

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

KUMASI, GHANA

ASSESSMENT OF PHYSICOCHEMICAL PROPERTIES AND HEAVY METALS IN
WATER, SEDIMENT AND FISH (*Oreochromis niloticus*) FROM THE UPPER VOLTA
BASIN (STRATUM VII), GHANA

By

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A THESIS SUBMITTED TO THE DEPARTMENT OF THEORETICAL AND

APPLIED BIOLOGY,

KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF

MASTER OF SCIENCE IN ENVIRONMENTAL SCIENCE

DEPARTMENTMENT OF THEORETICAL AND APPLIED BIOLOGY

NOVEMBER, 2014

DECLARATION

I, Coffie John hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the qualification of any other degree or diploma of a university or other institution of higher learning, except where due acknowledgement is made.

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ABSTRACT

This study was carried out at the Upper Volta Basin (Stratum VII) to assess the levels of six (6) heavy metals, Arsenic, Lead, Copper, Cadmium, Zinc and Mercury in the water, sediments and fish as well as nutrients in the water (nitrates and phosphates) and sediments (nitrogen and phosphorus) from January to March, 2012. Three sampling locations, namely Korpedike (Upstream), Makango (Midstream) and Yeji (Downstream) were chosen to give adequate spatial coverage and obtain a comprehensive and representative assessment of the heavy metal as well as the nutrient levels of the study area. Physicochemical data gathered during the study at the three sampling locations were fairly similar over the sampling period with no significant spatial variations ($p>0.05$) in the assayed parameters. The nutrient levels were however variable with significant spatial variations in nitrate concentrations in the water with the highest concentration of 0.065 mgL^{-1} recorded at the Korpedike sampling location. The nutrients concentrations in the water were generally below the WHO (2011) Drinking Water Quality Standard for nitrate and phosphate. Nitrate values at some of the sampling stations however exceeded the guideline value for the protection of aquatic life of 0.05 mgL^{-1} . Concentration of metals in the water sediment and fish of the Basin were generally lower than their regulatory standards for their presence in the basin. Compared to the WHO (2002) Safety Reference Standards for Human Consumption, the fish samples from the three locations on the Volta Basin were considered wholesome for human consumption and are unlikely to cause harm to human consumers in these areas. Heavy metals in the water, sediment and fish from the Upper Volta Basin ranked in the order of; Upstream>Midstream>Downstream, indicating an influence of the artisanal mining on the Volta Basin.

DEDICATION

This work is dedicated to my parents; Mr. Emmanuel K.B. Coffie and Miss Cecilia Cobbinah. It is also dedicated to my siblings and my beloved family for their great kindness and devotion in building a strong and infallible educational foundation for me.

ACKNOWLEDGEMENT

I am very much indebted to Dr. Bernard Fei-Baffoe my supervisor and the programme coordinator of M.Sc. Environmental Science, KNUST, who criticised, offered useful suggestions, fruitful discussions which were vital for this work and encouraged me throughout my on campus. I am also very thankful to all lecturers of department of applied and theoretical biology for their care and fatherly advice during my stay at campus. My sincere thanks go to Mr. Kwasi Adu and Napoleon Jackson Mensah of Faculty of Renewable Natural Resources, KNUST for their assistance in diverse ways throughout this work. Lastly, I owe a great debt of gratitude to my siblings for their kindness and support. Above all my everlasting gratitude is to the Almighty God who made all this possible, I say to him alone I thank for the wonderful thing he has made. My prayer is that: my God I lift you high, by faith and grace on heaven's table land. For a higher place I have found. Lord, plant my feet on higher grounds. Amen.

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ACRONYMS

APHA	American Public Health Association
As	Arsenic
Cd	Cadmium
CdCl	Cadmium Chloride
Cu	Copper
ERP	Economic Recovery Program
EtHg	Ethyl Mercury
HCl	Hydrogen Chloride
Hg	Mercury
LDPE	Low Density polyethylene
mg/kg	Milligram per kilogram
mS/cm	Microsiemens per centimeter
ND	Non Detectable
Psu	Per litre of solution
TDS	Total Dissolved Solid
Zn	Zinc

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Pollution of the heavy metals in the environment has become a problem in the world this 21st century, because these metals are indestructible and most of them have toxic effects on aquatic systems (MacFarlane and Burchett, 2000). In the environment metals are concern, due to their ability to accumulate in aquatic ecosystems (Censi *et al.*, 2006).Metal concentrations are monitored in aquatic ecosystems by measuring their levels in water, sediments and fish (Camusso *et al.*, 1995). High levels of metals affect living organisms and poses considerable environmental risks (Cajaraville *et al.*, 2000; Ravera, 2001).

Heavy metals can exist in sediments and freshwater systems for several years and this can affect human health and the environment (Mackevičiene *et al.*, 2002).

Fish species can be used as one of the indicators in freshwater systems for the determination of metal pollution (Rashed, 2001).

Some metals are essential such as copper, zinc, etc because they play a role in biological systems, and cadmium, lead etc are also non-essential metals, as they become toxic in trace quantities (Fernandes *et al.*, 2008).

Upper Volta Basin can found in West Africa and has an area of 400,000 km². Eighty percent of the area lies within the territorial boundaries of Ghana and Burkina Faso, the basin is drained by numerous streams, (Barry *et al.*, 2005).

1.2 Problem Statement

Surface waters in Ghana such as rivers can serve of many purposes; including source for drinking, transportation, for irrigation, hydropower generation, recreational activities, fish as food supplement and protecting biodiversity, there is serious doubt about public health safety of water and organisms in river bodies due to increase in population, urbanization, industrialization and agricultural practices (Entsua- Mensah *et al.*, 2000).

There is a concern about the deteriorating state of surface waters in Ghana in reference to heavy metal pollution Tariq *et al.* (1996). Small mining activities based on the use of heavy metals for the amalgamation of gold are common and widespread along major rivers in Ghana with the Upper Volta Basin as no exception.

The basin is also a farming area and chemicals like fertilizer, herbicides, etc are mostly employed in the farming practices; however these chemicals enter the basin through surface runoff. Petrol powered water pumps used to irrigate farmlands in the dry season enables petroleum wastes to enter into the river body. Sewage and refuse from domestic activities also enter the basin, there is the likelihood of contamination of water, sediments and fish in the Upper Volta basin at the Stratum VII by heavy metals since fertilizers, herbicides and small mining activities effluents contain some heavy metals.

1.3 Justification for the research

Chemical pollution on its own is directly associated with heavy metal pollution and may adversely affect the physical, chemical and biological characteristics of water. Heavy metals, which are toxic or poisonous at low concentrations, can enter into certain reservoirs and may be released by some processes such as remobilization. In order to formulate laws that safeguard human health and the environment, it is necessary to understand the sources and quantities of various pollutants in the environment. However, it is therefore necessary to find contamination status at Stratum VII since there only scanty information available.

1.4 The Objectives of the Study

The overall objective of the study was to establish the physicochemical characteristics of the water and heavy metals contamination status of water, sediment and fish in the Volta basin at the Stratum VII in Ghana.

Specific objectives

1. To establish the levels of Arsenic, Cadmium, Lead, Mercury, Copper and Zinc in the fish, sediment and water of the Upper Volta Basin.
2. To establish the levels of nutrients in water and sediments of the Upper Volta Basin.
3. To determine the physicochemical parameter of the water from the Upper Volta Basin.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Environmental Pollution

Increasing concern regarding environmental quality can be seen in these years along global and local scale. Production of harmful substances has negative effects on the environment, man and producing agricultural (Gadzała-Kopciuch, 2004). When the consequences of environmental pollution become visible, it is often too late to prevent them and chronic toxic effects, impossible to notice at the initial stage of the process, may manifest after many years (Alloway and Ayres, 1998). Water constitutes the “trouble spot” of all ecosystems, as many pollutants are waterborne and also plays an important role as a solvent of various substances, and as a medium in the cycle: air-soil-plants-animals (Nałęcz-Jawecki and Sawicki, 1998).

Due to constant technological progress the natural environment undergoes numerous changes, deteriorating its quality, which often results in negative interactions between particular ecosystem components.

2.2 Heavy Metals

Heavy metal applies to the group of metals and metalloids with an atomic density greater than 4gcm^{-3} (Duffus, 2002).

Anthropogenic releases can give rise to higher concentrations of the metals relative to the normal background values. The anthropogenic releases of heavy metals to the environment come from mining, smelting, agricultural materials such as pesticides and fertilisers, irrigation and application of sewage water and sludge, fossil fuel combustion and metallurgical industries (Alloway 1995b).

Whether the source of heavy metals is natural or anthropogenic, the concentrations in terrestrial and aquatic organisms are determined by the size of the source and adsorption and/or precipitation in soils and sediments. The extent of adsorption depends on the metal, the absorbent, the physicochemical characteristics of the environment (e.g. pH, water hardness and redox potential) and the concentrations of other metals and complex chemicals present in the soil water, river or lake.

2.3 The Toxic Effects of Heavy Metals to the Humans

Toxicity of a metal is said to be the concentration required to cause an acute response or a sub-lethal response (Smith, 1986). Knowing the levels of metal exposure on living organisms is difficult to establish. Low concentrations of these metals can be as harmful as high concentrations (Newman and Clements, 2008).

The following subchapters review the toxic effects of heavy metals, especially the most studied metals on man and the environment.

2.4 Mercury

Mercury (Hg) occurs in nature due to erosion from earth crusts and volcanoes, but anthropogenic sources have increased the exposure in recent time (Clarkson, 2002). Elemental Hg is oxidized to mercuric mercury (Hg^{2+}), which can be methylated by some microorganisms forming MeHg, in a process which takes place mainly in aquatic environments (Harris *et al.*, 2003).

2.4.2 Effects of mercury to humans

Mercury can cause neurological and psychological symptoms, such as tremor, restlessness, anxiety and depression. Mercury is also an allergen, which may cause contact eczema. The kidneys are also known accumulate the high levels of mercury compared to brain and liver (Zahir *et al.*, 2005).

2.5 Cadmium

Cadmium is known to be a non-essential element, enters the aquatic environment from many processes such as chemical agricultural practices and mining activities (Sorensen, 1991; Wood, 2001).

Cadmium accumulation in gills, liver and kidney of fish has been reported in several literatures (Hollis *et al.*, 2000; Hans *et al.*, 2006) whereas accumulation of cadmium in fish muscles was reported in a few articles because of their biomagnifications in the food chain and its effect on humans (Mansour and Sidky, 2002).

2.5.1 Presence of Cadmium in Aquatic Environments

Cadmium in aquatic environments are enhanced by low pH, low hardness, low suspended matter levels, high redox potential and low salinity (Government of Canada, 1994). Cadmium is acutely toxic to fish and other aquatic organisms, resulting in mortality at lower concentrations than observed with other metals. This toxicity is attributed to the ability of cadmium to act as a calcium antagonist to gain entry into the body and subsequent disruption of calcium homeostasis (Verbost *et al.*, 1989).

2.5.2 Effect of Cadmium to human health

The kidney has been observed as the target organ, for both the general population and occupationally exposed populations. Studies over the past decade have indicated that renal tubular damage occurs at lower levels of cadmium body burden than previously observed. Some studies have suggested that cadmium alters calcium metabolism, contributing to osteoporosis (Järup *et al.*, 1998).

2.6 Arsenic

2.6.1 Presence of Arsenic in the Environment

Arsenic occurs widely in soil, rocks, sediments and metals ores in the form of oxyhydroxide, supplied or compounds of various metals in most part of world (Aronson, 1994). Humans are exposed to arsenic through ingestion, inhalation and dermal contact. Also occupation such as smelting and refining of metals expose people to arsenic (USPHS, 1989). In medicine patients and physicians are exposing to arsenic in

the treatment of some diseases like syphilis, asthma, rheumatism, cough, etc (Wong *et al.*, 1981; Ko, 1999).

2.6.3 Health Effects of Arsenic on Humans

Neurological effects, cardiovascular disease, chronic lung disease, cerebrovascular disease, reproductive effects and cancers of skin, lungs, liver, kidney and bladder are associated with humans at high concentrations of (Rahman *et al.*, 1998; Wang *et al.*, 2003). Children exposed to drinking water with high arsenic concentration of greater than 50 µg/l execute lower performance than children, using drinking water with low arsenic less than 5.5 µg/l and growth retardation in children (Wasserman *et al.*, 2004). Drinking water contaminated with arsenic is also responsible for spontaneous abortion, stillbirth and infant mortality (Aschengrau *et al.*, 1989).

