UNIVERSITY OF GHANA

COLLEGE OF BASIC AND APPLIED SCIENCES

ASSESSMENT OF THE LEVELS OF HEAVY METALS IN SEDIMENTS, WATER AND FISH FROM THE WEIJA DAM

BY

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THIS THESIS IS SUBMITTED TO THE UNIVERSITY OF GHANA,
LEGON IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE
AWARD OF MPHIL CHEMISTRY DEGREE

JULY, 2015

DECLARATION

It is hereby declared that this thesis is the outcome of research work undertaken by David Edem Dinku and that it has neither in part nor in whole been presented for another degree in this University or elsewhere except for references to works of other researchers which have been duly acknowledged.

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DEDICATION

I dedicate this work to the Almighty God and the entire Dinku family.

ACKNOWLEDGEMENT

I acknowledge with profound gratitude my supervisors, Prof. Vincent K. Nartey and Dr. Raphael K. Klake for their invaluable contributions throughout the work.

I also acknowledge the tremendous help given me by the lecturers of the Chemistry Department who did not only share their knowledge with me but also provided or directed me to very useful resource persons and materials.

Finally, I would like to appreciate Ms. Mercy Tindana and my colleagues in the Chemistry department for their immense contributions to my research. God bless you all.

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LIST OF ABBREVIATIONS

EC	Electrical Conductivity
UNEP	United Nation Environmental Programme
USEPA	United State Environmental Protection Agency
ANOVA	Analysis of Variance
APHA	American Public Health Association
AWWA	American Water Works Association
TDS	Total Dissolved Solid
DO	Dissolved oxygen
USGS	United States Geological Services
EPA	Environmental Protection Agency
T. Hardness	Total Hardness
Co. V	Co-efficient of Variation
WHO	World Health Organization
UV	Ultraviolet
HCl	Hydrochloric acid

ABSTRACT

This study was conducted to assess the levels of heavy metal contaminations within the Weija dam area of the Weija Lake. Sediments, water and fish samples were taken from ten different sites within the Weija dam in March, 2014 (dry season) and August, 2014 (wet season). The sediment, water and fish samples were analysed for Hg, Se, Fe, Cd, Mn and Pb using Atomic Absorption spectroscopy (AAS). Mercury was determined using a cold vapour technique with the AAS equipped with hydride generator (CV-ASS). Selenium was also determined by hydride generation atomic absorption spectrometry (HG-AAS). Water samples were analysed for pollution indicators using Standard Methods from the American Public Health Association (APHA) manual. Physicochemical parameters such as temperature, pH, conductivity, hardness and nutrients were all below WHO maximum permissible limits. The results of this study indicated that there were significant differences in concentrations of the physicochemical parameters between the two seasons. The Coefficients of Variation for physicochemical parameters were all below 50% for both seasons. Nutrient concentrations were also below the WHO maximum permissible limits. Total mercury (T-Hg) levels were below detection limit in sediments and water samples for the ten sites investigated, in both dry and wet seasons. However, all samples of the fish species studied showed mean T-Hg concentrations below the World Health Organization (WHO/FAO) limit of 0.5 mg/kg wet weight. The mean concentration of other heavy metals in the water were 0.155 mg/L (Fe), 0.021 mg/L (Cd), 0.031 mg/L (Mn) and 0.010 mg/L (Pb). Levels of all trace metals were below the WHO guideline values for drinking water. Apart from Hg and Se, the levels (mg/kg) of other metals in the sediment were higher than that of water and fish species. The results from this study therefore showed that the water in the Weija dam is relatively clean with regards to measured heavy metals.

CHAPTER ONE

1. Introduction

1.1 Background

Pollution of aquatic environments by heavy metals has been identified as a serious contamination problem (Larsson *et al.*, 1985; Mance, 1987; Langston, 1990; Yousafzai and Shakoori, 2008), not only because of the threat to water supplies to the public, but also causing damage to the aquatic life (Corbett, 1977; Mance, 1987; Leland *et al.*, 1978, Canli, 1998; Nasreen *et al.*, 1995; Jan *et al.*, 2002), which in turn, become unsafe for humans consumption (Karadede *et al.*, 2004; Mendil and Uluozlu, 2007).

