ASSESSMENT OF HEAVY METALS IN WATER, SEDIMENTS AND FISH FROM LAKE CHILWA, ZOMBA, MALAWI.

MASTER OF SCIENCE IN WATER RESOURCES AND SUPPLY MANAGEMENT DISSERTATION.

LAWRENCE LISTIDE JOSEPH KAMZATI.

UNIVERSITY OF MALAWI

THE POLYTECHNIC

August, 2017.

ASSESSMENT OF HEAVY METALS IN WATER, SEDIMENTS AND FISH FROM LAKE CHILWA, ZOMBA, MALAWI

Master of Science in Water Resources and Supply Management

By

LAWRENCE LISTIDE JOSEPH KAMZATI
BSc. (Water Resources Management & Development) - Mzuzu University

Submitted to the Department of Physics and Biochemical Sciences, Faculty of Applied Sciences, in partial fulfilment of the requirements for the degree of Master of Science in Water Resources and Supply Management.

University of Malawi

The Polytechnic

August, 2017.

DECLARATION

I declare that this research entitled `Assessment of Heavy Metals in Water, Sediments and Fish from Lake Chilwa, Zomba, Malawi` is my own work. It is submitted in partial fulfillment of the requirements for the Master of Science Degree in Water Resources and Supply Management at University of Malawi, The Polytechnic. It has not been submitted for any other degree to any University.

SIGNATURE :

DATE :

CERTIFICATE OF APPROVAL

The undersigned certify that they have read and approved for acceptance by University of Malawi, The Polytechnic this thesis entitled `Assessment of Heavy Metals in Water, Sediments and Fish from Lake Chilwa, Zomba, Malawi`.

Postgraduate Dean **:** Peter M. Mhagama, PhD

Signature **:**

Date **:**

Name of Main Supervisor **:** Chikumbusko C. Kaonga, PhD

Signature **:**

Date **:**

Name of Co-Supervisor **:** Harold W.T. Mapoma, PhD

Signature **:**

Date **:**

Name of Head of Department **:** Chikumbusko C. Kaonga, PhD

Signature **:**

Date **:**

DEDICATION

This thesis is dedicated to my wife Tapiwa for always being there for me during tough times. To my loving parents (Mr. and Mrs. Kamzati), I dedicate this work for laying a good educational foundation in my life.

ACKNOWLEDGEMENT

This Master of Science thesis would not have been possible without the ongoing support and advice from various people. Although it is impossible to mention all the names, the following have been of great assistance towards the success of this work.

First and foremost, I would like to thank a team of young men led by Juma Kamchacha based at Kachulu near Lake Chilwa who were of great assistance during sample collection. I would also like to thank Mr. F. Kunkundi and Mr. M. Chikafa, from The Polytechnic for their tireless support in the laboratory analysis. Let me also thank my friend Anthony Mwale for helping me with laboratory protective gear.

I am very grateful to my supervisors Dr. C.C Kaonga and Dr. H. W. T Mapoma for their ongoing support and valuable ideas during the research process.

Lastly, am most grateful to my family for their patience and encouragement during the whole study.

ABSTRACT

An assessment of heavy metals in water, sediments and fish was done in Lake Chilwa (2015 to 2016), Zomba, Malawi. Five sampling points namely Bonga, Chaone, Thunde, Mchenga and Kachulu were selected. These areas were chosen because of their easy accessibility and also are the fishing sites. Samples were analyzed for pH, electrical conductivity (EC), total dissolved solids (TDS), temperature, nitrates (NO_3^-), phosphates (PO_4^{2-}), lead (Pb), cadmium (Cd), manganese (Mn), copper (Cu), zinc (Zn) and iron (Fe) using American Public Health Association (APHA) prescribed standard methods. The sample collection and analysis happened in dry season and wet (rainy) season. Generally, physicochemical parameters were higher in the dry season than the rainy season which was attributed to low water volumes. The results further revealed that Pb was undetectable in water, sediments and fish. However, Mn and Cu were detected in fish and sediment samples ($Mn_{sediments}$= 2.25 – 10.66 mg kg^{-1} dry weight (dw); Mn_{fish} = 0.015 – 1.18 mg kg^{-1} dw; $Cu_{sediments}$ = n.d – 1.63 mg kg^{-1} dw; Cu_{fish} = 0.41 – 0.92 mg kg^{-1} dw). The concentrations of heavy metals in fish samples were below the maximum limits for edible fish recommended by FAO / WHO: Cd (0.1 mg kg^{-1}), Cu (3 mg kg^{-1}), Fe (43 mg kg^{-1}), Pb (0.2 mg kg^{-1}), Mn (2 – 9 mg kg^{-1}) and Zn (60 mg kg^{-1}). Generally, the levels of heavy metals were ranked in the order sediments > fish > water. The study further revealed significant differences in metal concentration between dry season and rainy season. Mn, Cu and Zn in sediments were significantly higher in the dry season than rainy season ($p < 0.05$). Conversely, Fe in sediments was significantly higher in the rainy season than the dry season ($p < 0.05$). Results of this study indicate that the main sources of heavy metals in Lake Chilwa are the use of fertilizers, burning of fossil fuels and disposal of metal products. Therefore, there is a need for an integrated approach towards controlling pollution activities in the area.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATION / ACRONYMS

AAS	Atomic Absorption Spectrometer
ANOVA	Analysis of Variance
APHA	American Public Health Association
AR	Analytical Reagent
ATSDR	Agency for Toxic Substances and Disease Registry
DNA	Deoxyribonucleic Acid
EC	Electrical Conductivity
EPA	Environmental Protection Agency
FAO	Food Agricultural Organization
GoM	Government of Malawi
GIS	Geographical Information System
GPS	Geographical Positioning System
IBM	International Business Machine
MBS	Malawi Bureau of Standards
NAS/IOM	National Academy of Sciences/Institute of Medicine
ND	Not Detected
NSO	National Statistical Office
SPSS	Statistical Package for the Social Sciences
TDS	Total Dissolved Solids
UN WWAP	United Nations World Water Assessment Programme
U.S. EPA	United States Environmental Protection Agency
WHO	World Health Organization

APPENDICES

Appendix 1: ANOVA Table

Table 1: ANOVA for physicochemical parameters

Appendix 2: Paired T – test tables

Table 1: Comparison of heavy metals in water between dry and rainy season

Table 2: Comparison of heavy metals in sediments between dry and rainy season

Table 3: Comparison of heavy metals in fish between dry and rainy season

Table 4: Comparison of heavy metals in water, sediments and fish for both seasons

Appendix 3: Pearson Correlations

Table 1: Relationships between cadmium and physicochemical parameters in water

Table 2: Relationships between zinc and physicochemical parameters in water

Table 3: Relationships between iron and physicochemical parameters in water

Table 4: Relationships of heavy metals in water, sediments and fish

Appendix 4: Pictures for the research study

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the study

Globally, freshwater pollution is increasingly becoming an issue of great concern. According to United Nations World Water Assessment Programme (UN WWAP, 2003), the water bodies receive 2 million tons of sewage, industrial and agricultural wastes every day, which is equivalent to the weight of 6.8 billion people. Furthermore, it is estimated that about 1,500 km^3 of wastewater is produced every year, which is six times more water than exists in all rivers of the world.

Freshwater pollution is even worse in developing countries where there are no or less efficient wastewater treatment systems. According to UN-Water (2009), 70% of untreated industrial wastes produced in developing countries are disposed of directly into waters, thus contaminating existing fresh water sources. The uncontrollable disposal of waste effluents to water bodies has negatively affected both water quality and aquatic life (Abida et al., 2008).

The three sources of water pollution namely: industrial, agricultural and sewage wastes are associated with the increased levels of trace elements or heavy metals such as lead (Pb), zinc (Zn), iron (Fe), manganese (Mn), copper (Cu) and cadmium (Cd) in freshwaters (Sajidu, 2008). Similarly, Gupta *et al.* (2009) noted that industrialization, agriculture, increased population, urbanization and lack of environmental regulations aggravate high levels of heavy metals in surface waters.

The rate at which heavy metals are polluting the freshwaters and environment is a global problem (Malik *et al.*, 2010). In Malawi, just like many developing countries there are growing concerns of heavy metal pollution in its surface waters, particularly those that are proximal to cities and towns. Recently, Ullberg (2015) found that the levels of Pb, Mn and Fe in Likangala River were higher than the guideline values of drinking water from WHO (2011) and Malawi Bureau of Standards (MBS, 2005). On the other hand, Kumwenda *et al.* (2012) found that most parameters in Mudi River were above the European Commission Standards of 1994 for maintenance of aquatic life, irrigation and domestic use. Similarly, Kaonga (2007) carried out a study in streams of Blantyre (Chirimba, Mudi, Nasolo, Michiru, Mangunda, Limbe and Naperi) and found that the levels of Pb, Fe, Cd and Mn for both rainy and dry season samples were above the WHO and MBS standards for drinking water. Additionally, a water quality study conducted in Lilongwe

River found that the values for Pb (0.07±0.02 mgL^{-1}) and Cd (0.14±0.08 mgL^{-1}) were above the acceptable limits of the Malawi Bureau of Standards (MBS) (Nyasulu, 2010).

According to Sterner (2003) Cd, Cu, Zn, Fe, Mn, Pb and Cr are all heavy metals. Heavy metals are defined as metals with a density higher than 5 g/cm^3 (Weast, 1984). Some of these metals such as Zn, Fe, Mn and Cu are important for body organs at very low levels, while others such as Pb, Cd and Cr are directly harmful even in small doses (Sterner, 2003).

Generally, heavy metals are toxic to animals either through direct uptake or bio magnification. The reason is that heavy metals, unlike other pollutants, are non-biodegradable (Wepener *et al.*, 2001). Consequently, aquatic organisms such as fish may accumulate very high concentration of heavy metals than the surrounding environment (Olaifa *et al*., 2004). In addition to that, metals are prone to bind to sediments, soils and other particles or precipitate because they have few gaseous paths. Therefore, plants, algae and bacteria, which are food for fish, are likely to uptake metals (WHO, 2011).

Both natural and anthropogenic activities introduce heavy metals into the environment. These activities include natural weathering of the earth's crust and soil erosion, mining, industrial discharge, urban runoff, sewage effluents, and pest or disease control agents applied to plants, air pollution fallout among others (Ming-Ho, 2005).

The existence of these metals at high levels in the environment may cause serious health hazards to both humans and the ecosystem (WHO, 2004). Therefore, the WHO recommended that all nations should include in their policies the maximum allowable concentration of these trace elements in drinking water, wastewater, and water used for irrigation and recreation.

1.2 Problem statement

Heavy metals are different from organic pollutants in that natural processes of decomposition cannot remove them. Additionally, they accumulate in tissues of aquatic organisms, which may lead to increase in toxicity once converted into organic complexes (Chiodi *et al.*, 2011).

In an effort to achieve sustainable economic growth, recently the government of Malawi made a deliberate policy to "transform Malawi from a predominantly importing and consuming to a producing and exporting nation." In this context, the country would seek to increase investments in the productive sectors (Government of Malawi, 2006). Consequently, this would result in increased industrial and agricultural activities that promote pollution of water bodies by heavy metals.

Some studies that assessed surface and ground water quality in Zomba have already shown heavy metal pollution (Chidya, 2010; Saka, 2006; Ullberg, 2015). Although past studies on pollution of the rivers that feed into Lake Chilwa on the Zomba side exist, there is little literature on pollution of the Lake itself and impact on organisms like fish hence the need for this study. The study was conducted on the Zomba side because that was where pollution activities have been reported and the district itself is a municipality hence a lot of activities take place compared to Machinga and Phalombe.

1.3 Research questions

To achieve the set objectives, the study sought to answer the following research questions:

i. What are the levels of pH, electrical conductivity, total dissolved solids, temperature, nitrates and phosphates in Lake Chilwa?
ii. What are the levels of heavy metals in water, sediments and fish in Lake Chilwa?
iii. Do the levels of parameters studied vary due to seasons?
iv. Are there any significant differences between the parameters studied and the standards?
v. Is there correlation of heavy metals in water, sediments and fish in Lake Chilwa?

1.4 Objectives

1.4.1 General objective

The general object of the study was to assess the levels of selected heavy metals in water, sediments and fish from Lake Chilwa, Zomba, Malawi.

1.4.2 Specific objectives

The research project sought to achieve the following specific objectives:

i. To evaluate the water quality conformance of Lake Chilwa based on prescribed standards
ii. To compare the levels of heavy metals (lead, cadmium, manganese, copper, zinc and iron) in water, sediments and fish in Lake Chilwa; and
iii. To assess seasonal (wet and dry) differences of the heavy metals in Lake Chilwa.

1.5 Significance of the study

This study is significant in that the results provides a significant contribution to academic literature on heavy metals in lakes and the data may be used as baseline information in policymaking. Furthermore, the results of the study provide evidence of the anthropogenic impact on ecosystems, which helps in making viable policies regarding environmental protection.

1.6 Scope and limitations

Water quality degradation in surface waters of the world is attributed to rapid population growth, industrial and economic growth. Recently, surface waters of Malawi including Lake Chilwa are exposed to heavy metal pollution due to anthropogenic factors. This study focused on six metals (Pb, Cd, Mn, Cu, Fe and Zn) which, according to literature, are the most reported heavy metals in water and sediments of surface waters of southern region of Malawi. Physical parameters (pH, EC, TDS and temperature) and other chemical parameters (nitrates and phosphates) were analysed. The study narrowed its coverage of five sampling sites to the Zomba side of Lake Chilwa due to financial constraints.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Introduction

Worldwide, it was estimated that 45,000 m^3 of wastewater were discharged in surface water bodies (UN World Summit, 2002). According to the SADC (2007), fresh water bodies in Southern Africa are exposed to high risk of pollution particularly in urban and industrial areas.

Harrison (1992) defined pollution as the introduction of substances or energy liable to cause hazards to human health, to cause harm to living organisms and ecological systems, damage to structures or amenities or interference with legitimate uses of the environment. Water pollution occurs when there is a change in its composition and quality due to natural or anthropogenic activities rendering it less suitable for drinking, domestic, agricultural, industrial, recreational, wildlife and other uses (Goel, 2009).

High levels of water pollution have been attributed to rapid population growth, urbanization, industrialization and agriculture (Sajidu, 2008; Calhoun, 2005; Goel, 2009). Water pollution poses a serious threat to human health and environment therefore it is important to implement techniques for its assessment, prevention and remediation (Calhoun, 2005). Water pollution can be in form of physical, chemical and biological (Cunningham, 2003).

According to Cunningham (2003), water quality parameters are categorised into physical, chemical, and biological parameters. Physical parameters are defined as characteristics of water that respond to the sense of sight, touch, taste or smell, such as turbidity, temperature, dissolved and suspended solids. The study concentrated on the physical and chemical parameters of water.

2.2 Physicochemical parameters

2.2.1 pH

pH, or the "potential of hydrogen", is a measure of the concentration of hydrogen ions in the water. pH value of water is determined by the relative concentrations of H^+ ion and OH^-. It indicates acidity or alkalinity of the water. On the pH scale of 0 - 14, a reading of 7 is considered to be "neutral". Readings below 7 indicate acidic conditions, while readings above 7 indicate that the water is alkaline or basic (Chapman, 1996). Water pH can be affected by rainfall, algal blooms, level of hard water minerals, effluents from industrial processes, detergents released into water, carbonic acid from respiration or decomposition, and oxidation of sulphides in sediments (Chapman & Hall, 1992). According to Johnson *et al.* (1999) the expected levels of pH values in lakes and rivers is between 7 and 8. On the other hand, WHO (2011) recommends pH ranges of 6.5 to 8.5 as acceptable for drinking water standards.

The pH of water has been considered to be the most important parameter for heavy metal adsorption to solids (Sparks, 2003). A study conducted to determine the dependency behavior of heavy metals on pH revealed that the adsorption capacity varied directly with pH of the solution (Eliot *et al*., 1986). Therefore, in aquatic environments, high pH values encourage metal adsorption onto sediments while low pH values depress metal adsorption (Belize *et al*., 2004). However, heavy metals have different pH values for precipitation (Adriano, 2001). For example, there is higher accumulation of copper at lower pH (Cogun & Kargin, 2004). In other words, the precipitation of heavy metals is very sensitive to the pH of the solution (Bradl, 2004). On the other hand, pH of water influences the solubility of heavy metals in surface waters (Iwashita & Shimamura, 2003; Osmond *et al.*, 1995). Thus, the decrease in water pH leads to the increase in the solubility of toxic metals i.e. from surface to depth or from alkaline to acidic (Radulescu *et al*., 2014). Li *et al.* (2013) conducted a study on factors that affect the release of heavy metals (Zn, Cu, Cd, Cr and Pb) from sewer sediments and found that the release of metals were affected greatly at low pH (4 – 7) than high pH (8 – 10).

2.2.2 Temperature

Temperature is a measure of how cold or hot something is, expressed in degrees Celsius (^{o}C). Temperature in water bodies is affected by air temperature, amount of shade, soil erosion increasing turbidity, thermal pollution from human activities and unknown chemical reactions that were not previously occurring in water (Chapman & Hall, 1992).

Temperature in water bodies affect solubility of dissolved oxygen. More gas dissolves in cold water than warm water thus making animals requiring high levels of oxygen to survive in cold water. In addition, temperature in water affects the rate of plant growth, metabolic rate of organism and their resistance to environmental factors (Chapman & Hall, 1992). Water temperature above 18 ^{o}C has a harmful effect on numerous species of fish in rivers (Canter, 1985). Changes in water temperature could indicate pollution from human activities that can lead to increase in overall temperature. High temperature ranging from 30 – 35 ^{o}C was found to increase the release rate of heavy metals in water (Li et al., 2013). Papafilippaki *et al.* (2008) observed a positive correlation between heavy metals and water temperature in their study of heavy metal in surface waters.

2.2.3 Total Dissolved Solids (TDS)

Total dissolved solid (TDS) is a measure of the amount of particulate solids that are in solution. Dissolved solids in freshwater include soluble salts that yield ions such as Na^{+}, Ca^{2+}, Mg^{2+}, HCO^{3-}, SO_4^{2-}, or Cl^{-1}. Total dissolved solids are sometimes used as a “watchdog” environmental test. TDS is measured using the standard TDS meter and is expressed in mg/L (Chapman, 1996).

Sources of dissolved solids are hard water ions (Ca^{2+}, Mg^{2+}, HCO^{3-}), fertiliser in agricultural runoff (NH^{4+}, NO^{3-}, $PO4^{3}$, SO_4^{2-}), urban runoff (Na^{+}, Cl^{-}), salinity from minerals or returned water from irrigation (Na^{+}, K^{+}, Cl^{-}), and acidic rainfall (H^{+}, NO_3^{-}, $SO_3^{2-}SO_4^{2-}$). TDS mainly comprises of naturally occurring elements, mostly organic salts such as calcium, magnesium, potassium, sodium, bicarbonates, chlorides, sulphates or metals dissolved in a certain volume of water (U.S EPA, 2012). In general, the total dissolved solids concentration is the sum of the cations (positively charged) and anions (negatively charged) in the water (Bishop, 1998). Determining TDS in water purification system is very important because it shows the amount of ions present in water that help to estimate the water quality (U.S EPA, 2012).

Normally, the levels of TDS in lakes and streams range from 50 to 250 mg/L. However, it may go as high as 500 mg/L in areas of hard water or high salinity. In drinking water TDS tends to be 25 to 500 mg/L (Chapman & Hall, 1992; Johnson *et al.,* 1999).

