	Hotels	Wood &
		Beverages	Chemicals		& Pulp	&	Wood
					-	Resorts	Processing
pН	6-9	6-9	6-9	6-9	6-9	6-9	6-9
Oil & Grease	5	5	10	5	10	5	5
(mg/l)							
Temperature	< 3° C	< 3° C	< 3° C	< 3° C above	< 3° C	< 3° C	< 3° C
L.	above	above	above	ambient	above	above	above
	ambient	ambient	ambient		ambient	ambient	ambient
Colour	400	200	300	150	200	150	250
(TCU)							
COD (mg/L)	250	250	250	250	250	250	250
BOD (mg/L)	50	50	50	50	50	50	50
TDS (mg/L)	1000	1000	1000	1000	1000	1000	1000
Chromium	0.1		C.L.	117	0.1	0.1	0.1
(mg/l)							
Sulphide	1.5	1.5	1.5	1.5	1.5	1.5	1.5
(mg/l)							
Phenol (mg/l)	2	2	2	2	2	2	2
Total	400	400	400	400	400	400	400
Coliforms			FU	JE	7		
(MPN/100ml)		15	Xt >	1300			
E. Coli	10	10	10	10	10	10	10
(MPN/100ml)		R	Carto				
Turbidity	75	75	75	75	75	75	75
(NTU)			5				
TSS (mg/L)	50	50	50	50	50	50	50
Lead (mg/L)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Nitrate (mg/	50	50	50	50	50	50	50
L)		TP3 A	7	5 BAY			
Total	2	2	2	2	2	2	2
Phosphorus			JAN				
(mg/L)							
Conductivity	1500	1500	1500	1500	1500	1500	1500
(µS/cm)							
Mercury	0.005	0.005	0.005	0.005	0.005	0.005	0.005
(mg/L)							
Ammonia as	-	1.0	-	-	-	1.0	1.0
N (mg/L)							
Total	-	0.5	-	-	-	0.5	0.5
Pesticides							
(mg/l)							

**Appendix 2.** Sector Specific Effluent Quality Guidelines for Discharges into Natural Water Bodies (Maximum Permissible Levels).

# Appendix 2 Continued.

Total	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Arsenic							
(mg/L)							
Soluble	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Arsenic							
(mg/L)							
Alkalinity	150	150	150	150	-	-	-
as CaCO <sub>3</sub>							
(mg/L)							
Fluoride	-	10				-	-
(mg/L)							
Chloride	250	250	250	250	250	250	250
(mg/L)							
Total Iron	-	-			10	10	10
(mg/L)			M	2			
Free	-	-	N-	11 14-	-	0.2	-
Cyanide			Cil	117			
(mg/L)							
Aluminium		-		-	-	-	5.0
(mg/L)							
Copper				2 mg	5	5	5
(mg/L)	2	~		-	Th	5	

Source: Ghana EPA (2011)