Heavy metals in trace amounts are usually present in fresh waters due to the weathering of rocks and soils (Muwanga, 1997; Anderson, 2003; Babel and Opiso, 2007; Samarghandi *et al.*, 2007; Igwe *et al.*, 2008; Al-Juboury, 2009). The main sources of trace metal pollution in aquatic ecosystems are natural sources and anthropogenic activities. These trace metals are continuously added into aquatic systems, causing a serious threat to aquatic life due to their toxic nature (Dutton *et al.*, 1988, Bowlby *et al.*,1988, Bhuvaneshwari *et al.*, 2012). Moreover, they do not only affect the ecosystems, but also human life through bioaccumulation and bioaugmentation in the food chain as well as their non-biodegradable nature in ecosystems (Sastry, 1982; Puel *et al.*, 1987, Eisler, 1988; USEPA, 1991; Yousafzai and Shakoori, 2008). Trace metals are deposited, assimilated or incorporated in water, sediments and in aquatic organisms since they cannot be degraded (Abdel-Baki *et al.*, 2011).

According to Guy and Kean (1980), trace metals in the aquatic system occur in sediments, suspended particulates, hydrous oxides and humic colloids. Many of these trace metals are toxic even at very low concentrations (Volesky, 1990; Alkorta *et al*., 2004) and generally occur in low concentrations in water and attain appreciable concentrations in sediments (Naminga and Wilhelm, 1976).

Loizidou *et al*., (1992), reported that the contamination of sediments by trace metals and other pollutants is one of the major threats to aquatic ecosystems and leads to serious environmental problems. Sediments act as substrates for most aquatic organisms; therefore they are important sinks and reservoirs for a variety of environmental substances such as nutrients and trace metals (Baldwin and Howitt, 2007). Trace metals once absorbed in the sediments are not freely available for aquatic organisms. These toxic metals are released back to the aqueous phase under changing environmental conditions including temperature, pH, redox potential of the overlying water (Soares *et al*., 1999).

Aquatic sediments absorb persistent and toxic chemicals to concentrations many times higher than the level of the water column; hence they can incorporate and accumulate many metals to be added to a body of natural water (Milenkovic *et al*., 2005).

Sediments play an important role in the remobilization of pollutants in aquatic environments under conditions which are favourable and are therefore used for monitoring the health of aquatic ecosystems (Sigh *et al*., 1997; Abraha *et al*., 2012). They act as both carrier and sources of pollutants in aquatic ecosystem (Shuhaimi, 2008). Sinclair *et al*., (1989) reported that water quality studies have always focused on point source pollution with much attention being paid to dissolved pollutants. However, the sediments and suspended load can be more significant in transportation of contaminants and nutrients than the dissolved load (Shear and Watson, 1977; Cullen *et al*., 1979; Allen, 1986).

Fish is considered as one of the indicative factors for the estimation of metal pollution in the aquatic ecosystems (Amaraneni, 2006; Yang *et al*., 2007; Yousafzai *et al*., 2010). Fish has also been identified as good bio-accumulators of organic and inorganic contaminants since they are a major component of most aquatic ecosystem (King and Jonathan, 2003). Karadede *et al*., (2004) report indicates that metals have the tendency to accumulate in various organs of the aquatic organisms, particularly in fish, which in turn can enter into the human metabolism through the consumption of fish causing serious health problems (Puel *et al*., 1987; USEPA, 1991). Metals are accumulated in the tissues of fish through absorption and humans can be exposed to these metals through the food web. This can cause acute and chronic effects in humans (Nord *et al.*, 2004). The use of fish as a bio-indicator can determine the actual situation of the contamination level before and during monitoring (Rashed, 2001).

1.2 Problem statement

The monitoring and assessment of water pollution has become a very important area of study because of the direct implications of water contamination on the aquatic life, as well as on human beings. The pollution of surface water by heavy metals is a serious environmental problem as some of the metals such as Hg and Pb are toxic even at low levels and are non-degradable. Although metals such as Fe, Cu and Zn are essential micronutrients, they may be detrimental to the physiology of the living organisms at higher levels (Kar *et al.,* 2008; Nair *et al*., 2010).

The Weija dam plays an important role in the livelihood of the population of the Accra metropolis and its environs. It provides water to the western parts of Accra, supports irrigation projects, as well as fisheries; however, the water is variable in quality due to contamination

(DFID, 1999). The dam has been subjected to various forms of degradation due to pollution arising from stone quarrying, dumping of domestic wastes, industrial effluents, as well as agricultural run offs (Asante *et al.*, 2005). Among these pollutants, metals are of particular concern, due to their potential toxic effect and ability to bioaccumulation in aquatic ecosystems (Miller *et al.*, 1993; Censi *et al*., 2006). Hence, it has public interest (Gibbs, 1972; Niemi *et al.*, 1990). The use of fertilizers during farming within a dam's catchment is a potential source of heavy metals discharged into the water bodies. As a result of the rate and extent of anthropogenic activities impacting on the water quality of the dam, it is imperative to assess the quality of the water from the dam to ascertain the level of pollution.