2.2.4 Electrical Conductivity (EC)

According to Mushatq *et al.* (2013), conductivity is the measure of capacity of a substance or solution to conduct electric current, and is an indirect measure of the ion concentration. If there are more ions present in water, it implies that more electricity can be conducted by water. This means that EC is directly proportional to Total Dissolved Solids. Therefore, EC is also an indirect measure of Total Dissolved Solids. EC is detected using a conductivity meter and expressed in Micro Siemens per centimeter (μS/cm).

2.2.5 Nitrate (NO_3^-)

Nitrates are an important source of nitrogen necessary for plants and animals to synthesize amino acids and proteins. Nitrate is the main component of farm fertilizer and a necessary element for crop production. Nitrate ions (NO_3^-) that are found in freshwater samples result from a variety of natural and manmade sources. The sources are agricultural runoff, urban runoff, animal feedlots and stock yard, municipal and industrial wastewater, automobile and industrial emission, and decomposition of plants and animals (Lutz, 2004).

In fresh water, nitrate levels are usually less than 1 mg/L but human activities can elevate the levels to above 3 mg/L. The nitrate levels above 10 mg/L can potentially cause a fatal disease in infant called Methemoglobinemia or Blue Baby Syndrome. Additionally, high levels of nitrate combined with phosphate can lead to excessive growth of plant and algae that can have an effect on odour and taste of water. Eventually, the decaying of dead biomass at the bottom of waters may lead to algal bloom (Chapman & Hall, 1992).

2.2.6 Phosphates (PO_4^{3-})

Phosphates are the naturally occurring form of the element phosphorus, found in many phosphate minerals. The most common sources of phosphates in water are: human and animal waste; industrial wastes; agricultural waste; and human disturbances of land. Natural waters have a phosphorus concentration of approximately 0.02 parts per million (ppm) which is a limiting factor for plant growth. The concentration of phosphates above 100 mg/L may adversely affect the coagulation processes in drinking water treatment plants (Hochanadel, 2010).

Phosphates stimulate plankton growth that lead to increase in fish population through abundant feed. However, high levels of phosphates in water will result in eutrophication resulting in death of fish and aquatic organisms.

2.2.7 Heavy metals

According to Weast (1984), heavy metals are defined as metals with a density higher than 5 g/cm^3. Although some metals are essential for health at low levels, high doses can be harmful. On the other hand, cadmium, chromium and lead are termed as non-essential heavy metals which are toxic and can cause severe health effects upon consumption. In accordance with Kishe and Machiwa (2003) cadmium, lead, copper and zinc are hazardous to aquatic organisms because of their persistence in the environment, toxicity and ability to bio-concentrate and accumulate in food chains.

Heavy metals are among surface water pollutants from industrial, agriculture and sewage effluents (Sajidu, 2008). Its pollution occurs when the heavy metal pollutants reach toxic levels in the aquatic environment (Bose & Hemantranjan, 2005).

Heavy metals in fresh water ecosystems are very dangerous because of their potential to bio-accumulate and bio-magnify in the system. Many researchers in the world have a keen interest on heavy metal pollution because of their harmful effects on living organisms (Misra & Mani, 2009). The nature of being toxic, persistent, and non-biodegradable makes researchers to categorise heavy metals as serious pollutants that pose a serious threat to humans and other living organisms (Adeleken & Abegunde, 2011). There are many instances in human biology where mass deaths occurred due to heavy metal toxicity (Shrivastav, 2001).

The concerns regarding metal pollution are currently increasing in surface waters of Malawi. Several studies conducted in rivers and streams of Malawi have indicated heavy metal contamination (Ullberg, 2015; Kumwenda *et al*., 2012; Chidya, 2010; Nyasulu, 2010; Kaonga, 2007; Saka, 2006). Lake Chilwa is one of the most exposed lakes to different sources of pollutants. According to Saka (2006) the major sources of pollution in Lake Chilwa basin are agricultural and horticultural materials, use and disposal of metal commodities, fossil fuel combustion, use and disposal of electronic appliances, waste disposal, and waste products derived from military training.

Heavy metal pollution in Lake Chilwa might also originate from Likangala River which discharges its waters directly into the lake. According to Njaya (2001), Likangala River drains and influences the hydrochemistry of a tropical endorheic Lake Chilwa, which is a designated wetland of international importance ratified by the Ramsar Convention in 1997. This river has already shown high levels of some metals such as lead, manganese and iron that were attributed to poor waste management and effluents from sewage treatment works in Zomba city (Ullberg, 2015).

On the other hand, low amounts of zinc and cadmium were reported at few sites in Likangala River (Chidya, 2010). The major factors of pollution is that the middle section of the river passes near Zomba Mental Hospital, the Zomba Central Hospital, commercial and residential areas and the wastewater treatment plant which discharges its effluent directly into the river (Ullberg, 2015). In addition to that, water from Zomba municipal and Chancellor College wastewater treatment plants is discharged directly into Likangala River, which runs approximately 50 km all the way down to Lake Chilwa (Masamba & Mulwafu, 2008).

Kwanjana (2003) found that the levels of manganese and cadmium were above the standards for irrigation water as set by the FAO for Zomba municipal sewage effluent. Furthermore, Chidya *et al.* (2011) found elevated levels of manganese and nitrate near the municipal waste water treatment plant. Similar studies in Lake Chilwa have shown elevated levels of iron, sodium and chloride (Masamba & Mulwafu, 2008; Chidya et al., 2011).

Like all Malawians, people in Zomba, Phalombe and Machinga rely on farming. Due to deterioration in soil fertility, most farmers use inorganic fertilizers to improve their yield. The introduction of farm input subsidy program (FISP) in 2005 / 2006 farming season has seen many people using inorganic fertilizers that have nitrogen, phosphates, potassium and sulphur. Poor absorption of fertilizers by plant or flooding conditions lead to wash away of the fertilizers to the receiving water bodies such as streams (Farhadinejad *et al*., 2014). Some of these nutrients from land have the potential to end up in Lake Chilwa.

Recently, Malawi has experienced one of the worst flooding events in history. Among the most hardly hit districts were Zomba, Phalombe and Machinga that forms a large percentage of Lake Chilwa catchment area (Government of Malawi, 2015). Zaghloul *et al.* (2005) found that contamination of aquatic ecosystems by heavy metals such as cadmium, lead, manganese, mercury, zinc and others occur due to application of fertilizer and pesticides containing heavy metals in agricultural fields.

2.2.7.1 Heavy metals in sediments

According to Davies and Abowei (2009) sediments are the loose sand, clay, silt and other soil particles that settle at the bottom of a body of water. Aquatic organisms utilize sediments as a habitat as well as a major source of nutrients (Davies & Abowei, 2009). On the other hand, sediments from water bodies act as reservoirs for heavy metals; therefore, marine sediments can be used as indicators for monitoring pollutants in water (Pekey *et al*., 2004).

The concentrations of heavy metals in sediments are determined by local geology, through weathering of minerals and anthropogenic sources such as use of fertilizers and herbicides, irrigation, industrial effluent, and pipe leakages (Aprile & Bouvy, 2008). These natural and anthropogenic processes lead to the deposition of heavy metals into water bodies where they spread in water, suspended solids, sediments and biota (Anim-Gyampo *et al.,* 2013). It has been reported that higher incidences of heavy metals in sediments may be regarded as an indicator of human induced perturbations rather than natural processes (Eja *et al*., 2003).

Elsewhere, studies on bottom sediments of water bodies have shown elevated levels of lead, cadmium, zinc, copper, iron and manganese at some sites which were attributed to untreated sewage effluents, industrial effluents, agricultural activities and domestic waste water (Nasr *et al.,* 2006; Szefer *et al*., 1999). Similarly, Olubunmi and Olorunsola (2010) conducted an evaluative study on the status of heavy metal pollution of sediments of Agbabu Bitumen Deposit Area, Nigeria which compared the level of contamination of heavy metals in dry and wet season. The study revealed higher levels of copper, manganese, zinc, lead and cadmium in dry season than in wet season which was attributed to rainwater dilution that affected concentration and heavy metal mobility. Contrary, the levels of iron were elevated in wet season than dry season which was attributed to rainfall and surface run off. The seasonal variations in concentration of heavy metals in waters have also been reported by (Iwashita & Shimamura, 2003).

Some studies in Malawi have revealed heavy metal pollution in soils (Kadewa *et al*., 2001; Lakudzala *et al.*, 1999). Soil samples that were collected along main roads in Blantyre have indicated elevated levels of heavy metals that may be carried by surface run off into water bodies to form part of bottom sediments (Masamba & Chimbalanga, 2001). Similarly, Kaonga (2007) found higher concentration of heavy metals in soils than earthworms in the streams of Blantyre namely: Chirimba, Mudi, Nasolo, Michiru, Mangunda, Limbe and Naperi.

2.2.7.2 Heavy metals in fish

Industrial development and agricultural activities have contributed to increase in heavy metals in the environment which is threatening the lives of many invertebrates, fish and humans (Uluturhan & Kucuksezgin, 2007). Inorganic and organic chemicals that contaminate the aquatic environment are creating a hazardous environment for the survival of aquatic organisms particularly fish (Saeed & Shaker, 2008).

Since fish live and feed in the aquatic environment, it is exposed to the detrimental effects of environmental pollution (Saleh & Marie, 2014). Fish are known to be more sensitive to poisonous substances and are regarded as good indicators for testing ecosystems health compared to invertebrates (Zaki *et al*., 2014).

According to Almeida *et al*. (2002) the deposition of metals into rivers and agricultural drainage systems may lead to the accumulation and biomagnification in the aquatic food chain leading to sub lethal effects of death of fish. The reason is that aquatic organisms and others at different trophic levels tend to accumulate contaminants in their tissues and organs (Taylan & Ozkoc, 2007). The accumulation of heavy metals in fish depends on various factors such as level of pollution in aquatic environment and species of fish (Jezierska & Witeska, 2001).

Fish absorb heavy metals into their bodies either by ingesting contaminated food or through the gills and skin (Sfakianakis *et al.*, 2015). Furthermore, Nussey (2000) mentioned five ways in which fish accumulate heavy metals as: food, suspended particles, gills, intake of water and integuments. Eventually, metals accumulate in organs and tissues through the blood stream (Fazio *et al.,* 2014). The accumulation of heavy metals in the aquatic organisms is a sign of past as well as present pollution of the environment (Ravera *et al.,* 2003).

Several studies have provided evidence of heavy metal contamination in fish. A study that assessed the concentration of heavy metals in water, sediments and fish in Turkey revealed higher levels of Cu, Cd, Pb, Zn and Cr in gills and muscles of fish (Demirak *et al*., 2005). Similarly, Saeed and Shaker (2008) conducted a study on the effect of heavy metals on Nile tilapia *(Oreochromis niloticus)* in the Nile delta lakes of Egypt and found higher concentrations of Fe, Zn, Cu, Mn, Cd and Pb in fish gills and liver than in the muscles.

In Malawi, Puchase and Jamu (2009) conducted a study that determined the levels of lead in farm – raised fish in Zomba and found greater concentration of it in fish samples. A related study, on aquatic living organisms, in streams of Blantyre namely: Chirimba, Mudi, Nasolo, Michiru, Mangunda, Limbe and Naperi has shown accumulation of heavy metals in invertebrates, and elevated levels of heavy metals in the filamentous green algae (*Spirogyra aequinoctialis*) which are one of the major feeds for fish (Kaonga, 2007).

2.3 Effects of specific heavy metals on health

2.3.1 Lead

Lead is among the most commonly distributed trace elements that exist in form of inorganics and numerous oxidized states (Jackson *et al.,* 2005). It originates from different sources such as storage batteries, ceramics, radiation shield, insecticides, bearing alloys, plastics, paints and lead based petroleum fuels (Mutwiri, 2001).

According to Ferner (2001) lead is the most toxic among heavy metals and it gets in the body of living things through ingestion by food and water, and inhalation. The toxicity of lead in aquatic environment is influenced by pH, age of fish and water hardness (Nussey *et al*., 2000).

Exposure to high levels of lead may have biochemical effects on humans that result into problems of hemoglobin synthesis, kidney problems, gastrointestinal tract, reproductive system, joints and acute or chronic damage to the nervous system (Tirkey *et al*., 2012). The effects of chronic exposure to lead include: fatigue, anemia, kidney damage, headache, and hearing and speaking problems (Simeonov *et al*., 2010). In children, lead is known to reduce physical and mental growth (Simeonov *et al.*, 2010). Additionally, higher exposure of lead to pregnant women may lead to miscarriages, still births and infertility (Ediin *et al*., 2000).

2.3.2. Cadmium

According to Challa and Kumar (2009) cadmium is abundantly spread in the environment through mining and smelting of metal ores, combustion of fossil fuels and the use of phosphate fertilizers. Additionally, tobacco farming increases the level of cadmium in the environment since tobacco has proven to accumulate Cd in tissues (Selinus & Alloway, 2005).

Cadmium is among the heavy metals that are highly toxic through food poisoning to an extent that it causes adverse changes in the arteries of human kidneys even in small quantities (Mehbrahtu & Zerabruk, 2011). Furthermore, Cd biochemically substitutes Zn resulting to high blood pressures and kidney damages (Mehbrahtu & Zerabruk, 2011).

Chronic exposure to Cd can cause calcium metabolism disorders, some forms of cancer and renal dysfunction (Selinus & Alloway, 2005). Furthermore, high exposure to Cd causes obstructive lung disease that can lead to lung cancer and bone defects in humans and animals (Tirkey *et al*., 2012).

2.3.3 Manganese

Manganese minerals such as pyrolusite (MnO_2), sulfides, oxides, carbonates, silicates, phosphates, arsenates, tungstate and borates are widely distributed in rocks, soils and the bottom of surface waters (Damodharan, 2013). Exposure to low doses of Mn is vital for human and animal health since it has nutritional benefits for normal physiological functions (Calkins, 2009).

Mn is a metal of low toxicity which appears to accumulate in fish (Kumar *et al.,* 2011). Chronic exposure to high doses of Mn is hazardous to human health (Calkins, 2009). The toxicity of Mn at higher levels differs with chemical species, route of exposure, animal species, age and sex (EPA, 2004; Kohl & Medlar, 2007).

High concentration of Mn affects the nervous system of vertebrates that lead to neurological disorders, thus posing a serious health risk to the consumers of Mn contaminated fish (EPA, 2004; Krishna *et al.*, 2014). Similarly, high concentration of Mn can cause liver cirrhosis and lead to a condition called Parkinson disease (Bradi, 2005).

2.3.4 Copper

The sources of copper in the aquatic environment are mining, smelting, domestic and industrial wastewaters, steam electrical production, incinerator emissions, and the dumping of sewage sludge (Denton, *et al*. 1997).

Copper elements are widely distributed in surface water, groundwater, seawater and drinking water (ATSDR, 2002). According to Carolyn *et al.* (2004) copper is vital for good health and is a crucial component of living systems.

Exposure to high levels of Copper can cause liver and kidney damage, anemia, stomach and intestinal irritation (Tirkey *et al*., 2012). Furthermore, exposure to higher doses of Copper can be lethal and chronic exposures can result to irritation of the mouth, eyes and nose, diarrhea and headache (Denton, et al. 1997).

2.3.5 Zinc

Zinc is an important element found in food and water, and its low doses in form of salts and organic complexes is vital for plants, animals and human health (Swaminathan *et al*., 2011).

Sources of zinc in the aquatic environment include products of paints, fertilizers, wood preservatives containing Zinc and discharges of smelter slag and wastes (Lew, 2008).

According to Al-Weher (2008) the zinc concentration of up to 40 mg L^{-1} may induce toxicity leading to irritability, stiffness of muscles and pain. In addition to that, high levels of zinc in drinking water can cause stomach cramps, nausea and vomiting (Damodharan, 2013). It has also been reported that zinc toxicity can result into kidney failure, liver failure, diarrhea, bloody urine and anemia (Duruibe *et al.*, 2007).

2.3.6 Iron

Iron is an essential element for growth and development of nearly all living organisms (Valko *et al.*, 2005). Increased levels of iron are due to anthropogenic activities that involve production of sulphuric acid and discharge of ferrous (Fe^{2+}) as a result of oxidation of iron pyrites (FeS_2) from coal seams (Valko *et al.*, 2005). According to Phippen *et al.* (2008) iron undergoes several biological redox processes due to transformation between ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions.

Excess consumption of iron leads to reactions that produces free radicals which attach to the DNA to cause cellular damage, mutation and malignant transformations (Paponikolaou & Pantopoulos, 2005). Therefore, exposure to excess iron doses during intrauterine life may have an effect on the alteration of genetic structure of the phenotype, which predisposes susceptibility to a wide range of common diseases (Phillips, 2006).

Additionally, chronic exposure to high iron doses, as seen in primary and secondary hemochromatosis, may lead to hepatic fibrosis, diabetes mellitus, and cardiac failure (Bassett, 2001; Hash, 2001; Schumann, 2001). It should be noted that individuals with hemochromatosis (iron storage disease) may suffer from hepatic cirrhosis and risks developing hepatocarcinoma (NAS/IOM, 2003).

2.4 Relationship between heavy metals and physicochemical parameters

The levels of heavy metals in water depend on physicochemical parameters of water like pH, electric conductivity, temperature and total dissolved solids (Radulescu *et al.*, 2014). Physical and chemical factors such as pH, electrical conductivity, temperature, salinity, dissolved oxygen, redox potential, and ionic strength influence the concentration of heavy metals in water and sediments (Goksu, 2003). Furthermore, the toxicity of heavy metals on aquatic organisms and its balance in water depend on limunological factors like pH, alkalinity, hardness, salinity, organic matter, total solids and sedimentation load influence (Golterman, 2004).

Studies have proved that inorganic fertilizers contain heavy metals (CDFA, 2004; WSDA, 2007). Laboratory analyses of various types of fertilizers have shown that phosphate fertilizers contain higher levels of cadmium, lead and arsenic than other types e.g. Nitrogen, potash and gypsum. While micronutrient fertilizers tend to have the higher levels of iron, manganese and zinc (WSDH, 1998a).

In conclusion, water pollution is a worldwide problem that has seen a prominent outcry from the countries in the southern African region in which Malawi belongs. Recently, researchers have shown much interest on heavy metal pollution because of the deleterious effects that they cause on humans and environment. Some of these effects particularly caused by non - essential metals are fatal. Many studies conducted in surface waters in Malawi have indicated heavy metal pollution in water, sediments and some cases fish samples. Therefore, it was necessary to carry out a study of heavy metal pollution in Lake Chilwa which is a reliable source of water to people around the lake, and fish to larger population of Malawi.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Description of the study area

3.1.1 Location

Lake Chilwa is found in the southern districts of Malawi namely: Zomba, Machinga and Phalombe. It also lies on the border with Mozambique (Zegreen & Munyenyembe, 1998). It is the second largest lake in Malawi situated in the center of the low-lying Chilwa-Phalombe plain at 35°45’ E and 15°15’ S (Ratcliffe, 1971). The lake is roughly oval in shape, about 40 km from north to south and 30 km from west to east. It is an inland drainage basin lake which is less than 5 m deep (Zegreen & Munyenyembe, 1998). Its open water area is around 678 km^2, which is surrounded by about 600 km^2 of *Typha* swamps, 390 km^2 of marshes and 580 km^2 of seasonally inundated grassland of floodplain (Lake Chilwa Wetland Project, 1999).

The perennial rivers that feed the lake are: Domasi, Likangala, Thondwe, Namadzi and Phalombe (Wetlands International, 2011). The lake has several islands but only two are inhabited i.e. Chisi and Tongwe. Chisi Island is located to the western shore near Kachulu harbor. It is 4 km across and rises to 430 m above the level of the lake (Burgis & Symoens, 1987). Zomba is the nearest city which is approximately 30 km from Kachulu harbor. Figure 3.1 shows the location of Lake Chilwa and its catchment area.