2.7 Lead

2.7.1 Environmental Fate of Lead

The distribution of lead from fixed, mobile and natural sources is primarily through air, although there is a continuous transfer of lead between air, water and soil. This interaction depends on the physicochemical properties of both lead and the environment (MOEE, 1994). Lead exists in aquatic medium in three phases: dissolved lead, suspended particulate and sediment. Most of the lead in water eventually goes to the sediment phase. Lead is slightly soluble in water, so there is a potential for human exposure through drinking water and can be toxic to fish or to those consuming fish (MOEE, 1994).

2.8 Zinc

2.8.1 Zinc Distribution in the Environment

Zinc is widely used in our social lives such as coating or galvanizing iron to prevent corrosion, they are mixed with other metals to form alloys for example brass and particles released from vehicle tyres and brake linings are a major source of zinc in the environment (WHO, 2001).

2.8.2 Effects of Zinc to humans

High concentrations of zinc (ANZECC, 2000) cause gastrointestinal distress and diarrhoea has been reported following ingestion of beverages standing in galvanized cans (WHO, 2001). Symptoms such as slow reflexes, shakes, paralyzation of extremities, anaemia, metabolic disorder, terratogenic effects and increased mortality are associated with zinc (Klaassen, 1996).

2.9 Copper

Copper is one of the essential trace metals for plants and animals, it is required in synthesis of chlorophyll and haemoglobin. It is also used in maintaining optimum plant metabolism. Copper becomes toxic to aquatic organisms when biological requirements are exceeded.

2.9.1 Properties of Copper

Copper is also known to be one of the noble metal as silver and gold and can be found in nature in the elemental form. It has high thermal conductivity, high electrical conductivity, and malleability, low corrosion, alloying ability, and aesthetically pleasing appearance.

2.9.2 Copper in water

Natural and anthropogenic sources contribute copper to water example natural weathering of soil, atmospheric deposition, and discharges from industry and wastewater treatment plants and the major source is from land runoff through natural weathering (U.S. Department of Health & Human Services, 1990).

2.9.3 Concentration of Copper in sediments

Concentrations of copper in freshwater sediments ranged from 12 to 57 mg/kg (Spear and Pierce 1979).

2.10 Physicochemical Parameters

2.10.1 pH

pH is a measure of hydrogen ion concentration. Water bodies with pH of less than 4.8 or greater than 9.2 can be harmful to aquatic life. Most freshwater fish prefer water with a pH range between 6.5 and 8.4, optimum pH for river water is should be 7.4, extreme pH can make a river inhospitable to life and low pH is especially harmful to immature fish and insects (Moore, 1989).

2.10.2 Temperature

Temperature is a measure of the hotness a substance could be, physical, biological and chemical characteristics of surface water are dependent on temperature. The optimal health of aquatic organisms from microbes to fish depends on temperature. If temperatures are outside the optimal range for a prolonged period, organisms are stressed and can die. For fish, the reproductive stage (including spawning and embryo development) is the most temperature-sensitive period (Ecology, 2011b).

2.10.3 Conductivity

Conductivity of water is directly related to the concentration of dissolved solids in the water. Dissolved ions in water influence the ability of that water to conduct an electrical current (Michaud, 1991).

2.10.4 Total Dissolved Solids (TDS)

Total dissolved solid is a measure of the total amount of all the materials that are dissolved in the water. The materials can be natural or anthropogenic which are mainly inorganic solids and a minor amount of organic material. Total dissolved solids can vary greatly from a few milligrams per liter to percent levels (tens of thousands of milligrams per liter), depending on the type of water. Seawater contains 3.5 percent (35,000 mg/L) total dissolved solids (Michaud, 1991).

2.11 Nutrient Pollution of Surface Waters

Nutrients are major environmental stressors in river and lake ecosystems. Levels nutrients in rivers impact the trophic status thus influencing the sedimentation of abiotic and biotic particles. High levels of nutrients in water bodies can potentially cause eutrophication and hypoxia (USGS, 2006). The major nutrient that causes eutrophication is nitrogen and phosphorus (Howart *et al.*, 2000).

2.12 Types of Nutrient Pollutants

Investigating water quality the various forms of nitrogen and phosphorus are the nutrients of interest. They include nitrate, nitrite, ammonia, organic nitrogen (in the form of plant material or other organic compounds) and phosphates (orthophosphate and others). Nitrate is the most common form of nitrogen and phosphates are the most common forms of phosphorus found in natural waters (Skei *et al.* 2000).

2.12.1 Phosphorus

Phosphorus as an essential nutrient for living organisms is required by plants for growth and reproduction and often is added to agricultural soils to increase crop yields and in the aquatic ecosystem, phosphorus can be found in the water column, within the bodies of aquatic organisms, or attached to particles such as in sediment in the water (Caumette *et al.*, 1996).

2.12.2 Nitrate

Man's uses of synthetic or inorganic fertilizers has caused the single largest change in the global Nitrogen cycle and the burgeoning fertilizer use accounts for more than half of the total human-driven alteration of the Nitrogen cycle (Selman and Greenhalgh, 2009). These activities of burning fossil fuels such as coal and oil and extensive plantings of nitrogen-fixing crops such as soybeans, peas and alfalfa has caused high nitrate levels in rivers (Howarth *et al.*, 2000).

2.13 Impacts of Nutrients on Water Quality

The primary limiting nutrients in surface waters are phosphorus and nitrogen. Phosphorus and nitrogen have different chemical properties and are involved in different chemical processes. Excess nutrients in surface water may contribute to eutrophication of surface water, particularly lotic waters. Nutrient enrichment can over-stimulate algal production creating algal blooms that may reduce the aesthetic and recreational value of the water, create taste and odor problems in drinking water, and, in severe cases, stress or kill aquatic organisms as a result of dissolved oxygen depletion or the release of toxins when algal blooms die (Sharpley, 1995).

2.14 Pollution of Natural Waters in Ghana

Surface waters in Ghana serve as valuable means such as include as absorbing floodwaters and protecting biodiversity (Entsua-Mensah *et al.*, 2000). These surface waters have a great influence on the socio-economic well-being and health of communities that live close to and beyond them. The existing balance between the input of inorganic nutrients from different sources and their use or transport through assimilation, sedimentation or export from the system is important in evaluating trophic state of surface waters (Ansah-Asare *et al.*, 2008).

The present rate of urbanization in Ghana raises concern about the impact of urban development on the environment, particularly the aquatic environment (UNCHS, 2001; Rakodi, 1997). Most surface waters in Ghana are associated with very intensive land use and waste disposal. Surface waters for instance, serve as conduits for the transport of both solid and liquid waste from most parts of the cities into the sea. Almost all the surface waters are used in artisanal fisheries and they play an important role in the economy of some inhabitants (Entsua-Mensah *et al.*, 2004). There is however growing evidence that these freshwater systems are under stress from human-induced interference. The pollution of most of the surface waters in Ghana can be attributed to the uncontrolled discharge of domestic effluents and industrial emissions, which has worsened since 1983 when the Government introduced the Economic Recovery Programme (ERP) (Amuzu, 1997).

A review of researches carried out in Ghanaian lagoons indicate moderate to gross pollution, mainly as a result of anthropogenic activities. At one extreme, the Korle lagoon, near Accra, has been described as one of the most polluted water bodies on earth

(Boadi and Kuitunen, 2002). Up to the 1960s, the Korle Lagoon supported a thriving fishery, but presently it supports only a few fish species which are restricted to its estuary, including *Mugilcephalus* and *Seriola sp.* (Agbo *et al.*, 2011). Excessive pollution has been implicated as the main cause of the near-collapse of the Lagoon's fishery. Oxygen is depletion in the lagoon and BOD levels are high. The lagoon has been described by CSRM (2002) as the most polluted water body in Tema due to the constant discharge of industrial and domestic effluents into the lagoon.

2.15 National Environmental Plans of Action

Implementation of the environmental policies in Ghana, describes the activities and policies which were implemented to affect the environment in a significant way. The institution of some governmental and environmental agencies like the Ministry for the Environment, Science and Technology in 1993 and Environmental Protection Agency (EPA) in 1995 were mainly in response to the environmental harm caused by the ERP in 1983. The EPA was set up on the basis of the 1994 Environmental Protection Agency Act (Act 490). This act defines a set of policy actions, related investments and institutional strengthening activities that will help make Ghana's development strategy more environmentally compatible. In the recent past, Ghana in response to the NEAP, instituted a 10-year Environmental Action Plan (EAP), which covered the period 1991-2000 and involved the management and sustainable use and management of Ghana's drainage basins.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Study Area

Stratum VII of the Volta Lake was chosen for this contaminant analysis. It was divided into three sampling stations; Korpedike (upstream), Mankango (midstream) and Yeji (downstream) as shown in figure 3.1. In choosing the sampling stations, preference was given to factors such as runoff from agricultural fields at both Korpedike and Mankango, artisanal mining activities carried around the White Volta at Korpedike, fishing harbour at Yeji and nearness of sampling station to settlement.

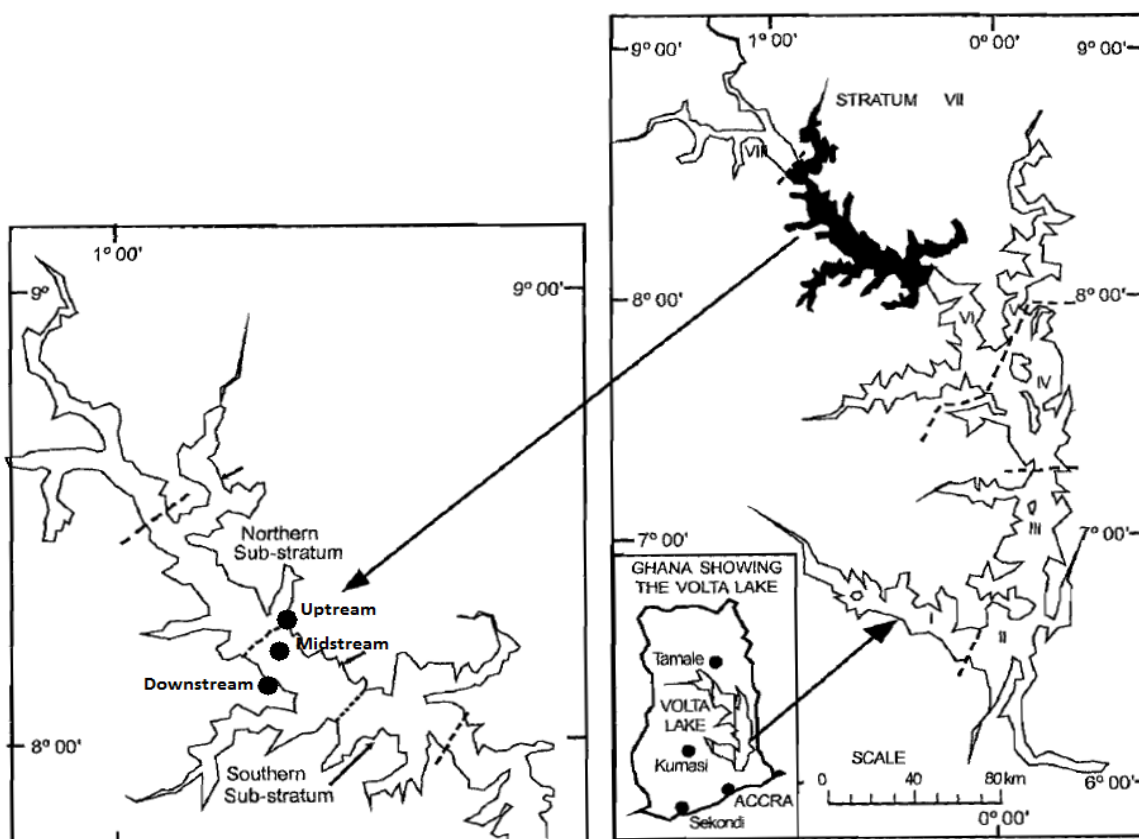


Figure 3. 1Modified map of Stratum VII. Inset is the map of Ghana indicating portion of Upper the Volta Basin.