1.3 Justification

Evaluation and assessment of water quality in reservoirs is essential because reservoirs are often one of the main sources of water for human consumption and irrigation. It is therefore necessary to assess the quality of water from the Weija dam to determine the levels of contaminants of various pollutants in the dam. This will in turn provide appropriate solutions to problems that may arise as a result of pollution within the dam which may impact on humans that depend on the dam. The dam is vital in the supply of water (91,000 m^3/day) to about 340,000 people in western Accra (Ghana Water Sewerage Company, 2003) and to its growing environs. The functions of the catchment are being impaired as a result of high population growth associated with its increased human activities since the 54.32 km^2 restricted zone demarcated under the Executive Instrument 130 of 1977 for the Weija Lake has been seriously encroached upon according to the recent government committee report (Akuffo, 2003). Sediments of a dam can act as a sink for Pollutants such as metals of anthropogenic origin transported by rivers and by atmospheric precipitation are accumulated in the sediments of a dam (Sigg, 1985). In the sediments, heavy metals are accumulated in different forms which affect their recycling between solution and sediment.

Heavy metals accumulated in an aquatic ecosystem has direct effects on man and the ecosystem. Toxicity is the most important problem associated with trace metals in the environment aside its accumulation through the food chain and its persistence in nature (King and Jonathan, 2003; Dimari *et al*., 2008. Several studies have showed enhanced concentration of essential and non-essential trace metal load in muscle and liver tissues of fish (Obasohan, 2007; Adeniyi *et al*., 2008). It is important to always determine the bioaccumulation capacity of heavy metals in organisms especially the edible ones in order to assess potential risk to human health (Otitoloju, 2002). Fish also act as bio-indicators of trace metal concentrations in such ecosystems, and could be used to evaluate the health of such aquatic ecosystems.

1.4 Objectives of the study

The main objective of this study is to determine the levels of mercury and selenium in water, fish and sediments and how these elements affect each other if present.

Specifically, the study seeks to:

- Determine the concentration of mercury (Hg), selenium (Se), cadmium (Cd), lead (Pb), iron (Fe) and manganese (Mn) in the environmental compartments; water, sediment and fish.
- Assess the relationship between Hg and Se on certain physico-chemical parameters like pH in the study area.

- Determine physicochemical parameters such as pH, electrical conductivity, total dissolved solids, total hardness, phosphate, chloride and nitrate levels of water from the Weija dam.

CHAPTER TWO

2. Literature review

2.1 Importance of dams

Dams, which are man-made lakes, are vital aquatic ecosystems that serve important environmental and economic purposes, including a potable water supply, hydroelectric power generation, irrigation for agriculture and fisheries (Asante *et al*., 2005; Smith, 2006). According to ICOLD (1998), 48% of the world's dams are used for irrigation, and 20% for hydropower generation. The rest are mainly for flood control, domestic and industrial water supply, and recreation. The health of a community is also influenced by safe water and sanitation through a potable water supply, safe food preparation, hygiene and improved nutrition (van der Hoeck, 2001).

Water supply dams (including Weija Dam) in several parts of Ghana ensure adequate and sustainable sources of raw water throughout the year for treatment to provide potable water to major cities and towns as well as for agricultural purposes (Asante *et al.*, 2013). According to DFID (1999), fresh water obtained directly from these dams to satisfy the needs of rapidly growing urban populations are in quality due to pollution.

2.2 Pollution of dam and water quality

Water pollution is usually defined as any physical, chemical or biological change in water quality which adversely impacts on living organisms in the environment or which makes a water resource unsuitable for one or more of its beneficial uses (UNEP/WHO, 1988).