3.1.2 Geology and soil

Malawi is underlain by the basement complex of precambrian metamorphic and igneous rocks (Mapoma & Xie, 2014; Monjerezi & Ngongondo, 2012). These precambrian rocks of Malawi consists of various proterozoic lithologies and structures such as: paragneisses, quartzites and marbles of the neoproterozoic Mozambique belt, rock sequences of the mesoproterozoic irumide belt, including granulite facies rocks in southern Malawi (Dill *et al.*, 2005).

Based on Swazie and Stubbs (1972) study, the area around Lake Chilwa contains carbonatites intrusions containing rare earth elements, apatite, limestone and marble and pyrochlore. According to Garson (1960), Lake Chilwa catchment area and the Chisi Island were found with carbonatites containing sovites with silicates, sovites with small amounts of siderite, ankeritic sovites and sideritic carbonatites, locally rich in manganese oxides.

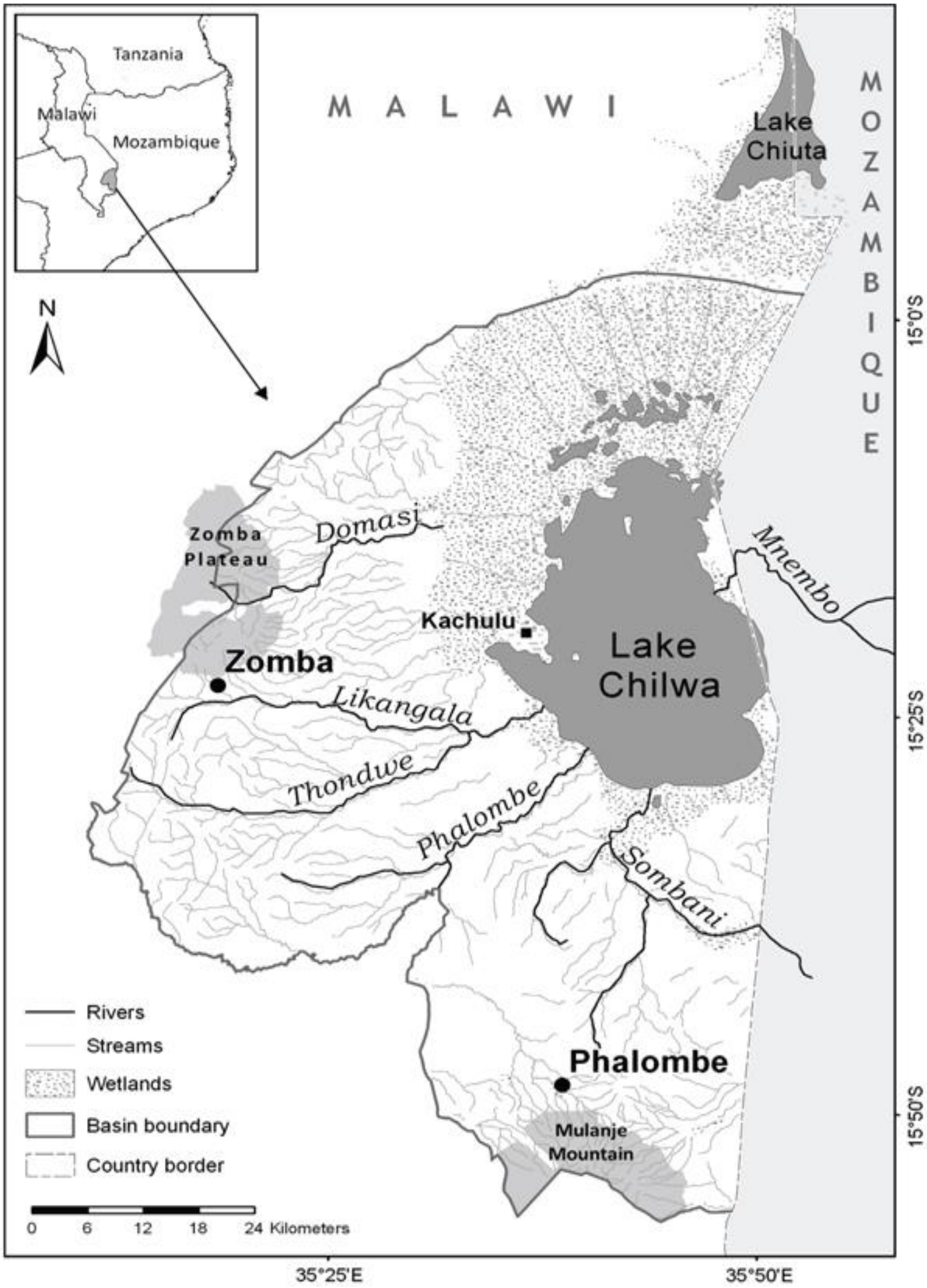

Figure 3.1: Map of Lake Chilwa basin in Malawi (Njaya *et al*., 2011)

A recent study in areas around Lake Chilwa - Phalombe plain found the mineral deposits such as: fluorite, limestone, nepheline syenite and niobium (Ministry of Energy and Mines of Malawi, 2009). The main soils that surround Lake Chilwa basin are hydromorphic black cotton soils, and vertisols, in mixture with gleysols (Macmillan Malawi, 2001; FAO, 2006).

3.1.3 Climate

According to Burgis and Symoens (1987) Lake Chilwa catchment area has a strong seasonal pattern characterized by cool with little rain over high ground in May to September, hot and dry September to November period, and hot and wet November to May. The area experience an annual mean temperature of 24 ^{o}C. The hottest months are from October to December with a monthly mean of 32 – 34 ^{o}C and the coolest from May to August with a monthly mean of 24 – 25 ^{o}C. Wind is predominantly from east, blowing from north and north east from September to November and from south and south east from March to September. The area receives unreliable rainfall with great annual variations i.e. annual mean ranging from 800 – 900 mm.

3.1.4. Vegetation

The five major natural vegetation types of the Lake Chilwa wetland are: the floodplain grassland, neutral to acid marsh, alkaline marsh, swamp transition and swamp which borders with the open water (GoM, 2000). The grassland floodplain located on the periphery of the Chilwa wetland, is a grass dominated habitat. The principal species include: *Hyparrhenia rufa*, *Cynodon dactylon* and *Sporobolus pyrramidalis.* To date, the floodplain is partly under cultivation. The neutral to acid marshes vegetation occur opposite perennial river mouths where *Cyperus papyrus* (the dominant species) is surrounded by a zone of tall grasses such as *Phragmites maurittianus* and *Vossia cuspidata*. On the western side of the lake, between the rivers is the marsh habitat dominated by *Cyperus procerus*, which grows together with marsh grass *Leersia hexandra*. The alkaline marsh occurs widely at the southern end of Lake Chilwa, where *Vossia cuspidata* and *Cyperus longus* are interspaced with large clumps of *Aeshinomene phundii* (GoM, 2000).

The grasses *Diplachne fusca* and *Panicum repens* form the bulk of plant biomass of the swamp transition vegetation belt, which occurs in the northern half of Lake Chilwa. Lake Chilwa open waters are surrounded by the swamp which is uniquely dominated by *Typha domingensis* (rather than *Cyperus papyrus* as is the case in similar lakes elsewhere). Free floating species such as *Pistia stratiotes*, *Ceratophyllum demersum* and *Utricularia* spp. are found on the lake edge of the swamp. The large sedge *Scirpus littoralis* and the aquatic grass *Paspalidium germinatum* commonly occur on open water. The vegetation of Lake Chilwa is greatly influenced by the seasonal fluctuations of water levels which in drier years have seen disappearance of some species due to human activities such as farming (GoM, 2000).

3.1.5 Land use system

The wetland in the Lake Chilwa basin is mainly used for subsistence agriculture. Crops that are commonly grown in this area include maize, rice, groundnuts, cassava and tobacco (NSO, 2008). According to Jamu et al. (2003), more land is exposed to crop farming and livestock grazing when the waters in the lake have receded. The land in the Lake Chilwa basin is also used for settlement. There are crowded fishing villages that were attracted by the wetland that makes the basin to be one of the most densely populated wetlands in Africa with 321 persons per km^2 (NSO, 2008).

3.1.6 Economy

Fishing and farming are the major economic activities in the area around Lake Chilwa. According to NSO (2008), 80% of the people living in the basin are fishermen and small holder farmers. The lake supports over 1.5 million people through agriculture and natural resources goods and services (Njaya *et al*., 1996). Fish is regarded as the major natural resource in the area with an annual yield of about 25,000 tons contributing to $17 million a year to Malawi's economy (Bhima, 2006). The fish from the Lake are sold throughout Malawi. The fish species include *Barbus paludinosus, Clarias gariepinus, Sarotherodon shiranus chilwae, Haplochromis callipterus* and *Hemigrammopetersius barnardi*. Out of 27 fish species found, the most important fish species of Lake Chilwa are a small minnow, *Barbus paludinosus*, the African catfish, *Clarias gariepinus* and two tilapiine species, *Oreochromis shiranus chilwae* and *Tilapia rendalli* (ILEC, 2011; Kalk, McLachlan & Howard-Williams, 1979).

3.2 Sampling

3.2.1 Sampling points

Figure 3.2 is a map of Lake Chilwa catchment area showing location of sampling points and other features to the Zomba side. The sampling points were located using Global Positioning System (GPS) as shown in Table 3.1. The Geographical Information System (ArchGIS, version 10.2) was used to produce a map showing the sampling points within the lake. In order to assess spatial variation of water quality, the study had five sampling sites namely: Bonga, Chaone, Thunde, Mchenga and Kachulu. These sites were selected based on the existence of human activities that were assumed to be the contributing factors to heavy metal pollution such as cultivation, poor waste management and previous pollution reports. Additionally, some sites were selected to appreciate the influence of nature on the reservoir. Bonga is an area where Likangala River joins Lake Chilwa. Chaone is an area where there are settlements on Chisi Island. Thunde is an area on the other side of Chisi Island with less human activities. Mchenga is on the shores of the main land where farming activities are dominant. Kachulu is the harbor on the main land shore where mixed human activities take place.

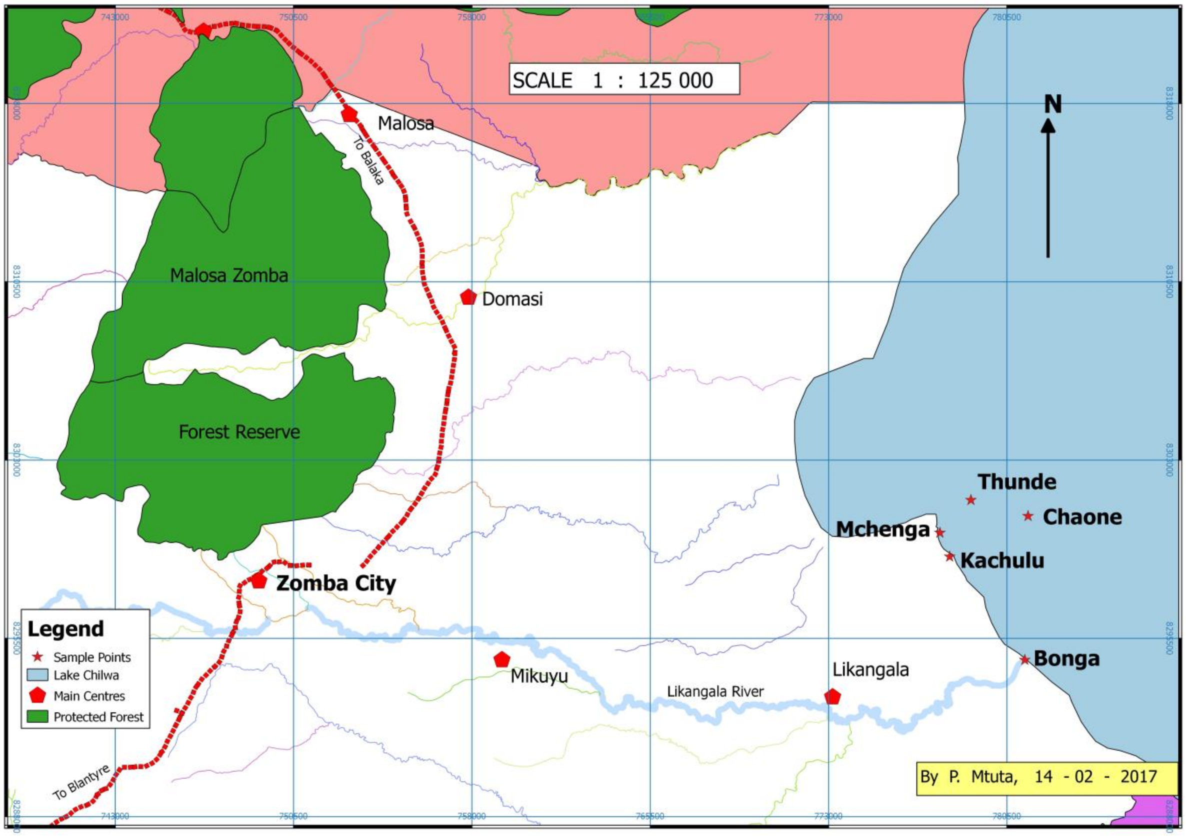

Figure 3.2: Map of Lake Chilwa to the Zomba side showing sampling points

3.2.2 Water sampling

Samples of water from all five sampling sites for both dry (November) and rainy (March) seasons were 40. Water samples were collected using grab sampling at a depth of about 0.3 m below the surface into 1 litre plastic bottles in order to get a clear sample. The bottles were cleaned with 10% nitric acid and rinsed with distilled water before sampling. At each sampling site the bottles were again rinsed three times with water from the lake. The bottles were then immersed directly in water to grab the samples. Samples meant for heavy metal analysis, nitrates, phosphates, pH, EC, TDS and temperature were collected in triplicates. The probe method on the field was used to determine the physical parameters. Temperature, pH, Electrical Conductivity (EC) and Total Dissolved Solids (TDS) were determined with a portable pH meter model Wagtech International WE 30200 and EC Meter Hatch model MP4.

In case of samples for heavy metal analysis, water samples collected in 1-litre plastic bottles were immediately treated with 1.5 mL concentrated nitric acid (AR) to lessen the adsorption of metals onto the wall of the bottles (APHA, 1985). The bottles were then labeled to indicate the site and date of sampling. Samples were temporarily stored in a cooler box with ice packs awaiting transportation to the University laboratory where they were stored in refrigerator at 4 ^{o}C before analysis.

3.2.3 Sediment sampling

Sediment samples were collected using Eckman grab as described by (Osman & Kloas, 2010). Samples were taken at a depth of 1-2 cm from the bottom of the lake. Divers were used to collect the sediment samples at the bottom of the lake. At each sampling site, three sediment samples were randomly taken, homogenized and kept in clean polyethylene bottles. The bottles were then labeled to indicate site and date of sampling. Samples were then stored in cooler box with ice packs for transportation to the University laboratory. In the laboratory, the samples were kept in a freezer at – 20 ^{o}C until they were processed for heavy metal analysis.

3.2.4 Fish sampling

In both seasons, fresh fish samples were bought directly from fishermen at the lake. The study sampled the common species of fish found in Lake Chilwa namely: *Barbus paludinosus , Clarias gariepinus and Oreochromis shiranus chilwae* as shown in Figure 3.3. Three from each species were collected in both seasons. Immediately after buying the fresh fish from the fishermen, they were kept in a cooler box with ice packs in as in figure 3.4 (a) awaiting transportation to the university laboratory to be stored in a freezer at – 20 ^{o}C before analysis.

Figure 3.3 Fresh fish samples just bought at the lake (a) and samples being prepared in the laboratory (b) and (c)

Figure 3.4: researcher testing pH meter on a cooler box with ice packs (a) and standing in front of canoe used for sampling (b)

3.3 Analytical methods

3.3.1 Instrumentation

i. pH meter model Wagtech International WE 30200 and EC Meter Hatch model MP4 were used for pH, electrical conductivity (EC), total dissolved solids (TDS) and temperature measurements.

ii. Atomic Absorption Spectrophotometer (GBC932 model) was used for heavy metal analysis.

iii. UV/Vis Spectrophotometer (spectronic 20 model) was used for analysis of phosphates and nitrates (APHA, 2005).

3.3.2 Nitrate

Nitrate (NO_3^-) was determined by reacting it with sodium salicylate under strong acid conditions. Addition of excess sodium hydroxide solution produced the sodium salt of the organic nitro complex. The nitro compound was soluble in water and produced a strong yellow solution. The intensity of the colour was proportional to the amount of nitrate in the sample and was measured at 410 nm on a spectrophotometer.

3.3.2.1 Preparation of reagents

Sodium salicylate (0.5% w/v) was made by dissolving 0.5 ± 0.01 g laboratory reagent grade sodium salicylate in 100ml distilled water that was stored in a cool place for less than 10 days. Sodium hydroxide (25% w/v) was made by dissolving 25 ± 0.01 g of sodium hydroxide (NaOH) in 70mL of distilled water. When cool it was diluted to 100 mL with distilled water. Sulphuric acid analar grade, S.G. 1.84 was used.

3.3.2.2 Standard Solution

Standard nitrate (stock) solution, 1ml = 500 μg NO_3^- was made by dissolving 0.815 ± 0.001g of Analar potassium nitrate, previously dried at 110 °C, in approximately 100mL of distilled water. It was then transferred to a 1 litre volumetric flask, and dilute to the mark with distilled water and mixed well. Standard nitrate (working) solution (A), 1mL = 50 μg NO_3^- was made by pipetting 10.0 mL of standard nitrate (stock) solution into a 100 mL volumetric flask, diluted to the mark with distilled water and mixed well. Standard nitrate (working) solution (B), 1mL = 5 μg NO_3^- was made by pipetting 10.0 mL of standard nitrate (working) solution (A) solution into a 100 mL volumetric flask, diluted to the mark with distilled water and mixed well. The volumes for standard working solution (A) were 2.00, 4.00, 6.00 and 8.0 mL while for working solution (B) was 0.00, 1.00, 2.00, 5.00 and 10.0.

3.3.2.3 Treatment of standard solutions and measurement

The sample of 5.00 mL was pipetted into a 100 mL pyrex beaker. If more than 80mg/L nitrate is expected, a smaller aliquot was pipetted or dilute sample accordingly. Then 2.0 mL of sodium salicylate solution (0.5% w/v) was added using a pipette. It was mixed well and evaporated to dryness on water bath. The beaker was removed from water bath and added using a pipette and safety pipette filler 1.0 mL of concentrated sulphuric acid. It was mixed well and allowed to stand for 10 minutes. The mixture was diluted to approximately 50 mL with distilled water. Using a measuring cylinder, 10 mL of sodium hydroxide solution (25% w/v) was added and mix thoroughly. When cool, the solution was transferred to a 100mL volumetric flask and diluted to the mark with distilled water.

3.3.2.4 Nitrate measurement and preparation of calibration curve

The standard solutions and water samples versus the blank were determined. The absorbance was measured on spectrophotometer against the blank (100%) transmission), in either 10 or 40 mm cell at 410 nm wavelength. The same procedure was followed to measure nitrate in the rest of the standard solutions (2, 4, 6, 8, 10, 12 mg/L NO_3^-) and water samples. Finally, the determination of nitrate concentration in each of the water samples was done by referring to the calibration curves that was prepared.

3.3.3 Phosphate

Phosphate (PO_4^{3-}) in water samples was determined by Ascorbic Acid method (APHA, 1995). Measurements were carried out with the aid of UV/Vis spectrophotometer (spectronic 20 model) at 880 nm wavelength, providing light path of 2.5 cm or longer.