Yeji is characterized by vibrant fish market centres along the basin shoreline which contribute significantly to the livelihoods of the population in the informal sector. There is also poor waste management and the waste generated usually end up in the river. Sections of the lake adjacent to the market yards are polluted with organic and plastic wastes as well as faecal matter as can be seen in Figure 3.2 below.



Figure 3. 2Waste at a market yard in Yeji; a common feature at all the markets centres

3.1.1 Topography, Climatic Conditions and Soil Characteristics

The study area is generally flat with isolated hills and valleys sparsely scattered on the land surface. It is generally a low lying terrain and the presence of the Volta basin gives it

sloppy appearance towards the lake region. The vegetation is generally the Guinea Savannah type, with scattered patches of forest. The climate is generally hot and is made up of two major seasons; the dry and rainy seasons. The dry season begins with the harmattan winds in November and persists until February, when the rains set in. The rainy season, normally records a double maximum in June/July and in September/October. Temperature averages range between 22 – 34°C, while rainfall averages is 30 mm. The sampling locations of the study area have rich fertile soils, which support the growth of food crops, vegetables and other cash crops (Barry *et al.*, 2005)

3.2 Sample Collection

A canoe was used as sampling craft with the help of local fishermen and at each station the canoe was stopped for fish, sediment and water samples. Fish samples (*Oreochromis niloticus*) were collected with cast net. Fish samples were wrapped with polythene bags and kept on ice in an ice-chest and subsequently transported to the laboratory and frozen at 4 °C before further analysis.

Sediment samples were collected at the bottom of the river with an Ekman grab at each sampling station and stored immediately in polythene bags. Sediments collected were stored at 4 °C in an ice-chest and transported to the laboratory before analysis. Sampling was done once a month from January to March of 2012.

3.3 Analysis of Samples

3.3.1 Determination of Physicochemical Parameters

Monthly measurement of temperature, salinity, pH, total dissolved solids (TDS), and conductivity of the overlying water were taken at all the sampling locations for the study period using a Hanna (HI 9828) multi-parameter probe.

3.3.2 Sediment Preparation for Nutrient Analysis

Sediment samples were dried in the sun on clean polythene sheets, and with aid porcelain mortar and pestle it was ground into a powdery form and they were sieved. The sediment samples were then stored in labeled polythene bags for Nitrogen and Phosphorus analysis.

3.3.2.1 Determination of Sediment Nitrogen

Nitrogen in the sediment was determined at the Faculty of Renewable Natural Resources Laboratory, KNUST.

The Kjeldahl method (figure 3.4) was used for the determination of Nitrogen. Approximately 1.00 g sample was digested in concentrated Sulphuric acid with Selenium based catalyst tablet (contains 3.5 g Potassium sulphate and 3.5 mg Selenium). The samples were digested in a Tecator Instrument AB digester. Each of the digested samples was distilled with Kjeldahl distiller after reacting with 50 ml Sodium hydroxide sodium thiosulphate ($\text{NaOH} \cdot \text{Na}_2\text{S}_2\text{O}_2$). The liberated nitrogen was collected in 50 ml boric acid

and titrated with 0.1N HCl solution with bromocresol green as indicator and traces of nitrogen in the reagents and water used were taken care of by carrying out a blank distillation and titration.



Figure 3. 3 Sample distillation using the Kjeldahl Distiller

Percent nitrogen was calculated using the equation below:

$$\% N = \frac{14 \times (A - B) \times N \times 100}{1000 \times 1}$$

Symbols meaning;

A = ml HCl used in sample titration

B = ml HCl used in blank titration

N = concentration of HCl used in titration.

14 = atomic weight of nitrogen

1 = wt. of soil sample in gram

3.3.2.2 Determination of Sediment Phosphorus

In determining the sediment phosphorus, the first procedure that was carried out was the dry ashing method.

Two (2) g of the sieved (2 mm) sediment was weighed into a crucible and ashed at a temperature of 550 °C in a muffle furnace for 4 hours. The ashed residue was dissolved in a diluted HCl, filtered through acid- washed filter paper into a 50 ml volumetric flask and the volume made up to the mark.

Phosphorus in Phosphate ion was then determined by the Ascorbic acid-Molybdate method with the aid of a spectrophotometer (SP 300).

3.3.2.3 Determination of Nitrate in Water

Nitrate concentrations in the water samples were determined at the Faculty of Renewable Natural Resources Laboratory. Photometric method was used to determine the concentrations of nitrate in the water samples. Round test tubes were filled with the sample to the 10 ml mark. Nitricol tablet was crushed and mixed to dissolve. The solution was left to stand for 10 minutes to allow for full colour development. The absorbance of the Photometer (Wagtech Photometer 7100) was set at a wavelength of 520 nm. The Nitrate in the water was determined by multiplying the absorbance by 4.4 using a Nitricol calibration chart.

3.3.2.4 Determination of Phosphate in Water

The Phosphate concentration of the water of the Volta basin was determined using a Viscolor® Phosphate 50 Test Kit with a comparator cell and colour scale at the laboratories of Anglogold Ashanti Limited at Obuasi, Ashanti Region.

Apparatus and Reagents used

- i. Comparator cell
- ii. Phosphate-1 solution
- iii. Phosphate-2 powder
- iv. Measuring spoon
- v. 1ml syringe
- vi. Colour scale

Procedure:

1. The comparator cell was rinsed several times with each test sample and filled up to the upper mark (10 ml).
2. Ten (10) drops of Phosphate-1 solution was added to the sample in the comparator cell and mixed.
3. One spoonful of Phosphate-2 powder was added to the mixture and thoroughly mixed for 30 seconds.
4. The mixture was then allowed to stand for 5 minutes for the colour to develop.

5. After the 5 minutes, the comparator cell was held at eye level against light and the colour of the solution matched with the corresponding colour on the colour scale. The Phosphate concentration of the sample was then read off and expressed as mg/l NO_3^- .

3.3.3 Preparation and Digestion of Sediment and Fish Samples for Heavy Metal Analysis

Wet digestion was carried out for the fish samples. Approximately 1 g of each completely homogenized fish was taken and digested following the procedure below.

Each fish sample was homogenized using a food blender with stainless steel cutters. The sediment samples on the other hand, were dried on clean polythene sheets and ground into a powdery form with a porcelain mortar and pestle for the digestion for the metal analysis. 1 g of the finely ground sediment was weighed and placed into 500 ml conical flask and 20 ml of di-acid mixture of HNO_3 and HClO_4 with ratio 9:4 was added and the contents well mixed by swirling thoroughly. The flask with contents was then placed on a hotplate in the fume chamber and heated at an initial temperature of 85°C and then raised to 150°C . The mixture was heated until the production of red NO_2 fumes ceased. The contents were further heated until volume was reduced to 3-4 ml and became colorless or yellowish. The completely digested samples were allowed to cool at room temperature, and the undigested portions of the sediments filtered off through a Whatmann Glass Microfibre filter paper (GF/C) to obtain a clear solution. The resulting solution was then diluted to 100 ml in volumetric flasks with double distilled water and stored in LDPE bottles for metal analysis. The resulting solution was preserved at 4°C for heavy metal determination.

3.3.4 Digestion of water samples for Heavy Metal Analysis

Each sample was thoroughly mixed by shaking prior to transferring 100 ml into a conical flask. Five (5) ml of concentrated HNO_3 and a few boiling chips were added (APHA, 2005). The mixture was then heated until the volume was reduced to about 15 ml and complete digestion was indicated by either a light colored or clear solution. Contents were washed down with double distilled water and then filtered. The filtrate was transferred into 100 ml volumetric prior washed plastic containers and volume finally adjusted to 100 ml with double distilled water and stored at 4 °C, ready for heavy metal analysis (APHA, 2005). The digested samples were transported to the Environmental Laboratory of Anglogold Ashanti at Obuasi for the determination of heavy metals.

3.3.5 Determination of Total Mercury (THg)

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 253.7nm 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 ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) 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.

3.3.6 Quality Control and Assurance

All fish, sediment and water analytical batches for the determination of As, Pb, Cd, Zn, Cu and Hg concentrations were accompanied by blanks. Replicate analyses were conducted on 10% of the samples to assess precision of the analytical techniques. The preparation of the blank solutions were according to the following procedure: Approximately 2 ml of distilled water was poured into a digestion tube and 5 ml of nitric acid and perchloric acid ($\text{HNO}_3\text{-HClO}_4$) mixture in the ratio of 1:1 was added and swirled to mix. 5 ml of sulphuric acid was subsequently added and the mixture was shaken well to mix and heated at 200 °C for 30 minutes. The blank solution (1 ppm) was prepared by diluting an appropriate aliquot of the stock solution to 50 ml with distilled water.

To minimize contamination, all glassware for the digestion process were first cleaned under running tap water and soaked in 10% (v/v) Nitric acid (HNO_3) for 24 hours. They were then rinsed with distilled water followed by 0.5% (w/v) potassium permanganate (KMnO_4). Distilled water was used to finally rinse the glassware which was subsequently dried using an electric drier.

3.4 Statistical Analysis

Data were presented in tables as means \pm SD. Data obtained in this study for the levels of nutrients and heavy metals in the Lake's fish, water and sediments were analyzed by the Kruskal-Wallis non-parametric test to determine the variability in levels recorded at the various sampling stations over the sampling period. In all cases, standard error difference (s.e.d) at 5% was used to compare treatment means. All descriptive statistics and graphs were executed using the Graph-Pad Prism 5 Software.

CHAPTER FOUR

4.0 ANALYSIS OF RESULTS

4.1 Physicochemical Parameters of the Water

The physicochemical parameters of the samples collected from the three sampling locations over the study period are presented below (Table 4.1). The values recorded for the studied parameters were fairly similar and generally did not exhibit significant spatial variations over the three month period.

4.1.1 Korpedike Sampling Station (Upstream)

pH for the Korpedike (upstream) sampling site (Table 4.1) ranged from 6.13 in January, 2012 to 7.13 in March, 2012 and values of pH were fairly constant from February, 2012 to March, 2012 (table 4.1). Temperature values over the three (3) months period were constant with 24 °C ranging from January, 2012 to March, 2012 as shown in table 4.1. Salinity values varied between a narrow range of 0.031 to 0.042 psu in January, 2012 and March, 2012 respectively also as in table 4.1. Concentrations of Total Dissolved Solids (TDS) indicated in table 4.1 were fairly constant with values ranging from 0.035 mgL⁻¹ to 0.046 mgL⁻¹ over the sampling period. In table 4.1 there was a progressive increase of conductivity from 0.075 mS/cm to 0.076 mS/cm for January, 2012 and February, 2012 respectively. Conductivity value dropped to 0.071 mS/cm for the sampling period of March, 2012 (table 4.1).

4.1.2 Mankango Sampling Station (Midstream)

At Mankango (midstream) sampling site pH values were similar to the values recorded at Korpedike over the sampling period although values were generally slightly higher during most of the sampling period (table 4.1). The pH values ranged between 6.98 in March, 2012 and 7.52 in February, 2012 (table 4.1). Temperature values ranged between a very narrow range of 23.00 °C in February, 2012 but increase marginally in March, 2012 (table 4.1). TDS values were almost constant over the sampling period. Conductivity values were between 0.063 mS/cm to 0.067 mS/cm during the sampling period similar to the values recorded at Korpedike but were generally narrow (table 4.1). (Table 4.1) also shows that salinity was fairly constant at 0.031 psu for all the months from February, 2012 to March, 2012 except January that same year, which recorded a slightly lower value of 0.027 psu.

4.1.3 Yeji Sampling Station (Downstream)

At Yeji (Downstream) sampling site which was close to the fishing harbour, had pH values which were almost similar to the values recorded for both Korpedike and Mankango sampling sites over the sampling period although values were generally slightly higher during most of the sampling period (table 4.1). The pH values were ranging between 6.83 in January, 2012 to 7.42 in March, 2012 (table 4.1). Temperature values ranged between a narrow range of 24 °C to 25 °C in January, 2012 and March, 2012 respectively (table 4.1). TDS was constant between the sampling period of January, 2012 to February, 2012 but increase steadily from 0.032 mgL⁻¹ to 0.052 mgL⁻¹ in March, 2012 due to overload from municipal waste (table 4.1). Conductivity values dropped

slightly from 0.064 mS/cm in January, 2012 to 0.052 mS/cm in February, 2012 and there was an increase in March, 2012 with 0.08 mS/cm (table 4.1). Salinity increase narrowly from 0.025 psu to 0.028 psu in January, 2012 and February, 2012 respectively, however, the value for salinity in March, 2012 was a bit higher than all of the sampling period (table 4.1).