Pollution could come from natural processes such as weathering and soil erosion. However, contamination of water quality is either directly (point source pollution) where the source of pollution is known, or indirectly (non-point source), where the source of pollution is diverse and diffuse and the result of human activities (Dix, 1981). GESAMP (1988), also states that pollution of the aquatic environment occurs when humans introduce, either by direct discharge to water or indirectly (for example through atmospheric pollution or water management practices), substances or energy that result in deleterious effects such as hazards to human health, harm to living resources, hindrance to aquatic activities such as fishing, impairment of water quality with respect to its use in agriculture, industry or other economic activities, or the reduction of amenity value. Direct contamination from agricultural chemical contamination of water sources in Seke, Zimbabwe, has been reported by Hussein *et al.*, (2000). Mandizha (1995), also reports indirect contamination through discharge from dip tanks into nearby water bodies, which raises the potential danger posed to aquatic ecosystems. Pathogenic organisms, oxygen demanding organic substances, plant nutrients that stimulate algal blooms, inorganic and organic toxic substances are the common types of pollutants (Cornish and Mensah, 1999). According to Qadir *et al.*, (2008), contamination of water quality affects the health of aquatic organisms and human beings.

2.3 Water quality indicators

2.3.1 Temperature

Temperature changes largely affect the chemical characteristics of water. Chemical and biological reaction rates, mineral solubility, and growth of aquatic organisms can be increased due to increased temperatures in water bodies (Ellis *et al.*, 1989). Tchobanoglous (1985) states that gas solubility and respiration rates are also decreased as a result of higher temperatures. Water temperature changes are due to seasonal variations and daily temperature changes with air temperature (UNEP/GEMS, 2006). Seasonal variations are slower processes, especially in larger water bodies where the deeper water experiences little change in temperature due to ground insulation (Spellman and Drinan, 2000). Rise in temperature during the dry season lowers the dissolved oxygen solubility or amount of oxygen that the water can hold even though the rate at which atmospheric oxygen is able to re-dissolve into de-oxygenated water increases (Ellis *et al.*, 1989).

2.3.2 pH

The acidic or basic characteristics of a water body are described by pH (APHA, 1998). pH indicates the concentration of free hydrogen ions in drinking water and is affected by acid rain, surrounding rock formations, and certain wastewater discharges. A dam's general state can be estimated by pH (Tilman *et al.*, 1982). Biological availability and solubility of elements in water are affected by pH of the water (WOW, 2004; Chapman, 1996).

Freshwater aquatic species survive within a pH range of 6.5 to 8.5; although, they may thrive slightly outside this range as well (Wilber, 1969).

According to EPA (2005), a low pH may cause the mobilization of toxic elements and compounds to make them available for uptake by organisms. Small changes in pH often causes large changes in the level of available metallic complexes and can lead to significant increases in the availability and toxicity of most metals (DWAF, 1996).

2.3.3 Conductivity

Conductivity describes the ability of aqueous solution to carry electric current (APHA, 1998). The amount of ions or total dissolved salts in water is an indicator of conductivity, meaning that conductivity increases as the concentration of ions increases (Tchobanoglous, 1985).

In freshwater ecosystems, the conductivity is regulated by the size of the watershed, rocks' mineral composition and other source of ions (Hudson-Edwards *et al*., 2003; Nielsen *et al*., 2003). Sources that contribute to in-stream conductivity include wastewaters from industries, sewage treatment works as well as non-point sources from settlements and agriculture (Roelofs, 1991; Nielsen *et al*., 2003). The kind of biological activity in surface water can also influence the conductivity (Copertino *et al*., 1998). Solutions with mostly inorganic compounds tend to be better conductors while solutions with organic compounds do not conduct currents well (APHA, 1998).

2.3.4 Dissolved Oxygen

Dissolved oxygen (DO) is a measure of the amount of oxygen gas dissolved in water (Malia, 2005). DO levels indicate the concentration of oxygen demanding pollutants that may be entering surface water through a point and non-point sources (Elbag, 2006). Generally, fast moving waters have a higher DO due to mixing with air when the water comes into contact with debris such as rocks and logs (Vigil, 2003). Dissolved oxygen can be depleted by the demand from organic decomposition and use from plant and animal respiration. Different amounts of DO are needed by different types of fish to survive. According to Best *et al*., (2007), although DO is essential to the respiratory metabolism of most aquatic species, it however affects the solubility and availability of nutrients and thus aquatic ecosystems productivity. Low DO levels negatively affect plant and aquatic species within the water and change the character of a water body (Wilber, 1969; Kailasam and Sivakami, 2004; Best *et al*., 2007).

2.3.5 Alkalinity

Alkalinity is a measure of the acid-neutralizing capacity of water. Although the alkalinity may in theory be caused by any weak acid anion, it is usually only carbonate or more strictly bicarbonate, alkalinity that is important in freshwaters (Wetzel and Likens, 1991). However, if present, borates, phosphates, silicates, and other bases also contribute to alkalinity. Fresh water systems usually have an alkalinity level range of 20 and 200 mg/L (Chapman, 1996).