3.3.2.1 Preparation of reagents

Sulfuric acid, H_2SO_4, 5N was made by diluting 70 mL concentrated H_2SO_4 to 500 mL with distilled water in a volumetric flask. Potassium antimonyl tartrate solution was made by dissolving 1.3715g $K(SbO)C_4H_4O_6.1/2H_2O$ in 400 mL distilled water in a 500 mL volumetric flask that was diluted to volume and stored in a glass stoppered bottle. Ammonium molybdate solution was made by dissolving heated 20 g $(NH_4)_6Mo_7O_{24}.4H_2O$ in 500 mL distilled water and stored in a glass - stoppered bottle. Ascorbic acid, 0.01M was made by dissolving 1.76 g ascorbic acid in 100 mL distilled water and stored at 4^oC.

The combined reagent was produced by mixing the above reagents in the following proportions for 100 mL of the combined reagent: 50 mL 5N H_2SO_4, 5 mL potassium antimonyl tartrate solution, 15 mL ammonium molybdate solution and 30 mL ascorbic acid solution. All the the reagents were let to reach room temperature before being mixed in the order given. If turbidity formed in the combined reagent, it was shaken and let it stood for few minutes until turbidity disappeared before proceeding.

3.3.2.2 Standard solutions (0, 2.0, 4.0, 6.0, 8.0 PO_4^{3-})

Phosphate stock solution was made by dissolving 219.5 mg unhydrous KH_2PO_4 and dilute to 1000 mL; 1.00 mL = 50.0 g PO_4^{3-} -P. Standard stock solution was made by diluting 50.0 mL stock phosphate solution to 1000 mL with distilled water; 1.00 mL = 2.50 μg P. To prepare phosphate calibration standard solution series, exactly 0, 2, 4, 6, 8 mL of stock solution (50 mg/L PO_4^{3-}) were separately transferred into respective 100 mL volumetric flasks. The solutions were then diluted to the mark with distilled water to get final standard solutions of concentrations 0, 2, 4, 6, 8 mg/L PO_4^{3-} respectively.

3.3.2.3 Treatment of standard solutions and water samples: color development

Water sample of 50.0 mL was pipetted into a clean, dry test tube or 125 mL erlenmeyer flask. Then 0.05 mL (1 drop) phenolphthalein indicator was added. If a red colour developed 5N H_2SO_4 solution was added in form of drops just to discharge the colour. The combined reagent of 8.0 was added and mixed thoroughly. The mixture was kept for 10 minutes but not more than 30 minutes before measuring absorbance.

3.3.2.4 Phosphate measurement and preparation of calibration curve

Within 10 to 30 minutes the absorbance of the standard solutions and water samples versus the blank were determined. This done by pouring 0 mg/L PO_4^{3-} standard solution into clear test tube that was inserted in the absorption cell of the photometer and measured its absorbance using UV/Vis spectrophotometer at 880 nm wavelength. The same procedure was followed to measure phosphate in the rest of the standard solutions (2, 4, 6 and 8 mg/L PO_4^{3-}) and water samples. Finally, the determination of phosphate concentration in each of the water samples was done by referring to the calibration curves that was prepared.

3.3.3 Determination of heavy metals in water samples

All the water samples for metal analysis were digested using concentrated nitric acid (AR) 5mL of Nitric acid to 50mL of sample water in a 100mL volumetric flask and then heated on hot plate to boil until the volume reduces to 20mL. Another 5mL of concentrated Nitric acid was added and then heated for 10 minutes and allow cooling. The solution was filtered (APHA, 1985). The filtrate was then diluted to volume with distilled water in a 50 ml volumetric flask.

3.3.4 Determination of heavy metals in sediment samples

Sediment samples were thawed at room temperature (25 ^oC) and put in beakers. The samples were then put in an oven set at 50 ^oC to dry until a constant weight was reached. A porcelain mortar and pestle were used to grind the sediment samples. The ground samples were then sieved using a 2 mm mesh plastic sieve. 2 g of sediments from each sample were weighed in a beaker cleaned with nitric acid. The weighed samples were then digested using 5 mL concentrated nitric acid (analytical grade) and few drops of 30% hydrogen peroxide. The digested samples were filtered using filter paper into a 50 mL volumetric flask and filled up to the mark with distilled water. AAS was used to analyse the filtrate for each sample. Similarly, a blank solution was prepared using distilled water.

3.3.5 Determination of fish samples

Frozen fish samples were thawed before being cut into small pieces by a plastic knife. A plastic knife was used to avoid metal contamination. The pieces were then put in pre-acid washed oven dried-crucibles. The samples were put in an oven set at 50 ^{o}C to dry until a constant weight was reached. The dried samples were allowed to cool in a desiccator to avoid absorption of any moisture from the environment. The cooled fish samples were slightly ground using a porcelain mortar and pestle before being crushed into powdered form using a nima magic blender. Next 2g of the powdered fish samples was weighed on an electronic balance and the samples were then transferred into a clean beaker.

The samples for each fish species were digested in triplicates (APHA, 2005). 18 mL of concentrated nitric acid was then added to each sample and heated on a hot plate at 100 ^{o}C in a fume hood chamber. A few drops of 30% hydrogen peroxide (analytical grade) were added until there were no brown fumes. The fish sample solution from digestion process was filtered using 541 hardened Ash less circles, 125 mm filter paper into a 25 mL volumetric flask and filled to the mark with distilled water. The filtrate was then put into pre – acid cleaned plastic bottles and metal analysis was done using an Atomic Absorption Spectrophotometer (model GBC932).

3.3.6 Preparation of standard stock solutions

Standard stock solutions for selected six metals namely: lead, cadmium, manganese, copper, iron and zinc were prepared. The six metals were selected based on the frequency reported in literature of previous studies done in surface waters and sediments of southern region of Malawi.

3.3.6.1 Lead

1.598 g of lead nitrate (AR), $Pb(NO_3)_2$ was weighed on an electronic balance and dissolved in about 200 mL of distilled water. Then 1.5 mL of concentrated nitric acid (AR), (HNO_3) was added to completely dissolve lead nitrate to solution. The resultant solution was diluted to 1000 mL in a volumetric flask to make a stock solution. The 100 mg L^{-1} intermediate stock solution was prepared from this stock solution. The working standard solutions were then prepared from the intermediate stock solution. The final standard solutions used were 0.00, 1.0, 2.0, 4.0 and 6.0 mgL^{-1}. The AAS was set at 283.3 nm to read the absorbance of the working standards.

3.3.6.2 Cadmium

1.000 g cadmium metal (AR) was weighed on an electronic balance and dissolved in a minimum of 1 + 1 HCL (AR). The resultant solution was diluted to 1000 mL in a volumetric flask to make a cadmium stock solution. The 100 mg L^{-1} intermediate stock solution were prepared from this stock solution. The working standard solutions were then prepared from the intermediate stock solution. The final standard solutions used were 0.00, 0.5 and 1.0 mg L^{-1}. The AAS set at 228.8 nm was used to read the absorbance of the working standards.

3.3.6.3 Manganese

3.076 g manganous sulfate (AR), $MnSO_4.H_2O$, was weighed on an electronic balance and dissolved in about 200 mL distilled water. Then 1.5 mL of concentrated nitric acid (AR), (HNO_3) was added to completely dissolve manganous sulfate to solution. The resultant solution was diluted to 1000 mL in a volumetric flask to make a stock solution. The 100 mg L^{-1} intermediate stock solution was prepared from this stock solution. The working standard solutions were then prepared from the intermediate stock solution. The final standard solutions used were 0.00, 0.5, 1.0, 2.0, 5.0 and 10.0 mg L^{-1}. The AAS set at 279.5 nm was used to read the absorbance of the working standards.

3.3.6.4 Copper

1.000 g of copper metal (GPR) was weighed on an electronic balance and dissolved in 15 mL of 1 + 1 HNO_3 (AR). The resultant solution was diluted to 1000 mL in a volumetric flask to make a copper stock solution. The 100 mg L^{-1} intermediate stock solution was prepared from this stock solution. The working standard solutions were then prepared from the intermediate stock solution. The final solutions used were 0.0, 2.0, 4.0, 6.0, 8.0 and 10.0 mg L^{-1}. The AAS was set at 324.8 nm to read the absorbance of the working standards.

3.3.6.5 Zinc

1.000 g zinc metal (AR) was weighed on an electronic balance and dissolved in 20 mL 1 +1 HCl. The resultant solution was diluted to 1000 mL in a volumetric flask to make a zinc stock solution.

The 100 mg L^{-1} intermediate stock solution was prepared from this stock solution. The working standard solutions were then prepared from the intermediate stock solution. The final standard solutions used were 0.00, 0.5, 1.0, and 5.0 mg L^{-1}. The AAS set at 213.9 nm was used to read the absorbance of the working standards.

3.3.6.6 Iron

1.000 g iron wire (GPR) was weighed on an electronic balance and dissolved in 50 mL of 1 + 1 HNO_3 (AR). The resultant solution was diluted to 1000 mL in a volumetric flask to make an iron stock solution. The 100 mg L^{-1} intermediate stock solution was prepared from this stock solution. The working standard solutions were then prepared from the intermediate stock solution. The final solutions used were 0.0, 2.0, 4.0, 6.0, 8.0 and 10.0 mg L^{-1}. The AAS was set at 248.3 nm to read the absorbance of the working standards.

3.4 Data Analysis

Statistical analysis was done using IBM SPSS Version 20 computer package. One way ANOVA and t-test were applied to compare the mean concentration of metals at different sites at 95% confidence interval. In addition to that, Pearson correlation coefficients were determined to examine the relationship between the levels of analytes in water, sediment and fish samples. Pearson correlation coefficient was also determined to examine the relationship between heavy metals and other physico-chemical parameters.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

In this study, the following physicochemical parameters were analysed: pH, temperature, total dissolved solids, electric conductivity, nitrate and phosphate (Table 4.1). It should be noted that the appendix section provides detailed statistical analysis results.

4.1 Water pH

Table 4.1 shows the mean pH values for five sampling sites in Lake Chilwa. All the sampling sites recorded higher pH levels in dry season than in rainy season. The possible reason could be that rain water and surface run-off to the area is slightly acidic which could decrease the pH. Thunde recorded the highest levels of pH for dry and rainy seasons (9.7 ± 0.1) and (9.4 ± 0 .01), respectively while Bonga had the lowest for dry season (8.6 ± 0.01) and rainy season (6.9 ± 0.01). One way ANOVA revealed that there were significant differences in mean pH values among five sites for both seasons, Table 4.1).

In both seasons, all the sampling sites but Bonga in rainy season were not within the WHO acceptable pH drinking water values (pH = 6.5 – 8.5) (WHO, 2011). On the other hand, all the sampling sites except Thunde (pH = 9.7) in the dry season were within the Malawi Standard drinking water values (pH = 5.0 – 9.5) (MBS, 2005). However, in natural fresh waters pH ranges between 6.0 and 8.0 (Osman & Kloas, 2010). The possible reason for having slightly low pH at Bonga could be because the site is an inlet of Likangala River to Lake Chilwa where depositions of organic materials occur. With time the organic substances decompose and release carbon dioxide (CO_2) which combines with water to produce carbonic acid which decreases the pH of water.

Generally, the water samples from Lake Chilwa indicated high pH values (alkaline conditions). According to Garson (1960) the high pH levels in Lake Chilwa were attributed to the bedrock and soil composition of the catchment area that contains limestone ($CaCO_3$) through which the water moves. In the aquatic environment pH is one of the main factors that influence the solubility of heavy metals in surface waters (Iwashita & Shimamura, 2003). According to Radulescu *et al*. (2014) the decrease in water pH lead to the increase in the solubility of toxic metals i.e. from surface to deep layers or from alkaline to acidic.

Table 4.1: Seasonal results for physicochemical parameters in water samples with minimum and maximum values compared with WHO and Malawi standards threshold limit values

Parameter	Bonga		Chaone		Thunde		Mchenga		Kachulu		Min	Max	p-value	WHO	MS
	DS	RS	DS	RS	DS	RS	DS	RS	DS	RS					
pH	8.570	6.937	9.360	9.233	9.700	9.437	9.333	8.587	9.433	8.747	6.937	9.70	< 0.001	6.5 – 8.5	5.0 – 9.5
Temp (^{o}C)	32.53	30.70	33.77	31.70	32.10	31.70	33.23	32.83	33.73	32.60	30.70	33.77	< 0.001		
TDS (mgL^{-1})	2064	77	1948	2047	2045	1818	2158	1272	2119	1657	77	2119	< 0.001		450 – 1000
EC (µS/cm)	2808	123	2701	2777	2814	2493	2936	1788	2878	2300	123	2936	< 0.001	700	700 – 1500
NO_3 (mgL^{-1})	0.632	2.033	1.084	2.166	0.865	5.290	0.896	6.565	3.201	0.388	0.388	6.565	0.027	50	6.0 – 10
PO_4 (mgL^{-1})	0.336	0.249	0.288	1.107	0.270	1.209	0.321	0.945	0.233	1.274	0.233	1.274	< 0.001		

DS = dry season, RS = rainy season, p-values for ANOVA test

Table 4.2: Seasonal results for sediment samples with maximum and minimum values

Parameter (mg kg^{-1})	Bonga		Chaone		Thunde		Mchenga		Kachulu		p-value	Min	Max
	DS	RS	DS	RS	DS	RS	DS	RS	DS	RS			
Mn	5.396	3.250	7.746	10.656	9.775	9.785	4.788	2.253	5.509	3.967	0.233	2.253	10.656
Cu	1.273	1.629	0.575	0.000	0.637	0.000	0.249	0.000	0.548	0.405	0.021	0.000	1.629
Zn	1.659	1.527	1.078	0.209	1.825	0.245	0.153	1.086	1.289	0.000	0.029	0.000	1.825
Fe	392.3	445.9	282.8	376.2	357.4	371.6	156.5	232.7	235.3	307.2	< 0.001	156.5	445.9

4.2 Water Temperature

Table 4.1 also shows the mean temperature values for five sampling sites in Lake Chilwa. All the sampling sites recorded higher temperatures in dry season than in rainy season. This is attributed to heat from the sun during dry season and the cooling effect of rain in rainy season. Chaone recorded the highest temperatures for dry season (33.8 ± 0.06 ^{o}C) while Thunde had the lowest (32.1 ± 0.10 ^{o}C). In the rainy season, Mchenga recorded the highest temperatures (32.8 ± 0.06 ^{o}C) while Bonga had the lowest (30.7 ± 0.10 ^{o}C).

One way ANOVA revealed that there were significant differences in mean temperature values among the five sites for both seasons ($p < 0.05$, Table 4.1). In aquatic environment temperature is one of the main factors that influence the solubility of heavy metals in surface waters (Iwashita & Shimamura, 2003).

Generally the water temperatures for both seasons were high which imply that the weather condition during the study period were relatively hot.

4.3 Total dissolved solids (TDS)

According to Table 4.1 the mean concentration of total dissolved solids (TDS) for five sampling sites in Lake Chilwa. The mean concentration of total dissolved solids (TDS) for four sampling sites were higher in dry season than in rainy season. This could be attributed to low water levels in dry season that lead to increase in concentration of dissolved solids. On the other hand, in rainy season the water levels were high and there was dilution effect on total dissolved solids. Mchenga recorded the highest TDS (2158 ± 1.15 mg L^{-1}) while Chaone recorded the lowest (1947 ± 1.53 mg L^{-1}) in the dry season. In the rainy season, Chaone recorded the highest TDS (2047 ± 0.58 mg L^{-1}) while Bonga had the lowest (77 ± 0.02 mg L^{-1}). The reason for having very low TDS levels at Bonga in rainy season could be attributed to large volumes of water that were continuously flowing into the lake from Likangala River that reduced the concentration of suspended solids at the site.

ANOVA revealed that there were significant differences in the mean of total dissolved solids among five sites for both seasons ($p < 0.05$, Table 4.1). The study indicated that all the sites but

Bonga in the rainy season, were above the Malawi Standards drinking water values for TDS (450 – 1000 mg L^{-1}) (MBS, 2005).

In this study the trends for EC and TDS have shown similarities which support the assertion that there is a direct relationship between TDS and EC (Bishop, 1998).

4.4 Electrical conductivity (EC)

Table 4.1 also shows the mean concentration of electrical conductivity (EC) for the five sampling sites in Lake Chilwa. The mean electrical conductivities (EC) for the four sampling sites were higher in dry season than in rainy season. The possible reason could be attributed to low water levels in dry season that lead to increase in concentration of ions. On the other hand, in rainy season the water levels were high and there was dilution effect on ions. According to Jain *et al.* (2005) EC is used as an important indicator of the mineralization in water. Mchenga recorded the highest EC (2936 ± 1.53μS/cm) and Chaone recorded the lowest (2701 ± 0.58 μS/cm) in the dry season. In the rainy season, Chaone recorded the highest EC (2777 ± 1.00 μS/cm) while Bonga had the lowest (123 ± 0.06 μS/cm).

The highest recording in rainy season at Chaone could be as a result of weathered rock material from Chisi Island where Chaone is located. The rock material could be carried down the lake by surface runoff where mineralization of water occurs. Chisi Island was found with various rock minerals such as carbonatites containing sovites with silicates, sovites with small amounts of siderite, ankeritic sovites and sideritic carbonatites, locally rich in manganese oxides (Garson, 1960).

ANOVA revealed that there were significant differences in the mean electrical conductivities among five sites for both seasons ($p < 0.05$, Table 4.1). The study indicated that water from Bonga in the rainy season was the only site suitable for domestic use because the limit for EC for drinking and potable water set by WHO is 700 μS/cm (WHO, 2003) and 700 – 1500 μS/cm according to the Malawi Standards (MBS, 2005). Conductivity is directly related to total suspended solids in water.

4.5 Nitrate levels in water and sediment samples for dry and rainy seasons

In the dry season, the levels of nitrate in water samples ranged from 0.388 – 6.565 mg L^{-1} while in rainy season the range was 0.632 – 3.201 mg L^{-1} (Table 4.1). In both seasons all the sampling sites had nitrate levels below WHO drinking water standard (50 mg L^{-1}) (WHO, 2011). On the other hand, Mchenga was the only site that had nitrate levels within Malawi drinking water standards (6.0 – 10 mg L^{-1}) (MBS, 2005). The sources of nitrates in water samples could be the use of inorganic fertilizers. The highest level of nitrate was observed in the dry season at Mchenga while the lowest was at Kachulu in the same season. This could be attributed to irrigation farming that involves the use of fertilizers in the area around Mchenga as compared to Kachulu where people concentrate on fishing.

The study indicated significantly higher levels of nitrates in water samples for rainy season than dry season ($p = 0.027$, Table 4.1). The possible reason for increased levels of nitrates in rainy season could be the application of nitrogenous fertilizers in the upland farms that were carried down to the lake by surface run off. On the other hand, the area has had reports of cholera out breaks which is an indicator of poor sanitation (UNICEF, 2015). Therefore, the presence of high levels of nitrates in rainy season could also be attributed to poor sanitation ranging from open defecation to uncontrollable dumping of solid wastes that were carried into the lake by surface run off.

4.6 Phosphate levels in water samples for dry and rainy seasons

In the dry season, the levels of phosphate in water samples ranged from 0.233 – 0.336 mg L^{-1} while in rainy season the range was 0.249 – 1.274 mg L^{-1} (Table 4.1). The sources of phosphates in water samples are the use of inorganic fertilizers and geology of the area. The Lake Chilwa basin is made up of igneous rocks associated with carbonatites and mica pyroxenites which are the major resources of phosphates in Malawi (Garson 1962). According to Garson (1996) the observation was made by many geoscientists who studied the Tundulu carbonatite complex at the southern end of Lake Chilwa, close to the border with Mozambique.