Table 4. 1 Physicochemical Parameters of the Water Samples from the Volta Basin

	Temp (°C)	pH	Cond (mS/cm)	TDS (mg/L)	Salinity (PSU)
January					
Upstream	24.00±0.00	6.13±0.06	0.075±0.001	0.035±0.001	0.031±0.001
Midstream	23.00±0.00	7.06±0.002	0.067±0.001	0.032±0.001	0.027±0.001
Downstream	24.00±0.00	6.83±0.06	0.064±0.001	0.033±0.001	0.025±0.001
February					
Upstream	24.00±0.00	7.31±0.01	0.076±0.002	0.046±0.002	0.039±0.001
Midstream	23.00±0.00	7.52±0.01	0.065±0.002	0.035±0.001	0.036±0.002
Downstream	25.00±0.00	7.42±0.02	0.052±0.002	0.032±0.002	0.028±0.002
March					
Upstream	24.00±0.15	7.31±0.01	0.071±0.001	0.043±0.002	0.042±0.002
Midstream	25.00±0.00	6.98±0.03	0.063±0.001	0.032±0.001	0.031±0.002
Downstream	25.00±0.00	7.11±0.01	0.080±0.002	0.052±0.002	0.052±0.001

4.2 Nutrients Concentrations in Water

The nutrient concentration of the water in the lake has been presented in (table 4.2).

4.2.1 Nitrate

Nitrate (NO_3^-) in water at Korpedike sampling site increase gradually ranging from values of 0.043 mgL^{-1} in January, 2012 to 0.065 mgL^{-1} in March, 2012 as compared to the other sampling sites (table 4.2). Nitrate values for the sampling site Mankango and Yeji were fairly constant from January, 2012 to March, 2012 except for the sampling site at Yeji where the nitrate value was lower with 0.022 mgL^{-1} compared to Korpedike and Mankango sampling sites (table 4.2). Overall there were significant differences ($p < 0.05$) in nitrate concentrations recorded at the three sampling stations over the sampling period. The Dunn's multiple comparison tests revealed that the actual difference in nitrate concentrations was between the upstream sampling station (Korpedike) and the downstream sampling station (Yeji). Nitrate concentration in the Volta Lake at the study locations ranked in the following order; Upstream > Midstream > Downstream over the study period (Appendix 4.1).

4.2.2 Phosphate

The highest phosphate (PO_4^-) concentration for the three months sampling period was recorded at Korpedike. Mean phosphate concentrations ranged from 0.321 mgL^{-1} to 0.545 mgL^{-1} in January, 2012 and March, 2012 respectively (table 4.2). At Mankango values for phosphate were similar to those recorded at Korpedike over the sampling period though values were generally slightly lower during most of the sampling period. The phosphate

values ranged between 0.256 mgL⁻¹ in January, 2012 to 0.545 mgL⁻¹ in March, 2012 (table 4.2). The Yeji sampling station recorded similar phosphate concentrations although they were slightly lower than the concentrations recorded at Korpedike and Mankango. Overall, there were no significant variations (P>0.05) in the phosphate concentrations recorded at the three sampling stations. Phosphate concentration in the Volta Lake at the study locations ranked in the following order; Upstream>Midstream>Downstream over the study period (appendix 4.1).

Table 4. 2 Nutrients Concentration in Water Samples

	NO₃⁻ (mg/L)	PO₄⁻ (mg/L)
January		
Upstream	0.043±0.001	0.321±0.002
Midstream	0.038±0.001	0.256±0.001
Downstream	0.033±0.001	0.128±0.002
February		
Upstream	0.052±0.001	0.322±0.002
Midstream	0.042±0.002	0.281±0.002
Downstream	0.036±0.001	0.186±0.001
March		
Upstream	0.065±0.001	0.545±0.001
Midstream	0.043±0.002	0.464±0.002
Downstream	0.022±0.002	0.474±0.002
ANZECC* (2000)	<0.05	10
WHO† (2011)	50	

*Water Quality Guidelines for the Protection of Aquatic Life

† Human Drinking water Quality Guidelines

4.3 Nutrient Levels in the Bottom Sediments

Bottom sediment nutrient concentrations in the lake are in table 4.3.

4.3.1 Nitrogen

The recorded sediment nitrogen (N) levels were fairly similar over the study period with the Upstream sampling station (Korpedike) recording the highest nitrogen concentrations over the three month period (table 4.3). Nitrogen levels at Korpedike ranged from 2.56 mgkg⁻¹ to 5.85mgkg⁻¹ in January, 2012 and February, 2012 respectively but there were a slight decrease to 4.17 mgkg⁻¹ in March, 2012 (table 4.3). The Mankango sampling station (midstream) recorded fairly similar but slightly lower nitrogen levels as compared to the Korpedike (Upstream) sampling station (table 4.3). The sediment nitrogen levels recorded at Yeji values were lower than the levels recorded at the Korpedike and Mankango sampling site with values of 0.95 mgkg⁻¹ in January, 2012 and 2.87 mgkg⁻¹ in March, 2012 (table 4.3). Overall, however, there were no significant differences ($p>0.05$) in the sediment nitrogen concentrations recorded at the three sampling stations with levels ranking in the following order; Upstream>Midstream>Downstream (appendix 4.2).

4.3.2 Phosphorus

Phosphorus (P) content of the bottom sediments at the upstream sampling site, Korpedike decreased from 432.13 mgkg⁻¹ in January, 2012 to 322.00 mgkg⁻¹ in February, 2012, with an appreciable increased to 669.09 mgkg⁻¹ in March, 2012 (table 4.3). At Mankango, similar mean phosphorus levels of 256.73 mgkg⁻¹ and 255.90 mgkg⁻¹ were recorded for the

months of January and February respectively (table 4.3). For the month March, 2012, a slightly lower mean phosphorus level of 157.27 mgkg^{-1} was recorded (table 4.3). The Yeji sampling site (downstream) recorded the lowest sediment phosphorus levels over the sampling period (table 4.3). The lowest mean phosphorus concentration of 41.23 mgkg^{-1} was recorded in March with the highest concentration of 184.06 mgkg^{-1} was recorded in January (table 4.3). Similar to the sediment nitrogen levels, the phosphorus levels recorded at the three sampling stations over the study period ranked in the following order; Upstream>Midstream>Downstream (appendix4.2).

Table 4. 3 Nutrient Levels in the Bottom Sediments

	N(mg/kg)	P (mg/kg)
January		
Upstream	2.56 ± 0.006	432.13 ± 0.058
Midstream	1.86 ± 0.015	256.73 ± 0.115
Downstream	0.95 ± 0.011	184.06 ± 0.124
February		
Upstream	5.85 ± 0.010	322.00 ± 2.00
Midstream	3.26 ± 0.002	255.90 ± 2.00
Downstream	2.12 ± 0.020	183.61 ± 0.34
March		
Upstream	4.17 ± 0.058	669.09 ± 0.27
Midstream	3.48 ± 0.153	157.27 ± 0.24
Downstream	2.87 ± 0.026	41.23 ± 2.40

4.4 Metal Concentrations in the Fish

When all samples were analysed by the Kruskal-Wallis parametric test to determine the variability in levels in fish recorded at the various sampling stations over the sampling period graphs executed using the Graph-Pad prism 5 software are presented in (table 4.4) and appendix 5.1.

4.4.1 Arsenic

Mean Arsenic concentrations in the *Oreochromis niloticus* samples from the three sampling locations exhibited similar trends over the three month period, with fairly similar Arsenic levels being recorded in the fish. Fish samples from the Korpedike (Upstream) sampling station generally recorded the highest mean Arsenic concentrations over the three month period. There was also a noticeable trend of Yeji (Downstream) recording the lowest mean Arsenic concentrations over the sampling period.

The Arsenic concentrations in the fish samples from the Korpedike sampling station varied from a lowest concentration of 0.28 mgkg^{-1} to a highest of 0.35 mgkg^{-1} in January and March, 2012 respectively (table 4.4). The fish samples from the Mankango (midstream) sampling station recorded slightly lower Arsenic concentrations as compared to the levels in the fish samples from Korpedike. The highest and lowest values of 0.27 mgkg^{-1} and 0.13 mgkg^{-1} were recorded in January and March respectively, similar to the trend observed at Korpedike (table 4.4). Yeji recorded its overall highest mean Arsenic concentration of 0.19 mgkg^{-1} in the February and March sampling periods (table 4.4). The statistical analysis revealed no significant differences ($p > 0.05$) in the mean As

concentrations recorded at the three sampling stations. Mean As concentrations in the fish samples from the three locations ranked in the following order; Upstream>Midstream>Downstream (appendix 5.1).

4.4.2 Lead

Lead levels in the fish samples from the three sampling locations were detected only in all the sampling months during the study period. January recorded the highest concentrations of Lead in the tissues of the *Oreochromis niloticus* from the Upstream and Downstream sampling stations. Similar to the trend observed for the Arsenic concentrations in the fish tissues, Korpedike (Upstream) recorded the highest Lead concentration of 0.70 mgkg^{-1} in the fish samples (table 4.4). Mankango and Yeji, the midstream and downstream portions recorded mean Lead concentrations of 0.40 mgkg^{-1} and 0.55 mgkg^{-1} respectively for the January sampling period (table 4.4). The March sampling period recorded the lowest Lead concentrations for all the three sampling stations (table 4.4). The Kruskal-Wallis non-parametric Test revealed no significant differences ($p>0.05$) in the recorded Lead concentrations in the tissues of the *Oreochromis niloticus* samples over the sampling period. Overall, the mean Lead concentrations in the fish samples ranked in the following order; Upstream>Midstream>Downstream (appendix 5.1).

4.4.3 Copper

The general trend of Copper concentrations in the fish tissues at the three sampling stations as far as the sampling months were concerned was January

concentrations>February concentrations>March concentration (appendix 5.1). The Korpedike (Upstream) sampling station recorded the highest mean Copper concentration of 4.50 mgkg^{-1} as far as the three sampling stations were concerned (table 4.4). Copper concentrations in the tissues of the *Oreochromis niloticus* sampled at the Korpedike sampling station for the months of February and March were 4.37 mgkg^{-1} and 4.16 mgkg^{-1} respectively (table 4.4). The midstream (Mankango) sampling station consistently recorded lower Copper concentrations in the fish samples relative to the upstream portion. The highest mean Copper concentration in the fish samples from Mankango 4.23 mgkg^{-1} was recorded in the month of January, with February and March recording mean concentrations of 3.70 mgkg^{-1} and 3.61 mgkg^{-1} respectively (table 4.4). The downstream station (Yeji), similar to the observed trends at the upstream and midstream sampling locations, recorded a highest mean Copper concentration of 4.40 mgkg^{-1} in the month of January (table 4.4). The February and March sampling periods respectively recorded concentrations of 3.94 mgkg^{-1} and 3.66 mgkg^{-1} (table 4.4). Generally, there were no observed significant differences ($p>0.05$) in the mean Copper concentrations in the fish samples from the three sampling locations, with the concentrations ranking in the following order; Upstream>Downstream>Midstream (appendix 5.1).

4.4.4 Cadmium

Similar to the Copper concentrations recorded in the fish samples, Cadmium concentrations at the three sampling locations were highest in January with February recording the lowest mean concentration (table 4.4). The upstream sampling station (Korpedike) recorded the highest overall mean Cadmium concentration of 0.87 mgkg^{-1}

(table 4.4). The lowest Cadmium concentration in the tissues of the *Oreochromis niloticus* samples from Korpedike was 0.75 mgkg^{-1} recorded in the month of February (table 4.4). At the midstream sampling station (Mankango), the highest measurable and lowest mean Cd concentrations of 0.80 mgkg^{-1} and 0.55 mgkg^{-1} were recorded in January and February respectively (table 4.4). Mean Cadmium concentrations in the tissues of the fish samples from Mankango for the March sampling period was 0.77 mgkg^{-1} (table 4.4). The downstream sampling station (Yeji) also recorded trends of Cd concentrations in the fish tissues, similar to the one observed at Mankango and Korpedike sampling stations with the January sampling month recording the highest mean Cadmium concentration in the tissues of the *Oreochromis niloticus* samples. The fish samples from Yeji recorded highest and lowest mean measurable Cadmium concentrations of 0.73 mgkg^{-1} and 0.51 mgkg^{-1} respectively (table 4.4). Overall however, there were no significant differences ($p>0.05$) in the measured Cd concentrations in the fish samples from the three sampling stations ranking in the following order; Upstream >Midstream>Downstream (appendix 5.1).