According to Fianko (2003), alkalinity components such as carbonate/bicarbonate species will complex toxic heavy metals hence reducing their toxicity significantly.

2.3.6 Total Hardness

The term hardness is an indication of the presence of calcium, magnesium and iron carbonates that make it difficult for the lathering of soaps (Chapman, 1996). Ca^{2+} and Mg^{2+} are common cations found in hard water. Through leaching from minerals within an aquifer, these ions enter the water supply.

Hardness is more of a reflection of the amount of Ca and Mg entering the dam through the weathering of rocks such as limestone (Kreger, 2004). Water hardness indicates the geological formation of the catchment area hence an important indicator of water quality as suggested by

Akpabli and Drah (2001). The WHO recommends that hardness should not exceed 200 mg/L $CaCO_3$ but levels of 50-100 mg/L $CaCO_3$ are generally acceptable (WHO, 2011).

2.3.7 Total Dissolved Solids

This is a measure of the total ions in solution. The total dissolved solids consist mainly of carbonates, bicarbonates, chlorides, sulphates, phosphates and possibly nitrates of calcium, magnesium, sodium, potassium, with traces of iron, manganese and other substances. High TDS can reduce water clarity, affect photosynthesis, and increase water temperatures as well (USEPA, 1999).

2.3.8 Chloride

Chloride is the ionic form of the element chlorine and is a common, naturally occurring chemical that can be found at elevated concentrations in aquatic environments as a result of human activity. Natural background concentrations of chloride in surface water are generally no more than a few milligrams per litre, with some local or regional instances of higher concentration (CCME, 2011). Groundwater is a common natural source of chloride and anthropogenic sources such as road salts, water softeners, wastewater effluent, industry discharge and fertilizers can lead to pollution of water bodies by high levels of chloride (OMOE, 2003). Almost all chloride salts are soluble in water hence the chloride content in water ranges from 10-100 mg/L (Nkansah, 2005). The taste threshold for chloride varies depending on the associated cation that is present (e.g. sodium, potassium, etc.) and is generally in the range of 200 to 300 mg/L (Health Canada, 1996). Chloride concentrations in excess of 250 mg/L can give a detectable taste to water (WHO, 1996). Effects of chloride on human health may occur at very high levels above 200 mg/L by disturbance of the electrolyte balance and nausea. Infants are susceptible and fatalities due to dehydration may occur (DWAF, 1996).

2.3.9 Nitrate

Nitrate, a compound of nitric acid, is the most highly oxidized form of nitrogen found in aquatic environments. It is an essential nutrient for many photosynthetic autotrophs and, in some instances, functions as a growth-limiting nutrient (Akan *et al.*, 2013) however, it is necessary for plant uptake and essential to plant growth (Helen *et al.*, 2005). Algae and other aquatic plants use nitrate to form plant protein which, in turn, can be used by animals to form animal protein (Akan *et al.,* 2013). When it rains, varying nitrate amounts wash from farmland into the water body. Nitrates stimulate the growth of plankton that provides food for fish. This could increase the fish population. However, if algae grow too wildly, oxygen levels will be reduced and fish will die (Akan *et al.,* 2012).

Nitrate can be harmful when the level is high in water and as a result can be a good indicator of chemical polluted water (Peter, 1998). Reports by Spalding and Exner (1993) and USEPA (2012), indicate that, nitrate at high concentrations is toxic to infants and may cause /develop the blue baby syndrome also known as methemoglobinemia.

2.3.10 Phosphate

Phosphates are mostly caused by the use of fertilizers, pesticides, industry, and cleaning compounds USESB (2003). Phosphate represents both inorganic and organic forms of phosphorus. Natural sources include phosphate-containing rocks and solid or liquid wastes. Manmade sources of phosphate include human sewage, agricultural run-off from farms, sewage from animal feedlots, pulp and paper industry, vegetable and fruit processing, chemical as well as fertilizer and detergent manufacturing (Hochanadel, 2010; Laws, 1993; Froelich, 1988). Phosphates are present in almost all fertilizers and stimulate the growth of plankton and water plants that provide food for fish. Moreover, this may increase the fish population and improve the waterway's quality of life. Algae grow wildly, choke the waterways, and use up large amounts of oxygen when too much phosphate is present. Many fish and aquatic organisms may die as a result (Akan *et al.*, 2012). Phosphates may not be toxic to people or animals unless they are present in very high levels. Digestive problems could occur from extremely high levels of phosphates (USGS, 1970).