The highest level of phosphates was observed in the rainy season at Kachulu sampling site (1.274 mg L^{-1}). The possible reason for higher phosphate levels at Kachulu could be the use of phosphorus detergents for washing clothes and uncontrollable disposal of wastes. It was observed that people used the area near Kachulu harbor for laundry and bathing. There were significantly higher levels of phosphates in water samples for rainy season than dry season ($p < 0.05$, Table

4.1). This may be attributed to surface run off from agriculture fields that were applied with inorganic fertilizers containing phosphates. It may also be caused by uncontrollable dumping of solid wastes since the area does not have a specific dumping site.

4.7 Levels of heavy metals

4.7.1 Levels of metals in water and sediment for dry and rainy seasons

The study also analysed the water and sediment samples for possible presence of selected heavy metals namely: lead (Pb), cadmium (Cd), manganese (Mn), copper (Cu), zinc (Zn) and iron (Fe). The results for sediment samples are presented in Table 4.2.

4.7.1.1 Lead levels in water and sediment for dry and rainy seasons

The study indicated the absence of lead in water and sediments for dry and rainy seasons which implies that the levels of lead in the water samples were below the WHO drinking water standards for lead (0.01 mg L^{-1}) (WHO, 2011).

4.7.1.2 Cadmium levels in water and sediment samples for dry and rainy seasons

Cadmium was only detected in water in the dry season and in sediments in the rainy season at Kachulu sampling site. The levels in water for the dry season ranged from below detection limit to 0.002 mg L^{-1}. The concentration of cadmium in water samples were below the WHO drinking water standard (0.003 mg L^{-1}) (WHO, 2011). Paired t – test indicated that there was no significant difference in the levels of cadmium in water samples between dry and rainy season ($p = 1.000$).

Cadmium levels in sediments for the rainy season ranged from below detection limit to 0.04 mg kg^{-1} (Table 4.2). The possible sources of cadmium at Kachulu which is a harbor were anthropogenic activities such as the use of phosphate fertilizers, burning of fossil fuels and deposition of dry cell batteries and other metal products (Challa & Kumar, 2009).

The results in dry season do not concur with literature that sediments are the major depository of metals which hold up to 99% of total amount of metals in the system (Ademoroti, 1996; Garbarino *et al*., 1995). These results are also different from a study done in fives rift valley lakes in Kenya that had mean cadmium levels in sediment samples ranging from 0.2 – 1.18 mg kg^{-1} (Ochieng *et al*., 2007). These differences are attributed to the fact that Malawi is not highly industrialised as most countries in Southern and Eastern Africa as such pollution of heavy metals is still less as compared to these other countries.

4.7.1.3 Manganese levels in water and sediment samples for dry and rainy seasons

The study indicated the absence of manganese in water samples for both seasons which implies that the levels of manganese in the water samples were below the WHO drinking water standards (0.1 mg L^{-1}) (WHO, 2011).

On the contrary, in the dry season the level of manganese in sediments ranged from 4.788 - 9.775 mg kg^{-1} while in the rainy season the range was 2.253 - 10.656 mg kg^{-1} (Table 4.2). Paired t – test revealed that there was no significant difference in concentration of manganese in sediment samples between dry season (6.643 mg kg^{-1}) and rainy season (5.982 mg kg^{-1}) (Table 4.2). The possible sources of manganese in sediments are salts and mineral complexes commonly spread in rocks, soils and on the floors of the lake (Damodharan, 2013). According to Garson (1960) Lake Chilwa catchment area and the Chisi Island were found with carbonatites containing sovites with silicates, sovites with small amounts of siderite, ankeritic sovites and sideritic carbonatites, locally rich in manganese oxides. Additionally, anthropogenic activities such as deposition of metal products and use of inorganic fertilizers could be the likely sources of manganese in sediments.

4.7.1.4 Copper levels in water and sediment samples for dry and rainy seasons

The study indicated the absence of copper in water samples for both seasons which implies that the levels of copper in water samples were below the WHO drinking water standard (2 mg L^{-1}) (WHO, 2011).

On the contrary, in the dry season the level of copper in sediments ranged from 0.249 - 1.273 mg kg^{-1} while in the rainy season it ranged from below detection limit to 1.629 mg kg^{-1} (Table 4.2). Paired t – test revealed that the concentration of copper were significantly higher in dry season (0.656 mg kg^{-1}) than rainy season (0.407 mg kg^{-1}) (Table 4.2).

The possible sources of copper in sediments that were high at Bonga, an inlet from Likangala River, are domestic, industrial wastewaters and the dumping of sewage effluent (Denton, *et al.*, 1997). Copper pollution is through extensive use of fungicides, algaecides, insecticides and wood preservatives and in electroplating, dye manufacture, engraving, lithography, petroleum re-fining, pyrotechnics and discharge of waste (Michael, 1986). Additionally, copper compounds are used as food additives and can be added to fertilizers and animal feeds as nutrients to support plant and animal growth (Abbasi *et al*., 1998).

The findings of this study on copper in water samples concur with a study that assessed water quality in Likangala River and its catchment area in Zomba, Malawi. The study found that copper levels in water were below detection limit (Chidya, 2012). It should be noted that Likangala River drains its waters into Lake Chilwa.

4.7.1.5 Zinc levels in water and sediment samples for dry and rainy seasons

The study indicated the absence of zinc in water samples for dry season but the levels of the rainy season ranged from below detection to 2.308 mg L^{-1}. The zinc concentration detected in the rainy season was above the WHO drinking water standards (0.1 mg L^{-1}) (WHO, 2011).

The possible sources of zinc in water in the rainy season could be surface runoff from semi-urban areas, leaching from fertilizers and burning of waste materials at Kachulu harbour. According to Damodharan (2013) zinc is introduced into the water bodies through urban runoff, municipal sewages, burning of waste materials, leaching from fertilizers and effluents of commercial industries.

In the dry season the level of zinc in sediment samples from Lake Chilwa ranged from 0.153 – 1.825 mg kg^{-1} while in the rainy season the range was from below detection to 1.525 mg kg^{-1} (Table 4.2). Paired t – test indicated a significantly higher concentration of zinc in dry season (1.201 mg kg^{-1}) than in rainy season (0.613 mg kg^{-1}) (Table 4.2). Zinc levels in sediments were high in dry season possibly because in the rainy season there was churning effect in the lake that could uplift the sediments thereby leaving the metals ions in suspension. The possible sources of zinc in sediments were products of paints, fertilizers, wood preservatives containing zinc and waste discharges (Lew, 2008).

The result at Kachulu showed a notable switch of presence of zinc between water and sediment samples in both season where zinc was detected in water in the rainy season only and in sediments in the dry season only. This may be attributed to the capacity of sediments to accumulate heavy metals in dry season when water was calm before being remobilized back to water due to the churning effect of rain. According to WHO (2008) sediments have capacity for more heavy metal accumulation with time and remobilize them back to water and food chain.

4.7.1.6 Iron levels in water and sediment samples for dry and rainy seasons

In the dry season, the levels of iron in water samples ranged from 1.782 – 8.807 mg L^{-1} while in rainy season the range was 4.070 – 6.0 mg L^{-1}. In all the sampling sites iron levels were above WHO (0.3 mg L^{-1}) drinking water standards (WHO, 2011). The presence of iron in waters of Lake Chilwa could be attributed to the discharges of iron wastes produced in Zomba City and Kachulu Trading Center.

The range of iron concentration in sediment samples in Lake Chilwa for the dry season was 156.526 – 392.316 mg kg^{-1} while in the rainy season it was 232.667 - 445.930 mg kg^{-1} (Table 4.2). Paired t – test revealed significantly higher levels of iron in rainy season (346.72 mg kg^{-1}) than in dry season (284.86 mg kg^{-1}) (Table 4.2). The highest concentration of iron in sediments was at Bonga which is an inlet from Likangala River. This may be as a result of accumulation of sediments that contain iron elements originating from the inhabitants along the Likangala River.

4.7.2 Levels of metals in fish

The study also analysed the samples of three different species of fish for possible presence of selected heavy metals namely: lead (Pb), cadmium (Cd), manganese (Mn), copper (Cu), zinc (Zn) and iron (Fe). The results of different fish samples are presented in the Table 4.3.

Table 4.3: Seasonal results for fish samples with their minimum and maximum values compared with WHO/ FAO standards threshold limit values

Fish type	Cd (mg kg^{-1})		Mn (mg kg^{-1})		Cu (mg kg^{-1})		Zn (mg kg^{-1})		Fe (mg kg^{-1})	
	DS	RS	DS	RS	DS	RS	DS	RS	DS	RS
O. shiranus chilwae	0.000	0.003	0.246	0.065	0.406	0.544	2.078	4.815	18.637	18.631
C. gariepinus	0.000	0.003	0.467	1.178	0.406	0.917	2.214	1.712	32.314	9.683
B. paludinosus	0.000	0.006	0.015	0.206	0.416	0.683	2.004	2.698	16.342	11.780
Min	0.000	0.003	0.015	0.065	0.406	0.544	2.004	1.712	16.342	9.683
Max	0.000	0.006	0.467	1.178	0.416	0.917	2.214	4.815	32.314	11.780
Overall Mean	0.000	0.004	0.243	0.483	0.409	0.715	2.099	3.075	22.422	13.365
FAO/WHO	0.1		2 - 9		3		60		43	

4.7.2.1 Lead levels in fish samples for dry and rainy seasons

Lead was not detected in fish samples which imply that the levels of lead in fish samples were below FAO / WHO standards for lead in fish for consumption (0.2 mg kg^{-1}) (FAO / WHO, 1999).

A study that was conducted to determine the levels of lead in farm raised fish in Zomba found greater concentration of lead (0.68 mg kg^{-1}) in fish samples (Puchase & Jamu, 2009). Most of these studies reported in Malawi were in streams and rivers where the water volumes are much lower than in Lake Chilwa. This could indicate therefore that there is a dilution effect at play in Lake Chilwa which makes the lead levels to be below detection limit.

4.7.2.2 Cadmium levels in fish samples for dry and rainy seasons

In the dry season cadmium levels were not detected in all fish samples. On the contrary, fish samples for the rainy season showed the presence of cadmium ranging from below detection limit to 0.006 mg kg^{-1} (Table 4.3). The levels of cadmium in fish samples were below the maximum limit for the FAO / WHO standard for cadmium in fish for consumption (0.1 mg kg^{-1}) (FAO / WHO, 1999).

Barbus paludinosus recorded high levels of cadmium than the other two species. This may imply that *Barbus paludinosus* has more potential for accumulating cadmium metal than other species, possibly because of its feeding habit. According to Dadebo *et al.* (2013) *B. paludinosus* has an omnivorous habit. It fed on insects, detritus and zooplankton in the dry season while relying on detritus, insects and phytoplankton wet season. Also carnivorous and omnivorous fish tend to have high metal concentrations. Literature supports that omnivorous fish have elevated concentrations of Cd than carnivorous and herbivorous fish (Hashim *et al.*, 2014).

4.7.2.3 Manganese levels in fish samples for dry and rainy seasons

In the dry season manganese level in fish samples ranged from 0.015 - 0.467 mg kg^{-1}. Similarly, fish samples for the rainy season showed the presence of manganese ranging from 0.065 - 1.178 mg kg^{-1} (Table 4.3). In both seasons the levels of manganese in fish were below the FAO / WHO standards (2 – 9 mg kg^{-1}) (FAO/WHO, 1999). Paired t – test indicated that the concentration of manganese in fish samples were not significantly higher in rainy season than in dry season (p = 0.100, Table 4.3).

In both seasons *Clarias gariepinus* recorded highest levels of manganese 0.467 mg kg^{-1} for dry and 1.177 mg kg^{-1} for rainy season. This may indicate that *Clarias gariepinus* has more potential of accumulating manganese than the other sampled species. This could also be attributed to the fact that heavy metal accumulation in fish is affected by fish species (Jezierska & Witeska, 2001).

The presence of manganese in fish samples could also originate from ingestion of contaminated feed or through the gills and skin that eventually accumulate in organs and tissues through the blood stream (Sfakianakis *et al.*, 2015; Fazio *et al.*, 2014). Fertilizers, varnish, fungicides and livestock feed supplements are made of manganese compounds which bioaccumulate in lower organisms such as phytoplankton, algae, mollusks and some fish (Abbasi et al., 1998).

4.7.2.4 Copper levels in fish samples for dry and rainy seasons

Table 4.10 shows the mean concentration of copper in fish for dry and rainy season. In the dry season copper levels in fish samples ranged from 0.406 – 0.416 mg kg^{-1}. Similarly, fish samples for the rainy season showed the presence of copper ranging from 0.544 – 0.917 mg kg^{-1} (Table 4.3). In both seasons the concentration of copper in fish samples was below the FAO / WHO standards for copper in fish for consumption (3 mg kg^{-1}) (FAO / WHO, 1999). Paired t – test revealed that copper levels in fish samples were significantly higher in rainy season than dry season ($p < 0.05$, Table 4.3). This could be attributed to higher levels of copper found in the sediments in the rainy season that were consumed as detritus together with zooplankton and phytoplankton.

Clarias gariepinus recorded higher concentration of copper (0.917 mg kg^{-1}) than *Barbus* and *Oreochromis* species (Table 4.3). This may indicate that *Clarias gariepinus* has more potential of accumulating copper metals than the two species. The possible reason could be the habitat for *Clarias gariepinus.* The fish species usually live and feed on living organism and detritus found in the mud which is the major constituents of sediments.

The presence of copper in fish samples could originate from ingestion of contaminated feed or through the gills and skin that eventually accumulate in organs and tissues through the blood stream (Sfakianakis *et al.,* 2015; Fazio *et al.,* 2014). According to Cogun and Kargin (2004) lower pH levels lead to higher accumulation of copper in fish. Copper can be accumulated by fish either through diet or ambient exposure (Sfakianakis *et al*., 2015). According to Jezierska and Witeska (2006) copper shows a very distinct affinity to accumulate in fish liver even when the concentration is low in the environment.

4.7.2.5 Zinc levels in fish samples for dry and rainy seasons

In the dry season zinc levels in fish samples ranged from 2.004 – 2.214 mg kg^{-1}. Similarly, fish samples for the rainy season showed the presence of zinc ranging from 1.712 – 4.815 mg kg^{-1} (Table 4.3). In both seasons the concentration of zinc in fish samples was below the FAO / WHO standards for zinc in fish for consumption (60 mg kg^{-1}) (FAO / WHO, 1999). Paired t – test revealed that the concentration of zinc in the fish samples for rainy season was not significantly higher than in dry season ($p = 0.073$, Table 4.3). The presence of zinc in fish samples could also originate from ingestion of contaminated food or through the gills and skin that eventually accumulate in organs and tissues through the blood stream (Sfakianakis *et al.*, 2015; Fazio *et al.*, 2014).

Oriochromis shiranus chilwae had the highest levels of zinc in the rainy season than the other species. This may also indicate that *Oriochromis* species have high potential for accumulating zinc elements than other two species under study.

4.7.2.6 Iron levels in fish samples for dry and rainy seasons

In the dry season iron levels in fish samples ranged from 16.342 - 32.314 mg kg^{-1}. Similarly, fish samples for the rainy season showed the presence of iron ranging from 9.683 – 18.631 mg kg^{-1} (Table 4.3). In both seasons the concentration of iron in fish samples was below the FAO / WHO standards for iron in fish for consumption (43 mg kg^{-1}) (FAO / WHO, 1999). Paired t – test revealed that iron concentration in dry season was significantly higher than in rainy season (p = 0.03, Table 4.3).

Clarias gariepinus species recorded higher levels of iron than the other two species. Elevated levels of iron in humans result into toxic effects such as vomiting, cardiovascular collapse and diarrhoea, on the other hand, iron deficiency may lead to failure of blood clotting (Akan et al., 2009). The presence of iron in fish samples could originate from ingestion of contaminated food or through the gills and skin that eventually accumulate in organs and tissues through the blood stream (Sfakianakis *et al.*, 2015; Fazio *et al.*, 2014).

4.8 Relationships and comparison of heavy metal concentrations in water, sediments and fish

4.8.1 Correlation and paired T – test analysis of heavy metals in water, sediments and fish

There was a strong negative correlation of manganese levels in sediments and fish samples for the dry season (r = -1.000). This negative correlation indicated that as the levels of manganese in sediments were increasing, the levels in fish decreased. The possible reason could be that many types of fish relied on a wide variety of feed such zooplankton and phytoplankton than detritus (forming a larger part of sediments that bind metals) which in dry season was only available to benthic fishes due to calmness of the lake. In comparing the concentration of manganese in sediments (6.643 mg kg^{-1}) to fish samples (0.243 mg kg^{-1}) for dry season there were statistically significant differences ($p < 0.05$). Manganese levels were significantly higher in sediments than in fish in the dry season. The possible reason is that manganese elements may form part of the bed rock.

Similarly, there was a strong positive correlation of copper levels in sediments and fish samples for rainy season (r = 0.929). This positive correlation indicated that as the levels of copper in sediments were increasing, so were the levels in fish. This could be attributed to the churning effect of rains that renders the suspension of detritus to be readily available for feed to both benthic and pelagic fish. In comparing the levels of copper in sediments (0.656 mg kg^{-1}) to fish (0.715 mg kg^{-1}) samples for rainy season there were no significant differences (p = 0.461).

Additionally, zinc in sediments and water samples for rainy season were not strongly correlated (r = -0.521). This negative correlation indicated that as the levels of zinc in sediments were increasing, the levels in water decreased. The possible reason could be that metals bound to sediments as it settles to the bottom of the lake. Antagonistically, sediments may release more metal elements in water due to churning effect of the rains. In comparing the levels of zinc in sediment (0.613 mg kg^{-1}) to water samples for rainy season, there were no significant differences ($p = 0.676$).

Furthermore, zinc levels in sediments and fish samples for the dry season were not strongly correlated ($r = -0.046$). This negative correlation indicated that as the levels of zinc in sediments were increasing, the levels in fish decreased. In comparing the concentration of zinc in sediments (1.201 mg kg^{-1}) to fish samples (2.099 mg kg^{-1}) for dry season there were statistically significant differences ($p < 0.05$). Zinc levels were significantly higher in sediments than fish in the dry season. The possible reason is that zinc elements may form part of the bed rock and deposition of galvanized metals.

In addition to that, there was a strong negative correlation of zinc in sediments and fish samples for rainy season ($r = -0.760$). This negative correlation indicated that as the levels of zinc in sediments were increasing, the levels in fish decreased. The possible reason could be the churning effect of rains which detaches metal elements from sediments and increase its availability for pelagic fish consumption. This will lead to the increasing accumulation in body of fish while reducing its availability in sediments. In comparing the levels of zinc in sediment (0.613 mg kg^{-1}) to fish samples (3.075 mg kg^{-1}) for rainy season, there were significant differences ($p = 0.01$).

On the other hand, there was a strong negative correlation of iron in sediments and water samples for dry season ($r = -0.794$). This negative correlation indicated that as the levels of iron in sediments were increasing, the levels in water decreased. This could be attributed to the calmness of the lake during dry season which allows the metals to settle down together with sediments. In comparing the levels of iron in sediments (284.86 mg kg^{-1}) to water samples (3.867 mg L^{-1}) for dry season, there were statistically significant differences ($p < 0.05$). The levels of iron in dry season were significantly higher in sediments than in water.

On the contrary, iron in water and fish samples for rainy season was not strongly correlated ($r = -0.469$). This negative correlation indicated that as the level of iron in water was increasing, the levels in fish decreased. In comparing the levels of iron in water (4.807 mg L^{-1}) to fish samples (13.365 mg kg^{-1}) for rainy season, there were statistically significant differences ($p < 0.05$). The levels of iron in both seasons were significantly higher in fish than in water. The possible reason is that fish accumulate iron from water and sediments through ingestion of food particles and absorption through gills.