4.4.5 Zinc

Overall, the Zinc concentrations in the fish samples from Korpedike were generally higher than the concentrations recorded in Mankango and Yeji fish samples. The Korpedike fish samples recorded fairly similar zinc concentrations over the sampling period with the lowest mean Zinc concentration of 11.93 mgkg^{-1} recorded in March (table 4.4). February recorded the highest mean Zn concentration of 14.23 mgkg^{-1} in the tissues of the fish samples while January recorded a relatively lower concentration of 12.17 mgkg^{-1} (table 4.4). The Midstream station (Mankango) also recorded temporal trends in

mean Zn concentrations similar to the Korpedike trend, with February and March recording the highest and lowest mean Zn concentrations of 12.30 mgkg^{-1} and 11.40 mgkg^{-1} respectively (table 4.4). March recorded a much lower mean fish tissue Zn concentration of 6.37 mgkg^{-1} . The temporal trend of Zn in the tissues of the fish samples from Yeji was in the following order; January>February>March (appendix 5.1), with highest and lowest concentrations of 10.70 mgkg^{-1} and 5.57 mgkg^{-1} respectively (table 4.4). The Zinc concentrations in the fish samples from the three sampling stations did not vary significantly ($p>0.05$) over the sampling period.

4.4.6 Total Mercury

Total mercury concentration in fish samples from all the three sampling locations were relatively similar and low over the sampling period with March recording the highest mean total mercury concentrations for all the sampling stations. At Korpedike, the mean total mercury concentration over the sampling period ranged from 0.0006 mgkg^{-1} to 0.001 mgkg^{-1} (table 4.4). The measured total mercury concentrations at the midstream portion (Mankango) were slightly lower than the Korpedike concentrations. The February concentration of 0.0005 mgkg^{-1} was the lowest mean mercury concentration recorded at Mankango while the March concentration of 0.001 mgkg^{-1} (table 4.4) was the highest. The Hg concentrations recorded in the tissues of the fish samples from Yeji (downstream) were fairly similar to the concentrations in the fish samples from Mankango. There were no significant differences ($p>0.05$) in Hg in the fish samples from the Volta Lake as far as the three sampling locations were concerned and the

concentration of total mercury range in order of Upstream>Midstream>Downstream (appendix 5.1).

4.5 Heavy Metal Concentrations in the Bottom Sediment

Temporal trend in monthly concentration of As, Pb, Cu, Zn, Cd and Hg in bottom sediment at Korpedike, Mankango and Yeji sampling stations are presented in table 4.5 and appendix 5.2.

4.5.1 Arsenic

Arsenic concentrations in the bottom sediments of the Volta River followed a similar temporal trend as far as the three sampling stations were concerned. The mean Arsenic concentrations recorded at the three sampling stations were generally highest during the February sampling period. At the upstream sampling station (Korpedike), the highest and lowest mean Arsenic concentrations of 5.90 mgkg^{-1} and 4.39 mgkg^{-1} in February and January respectively (table 4.5). Mankango (Midstream) recorded a slightly higher Arsenic concentration of 4.57 mgkg^{-1} in January compared to Korpedike (table 4.5). The lowest measurable Arsenic concentration of 4.40 mgkg^{-1} was recorded in February (table 4.5). The Downstream station, (Yeji) recorded its highest mean Arsenic concentration of 5.00 mgkg^{-1} during the February sampling period (table). A mean Arsenic concentration of 4.74 mgkg^{-1} represented the lowest measurable concentration in the bottom sediment samples from Yeji (table 4.5). There were no significant differences ($p>0.05$) in the As

concentrations recorded at the three sampling stations with mean concentrations ranking in the following order; Upstream>Midstream>Downstream (appendix 5.2).

4.5.2 Lead

Concentrations of lead in the bottom sediments of the three sampling stations were highly measurable with the Downstream sampling station (Yeji) recording the highest mean concentration of 12.00 mgkg^{-1} (table 4.5). The Lead concentrations were however fairly similar among the sampling stations with the overall mean concentrations ranging from $9.10\text{-}12.00 \text{ mgkg}^{-1}$ (table 4.5) over the three month period. Mean concentrations at the Upstream sampling station for the January and February periods were 9.13 and 9.10 mgkg^{-1} respectively, with the March sampling period recording an increased mean concentration 11.07 mgkg^{-1} (table 4.5). The Midstream sampling station recorded progressively increasing mean Lead concentrations from 10.60 mgkg^{-1} to 11.12 mgkg^{-1} (table 4.5). The Downstream sampling station (Yeji) recorded its highest and lowest mean Lead concentrations of 12.00 mgkg^{-1} and 10.23 mgkg^{-1} in February and March respectively (table 4.5). The Kruskal-Wallis Test revealed no significant variations ($p>0.05$) in the mean Pb concentrations recorded at the three sampling stations and the mean concentration the following order; Downstream>Midstream>Upstream (appendix 5.2).

4.5.3 Copper

Comparatively, the Copper concentrations recorded in the sediment samples were higher than the concentrations recorded in the fish samples. The upstream portion recorded a

temporal trend of March>January>February (appendix 5.2) with the highest mean concentration being 15.35 mgkg^{-1} and the lowest being 10.70 mgkg^{-1} (table 4.5). A similar temporal trend was recorded for the Midstream sampling station for Copper in the sediment samples. March recorded the highest concentration of 11.22 mgkg^{-1} with February recording the lowest concentration of 9.87 mgkg^{-1} (table 4.5). Mean Copper concentration in the bottom sediments of the Midstream sampling station for the January sampling period was 10.97 mgkg^{-1} (table 4.5). At the downstream sampling station, the mean Copper concentrations in the sediments were fairly similar over the sampling months with January and March recording the highest and lowest concentrations of 10.23 mgkg^{-1} and 9.02 mgkg^{-1} respectively (table 4.5). The mean Copper concentration recorded for the month of February was 9.70 mgkg^{-1} (table 4.5). Overall, there were no significant variations ($p>0.05$) in the mean Copper concentrations recorded at the three sampling stations over the sampling period ranking in the following order; Upstream>Midstream>Downstream (appendix 5.2).

4.5.4 Cadmium

Temporal trends in mean Cadmium concentrations in the bottom sediments were fairly similar at the three sampling stations. At the Upstream sampling station (Korpedike), the highest mean Cd concentration of 1.97 mgkg^{-1} (table 4.5) was recorded during the February sampling period. A mean Cd concentration of 1.50 mgkg^{-1} was recorded in January, with March recording a mean Cadmium concentration of 1.42 mgkg^{-1} (table 4.5). At the Midstream sampling station (Mankango), the temporal trend was similar to the one

observed at the upstream station, with February recording the highest mean sediment concentration of 1.72 mgkg^{-1} and March recording the lowest concentration of 1.17 mgkg^{-1} (table 4.5). A similar trend was also observed for the downstream sampling station with February and March recording highest and lowest mean Cadmium concentrations of 1.81 mgkg^{-1} and 1.14 mgkg^{-1} respectively (table 4.5). The differences in the mean Cd concentrations between the three sampling stations were not significant ($p>0.05$).

4.5.5 Zinc

Zinc concentrations in the bottom sediments of the Volta Lake were considerably high over the sampling period. March consistently recorded the highest Zn concentration at the three sampling stations with February recording the lowest. The upstream station recorded sediment Zinc concentrations ranging between 24.41 mgkg^{-1} in January to 35.67 mgkg^{-1} in March (table 4.5). The highest and lowest mean Zinc concentrations recorded at the Midstream sampling station were 33.33 mgkg^{-1} and 20.13 mgkg^{-1} respectively (table 4.5). Zinc in the bottom sediments of the Midstream station followed a temporal trend similar to the one observed at the upstream station with the February and March sampling periods recording the lowest 20.63 mgkg^{-1} and highest 30.48 mgkg^{-1} respectively (table 4.5). The downstream station also exhibited the same trends in sediment Zn concentrations over the sampling months. The highest concentration of 30.48 mgkg^{-1} was recorded in March while the lowest concentration of 21.11 mgkg^{-1} was recorded in January (table 4.5). Mean sediment Zn concentrations ranked in the following order; Upstream>Midstream>Downstream (appendix 5.2). There were, however, no

significant differences ($p>0.05$) in the mean sediment Zn concentrations recorded at the three sampling stations.

4.5.6 Total Mercury

Mercury concentrations in the bottom sediments of the Volta Lake were generally very low with concentrations ranging between 0.001 mgkg^{-1} to 0.002 mgkg^{-1} at all the sampling stations over the sampling period (table 4.15). March, however, recorded the highest mercury concentrations in the bottom sediments at all the three sampling stations. There were no significant differences ($p>0.05$) in the mean sediment Mercury concentrations recorded at the sampling stations ranking in the following order; Upstream>Midstream>Downstream (appendix 5.2).

4.6 Heavy Metal Concentrations in the Water

Temporal trend in monthly concentration of As, Pb, Cu, Zn, Cd and Hg in the water at Korpedike, Mankango and Yeji sampling stations are presented in (table 4.6) and appendix 5.3.

4.6.1 Arsenic

Arsenic concentrations in the water samples were all below the detection limit of the Atomic Absorption Spectrophotometer (AAS) for the sampling periods for all the sampling stations (table 4.6).

4.6.2 Lead

Lead concentrations in the water samples, similar to the Arsenic concentrations, were all below the detection limit of the Atomic Absorption Spectrophotometer (AAS) for the sampling periods for all the sampling stations (table 4.6).

4.6.3 Copper

January recorded the highest Copper concentrations in the water at all the sampling stations. The spatial distribution of Cu in the water of the Volta Lake was as follows; Downstream>Upstream>Midstream (appendix 5.3). The Downstream station recorded a mean Copper concentration of 0.084 mgL^{-1} in January, with the Upstream and Midstream both recording mean Cu concentrations of 0.077 mgL^{-1} and 0.065 mgL^{-1} respectively (table 4.6). In February, with the upstream, midstream and downstream sampling stations recording mean concentrations of 0.032 mgL^{-1} , 0.031 mgL^{-1} and 0.022 mgL^{-1} respectively. March recorded a further decline in Cu concentrations in the water of all the sampling locations (table 4.6). Overall however, there were no significant variations in the Cu concentrations in the Volta Lake as far as the three sampling stations were concerned.

4.6.4 Cadmium

The concentrations of cadmium in the water samples from the three sampling stations were fairly similar over the sampling period with concentrations ranging between a narrow range of 0.001 and 0.002 mgL^{-1} (table 4.6). Spatial distribution of Cd was in the

following order; Upstream>Midstream>Downstream (appendix 5.3) and there were no significant variations ($p>0.05$) in the concentrations over the sampling period.

4.6.5 Zinc

The highest Zinc concentrations in the water samples from the three sampling locations were recorded in the February sampling period with March recording the lowest concentrations. At the upstream station, mean Zn concentrations ranged from a lowest value of 0.03 mgL^{-1} to a highest of 0.111 mgL^{-1} , while the midstream station recorded 0.026 mgL^{-1} and 0.073 mgL^{-1} as the lowest and highest Zn concentrations respectively (table 4.6). At the downstream station, the highest Zn concentration recorded over the sampling period was 0.09 mgL^{-1} while the lowest was 0.02 mgL^{-1} . The spatial comparison revealed no significant differences ($p>0.05$) over the sampling period as far as Zn in the water of the Volta Lake was concerned and rank the order of Upstream>Midstream>Downstream (appendix 5.3).

4.6.6 Total Mercury

Total Mercury concentrations in the water samples, similar to the Arsenic and Lead concentrations, were all below the detection limit of the Automatic Mercury Analyzer (Model HG 6000) for the sampling periods for all the sampling stations (table 4.6).

4.7 Contaminant Concentrations in Relation to Reference Standards

4.7.1 Nutrients

The nutrients concentrations in the water of the Volta Basin were generally below the WHO (2011) Drinking Water Quality Standard for nitrate and phosphate (table 4.2). Nitrate concentrations at the different sampling stations were more than a 1000-folds lower than the drinking water quality guideline value of 50 mgL^{-1} (table 4.2) indicating a relatively unpolluted state as far as using the water for drinking purposes is concerned. Nitrate values at some of the sampling stations however exceeded the guideline value for the protection of aquatic life of 0.05 mgL^{-1} . This phenomenon was observed at the upstream station (Korpedike) for the months of February and March. Overall, however, the nitrate concentrations at the other sampling stations were just below the standard value for the protection of aquatic life indicating the presence of considerable levels of nitrates in the water of the Volta Lake as far as the protection of aquatic life is concerned. No guideline value was found for phosphate in as far as consumption of the water by humans was concerned. Phosphate concentrations in the water, however, were lower than the guideline value for the protection of aquatic life (10 mgL^{-1}) at all the sampling stations (table 4.2). No guideline values were found for nitrogen and phosphorus in the bottom sediments of the Volta basin (table 4.3) although it can possibly be inferred from the nutrient levels in the water that the sediment nutrient levels are unlikely to cause any harm to the aquatic life in the Volta basin.

4.8 Heavy Metals

4.8.1 Heavy Metals in the Fish

Compared to the WHO (2002) Safety Reference Standards for Human Consumption, the metal concentrations in the tissues of the fish samples from the three locations on the Volta Lake were all found to be lower, and thus safe for human consumption. Lead concentrations in the tissues of the *Oreochromis niloticus* from the Korpedike sampling station in January. Lead concentrations in the fish samples from the other sampling stations were all found to be 2 and 4 times lower than the Safety Standard for human consumption. The highest mean Copper concentration of 4.50 mgkg^{-1} recorded during the January sampling period was more than two (2) times lower than the human safety reference standard of 10 gkg^{-1} . Cadmium values were consistently lower than the standard value of 1 mgkg^{-1} in the month of January. Zinc concentrations in the tissues of the fish, were all well below the WHO (2002) Safety Reference Standards for Human Consumption value of 1000 mgkg^{-1} . Mercury concentrations in the fish samples from the three sampling locations were also all below the WHO standard of 0.5 mgkg^{-1} (Table 4.4) details the mean concentrations of all the studied metals over the sampling period compared the WHO (2002) safety reference standards for human consumption

Table 4. 4Heavy Metal Concentrations in the Fish Compared to WHO Standards

	As	Pb	Cu	Cd	Zn	Hg
January						
Upstream	0.28±0.01	0.70±0.06	4.50±0.10	0.87±0.05	12.17±0.15	0.001±0.00
Midstream	0.27±0.00	0.40±0.10	4.23±0.15	0.80±0.20	11.40±0.06	0.001±0.00
Downstream	0.12±0.15	0.55±0.10	4.40±0.00	0.73±0.20	10.70±0.10	0.001±0.00
February						
Upstream	0.30±0.00	0.47±0.00	4.37±0.05	0.75±0.05	14.23±0.15	0.001±0.00
Midstream	0.26±0.00	0.42±0.00	3.70±0.10	0.55±0.00	12.30±1.07	0.001±0.00
Downstream	0.19±0.00	0.33±0.00	3.94±0.05	0.51±0.00	10.17±0.06	0.001±0.00
March						
Upstream	0.35±0.15	0.23±0.00	4.16±0.05	0.85±0.05	11.93±0.05	0.001±0.00
Midstream	0.13±0.20	0.23±0.00	3.61±0.36	0.77±0.06	6.37±0.05	0.001±0.00
Downstream	0.19±0.20	0.17±0.00	3.66±0.00	0.62±0.00	5.56±0.05	0.001±0.00
WHO (2002)	*	1	10	1	1000	0.5

4.8.2 Heavy Metals in the Bottom Sediments

Heavy metals in the bottom sediments of the Volta Lake were compared to the European Union Heavy Metal Regulatory Standards for Sediment and were generally found to be lower than their respective regulatory standards. Mean Arsenic and Cadmium concentrations at all the sampling stations were approximately two (2) times lower than the regulatory standards of 10 mgkg^{-1} and 3 mgkg^{-1} respectively. Mean Zinc concentrations in the sediments were 8 and 16 times lower than the regulatory standard of 300 mgkg^{-1} . Total Mercury concentrations of the bottom sediments of the three sampling stations were similar to the concentrations usually found in pristine aquatic environments. Mean total mercury concentrations recorded at the three sampling stations were between 500 and 1000 times lower than the guideline value of 1 mgkg^{-1} . (Table 4.5) shows the mean concentrations of all the studied metals over the sampling period compared the European Union Heavy Metal Regulatory Standards for Sediment.

Table 4. 5Heavy Metal Concentrations in the Bottom Sediment Compared to Standards

	As	Pb	Cu	Cd	Zn	Hg
January						
Upstream	4.39±0.01	9.13±0.15	12.10±0.10	1.50±0.10	24.41±0.20	0.002±0.00
Midstream	4.57±0.02	10.60±0.20	10.97±0.15	1.47±0.20	22.13±0.31	0.001±0.00
Downstream	4.74±0.01	11.76±0.15	10.23±0.15	1.35±0.15	21.11±0.17	0.001±0.00
February						
Upstream	5.90±0.00	9.10±0.00	10.70±0.10	1.97±0.01	22.32±0.02	0.001±0.00
Midstream	4.40±0.00	11.00±0.00	9.87±0.08	1.72±0.02	20.63±0.01	0.001±0.00
Downstream	5.00±0.00	12.00±0.00	9.70±0.10	1.81±0.01	18.65±0.31	0.001±0.00
March						
Upstream	5.10±0.01	11.07±0.00	15.35±0.05	1.42±0.03	35.67±0.06	0.001±0.00
Midstream	4.81±0.01	11.12±0.00	11.22±0.02	1.17±0.01	33.33±0.02	0.001±0.00
Downstream	4.90±0.20	10.23±0.00	9.02±0.00	1.14±0.02	30.48±0.02	0.002±0.00
EU*	10	35	30	3	300	1

4.8.3 Heavy Metals in the Water

The heavy metals in the water of the Volta Basin were compared to the WHO (2011) Guidelines for Drinking Water Quality and were found to be lower than their respective regulatory standards.

Copper levels at all the sampling stations were found to be over 20 times lower than the regulatory standard. Cadmium concentrations at all the sampling stations were, however, just below the regulatory standard of 0.003 mgkg^{-1} . No regulatory guideline value was found for Zinc, (Table 4.5) shows the mean concentrations of all the studied metals in the water over the sampling period compared to the WHO (2011) Guidelines for Drinking Water Quality.

Table 4. 6 Heavy Metal Concentrations in the Water Samples Compared to WHO Standards

	As	Pb	Cu	Cd	Zn	Hg
January						
Upstream	ND	ND	0.08±0.00	0.002±0.00	0.09±0.00	ND
Midstream	ND	ND	0.07±0.00	0.002±0.00	0.07±0.00	ND
Downstream	ND	ND	0.08±0.00	0.002±0.00	0.06±0.00	ND
February						
Upstream	ND	ND	0.09±0.00	0.002±0.00	0.11±0.00	ND
Midstream	ND	ND	0.09±0.00	0.002±0.00	0.07±0.00	ND
Downstream	ND	ND	0.06±0.00	0.001±0.00	0.09±0.00	ND
March						
Upstream	ND	ND	0.07±0.00	0.002±0.00	0.03±0.00	ND
Midstream	ND	ND	0.08±0.00	0.001±0.00	0.03±0.00	ND
Downstream	ND	ND	0.07±0.00	0.002±0.00	0.02±0.00	ND
WHO (2011)*	0.01	0.01	2	0.003	*	0.006

CHAPTER FIVE

5.0 DISCUSSION

5.1 Trends in the Physicochemical Water Parameters

The measured physicochemical parameters at the Upper Volta Basin compares fairly favourably with earlier studies conducted at that area although present study recorded lower readings. A study by Amakye (2001) revealed overall mean TDS and conductivity values of 69.40 mgL^{-1} and 142 mgL^{-1} compared to the highest mean TDS and conductivity values of 52.00 mgL^{-1} and 80 mgL^{-1} recorded in this study.

The temperature of the water recorded in this study was generally lower than previously recorded. A study by Ntow (2003) revealed higher mean temperature which varied between 29 and 31°C . According to Frempong, (1995) surface temperature measured along the axis of the basin over an eight year period did not exceed 33°C and the bottom temperature did not fall below 23°C in any season. Seasonal changes could also have an impact on water temperature with the rainy seasons recording cooler water temperatures. Amakye (2001) and Akongyuure *et al.* (2012) also recorded an overall mean temperature of 30.8°C and 30.2°C which are markedly higher than the temperature values recorded at the three sampling stations in this study. The lower temperatures recorded in this study relative to the earlier studies could be attributed to the differences in the time of collecting the temperature data (table 4.1).

The results of the physicochemical parameters of the Volta basin were generally within the acceptable guideline limits for unpolluted surface waters and compared favorably

with the finding of other studies at different locations in Ghana. The findings of this study appear to be in conformity with the findings of Hagan *et al.* (2011) who conducted studies at the Densu River Basin. The pH values ranged from 6.55 to 7.33 and were within the natural background level of 6.5-8.5, similar to the findings of this research (table 4.1). Only the Upstream sampling station (Korpedike) recorded a pH value below the regulatory guideline range, possibly due to the activities of the small scale miners at that location. The Total Dissolved Solids (TDS) values were below the World Health Organization (WHO) recommended value of 1000 mg/L. The Electrical Conductivity (EC) values were below the acceptable value for unpolluted surface waterbody, similar to the findings of this study.

5.2 Levels of Nutrients in Water and Sediments of the Upper Volta Basin

The nutrient levels in the water and sediments appeared to be relatively low at some sampling stations. The levels of Nitrate (table 4.2) in the water in this study were found to be much lower than the concentration ranges of 0.51-0.97 mgL⁻¹ recorded by Ntow (2003). The Total Phosphahate levels recorded in this study (table 4.2) were, however, similar to the Total Phosphate concentrations of 0.34-0.50 mgL⁻¹ recorded by Ntow (2003), indicating very little changes in Phosphate concentrations in the water of the Upper Volta Basin over the past decade.

The present concentrations of nutrients in the Volta Basin is possibly as a direct result of the dumping of solid wastes and the channeling of liquid waste into the river because of inadequate infrastructure and other resources for the efficient management of waste in the study area (figure 3.2). This current trend of channeling domestic wastes into the Basin

might in future represents an immense pressure on the fragile ecosystem and resources, and result in the steady degradation of the components of the Volta Basin. The pressure on the Volta Basin stems mainly from the unplanned human settlements around it. These informal settlements have led to sewage outfalls which are evidenced by the highly measurably nutrient levels in the water (table 4.2) and bottom sediments (table 4.3). According to Rakodi (1997) and UNCHS (2001), the present rate of urbanization and human settlement developments in Ghana raise concerns about the impact of urban development on the environment, particularly the aquatic environment. EPA of Ghana, revealed that only 6% of Ghana's water resources are unpolluted or recovering from pollution, 25% meet criteria and standard for most uses and 68.75% are either poor quality or grossly polluted, lend credence to the impacts of human settlements on the quality of surface water.

Evidence gathered from the field observation (figure 3.2) showed that residents of the study locations who did not have proper means of disposing refuse, human excreta, bath water and domestic waste water used the basin as an alternative, this enables leachates from the waste dumps, coupled with the discharges of domestic effluents into the Volta Basin (Ofori, 2012).

The present levels of nutrients in the water (table 4.2) of the Upper Volta Basin could well be as a result of the bottom sediments acting as a source of nutrients to the water. According to Wetzel (2001) and Brönmark & Hansson (2005), particulate-bound phosphates (phosphates bound to particles) can dissociate from its particle to become soluble in the water column. This form of internal nutrient loading can also have a significant influence on the water quality of shallow water bodies. Judging from the

relatively high phosphorus levels in the water of the Volta basin, it can possibly act as a source of phosphate to the water.