Contrary, there was a strong correction of iron levels in sediments and fish samples for the dry season ($r = 0.650$). This positive correlation indicated that as the levels of iron in sediments were increasing, so were the levels in fish. This may imply that fish relied much on detritus as feed. In comparing the concentration of iron in sediments (284.86 mg kg^{-1}) to fish (22.422 mg kg^{-1}) samples for dry season there were statistically significant differences ($p < 0.05$). Iron levels were significantly higher in sediments than in fish in the dry season.

Likewise, there was a strong negative correction of iron levels in sediments and fish samples for the rainy season ($r = -0.640$). This negative correlation indicated that as the levels of iron in sediments were increasing, the levels in fish decreased. The possible reason could be that fish relied on a wide range of feed than detritus. In comparing the concentration of iron in sediments to fish samples for rainy season there were statistically significant differences ($p < 0.05$). Iron levels were significantly higher in sediments than in fish in the rainy season. The possible reason is that iron elements may form part of the bed rock.

4.9 Relationship of heavy metal concentrations in water to other physicochemical parameters

4.9.1 Correlation of cadmium with physicochemical parameters in water

There was a strong negative correlation between cadmium and nitrate in water for the dry season ($r = -0.601$). This negative correlation indicated that as the levels of nitrates in water were increasing, the levels of cadmium decreased. The reason is that cadmium reacts with nitrates to produce nitrites (Margeson *et al*., 1980). Therefore, the levels of nitrates were reduced in the presence of cadmium.

Similarly, there was a strong correlation between cadmium and phosphate in water for the dry season ($r = 0.692$). This positive correlation indicated that as the levels of phosphates in water were increasing, so were the levels of cadmium. The reason is that phosphate rocks contain certain levels of cadmium. According to Roberts (2014) phosphorus fertilisers contain cadmium.

Likewise, a strong correlation existed between cadmium and pH in water for the dry season ($r = 0.618$). This positive correlation indicated that as the levels of pH in water were increasing, so were the levels of cadmium. The possible reason could be that some cadmium compound such as cadmium acetate reacts as bases.

On the contrary, cadmium and electrical conductivity in water for dry season were not strongly correlated (*r* = 0.192). Similarly, cadmium and total dissolved solids in water for dry season were not strongly correlated (*r* = 0.173). Also cadmium and temperature of water for dry season were not strongly correlated (*r* = -0.193).

4.9.2 Correlation of zinc with physicochemical parameters in water

There was a strong negative correlation between zinc and nitrates in water for the rainy season (*r* = -0.636). This negative correlation indicated that as the levels of nitrates in water were increasing, the levels of zinc decreased. Contrary, zinc and phosphates in water for rainy season were not strong correlated (*r* = 0.427). Similarly, zinc and pH in water for rainy season were not strong correlated (*r* = 0.090).

The analysis also revealed that zinc and electrical conductivity in water were also not strongly correlated (*r* = 0.214). Likewise, zinc and total dissolved solids in water were also not strongly correlated (*r* = 0.203). Equally, zinc and temperature in water were also not strongly correlated (*r* = 0.454).

4.9.3 Correlation of iron with physicochemical parameters in water

Pearson correlation showed that iron and nitrate in water for the dry season were not strongly correlated (*r* = -0.033). Also in the rainy season iron and nitrate in water were not strongly correlated (*r* = -0.370).

Similarly, iron and phosphates in water for the dry season were not strongly correlated (*r* = 0.079). Also in the rainy season iron and phosphates in water were also not strongly correlated (*r* = 0.308).

Likewise, iron and pH in water for the dry season were not strongly correlated (*r* = 0.330). Whereas in the rainy season iron and pH in water were also not strongly correlated (*r* = 0.089).

On the other hand, there was a strong correlation between iron and electrical conductivity in water for dry season (*r* = 0.746). While in the rainy season iron and electrical conductivity in water were not strongly correlated (*r* = 0.114).

Similarly, there was a strong correlation between iron and total dissolved solids in water for dry season (r = 0.675). This could possibly be as a result of metal accumulation in reduced volume of water since metals such as iron are the component of TDS in water. Whereas in the rainy season iron and total dissolved solids in water were not strongly correlated (r = 0.106).

On the other hand, iron and temperature of water for dry season were not strongly correlated (r = 0.116). Whereas in the rainy season iron and temperature in water were also not strongly correlated (r = 0.202).

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The study was intended to assess heavy metals in water, sediments and fish from Lake Chilwa in Zomba. This followed literature review that revealed the impacts of heavy metal pollution on environment. Also, studies done in surface waters of Zomba have shown heavy metal pollution. The overall objective of the study was to assess the levels of selected heavy metals in water, sediments and fish from Lake Chilwa in Zomba. Specifically: To determine the levels of selected physicochemical parameters (pH, EC, TDS, temperature, nitrates and phosphates) in water at Lake Chilwa; To determine the levels of Pb, Cd, Mn, Cu, Zn and Fe in water, sediments and fish in Lake Chilwa for dry and rainy season; and To compare the levels of the heavy metals (Pb, Cd, Mn, Cu, Zn and Fe) and physicochemical parameters (pH, EC, TDS, nitrates and phosphates) in dry and rainy season and also with standards.

The study revealed high pH levels in the dry season than rainy season. All the sampling sites had pH levels above the WHO and MBS limits for drinking water except Bonga in rainy season. Equally, there were higher temperatures in the dry season than the rainy season that was attributed to the weather during sampling. Similarly, there were higher EC in the dry season than rainy season except for Chaone sampling site. The EC of all sampling sites were above the WHO limits for drinking water in the rainy season except for Bonga. The possible reason could be the continuous flow of fresh water passing through Bonga which is an inlet into the Lake. Likewise, there were higher levels of total dissolved solids in water in the dry season than rainy season except for Chaone sampling site. The total dissolved solids of all sampling sites but Bonga in the rainy season were above the maximum level for drinking water as suggested by the WHO and Malawi Standards. In both seasons, all the sampling sites had nitrate levels below WHO drinking water standards. Phosphates were observed to be higher in the rainy season than the dry season. This could probably be as a result of fertilizers brought to the Lake by surface runoff.

The study also revealed that the concentration of Pb, Mn and Cu were undetectable in the waters of Lake Chilwa. The possible reason could be that the pH was slightly alkaline which might have an effect on the availability of dissolved metals in water as well as large volume of water. However, Cd and Zn were only detected at Kachulu in the dry and rainy season, respectively. Fe was the only metal that was found in water at all the sampling sites for both seasons. It was observed that Fe and Zn were above WHO drinking water standards but the rest of the metals were below. Further observation showed higher levels of heavy metals in water in the rainy season than dry season. The possible reason could be the churning effect of rain storms that led to the suspension of dissolved solids which constitutes heavy metals. Also during rainy season there was run-off which could potentially transport heavy metals from upland originating from fertilisers, burning fosil fuels and metal products.

Pb was also not detected in sediment samples. Generally, there was higher concentration of other heavy metals such as Mn, Cu, and Zn in the dry than rainy season except for iron which was the opposite. Cd was only detected in sediment samples at Kachulu in the rainy season. This could be an indicator of pollution activities at Kachulu harbour and the nearby settlements.

All heavy metals were detected in fish samples except Pb. Generally, the concentration of metals such as Mn, Cu and Zn were higher in the rainy season than dry season except for iron which was the opposite. Among the fish species that were sampled, *Clarias* species recorded higher levels of all the selected heavy metals except for Cd and Zn. The concentrations of heavy metals in fish were within the FAO/WHO limits of fish suitable for human consumption.

The study further revealed significant differences in metal concentration between dry season and rainy season. Mn, Cu and Zn in sediments were significantly higher ($p < 0.05$) in the dry season than rainy season. Conversely Fe in sediments was significantly higher ($p < 0.05$) in the rainy season than the dry season. The study also revealed strong correlations among water, sediments and fish in terms of the parameters studied. Nitrates, phosphates and pH were observed to have a strong correlation with Cd in water. Zn could only indicate a strong correlation with nitrates. Whereas EC and TDS were observed to strongly correlate with Fe. This could indicate that the presence of some heavy metals in water may be affected by other physicochemical parameters.

The study narrowed its coverage to the Zomba side of Lake Chilwa due to financial constraints. However, the general snapshot has indicated the presence of heavy metals in Lake Chilwa. Some metals (Pb, Mn, Cu) that were reported in streams of Zomba were not detected in water samples of Lake Chilwa possibly because of large volume of water. Results of this study indicated that the main sources of heavy metals in Lake Chilwa are the use of fertilizers, burning of fossil fuels and disposal of metal products as the higher levels were observed at sites near settlements where there were human activities. Heavy metals originating from these sources may contaminate the surface water resources nearby that could affect the health and livelihood of local population.

5.2 Recommendations

Based on the findings of this study, the following recommendations are therefore made:

- Bearing in mind the levels of heavy metals observed in sediments and fish in Lake Chilwa, it is recommended to have an integrated management plan that incorporate all stakeholders to help control pollution activities from the areas surrounding the lake.
- The presence of some heavy metals (e.g. cadmium in water at Kachulu) indicate a possibility of pollution from wastes, therefore, there is need for the city council to implement proper measures to reduce contamination of the lake by health hazardous chemicals. This may include removal of heavy metals in wastewater effluent which is released into Likangala River which eventually ends up in Lake Chilwa.
- Although the concentration of heavy metals in the fish were within the WHO/FAO limits, however there is a need for further evaluation of these contaminants in several fish species in the area.

5.2.1 Areas requiring further research

i. Further research should be done on planktons and earthworms at Lake Chilwa to determine the concentration of heavy metals.

ii. There is need to conduct a study that compares the levels of heavy metals in different species of fish in the lake. This is because due to time and financial constraints in this study, only three fish samples were assessed for heavy metals.

iii. There is need to conduct a similar study on the other sides of the Lake to have a clear picture of heavy metals in waters of Lake Chilwa i.e. Machinga and Phalombe.

REFERENCES

Abbasi, S. A., Abbasi, N., & Soni, R. (1998). *Heavy metals in the environment*. Delhi: Mittal Publications.

Abida, B., Harikrishna, S., Irfanulla, K., Ramaiah, M., Veena, K., & Vinutha, K. (2008). Analysis of flouride level in water and fish species of Sankey, Bellandur and Madi-vala lakes of Bangalore. Rasayan. *Journal of Chemistry*, 1 (3), 596-601.

Abulude, F. O., Obidiran, G. O., Elemide, O. A., & Abidakun, B. (2007). Trace metals distribution in Nigerian urban fishes. *Electronic Journal of Environment, Agriculture and Food Chemistry,* 6 (11), 2512-2516. Retrieved from http://www.ejeafche.uvigo.com

Adeleken, B., & Abegunde, K. (2011). Heavy metal contamination of soil and ground water at automobile mechanic village in Ibadan, Nigeria. *International Journal of the Physical Sciences*; 6: 1045 – 1058

Ademoroti, C. M. A. (1996), *Environmental chemistry and toxicology*. Ibadan: Fodulex press Ltd..

Adriano, D.C. (2001). *Trace elements in terrestrial environments biogeochemistry bioavailability and risk of metals*, (2nd edn). New-York: Springer-Verlag.

Alloway, B.J. (1995). The origin of heavy metals in soils. In *heavy metals in soils* (pp.38-57), (2nd Edn). London: Blackie Academic & professional, Chapman & Hall.

Almeida, J.A., Diniz, Y.S., Marques, S.F.G., Faine, L.A. Ribas, B.O., Burneiko, R.C., & Novelli, E.L.B. (2002). The use of oxidative stress responses as biomarkers in Nile tilapia (*Oriochromis niloticus*) exposed to in vivo cadmium contamination. *Environ. Int*. 27, 673-679

Anim – Gyampo, M., Kumi, M., & Zango, M.S.M. (2013). Heavy metals concentration in some selected fish species in tono irrigation reservior in Navorong. *Ghana J. Environ. Earth Sci.,* 3(1), 109-119

APHA (American Public Health Association). (1985). *Standard methods for the examination of water and wastewater*, (16th Edn), Washington DC, USA.

APHA, (2005). *Standard methods for the examination of water and wastewater*. (21^{st} Edn). Washington DC, USA: American Public Health Association, American Water Works Association (AWWA) & Water Environment Federation (WEF).

Aprile, F.M., & Bouvy, M. (2008). Distribution and enrichment of heavy metals in sediments at the Tapacurá river basin, northeastern Brazil. *Braz. J. Aquat. Sci. Technol*. 12(1), 1-8.

Akan, J.C., Abbagambo, M.T., Chellube, Z.M., & Abdulrahman, F.I. (2012). Assessment of pollutants in water and sediment samples in lake Chad, Baga, north eastern Nigeria. *Journal of Environmental Protection*. 3: 1428-1441 DOI:10.4236/jep.2012.311161 Published Online November 2012 (http://www.SciRP.org/journal/jep)

Al-Weher, M. (2008). Levels of heavy metal Cd, Cu and Zn in three fish species collected from the northern Jordan valley. *Jordan Journal of Biological Sciences*; 1: 41-46.

ATSDR (2002) *Toxicological profile for copper*. Atlanta, US: GA.

Bassett, M.L. (2001). Hemochromatosis: iron still matters. *Int. Med. J.* 31 (4), 237–242.

Belize, N., Chen, Y., Gunn, J., & Dixit, S. (2004) Sediment trace metal profiles in lakes of Killarney Park, Canada: from regional to continental influence. *Environmental Pollution* 130, 239-248

Binning, K., & Baird, D. (2001). Survey of heavy metals in sediments of Swartkops river Estuary Port Elizabeth South Africa. *Water* (27)4:261-466

Bishop, K.D. (1998). *Water quality and water toxicity*. Retrieved from http://www.toxicwatersolution.com/water-quality-and-water-toxicity/

Bose, B. & Hemantaranjan, A. (2005). *Developments in physiology, biochemistry and molecular biology of plants*. New Delhi, India: New India Publishing Agency.

Bradi, B.H. (2005). Heavy metals in the environment. *Interface Science and Technology,* (ed). Hubbard, A., 6. Neubrucke: Elsevier Academic Press.

Bradl, H.B. (2004). Adsorption of heavy metal ions on soils and soil constituents. *Journal of colloids and Interface sciences,* 277, 1-18.

Burgis, M.J., & Symoens, J. J. (Eds) (1987). *African wet lands shallow water bodies.* France: Institut français de recherche scientifique pour le développement en cooperation.

Calhoun, Y. (2005). *Water pollution.* New York, USA: Chelsea House Publishers.

Calkins, M. (2009). *Materials for sustainable sites: A complete guide to the evaluation.* Hoboken, New Jersey: John Wiley and Sons.

Canter W. (1985). *River water quality monitoring*. UK: Lewis Publishers.

Carolyn, S., Bentivegna, J.A., Sean, M. B., & Katarzyna, C. (2004). *Influence of sediment characteristics on heavy metal toxicity in an urban marsh department of biology*. South Orange: Seton Hall University.

CDFA. (2004). *Evaluation of heavy metals & dioxin in inorganic commercial fertilizers and california cropland soils, california department of food and agriculture*. Retrieved from https://www.cdfa.ca.gov/is/docs/MetalsReport12-23-04.pdf

Challa, S., & Kumar, R. (2009). *Nanostructured oxides*. Weinheim, Germany: Wiley.

Chapman, D. (1996). *Water quality assessments - A guide to use of biota, sediments and water in environmental monitoring,* (2nd Edn). London: UNEP

Chapman & Hall. (1992). *Water quality assessments: a guide to the use of biota, sediments and water in environmental monitoring.* London: UNESCO, WHO and UNEP.

Chidya, R.C.G., Masamba, W.R.L., Sajidu S.M.I., & Mwatseteza J.F. (2010). Evaluation and assessment of water quality in Likangala River and its catchment area. *Paper Presented at the 11th Waternet/WARFSA/GWP-SA Symposium*, Elephant Hills Hotel, Victoria Falls, Zimbabwe, 27th - 29th October.

Chidya, R.C.G., Sajidu, S.M.I., Mwatseteza, J.F., & Masamba, W.R.L. (2011). Evaluation and assessment of water quality in Likangala River and its catchment area, *Physics and Chemistry of the Earth*, 36, 865-871.

Chinyama, M.P.M., & Maldhopa, A. (1999). An assessment of municipal waste management in the city of Mzuzu, *Malawi. Malw.J.Sci and Techno,* 5, 40-49.

Chiodi, L.B., Escalante, A., Von Haeften, G., Moreno, V., & Gerpe, M. (2011). Assessment of heavy metals accumulation in two aquatic microphytes: a field study. *J. Braz. Soc. Ecotoxicol.,* 6 (1), 57-64. DOI: 10.5132/jbse.2011.01.009.

Cogun, H. Y., & Kargin, F. (2004) "Effects of pH on the Mortality and Accumulation of Copper in Tissues of *Oreochromis niloticus*," *Chemosphere*, 55 (2), 277-282. DOI:10.1016/j.chemosphere.2003.10.007.

Cunningham W.P., Cunningham M. & Saigo B.W. (2003); *Environmental Science: a global concern,* (7th Edn). New York :McGraw-Hill Higher Education.

Dadebo, E., Mohammed, A., & Sorsa, S. (2013). Food and feeding habits of the straightfin barb *Barbus paludinosus* (Peters, 1852) (Pisces: Cyprinidae) in Lake Ziway, Ethiopia. Ethiopian *Journal of Biological Sciences*. Retrieved March 12, 2017, from https://www.ajol.info/index.php/ejbs/article/view/115565

Damodharan, U. (2013). *Bioaccumulation of heavy metals in contaminated river water – Uppanar, Cuddalore South East Coast of India.* DOI:10.5772/5334.

Daly, M.C. (1986). *The intracratonic Irumide Belt of Zambia and its bearing on collision orogeny during the Proterozoic of Africa.* In: Coward MP and AC Ries (eds.) Collision Tectonics. Geol. Soc. Spec. Publ. 19, 321-328

Dauvalter, V.A. (1998), *Water Res.* 25, 451.

Davies, O. A., & Abowei, J. F. N. (2009). Sediment quality of lower reaches of Okpoka Creek, Niger Delta, Nigeria. *European Journal of Scientific Research.* 26(3), 437 – 442

De Freitas, J.M., & Meneghini, R. (2001). Iron and its sensitive balance in the cell. *Mutat. Res.* 475, (1-2), 153.

Demirak, A., Yilmaz, F., Tuna, A.L., & Ozdemir, N. (2005). Heavy metals in water, sediments and tissues of *Leuciscus cephalus* from a stream in Southwestern Turkey. *Chemosphere.* DOI; 10.1016/j. chemosphere. 2005.09.033

Denton, G.R.W., Wood, H.R., Concepcion, L.P., Siegrist, H.G., Eflin, V.S., Narcis, D. K., & Pangelinan, G.T. (1997). *Analysis of in-place contaminants in marine sediments from four* *harbor locations on Guam: A pilot study', water and environmental research institute of the western pacific, technical report no. 87*, Mangilao, Guam: University of Guam.

Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry (Subcontract No. ATSDR-205-1999-00024). Retrieved from https://www.atsdr.cdc.gov/

Dill, H., Ludwig, R.-R., Kathewera, A., & Mwenelupembe, J. (2005). A lithofacies terrain model for the Blantyre Region: implications for the interpretation of palae-osavanna depositional systems and for environmental geology and economic geology in southern Malawi. *J. Afr. Earth Sci.* 41, 341 – 393.

DRAE. (1994). *National environmental action plan*. Vol. 1: The Action plan, Vol. 2: Initial District Environmental Action suggestions. Retrieved from https://yandex.ru/images/search?text=DRAE.%20(1994).%20National%20environment.

Duruibe, J. O., Ogwuegbu, M.C., & Egwurugwu, J. N. (2007). Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences*, 2,112-118.