Another anthropogenic activity that can be implicated in the high nutrient levels as far as the protection of aquatic life is concerned is the marketing and trading activities at market centers along the Volta Basin. Wastes from the marketing activities are channeled directly into the river basin (figure 3.2).

The Volta basin is also booming crop farming area in both dry and rainy seasons, agrochemicals are widely employed in the agricultural activities around the Volta Basin and the washing of these inorganic chemical enter the water body through surface runoff can also result in the present levels of nutrients in the water.

5.3 Heavy Metal Levels in the Fish, Sediment and Water

The levels of metal contaminants in water, sediment and fish from the study areas appeared to correspond to the land-use activities around the sampling locations. It was realized from the study that small mining activities based on the use of certain heavy metal and other chemicals for the recovery of gold is common and widespread along the river basin, especially at Korpedike and Mankango. Small scale mining activities carried around the White Volta at Korpedike and Mankango can be directly implicated for the relatively higher metal concentrations at the two sampling stations compared to Yeji which is more of a commercial fishing centre. The concentrations of heavy metals at Yeji can be as a direct result of the downstream effect of the activities at Korpedike and Mankango.

5.3.1 Heavy Metal Levels in the Fish

Mercury concentrations in the tissues of the *Oreochromis niloticus* sampled in this study compares favorably with the findings of Kwaansa-Ansah *et al.* (2011) in the determination of mercury in seven different The levels of Mercury recorded in the tissues of the *Oreochromis niloticus* in this study (table 4.4), however was lower than the concentrations recorded by Kwaansa-Ansah *et al.* (2011) These to values are below the 0.5 mgkg^{-1} guideline recommended by the WHO/FAO.

An evaluation of heavy metal content in fresh and processed fish from Yeji by Essuman, (1998) revealed similar mercury concentrations in the tissues of some selected fish species from the Volta Lake at Yeji. The Mercury concentrations in the tissues of the fish species from two laboratories, the Ghana Atomic Energy Commission (GAEC) and the Société Générale de Surveillance (SGS) lab indicated very low levels of mercury in the fish sample, similar to the findings of this study. Mercury was not detected in any of the fresh, salted and smoked fish samples analysed at the Ghana Atomic Energy Commission in December 1996 and the results of the analysis at SGS laboratories in June 1997 indicated that the level of mercury in the samples was below 0.01 mgkg^{-1} .

The study by Essuman (1998) also revealed varying Lead concentrations in the tissues of *Oreochromis niloticus*. The concentration of Lead in the fish samples varied from less than 0.01 mgkg^{-1} to 1.03 mgkg^{-1} with the upper level just exceeding the WHO (2002) guideline value of 1 mgkg^{-1} . This study, similarly, recorded mean Lead concentrations in the tissues of *Oreochromis niloticus* below the guideline value. Lead, Cadmium and Arsenic concentrations were found in trace concentrations in the *Oreochromis niloticus*

sampled by Essuman, (1998). This study (table 4.4) recorded measurable concentrations of these three metals although all were found to be below their respective WHO Standards. The metal concentrations in the tissues compare favorably to the findings of Essuman (1998) and Kwaansa-Ansah *et al.* (2011) lending credence to the unpolluted state of the Upper Volta Basin as far as heavy metals are concerned.

Petrol powered water pumps used to irrigate farmlands in the dry season, can also serve as sources of petroleum products, some of which are known to contain amounts of heavy metals into the Volta basin.

5.3.2 Concentration of Metals in the Sediment

Sediments are also known to be important sinks for various pollutants like heavy metals and also play a significant role in the remobilization of contaminants in aquatic systems under favorable conditions and in interactions between water and sediment (Rashed, 2001). The concentrations of some of the metals could well be due to natural processes instead of anthropogenic activities as some metals, especially the essential ones which are known to occur mainly in the environment. According to Sholokovitz (1978), Wilson *et al.* (1986) and Din (1992), metal levels that originate from natural processes such as erosion and flocculation of metals may cause elevated levels in sediments and biota unrelated to anthropogenic sources.

Also, the concentrations of heavy metals in sediment increase as the amount of organic material increase (Tsai *et al.*, 2003). The pollutant concentrations in sediments increased with decreasing particle size in sediments. Sediment has certain limited capacity to

absorb different ions from waters percolating through it. This capacity is lowest for carbonate-sandy fractions of sediments and highest for clayey organic matter rich sediments.

Agricultural activities around the Volta Basin are usually limited mainly too small scale holdings and subsistence agriculture, and poverty often causes the farmers to open more land for cultivation. The environmental problems that arise from rural agriculture include absence of fallow periods, decline in soil fertility, deforestation and wetland drainage. These problems usually result in increased exportation of silt, organic material and nutrients from the surrounding agricultural lands in the Lake. Of the heavy metals investigated in this study, As and Zn are present in most of the agrochemicals used in Ghana (Otchere, 2003) and more specifically around the basin. The use of agrochemicals around the agricultural communities is widespread, and the major users of these agrochemicals had little, if any training or skills in application, use, storage or disposal. One possibility is that the relatively high concentrations of Cu and Zn in the sediment could be associated with the erosion and weathering of soils and parental rocks in the surrounding catchment as well as mobilisation of metals from the sediments. Another factor that can explain the observed heavy metal trends at the three sampling stations is the fishing season. During this period, heavy metals could be introduced into the basin as a result of the intense fishing activities from sources such as fuels leakages and fumes from outboard motors of the fishing boats. Metals could also be introduced from sources such as the paint coatings of the fishing boats since paints are known to contain some heavy metals. This trend is corroborated by Chouba *et al.*(2007) found higher levels of

heavy metals in the mullet, *Mugil cephalus* during high rainfall periods and the times for most intense fishing activities in Tunisia.

5.3.3 Levels of Heavy Metals in the Water

The recorded low concentrations of metals in the Volta basin could be to the fact that pollutant wash out due to the large surface area of the basin and the flow of water current at a distance. Metal dissolves as they move from one point to another, similarly when the pH in the water falls metal solubility increases and the metal particles become more mobile, that why metals are more toxic in soft water but in this study the pH were within the natural background levels (table 4.1).

The findings of this study appear to be in conformity with the finding of Hagan *et al.* (2011) who conducted studies at the Densu River Basin. Arsenic and Lead values were non detectable similar to the finding of this research in almost all the sampling stations despite the galamsey activities along the Densu Basin. The metals find in this research were in traces and values below WHO, (2011) recommended values for fresh water (table 4.6).

The maximum mean values of the measured metals in water (Cu and Zn) were recorded at korpedike and Mankango as well as (Cd and Hg). These levels are lower than the permissible limits (Table 4.6) recommended by (WHO,2011). Trace of these metals may be attributed to the huge amounts of raw sewage, agricultural and industrial wastewater

discharged into the Volta River. On the other hand, Zn and Cu values were below the allowable limits according to (WHO,2011).

Another principal factor that might explain the Zinc concentrations in the water is the use of galvanized sheets as the principal roofing material in the settlements surrounding the Volta basin. This could also account for the relatively high levels of Zn in the water, fish and sediments of the Volta basin. According to Otchere (2003), higher wet season levels of Fe and Zn might as well be due to import from surrounding settlements as most roofing in Ghana are made of galvanized iron sheets, most of which are presently rusty. Other environmental processes such as freshwater runoff, particulate matter re-suspension and primary production can affect the bioavailability of trace metals in the Volta Basin. Many of these processes are highly variable on monthly and even daily scales and could possibly account for the variations in monthly metal concentrations in the fish and in the sediment in particular.

CHAPTER 6

6.0 CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

From the study, it was realized that the nitrate and phosphate concentrations in the water of the Volta Basin at Stratum VII were generally below the WHO (2011) and ANZECC (2002) value for the protection of aquatic. For the nutrients as far as nitrate and phosphate are concern were also below the guideline values for fresh water bodies of 1.0 mgL^{-1} and 1.0 mgL^{-1} respectively according Ghana EPA (2002). Nitrate concentrations at the different sampling stations were more than a 1000-folds lower than the drinking water quality guideline value of 50 mgL^{-1} indicating a relatively unpolluted state of the Volta basin as far as using the water for drinking purposes. Again for recreation and domestic uses such as bathing and cooking for fresh water bodies standards the water in the Basin are safe. Nitrate values at some of the sampling stations however exceeded the guideline value for the protection of aquatic life of 0.05 mgL^{-1} . This phenomenon was observed at the upstream station (Korpedike) for the months of February and March (table 4.2). Overall, however, the nitrate concentrations at the other sampling stations were just below the standard value for the protection of aquatic life indicating the presence of considerable levels of nitrates in the water of the Volta Basin as far as the protection of aquatic life is concerned.

Heavy metals in the water, sediment and fish of the Volta Basin at Stratum VII were generally lower than their regulatory standards for their presence in the basin. Compared to the WHO (2002) Safety Reference Standards for Human Consumption, the fish

samples from the three locations on the Volta Basin were considered wholesome for human consumption and are unlikely to cause harm to human consumers in these areas.

Heavy metals in the water, sediment and fish generally ranked in the following order; Upstream>Midstream>Downstream, indicating the strong influence of the artisanal mining on the assessment of the heavy metals in the Upper Volta Basin.

6.2. Recommendations

- i. The results of this study can serve as baseline data for further research on the Upper Volta Basin as well as other freshwater bodies in Ghana.
- ii. Further studies could also be carried out at the same study area to include other heavy metals and nutrients that were not covered in this research and cover a much longer period.
- iii. Measures should be put in place to control the discharge of effluents especially untreated sewage from surrounding settlements and harmful chemical from the artisanal mining activities into the Volta Basin.
- iv. An increase in human population around the river basin means an increase in generation of liquid and solid waste and therefore an increase in demand for adequate sanitation infrastructure. It is therefore imperative that basic and essential sanitation infrastructures such as a sewage system that would carry effluents generated from domestic activities away from the basin be constructed by the District Assembly at the study areas.

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APPENDICES

Presented below are the tables for the various results generated in the course of the experimental study.

APPENDIX 1. Physicochemical parameters of the Volta Lake.

Parameters						
Period	site	temp (°C)	pH	Cond (mS/cm)	TDS(mg/L)	Salinity (psu)
Jan 2012	Ko	24	6.1	0.076	0.035	0.032
	Ma	23	7.05	0.068	0.032	0.028
	Ye	24	6.8	0.064	0.034	0.024
Feb 2012	Ko	24	7.3	0.075	0.046	0.040
	Ma	23	7.75	0.063	0.035	0.034
	Ye	25	7.40	0.051	0.032	0.026
Mar 2012	Ko	24	7.30	0.070	0.041	0.042
	Ma	25	6.90	0.064	0.031	0.030
	Ye	25	7.10	0.080	0.052	0.051

APPENDIX 2 Nutrients Concentration in Water of the Volta Lake

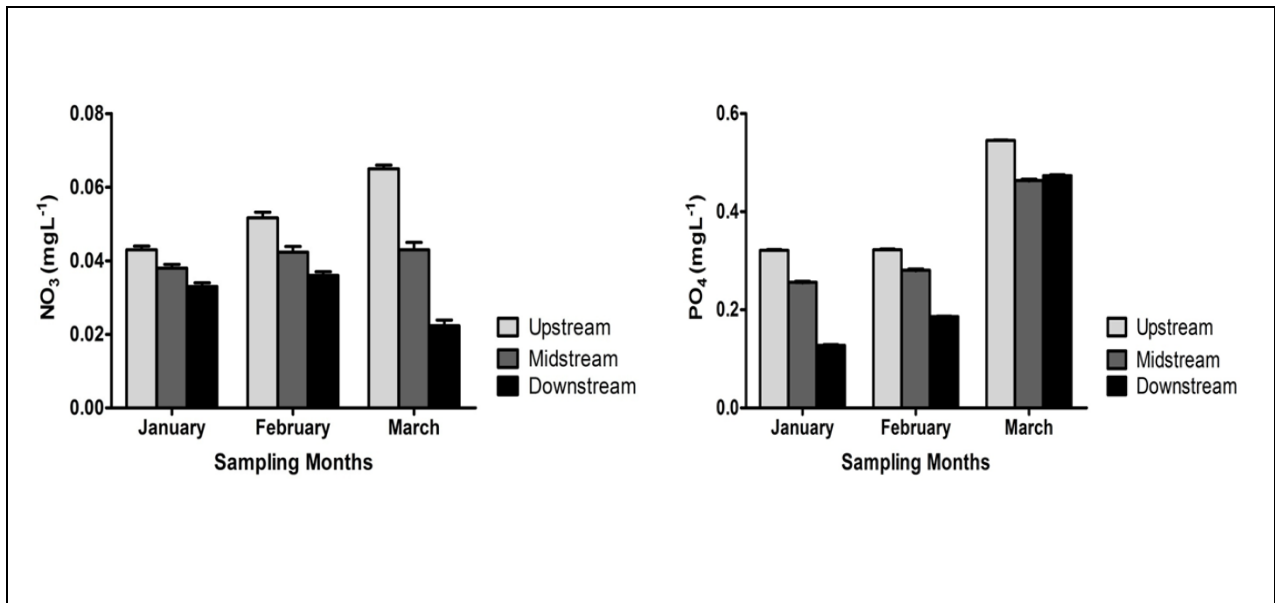
Parameters			
Period	site	NO₃⁻ (mg/L)	PO₄⁻ (mg/L)
Jan 2012	Ko	0.042	0.32
	Ma	0.037	0.25
	Ye	0.032	0.12
Feb 2012	Ko	0.052	0.32
	Ma	0.041	0.28
	Ye	0.036	0.18
Mar 2012	Ko	0.064	0.54
	Ma	0.045	0.46
	Ye	0.022	0.47

APPENDIX 3. Nutrient Levels in the Bottom Sediments of the Volta Lake

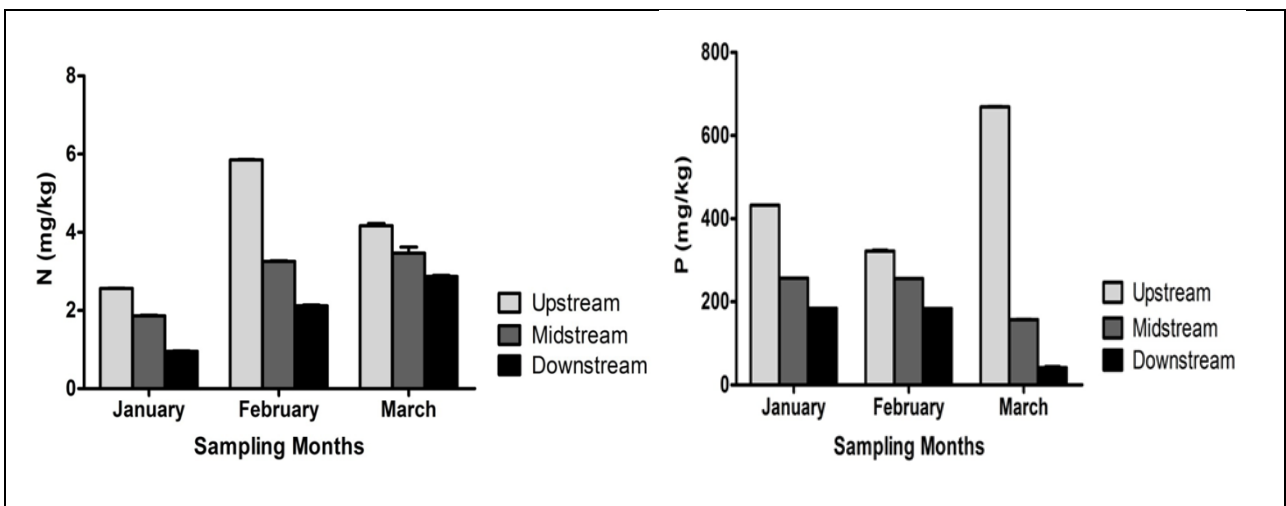
Parameters			
Period	site	N (mg/kg)	P (mg/kg)
Jan 2012	Ko	2.56	432.1
	Ma	1.86	256.8
	Ye	0.94	184.2
Feb 2012	Ko	5.84	322
	Ma	3.26	255
	Ye	2.12	183.4
Mar 2012	Ko	4.1	669
	Ma	3.5	157.4
	Ye	2.9	39.9
Key			
Ko represent Korpedike			
Ma represent Mankango			
Ye represent Yeji			

APPENDIX 4. Nutrients concentrations

APPENDIX 4.1 Spatial Variations in Nitrate and Phosphate Concentrations in the Water

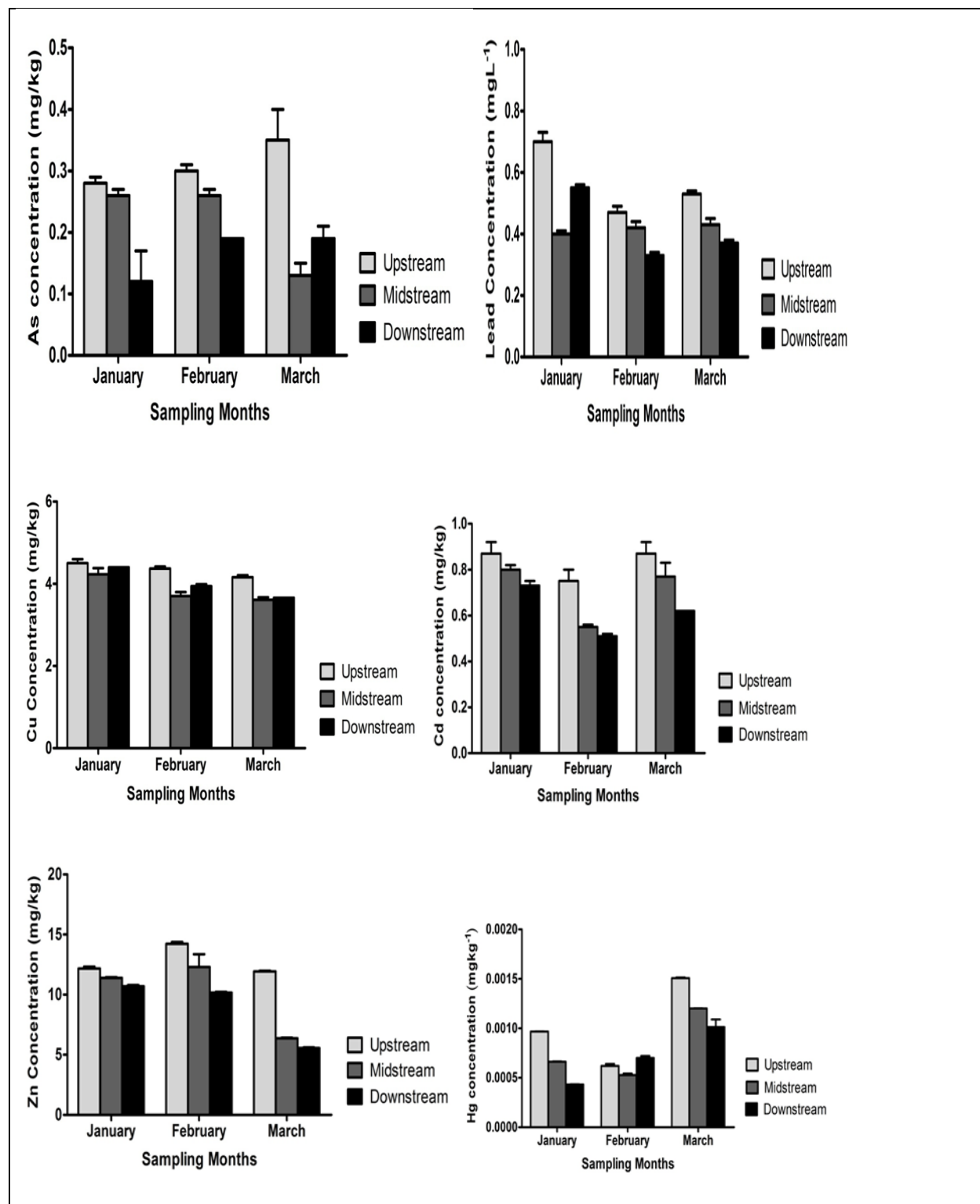


APPENDIX 4.2 Spatial Variations in Nitrogen and Phosphorus Concentrations in Bottom Sediment

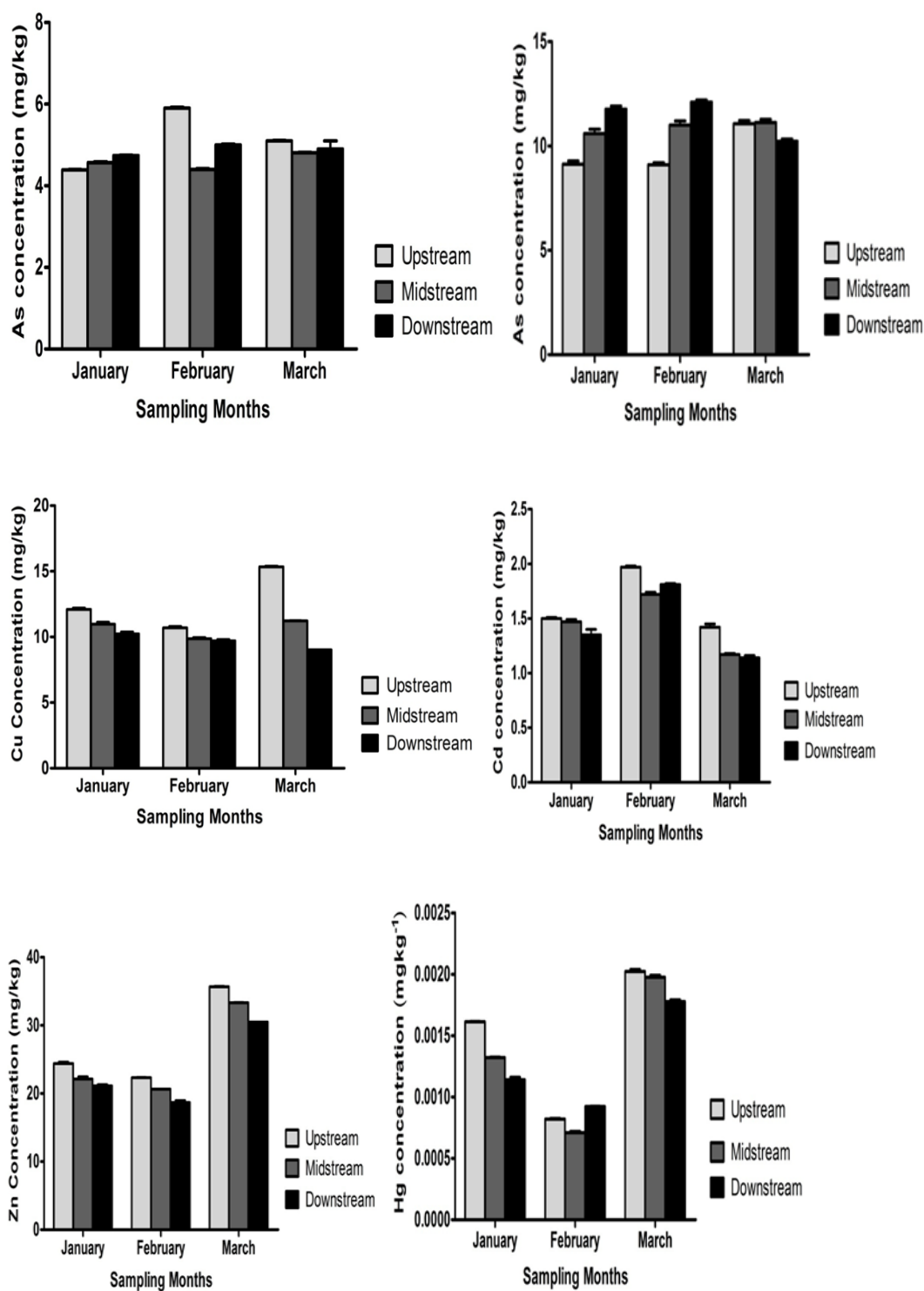


APPENDIX 5. Heavy Metals concentrations

APPENDIX 5.1 Spatial Variations of As, Pb, Cu, Cd, Zn and Hg Concentrations in Fish



APPENDIX 5.2 Spatial Variations of As, Pb, Cu, Cd, Zn and Hg Concentrations in Bottom Sediment



APPENDIX 5.3 Spatial Variations of As, Pb, Cu, Cd, Zn and Hg Concentrations in the Water