Eja, C.E., Ogri, O.R., & Arikpo, G.E. (2003). Bioconcentration of heavy metals in surface sediments from the Great Kwa river estuary, Calabar, Southeast Nigeria. *J. Nig. Environ. Soci*, 1: 247-256

Elliot, H.A., Liberati, M.R., & Huang, C.P. (1986). Competitive sorption of heavy metals by soils. *J. Environmental Quality*. 15 (3), 214 -218.

Environmental Protection Agency. (2004). *Drinking water health advisory for Mn*. Retrieved from http://www.epa.gov/safewater/

FAO (2006). *Country profile: Malawi. AQUASTAT Survey. Water report 29*. Retrieved 27.05.2016 from http://www.fao.org/ nr/water/aquastat/countries_regions/MWI/index.stm

Farhadinejad, T., Khakzad, A., Jafari, M., & Shoaee, Z. (2014). The study of environmental effects of chemical fertilizers and domestic sewage on water quality of Taft region, central Iran. *Arabian journal of geosciences,* 7, 221-229.

Fazio, F., Piccione, G., Tribulato, K., Ferrantelli, V., Giangrosso, G., Arfuso, F., & Faggio, C. (2014). Bioaccumulation of heavy metals in blood and tissue of striped mullet in two Italian Lakes. *J. Aquat. Anim. Health*, 26(4), 278-284.

Ferner, D.J. (2001). Toxicity, heavy metals. *eMed. J*. 2(5), 1.

Filep, G. (1999). *Soil chemistry: process and constituents*. Budapest, Hungary: Akademiai Kiado.

Food Agriculture Organization/World Health Organization (FAO/WHO). (1999). *Expert committee on food additives. summary and conclusions of the sixty-first meeting of the joint fao/who expert committee on food additives (JECFA).* Rome, 1-10 June. Page 15 of 22.

Garbarino, J. R. Hayes, H. Roth, D. Antweider, R. Brinton, T. I. and Taylor, H. (1995) *Contaminants in the Mississippi River, U. S.* Geological Survey Circular *1133*,Virginia, U.S.A. Retrieved from *www.pubs.usgs.gov/circ/circ1133/*

Garson, A. (1960). *The Geology of the Lake Chilwa Area*. Zomba, Malawi: Geological Survey Department

Garson, M.S. (1962). The Tundulu ring complex in southern Nyasaland. *Memoir Nyasaland Geol. Surv*. 2, 248.

Goel, P. (2009). *Water pollution*. New Delhi, India: New Age International.

Goksu, L.Z. (2003). *Water Pollution Lesson Book Cukurova University*, Adana: Faculty of Fisheries.

Golterman, H.L. (2004). *The chemistry of phosphate and nitrogen compounds in sediment*. Dordrecht/ Boston/London: Kluwer Academic Publishers.

Government of Malawi (GoM). (2000). *Lake Chilwa wetland state of the environment report*. Lilongwe, Malawi: Environmental Affairs Department.

Government of Malawi (2006). *Malawi growth and development strategy (MGDS). From poverty to prosperity 2006 - 2011*.

Government of Malawi. (2015). *Malawi 2015 post disaster needs assessment report*. *Global Facility for Disaster Reduction and Recovery*. Lilongwe: The World Bank, the United Nations and European Union.

Grieb, T. M., Driscoll, C. T., Gloss, S. P., Schofield, C. L., Bowie, G. L., & Porcella, D. B. (1990). Factors affecting mercury accumulation in fish in the upper Michigan peninsula, *Environmental Toxicology and Chemistry*, 9 (7), 919-930. DOI:10.1002/etc.5620090710

Gupta, A., Rai, D. K., Pandey, R. S., & Sharma, B. (2009). Analysis of some heavy metals in the riverine water, sediments and fish from river Ganges at Allahabad. *Environ. Moni. Assess.*157, 449-458.

Halliwell, B., & Gutteridge, T. M. (1999). *Free radicals in biology and medicine*. Oxford: Oxford University Press.

Harrison R.M. (1992). *Pollution, causes, effects and control*, (3rd Edn). UK: The Royal Society of Chemistry.

Hash, R.B., (2001). Hereditary hemochromatosis. *J. Am. Board Fam. Pract.*14 (4), 266–273.

Hashim, R., Song, T.H., Muslim, N.Z.M., & Yen, T.P. (2014). Determination of heavy metal levels in fishes from the lower reach of the Kelantan River, Kelantan, Malaysia. *Trop Life* Sci *Res*. 25(2), 21–39.

Health Canada. (2007). *Guidelines for Canadian drinking water quality: chemical and physical parameters.* Retrieved from: http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/doc_supappui/sum_guideres_recom/chemical-chimiques_e.htm1#4

Hochanadel, D. (2010). *Limited amount of total phosphorus actually feeds algae, study finds.* Lake Scientist. Retrieved from http://www.lakescientist.com/2010/limited-amount-of-total-phosphorus actually-feeds-algae-study-finds.

Horwitz, R.J., Ruppel, B., Wisniewski, S., Kiry, P., Hermanson, M., & Gilmour, C. (1995). Mercury Concentrations in Freshwater Fishes in New Jersey, *Water, Air, and Soil Pollution*, 80, (1-4), 885-888. DOI: 10.1007/BF01189739

ILEC (International Lake Environment Committee). (2011). *World lakes database; lake Chilwa.* Retrieved from http://www.ilec.or.jp/database/afr/afr-01.html on 2/01/16.

Iwashita, M., & Shimamura, T. (2003). Long-term variations in dissolved trace elements in the Sagami river and its tributaries (upstream area), Japan, *The Science of the Total Environment,* 312, 167–179.

Jackson, R.N., Baird, D., & Els, S. (2005). The effect of the heavy metals, lead (Pb2+) and zinc (Zn2+) on the brood and larval development of the burrowing crustacean *Callianasskraussi*. *Water S.A.,* 31(1), 107-116.

Jain, C. K., (2004). Metal fractionation study on bed sediments of River Yamuna, India. *Water Res.*, 38:569-578. DOI:10.1016/j.watres.2003.10.042.

Jamu, D., Chimphamba, J., & Brummett, R. (2003). Land use and cover changes in the Likangala catchment of Lake Chilwa basin, Malawi: implications for managing a tropical wetland. *Afr. J. Aquat. Sci.* 128, 119–132.

Jezierska, B., & Witeska, M. (2001). *Metal toxicity to fish*, Siedlce: Wydawnictwo Akademii Podlaskiej.

Jezierska, B., & Witeska, M. (2006). *The metal uptake and accumulation in fish living in polluted waters.* NATO Science Series. Netherlands: Springer.

Johnson, R.L., Holman, S., & Holmquist, D.D. (1999).*Water quality with CBL vernier software*, Oregon.

Kadewa, W. W., Henry, E. M., Masamba, W. R. M., & Kaunda, C. C., (2001). *Impact of sewage sludge application to horticulture: A case of the city of Blantyre.* In: proceedings of the first chancellor College Research dissemination conference, 291. Zomba, Malawi.

Kalk, M., McLachlan, A.J., & Howard-Williams, C. (1979). Lake Chilwa studies of change in a tropical ecosystem. *Monographae Biologicae,* 35, 17-227. The Hague, Boston, London: Dr. W. Junk Publishers.

Kaonga, C.C. (2007). Levels of selected heavy metals and related physico - chemical parameters of algae (*spirogyra aequinoctialis*), earthworms (*aporrectodea icteria*), soil and water in Blantyre city, Malawi. Unpublished Master of Science in Environmental Sciences, at Chancellor College, University of Malawi, Zomba.

Kishe, M. A., & Machiwa J. F. (2003). Distribution of heavy metals in sediments of Mwanza Gulf of Lake Victoria, Tanzania. *Environment International*, 28, 619– 625.

Kohl, P., & Medlar, S. (2007). *Occurrence of Mn in drinking water and Mn control*. New York, USA: IWA Publishing.

Krishna, P.V., Rao, K.M., Swaruparani, V., & Rao, D.S (2014). Heavy metal concentrations in Fish *Mugil cephalus* from Machilipatnam Coast and possiible health risks to fish consumers. *British Biotechnology Journal* 4(2): 126 –135.

Kumar, B., Mukherjee, D.P., Kumar, S., Mishra, M., Prakash, D., Sigh, S.K., & Sharma, C.S. (2011). Bioaccumulation of heavy metals in muscle tissue of fisheries from selected aquaculture ponds in east Kolkata etlands. *Annals of Biological Research*, 2(5), 125 –134.

Kumwenda, S., Tsakama, M., Kalulu, K., & Kambala, C. (2012). Determination of biological, physical and chemical pollutants in Mudi River, Blantyre, Malawi. *Journal of Basic and Applied Scientific Research*, 2 (7), 6833-6839.

Kwanjana, E.N. (2003). *Evaluation of sewage effluent use in horticulture: Zomba municipality wastewater treatment plant, Malawi*. (Unpublished Master of Science Thesis). University of Malawi, Zomba.

Lakudzala, D.D., Tembo, K.C., & Manda, I.K. (1999), An investigation of chemical pollutants in lower Shire river, Malawi, *Malawi Journal Of Science and Technology*, 5, University of Malawi.

Lalah, J.O., Ochieng, E. Z., & Wandiga, S.O. (2008).Sources of heavy metal input Into Winam Gulf, Kenya. *Bull. Environ. Contam. Toxicol*. 81, 277 –284.

Lew, K. (2008). *Understanding the elements of the periodic table: zinc*. New York, USA: Rosen Publishing Group.

Li, H., Shi, A., Li, M., & Zhang, X. (2013). Effect of pH, temperature, dissolved oxygen, and flow rate of overlying water on heavy metals release from storm sewer sediments. *Journal of Chemistry*. Hindawi Publishing Corporation, DOI: 10.1155/2013/434012s

Lutz, D. (2004); *Water Quality Studies - Red Rock Reservoirs*. USA: IOWA.

Macmillan Malawi (2001). *Senior secondary atlas*. Blantyre: Macmillan Malawi.

Malik, N., Biswas, A.K., Qureshi T.A., Borana K & Virha, R. (2010). Bioaccumulation of heavy metals in fish tissues of a freshwater lake of Bhopal. *Environ Monit. Assess.* 160: 267 – 267.

Mapoma, H.W.T, & Xie, X., (2014). Basement and alluvial aquifers of Malawi: an overview of groundwater quality and policies. *Afr. J. Environ. Sci. Technol*. 8, 190 – 202.

Masamba, W., & Mulwafu, W. (2008). *Water quality of the lake likangala and domasi river catchment areas, Malawi: Implication for domestic utilization,* BSCW: Chancellor College. Retrieved from http://www.bscw.ihe.nl/pub/bscw.cgi/d2607571/Masamba

Margeson, J.H., Suggs, J.C., and Midgett, M.R. (1980). Reduction of nitrate to nitrite with cadmium. *Anal. Chem.*, 52 (12), 1955–1957. DOI: 10.1021/ac50062a039

MBS (2005). *Drinking water – Specifications,* Malawian bureau of standards, MS214.

Mebrahtu, G., & Zebrabruk, S. (2011). Concentration of heavy metals in drinking water from urban areas of the Tigray Region, Northern Ethiopia. *Maejo international Journal of Science and Technology*. 3, 105-121.

Michael, P. (1986) *Ecological methods for field and laboratory investigations*. New Delhi: TATA McGraw-Hill Publishing Company Ltd.

Ministry of Energy and Mines of Malawi. (2009). *Mineral potential of Malawi*. BGS.

Ming-Ho, Y. (2005). *Environmental Toxicology: Biological and Health Effects of Pollutants,* (2nd Ed), Boca Raton, USA: CRC Press LLC.

Misra, S. & Mani, D. (2009). *Soil pollution.* New Delhi, India: S. B Nangia APH publishing corporation.

Monjerezi, M., & Ngongondo, C., (2012). Quality of groundwater resources in Chikhwawa, lower Shire valley. Malawi. *Water Qual. Exp. Health,* 4: 39-53.

Mumba, P. P., Chibambo, B. Q., & Kadewa, W. (2008). A comparison of the Levels of heavy metals in cabbages irrigated with reservoir and tap water. *Int. J. Environ. Res.*, 2 (1), 61-64, Mushatq, B., Raina, R., Yaseen, T., Wanganeo, A., & Yousuf, A.R. (2013). Variations in the physicochemical properties of Dal Lake, Srinagar, Kashmir. *African Journal of Environment Science and Technology,* 7 (7), 624 – 633.

Mutwiri, N. M. (2001). Determination of cadmium, chromium, lead and mercury in honey samples from Mbeere, Meru and Kirinyaga districts unpublished MSc Thesis Chemistry Department Egerton University Nakuru, Kenya.

Mwamburi, J. (2009). Trace metal concentration in water and sediments of satellite lakes within Lake Victoria (Kenya) basin. *Lakes and Reservoirs: Research and Management*. 14, 203-219.

Mwashote, B.M. (2003). Levels of cadmium and lead in water, sediments and selected fish species in Mombasa, Kenya. *Western Indian Ocean J. Mar. Sci.*, 2, (1), 25–34.

Nasr, S.M., Okbah, M.A., & Kasem, S.M (2006). Environmental assessment of heavy metal pollution in bottom sediments of Aden Port, Yemen. *International Journal of Oceans and Oceanography*. 1(1),99-109. Retrieved from http://www.ripublication.com/ijoo.htm.

NAS/IOM (National Academy of Sciences/Institute of Medicine). (2003). *Dietary reference intakes for Vitamin A, Vitamin K, arsenic, boron, chromium, copper, iodine, iron, manganese, molybdenum, nickel, silicon, vanadium, and zinc*. Washington, DC: Food and Nutrition Board, Institute of Medicine. Retrived from http://www.nap.edu/catalog/10026.html.

Narcis, D. K., & Pangelinan, G.T. (1997). *Analysis of in-place contaminants in marine sediments from four harbor locations on Guam: A pilot study. Water and environmental research institute of the western pacific, technical report no. 87*. Mangilao, Guam: University of Guam.

Nicolau, R., Galera – Cunha, A., & Lucas Y. (2006). Transfer of nutrients and labile metals from the continent to the sea by a small Mediterranean river. *Chemosphere*, 63, 469-476.

Njaya, F., Chiotha, S., & Kabwazi, H. (1996). *Lake Chilwa management plan*. In proc. of a workshop on the development of Lake Chilwa management plan. Lilongwe, Milawi: Government of Malawi.

Njaya, F. (2001). *Review of management measures for Lake Chilwa, Malawi. UNU – fisheries training programme*. Zomba, Malawi: Department of Fisheries.

Njaya, F., Snyder, K., Jamu, D., Wilson, J., Howard-Williams, C., Allison, E., & Andrew, N.L. (2011). The natural history and fisheries ecology of Lake Chilwa, southern Malawi. *J. Great Lakes Res.* 37(1), 15–25. DOI:10.1016/j.jglr.2010.09.008.

Nyasulu, T.H. (2010). Assessment of the quality of water in urban rivers -a case study of Lilongwe River in Malawi. Unpublished Master of Science in Integrated Water Resources Management of the University of Zimbabwe.

NSO. (2008). *Malawi housing and population census final report.* Zomba, Malawi: NSO.

Nussey, G., Vuren, V.J.H.J., & Preez, H.H. (2000). Bioaccumulation of chromium, manganese, nickel and lead in the tissues of the moggel, *(Labeoumbratus*) from Witbankdam. Mpumalanga. *Water S.A.*, 26 (2), 264-284.

Nzeve, J.K. (2015). A*ssessment of heavy metal contamination in masinga reservoir, kenya*. Unpublished Ph.D Thesis in Environmental Science, Department of Environmental Sciences, Kenyatta University, Kenya.

Ochieng, E. Z., Lalah, J.O., & Wandiga, S.O. (2007). Analyis of heavy metals in water and surface sediments in five Rift Valley lakes in Kenya for Assessment of recent increase in anthropogenic activities. *Bull. Environ. Contam. Toxicol.* 79, 570 -576.

Ochieng, E. Z., Lalah, J.O., & Wandiga, S.O (2008). Water quality and trace metal distribution in a Pristine lake in the lake Basin in Kenya. *Bull. Environ. Contam. Toxicol.* 80, 362 –366.

Olaifa, F.E., Olaifa, A.K., Adelaja, A.A., & Owolabi, A.G. (2004). Heavy metal contamination of *Clarias gariepinus* from a lake and fish farm in Ibadan, Nigeria. *Afric. J. of Biomed. Res.* 7: 145-148.

Olubunmi, F.E., & Olorunsola, O.E (2010). Evaluation of the status of heavy metal pollution of sediment of Agbabu bitumen deposit area, Nigeria. *European Journal of Scientific Research*, 41 (3), 373-382. Retrieved from http://www.eurojournals.com/ejsr.htm

Osman, A.G.M., & Kloas, W. (2010). Water quality and heavy metal monitoring in water, sediments and tissues of the African Catfish *Clarias gariepinus* (Burchell, 1822) from the River Nile, Egypt. *Journal of Environmental Protection*, 1, 389 – 400.

Osmond, D.L., Line, D.E., Gale, J.A., Gannon, R.W., Knott, C.B., Bartenhagen, K.A., Turner, M.H., Coffey, S.W., Spooner, J., Wells, J., Walker, J.C., Hargrove, L.L., Foster, M.A., Robillard, P.D., & Lehning, D.W. (1995). *Water, soil and hydro-environmental decision support system.* Retrived from http://www.water.ncsu.edu/watersheds/info /hmetals.hmtl.

Papafilippaki, A.K., Kotti, M.E., & Stavroulakis, G.G. (2008). Seasonal variations in dissolved heavy metals in the Keritis River, Chania, Greece. *Global NEST Journal*, 10 (3), 320-325.

Paponikolaou, G., & Pantopoulos, K. (2005). Iron metabolism and toxicity. *Toxicol. Appl. Pharmacol.* 202 (2), 199,

Pekey, H., Karakas, D., Ayberk, S., Tolun, L., & Bakoglu, M., (2004). Ecological risk assessment using trace elements from surface sediments of Ízmit Bay (Northeastern Marmara Sea) Turkey. *Marine Pollution Bulletin*, 48, 946–953.

Phillips, D.I. (2006). External influences on the fetus and their long-term consequences. *Lupus*. 15, 794.

Phippen, B., Horvath, C., Nordin, R., & Nagpal, N. (2008). *Ambient water quality guidelines for iron: overview.* British Columbia: Ministry of Environment Province.

Puchase, T., & Jamu, D. (2009). Determination of lead levels in farm-raised fish (*Oriochromis shrinus*) in Zomba district, Malawi. *Malawi j. aquac. fish,* 1, 2-5

Radulescu, C., Dulama, I.D., Stihi, C., Ionita, I., Chilian, A., Necula, C., & Chelarescu, E.D. (2014). Determination of heavy metal levels in water and therapeutic mud by atomic absorption spectrometry. Bucharest. *Rom. Journ. Phys.*, 59 (9–10),1057–1066.

Ratcliffe, C. (1971). The Fishery of the Lower Shire Area Malawi. *Fisheries Bulletin No. 3.* Government of Malawi, Ministry of Agriculture. Fisheries Department, Zomba. Lake Chilwa Wetland Project. 1999. Chilwa wetland basic information. DANIDA. 20 November, 2001 http://www.sdnp.org.mw/~chim/chilwa/basic_info.html

Ravera, R. C., Beone, G. M., Dantas, M., & Lodigiani, P. (2003). “Trace Element Concentrations in Freshwater Mussels and Macrophytes as Related to Those in Their Environment,” *Journal of Limnology*, Vol. 62, No. 1, pp. 61-70. DOI:10.4081/jlimnol.2003.61

Roberts, T.L. (2014) Cadmium and Phosphorous Fertilizers: The Issues and the Science. International Symposium on Innovation and Technology in the Phosphate Industry. *Procedia Engineering* 83 (2014) 52 – 59 1877-7058. Elsevier Ltd. DOI: 10.1016/j.proeng.2014.09.012.

SADC (2007). Technical report to inform and guide water resources policy and investments. Retrieved from http://www.sadc.int/files/7113/5293/3509/Regional_Water_Policy_Review_Reports

Saeed, S.M., & Shaker, I. M (2008). Assessment of heavy metals pollution in water and sediments and their effect on *Oreochromis niloticus* in the Northern delta Lakes, Egypt. *8th International Symposium on Tilapia in Aquaculture.*

Sajidu, S. M. I. (2008). *Characterisation and interaction of mixed alkaline clays and Moringa seeds with heavy metals in contaminated water.* Diss. Zomba: Chancellor College, University of Malawi.

Saka, J.D.K. (2006). A chemical study of surface and groundwater in the Lake Chilwa Basin, Malawi. In Y. Xu and B. Usher (Eds), *Groundwater Pollution in Africa* (pp. 229-238). AK Leiden, the Netherlands: Taylor and Francis/Balkema.

Saleh, Y.S., & Marie, M.A.S. (2014). Assessment of metal contamination in water, sediment, and tissues of *Arius thalassinus* fish from the Red Sea coast of Yemen and the potential human risk assessment. *Environ. Sci. Pollut. Res*., DOI: 10.1007/s11356-014-3780-0.

Schumann, K. (2001). Safety aspects of iron in food. *Ann. Nutr. Metab.* 45 (3), 91–101.

Selinus, O., & Alloway, B. (2005). *Essentials of medical geology: impact of the natural environment.* London, UK: Blackie Academic and Professional Publishers.

Simeonov, L., Kolhubovski, M., & Simeonov, B. (2010). *Environmental heavy metal pollution and effects on child mental development.* Dordrecht, Netherlands: Springer.

Sfakianakis, D.G., Renieri, E., Kentouri, M., & Tsatsakis, A.M. (2015). Effect of heavy metals on fish larvae deformities: A review. *Enviro. Res.*, 137, 246-255.

Shrivastav, R. (2001). *Atmospheric heavy metal pollution, development of chronological records and geological monitoring*. Retrieved from www.ias.ac.in.

Sparks, D.L. (2003). *Environmental Soil chemistry* (2nd Edn). San Diego: Academic Press.

Sterner, O. (2003). *Förgiftningar och miljöhot*. Lund: Studentlitteratur AB.

Szefer, P., Ali, A.A., Ba-Haroon, A.A., Rajeh, A.A., Geldon, J., & Nabrzyski, M. (1999). Distribution and relationships of selected trace metals in mollusks and associated sediments from the Gulf of Aden, Yemen, *Environmental Pollution*, 106, 299-314.

Tirkey A., Shrivastava, P., & Saxena, A. (2012). Bioaccumulation of heavy metals in different components of two Lakes ecosystem. *Current World Environment*, 7(2), 293-297

Taylan, Z.S., & Ozkoc, H.B., (2007). Bioavailibility of aquatic organisms in determination of potential heavy metal pollution. *Journal of BAU FBE*. 9, 17-33.

UNICEF. (2015). *Malawi cholera situation report. WHO update of Ministry of Health, Log of events surrounding cholera outbreak, Zomba District council 30th December, 2015*. Lilongwe: Epidemiology Unit.

Ullberg, M. (2015). *Temporal water quality of heavily human impacted Likangala River, Zomba,* .Malawi: Chancellor College, University of Malawi.

Uluturhan, E., & Kucuksezgin, F. (2007). Heavy metal contaminants in Red Pandora (*Pagellus erythrinus*) tissues from the Eastern Aegean Sea, Turkey. *Water Res*, 41, 1185-1192.

UN-Water. (2009). *World Water Day brochure*. Retrieved from http://www.unwater.org/worldwaterday/downloads/wwd09brochureenLOW.pdf.

UN World Summit. (2002). *World Summit on sustainable development*. Johannesburg, South Africa. Retrieved from http://www.johannesburgsummit.org

UN WWAP. (2003). *United Nations World Water Assessment Programme. The World Water Development Report 1: Water for People, Water for Life*. UNESCO: Paris, France. Retrieved from http://www.unesco.org/water/wwap/pccp/

United States Environmental Protection Agency. (2007). *The Water Sourcebooks: Grade Level 9 -12 Fact Sheets*. Retrieved from http://www.epa.gov/safewater/kids/wsb/index.html#about

U.S. Environmental Protection Agency. (1994a). *Watershed protection: TMDL Note #2 bioassessment and TMDLs.* Washington, D.C: U.S. Environmental Protection Agency, Office of Water.

US EPA (1999b). *Estimating risk from contaminants contained in agricultural fertilizers*. Office of Solid Waste, US Environmental Protection Agency, August 1999. Retrieved from http://www.epa.gov/epaoswer/hazwaste/recycle/fertiliz/risk/

US EPA. (2012). *Basic information about nitrate in drinking water, regulated drinking water contaminants, EPA 841-B-012-007*. Retrieved from http://water.epa.gov/drink/contaminants/basicinformation/nitrate.cfm

Valko, M.M.H.C.M., Morris, H., & Cronin M.T.D. (2005). Metals, toxicity and oxidative stress. *Curr Med Chem,* 12(10), 1161–1208.

Van Zegreen K., & Munyenyembe, M. P. (1998). *The Lake Chilwa environment, a report of the 1996 Ramsar site study.* Zomba, Malawi: Department of Biology, Chancellor College.

WDE (April, 1999). *Final report: screening survey of metals and dioxins in fertilizer products and soils in Washington State*. Washington: Washington Department of Ecology.

Weast, R.C. (1984). *CRC Handbook of chemistry and physics* (64th Edn). Boca Raton: CRC Press.

Wepener, V., Van Vuren, J. H. J., & Du Preez, H. H. (2001). Uptake and distribution of a Copper, Iron, and Zinc Mixture in Gill, Liver, and Plasma of a Fresh Water Teleost, *Tilapia sparmanii*: *Water SA,* 27 (1), 99 – 108.

Wetlands International. (2011). *Wetlands for water and life; Malawi - Lake Chilwa*. Retrieved from http://www.wetlands.org/reports/ris/1MW001en.pdf on 3/06/11.

WHO (2000). *Hazardous Chemicals in human and environmental health.* Geneva, Switzerland: World Health Organisation.

WHO (2003). *Guidelines for drinking water quality*. Geneva: World Health Organization.

WHO (2004). *Guidelines for drinking water quality* (3rd Edn). Geneva: World Health Organization.

WHO (2007). *pH in drinking-water. Background document for preparation of WHO Guidelines for drinking-water quality*. Geneva: World Health Organization (WHO/SDE/WSH/07.01/1)

WHO. (2008). *Guidelines for drinking water quality*. Geneva: World Health Organization.

WHO. (2011), *Guidelines for drinking water quality*. (4th Edn). Geneva: World Health Organization.

WSDH (1997). *Preliminary screening survey for metals and dioxins in fertilizers, soil amendments, and soils in Washington State*. Washington DC: Washington State Department of Ecology.

WSDH (1998a). *Screening survey for metals in fertilizers and industrial by-product fertilizers in Washington State*. Washington DC: Washington State Department of Ecology.

WSDA (2007). *Summary of metals analyses of fertilizer products conducted by the Washington state department of agriculture*. Washington DC: Washington State Department of Ecology.

Yang, H. N., & Chen, H. C. (1996). Uptake and elimination of cadmium by Japanese Eel, *Anguilla japonica*, at various temperatures, *bulletin of environmental contamination and toxicology*, 56 (4), 670-676. DOI:10.1007/s001289900098

Yang, J.E., Skogley, E.O., Schaff, B.E., & Kim, J.J. (1998). A simple spectrophotometric determination of nitrate in water, resin, and soil extracts. *Soil Science Society of America Journal,* 62, 1108-1115.

Yang, Y., Paterson, E., & Campbell, C. (2001). Accumulation of heavy metals in urban soils and impacts on microorganisms. *Huan Jing Ke Xue,* 22 (3), 44–48.

Zaki, M.S., Authman, M.M.N., Hammam, A.M.M., & Shalaby, S.I. (2014). Aquatic environmental pollution in the Egyptian countryside and its effect on fish production (Review). *Life Sci J,* 11, 1024-1029.

Zegeren, K., & Munyenyembe, M., (1998). *The Lake Chilwa environment. A report of the 1996 Ramsar site study.* Zomba: Chancellor College Publications.

Zheng, W., Aschner, M., & Ghersi-egea, J.F. (2003**).** Brain barrier systems: a new frontier in metal neurotoxicological research. *Toxicol. Appl. Pharmacol.* 192 (1), 1.

Zaghloul, K.H., Omar, W.A., & Abo-Hegab, S. (2005). Environmental hazard risk assessment on Oreochromis niloticus and Tilapia zilli fish. *J. Egypt. Ger. Soc. Zool.*, 46(A), 105- 139.

APPENDICES

Appendix 1: ANOVA Table

Table 1: ANOVA for physicochemical parameter

ANOVA

		Sum of Squares	Df	Mean Square	F	Sig.
pH in dry season	Between Groups	2.140	4	.535	227.312	.000
	Within Groups	.024	10	.002		
	Total	2.163	14			
EC in dry season	Between Groups	93198.267	4	23299.567	13979.740	.000
	Within Groups	16.667	10	1.667		
	Total	93214.933	14			
TDS in dry season	Between Groups	76911.067	4	19227.767	5546.471	.000
	Within Groups	34.667	10	3.467		
	Total	76945.733	14			
Temperature in dry season	Between Groups	6.543	4	1.636	245.350	.000
	Within Groups	.067	10	.007		
	Total	6.609	14			
pH in rainy season	Between Groups	11.666	4	2.917	87497.300	.000
	Within Groups	.000	10	.000		
	Total	11.667	14			
EC in rainy season	Between Groups	13357645.776	4	3339411.444	5004113.053	.000
	Within Groups	6.673	10	.667		
	Total	13357652.449	14			
TDS in rainy season	Between Groups	7267160.933	4	1816790.233	4541445.748	.000
	Within Groups	4.000	10	.400		
	Total	7267164.934	14			
Temperature in rainy season	Between Groups	8.643	4	2.161	249.308	.000
	Within Groups	.087	10	.009		
	Total	8.729	14			

Appendix 2: Paired T - test tables

Table 1: Comparison of heavy metals in water between dry and rainy season

		Paired Differences					T	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 2	Cadmium in water dry season - Cadmium in water rainy season	.000000	.001309	.000338	-.000725	.000725	.000	14	1.000
Pair 5	Zinc in water dry season - Zinc in water rainy season	-.461600	.955603	.246736	-.990795	.067595	-1.871	14	.082
Pair 6	Iron in water dry season - Iron in water rainy season	-.926333	3.045889	.786445	-2.613090	.760424	-1.178	14	.258
Pair 7	Nitrate in water dry season - Nitrate in water rainy season	-1.952933	3.061738	.790537	-3.648468	-.257399	-2.470	14	.027
Pair 8	Phosphate in water dry season - Phosphate in water rainy season	-.667200	.417598	.107823	-.898458	-.435942	-6.188	14	.000

Table 2: Comparison of heavy metals in sediments between dry and rainy season

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 3	Manganese in sediments dry season - Manganese in sediments rainy season	0.660667	2.05464	0.530506	-0.477155	1.798488	1.245	14	0.233
Pair 4	Copper in sediments dry season - Copper in sediments rainy season	0.2494	0.372218	0.096106	0.043273	0.455527	2.595	14	0.021
Pair 5	Zinc in sediments dry season - Zinc in sediments rainy season	0.587733	0.93444	0.241271	0.070258	1.105209	2.436	14	0.029
Pair 6	Iron in sediments dry season - Iron in sediments rainy season	-61.852	28.040232	7.239957	-77.380163	-46.323837	-8.543	14	0

Table 3: Comparison of heavy metals in fish between dry and rainy season

Paired Samples Test

		Paired Differences					T	Df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 2	Cadmium in fish dry season - Cadmium in fish rainy season	-.004333	.001581	.000527	-.005549	-.003118	-8.222	8	.000
Pair 3	Manganese in fish dry season - Manganese in fish rainy season	-.240444	.387926	.129309	-.538631	.057742	-1.859	8	.100
Pair 4	Copper in fish dry season - Copper in fish rainy season	-.305444	.163648	.054549	-.431236	-.179653	-5.599	8	.001
Pair 5	Zinc in fish dry season - Zinc in fish rainy season	-.976111	1.418475	.472825	-2.066448	.114226	-2.064	8	.073
Pair 6	Iron in fish dry season - Iron in fish rainy season	9.066333	10.363235	3.454412	1.100445	17.032221	2.625	8	.030

Table 4: Comparison of heavy metals in water, sediments and fish for both seasons

Paired Samples Test									
		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Cadmium in water rainy season - Cadmium in fish rainy season	-0.00433	0.001581	0.000527	-0.00555	-0.00312	-8.222	8	0
Pair 2	Zinc in water rainy season - Zinc in sediments rainy season	-0.15133	1.374806	0.354973	-0.91268	0.610009	-0.426	14	0.676
Pair 3	Zinc in water rainy season - Zinc in fish rainy season	-3.07489	1.373384	0.457795	-4.13057	-2.01921	-6.717	8	0
Pair 4	Zinc in sediments rainy season - Zinc in fish rainy season	-2.41533	1.914006	0.638002	-3.88657	-0.9441	-3.786	8	0.005
Pair 5	Zinc in sediments dry season - Zinc in fish dry season	-0.57822	0.356018	0.118673	-0.85188	-0.30456	-4.872	8	0.001
Pair 6	Manganese in sediments dry season - Manganese in fish dry season	7.396556	2.093272	0.697757	5.787525	9.005587	10.6	8	0
Pair 7	Manganese in sediments rainy season - Manganese in fish rainy season	7.414	4.030388	1.343463	4.31597	10.51203	5.519	8	0.001
Pair 8	Copper in sediments dry season - Copper in fish dry season	0.418778	0.339486	0.113162	0.157826	0.679729	3.701	8	0.006
Pair 9	Copper in sediments rainy season - Copper in fish rainy season	-0.17178	0.665925	0.221975	-0.68365	0.340098	-0.774	8	0.461
Pair 10	Iron in water dry season - Iron in sediments dry season	-280.99	89.76502	23.17723	-330.7	-231.28	-12.124	14	0
Pair 11	Iron in water dry season - Iron in fish dry season	-20.0804	8.35483	2.784943	-26.5025	-13.6584	-7.21	8	0
Pair 12	Iron in sediments dry season - Iron in fish dry season	321.7558	43.95389	14.6513	287.9698	355.5417	21.961	8	0
Pair 13	Iron in water rainy season - Iron in sediments rainy season	-341.916	74.60556	19.26307	-383.231	-300.601	-17.75	14	0
Pair 14	Iron in water rainy season - Iron in fish rainy season	-8.76856	4.437379	1.479126	-12.1794	-5.35768	-5.928	8	0
Pair 15	Iron in sediments rainy season - Iron in fish rainy season	384.5414	38.83007	12.94336	354.694	414.3889	29.71	8	0

Appendix 3: Pearson Correlations

Table 1: Relationships between cadmium and physicochemical parameters in water

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	Cadmium in water dry season & Nitrate in water dry season	15	-.601	.018
Pair 2	Cadmium in water dry season & Phosphate in water dry season	15	.692	.004
Pair 3	Cadmium in water dry season & pH in water dry season	15	.618	.014
Pair 4	Cadmium in water dry season & EC in water dry season	15	.192	.492
Pair 5	Cadmium in water dry season & TDS in water dry season	15	.173	.539
Pair 6	Cadmium in water dry season & Temperature of water dry season	15	-.193	.491
Pair 7	Cadmium in water rainy season & Nitrate in water rainy season	15	-.636	.011
Pair 8	Cadmium in water rainy season & Phosphate in water rainy season	15	.427	.112
Pair 9	Cadmium in water rainy season & pH in water rainy season	15	.090	.750
Pair 10	Cadmium in water rainy season & EC in water rainy season	15	.214	.443
Pair 11	Cadmium in water rainy season & TDS in water rainy season	15	.203	.468
Pair 12	Cadmium in water rainy season & Temperature of water rainy season	15	.454	.089

Table 2: Relationships between zinc and physicochemical parameters in water

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	Zinc in water rainy season & Nitrate in water rainy season	15	-.636	.011
Pair 2	Zinc in water rainy season & Phosphate in water rainy season	15	.427	.112
Pair 3	Zinc in water rainy season & pH in water rainy season	15	.090	.750
Pair 4	Zinc in water rainy season & EC in water rainy season	15	.214	.443
Pair 5	Zinc in water rainy season & TDS in water rainy season	15	.203	.468
Pair 6	Zinc in water rainy season & Temperature of water rainy season	15	.454	.089

Table 3: Relationships between iron and physicochemical parameters in water in dry and rainy season

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	Iron in water dry season & Nitrate in water dry season	15	-.033	.907
Pair 2	Iron in water dry season & Phosphate in water dry season	15	.079	.780
Pair 3	Iron in water dry season & pH in water dry season	15	.330	.230
Pair 4	Iron in water dry season & EC in water dry season	15	.746	.001
Pair 5	Iron in water dry season & TDS in water dry season	15	.675	.006
Pair 6	Iron in water dry season & Temperature of water dry season	15	.116	.681
Pair 7	Iron in water rainy season & Nitrate in water rainy season	15	-.370	.175
Pair 8	Iron in water rainy season & Phosphate in water rainy season	15	.308	.264
Pair 9	Iron in water rainy season & pH in water rainy season	15	.089	.753
Pair 10	Iron in water rainy season & EC in water rainy season	15	.114	.687
Pair 11	Iron in water rainy season & TDS in water rainy season	15	.106	.708
Pair 12	Iron in water rainy season & Temperature of water rainy season	15	.202	.470

Table 4: Relationships of heavy metals in water, sediments and fish

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	Cadmium in water rainy season & Cadmium in fish rainy season	9	.	.
Pair 2	Zinc in water rainy season & Zinc in sediments rainy season	15	-.521	.046
Pair 3	Zinc in water rainy season & Zinc in fish rainy season	9	.	.
Pair 4	Zinc in sediments rainy season & Zinc in fish rainy season	9	-.760	.017
Pair 5	Zinc in sediments dry season & Zinc in fish dry season	9	-.046	.906
Pair 6	Manganese in sediments dry season & Manganese in fish dry season	9	-.998	.000
Pair 7	Manganese in sediments rainy season & Manganese in fish rainy season	9	-1.000	.000
Pair 8	Copper in sediments dry season & Copper in fish dry season	9	-.372	.324
Pair 9	Copper in sediments rainy season & Copper in fish rainy season	9	.929	.000
Pair 10	Iron in water dry season & Iron in sediments dry season	15	-.794	.000
Pair 11	Iron in water dry season & Iron in fish dry season	9	-.614	.078
Pair 12	Iron in sediments dry season & Iron in fish dry season	9	.650	.058
Pair 13	Iron in water rainy season & Iron in sediments rainy season	15	-.054	.848
Pair 14	Iron in water rainy season & Iron in fish rainy season	9	-.449	.225
Pair 15	Iron in sediments rainy season & Iron in fish rainy season	9	-.640	.064

Appendix 4: Pictures for the research study

Photo: 1 *Barbus paludinosus* on drying rack

Photo: 2 Blender, mortar and pestle for grinding

Photo: 3 Pretesting EC and pH meters

Photo: 4 Lab analysis in process

Photo: 5. heating in fume hood chamber

Photo: 6 Sample filtrate

Photo: 7 cooling in a desiccator

Photo: 8 Filtration in labeled bottles