2.3.11 Fluoride

Fluoride is the most electronegative of all the elements (Hem, 1989), hence it has a strong tendency to acquire a negative charge, and in a solution forms F- ions. Fluorine has a density of 1.51 g/cm^3 and a melting point and boiling point at -220 ^{o}C and -188 ^{o}C respectively (Jones and Atkins, 1999; Saxena and Ahmed, 2001; WHO, 2004). Drinking water, which supplies 75-90 % of the daily intake, is commonly the main source of fluoride intake (Meenakshi *et al.*, 2004). Small amounts of fluoride can have a positive effect on our well-being. The WHO recommends that drinking water should ideally contain 0.5-1.0 mg/L fluoride, as it helps to prevent dental caries. WHO (2004) reports that, fluoride is especially effective on children who are still developing their teeth but over a long period of time will lead to a chronic fluoride poisoning, fluorosis If the drinking water has a fluoride concentration of 3-6 mg/L deformation of bones, skeletal fluorosis, can be observed (WHO, 2004).

2.4 Heavy metals

Heavy metal contamination has been a serious concern throughout the world (Romero *et al.*, 2001) as a result of the heavy metals' biochemical properties; they accumulate in environmental system (Kabata-Pendias, 2011). Heavy metals are a class of metallic elements which are abundant in the earth's crust, however, according to (Duffus, 2002), a valid definition for the term 'heavy metals' has never been established nor has the term 'trace metals, ever been defined exactly (Kabata-Pendias, 2011). Parker, (1989); Brewer and Scott, (1983); Lozet and Mathieu, (1991); Morris, (1992) all define heavy metals as elements with a density greater than 5 g/cm^3.

Trace metals can be sourced from both natural and anthropogenic influences; in some areas anthropogenic inputs are usually greater than those from natural sources with some academics (Ahmad, 2005, Holdgate, 1979, Alloway, 1994) suggesting these are often the by-products of mining, manufacturing, disposing of industrial metals and domestic waste that account for almost all environmental pollution. Weathering, volcanic eruptions and forest fires are important natural sources of trace metals in the environment (Biney *et al.*, 1992). Reports by (Singh, 1994; Fazeli *et al.*, 1998) also indicate that irrigation by effluents released from paper mills and fertilizer factories are adding various alkalis, ammonia, cyanides and trace metals into the water systems.

Heavy metal pollutions are important as a result of their potential toxicity to the environment and human beings (Gueu *et al.*, 2007; Lee *et al.*, 2007; Adams *et al.*, 2008; Vinodhini *et al.*, 2008). However, some of the metals like Cu, Fe, Mn, Ni and Zn are essential as micronutrients for the life processes in animals and plants. Moreover, these metals can be toxic if a specific concentration is exceeded (Alloway, 1999; Peralta-Videa *et al.*, 2009). Several other metals such as Cd, Cr, Pb and Co have no known physiological activities (Kar *et al.*, 2008; Suthar *et al.*, 2008; Aktar *et al.*, 2010).

Trace metal toxins contribute to a variety of adverse health effects (Romero *et al.*, 2004). A decline in the mental, cognitive, and physical health of an individual can be caused by the accumulation of heavy metals within the body (Aziz *et al.*, 2005).

Heavy metals are generally considered the most toxic to humans and animals; the severe human health effects associated with exposure to them, even at low levels, are diverse and inclusive, but are not limited to, neurotoxic and carcinogenic actions (ATSDR, 2003a, 2003b, 2007, 2008; Castro-González and Méndez-Armenta, 2008; Jomova and Valko, 2011; Tokar *et al.*, 2011). Trace metal distribution in water, sediments, and fish play a vital role in detecting sources of trace metal contamination in aquatic ecosystems (Forstner and Wittman, 1981; Odoh and Kolawole, 2011).

Persistent lipophilic organic compounds and trace metals are absorbed and accumulated in organism in a process known as bioaccumulation (Suess and Erlenkeueser, 1975; Taylor *et al.*, 1995). These bioaccumulated substances can be passed up the food chain to predator species in a process which is known as biomagnifications, hence one of the means that pollutants could become hazardous to people (Beiras, 2003).

2.4.1 Mercury

Mercury is one of the most toxic trace metals in the environment (Castro-González and Méndez-Armenta, 2008) that occurs in the atmospheric and in the, aquatic and soil systems (Yan *et al.*, 2013). Three oxidation states of Hg (0, I and II) occur in the environment (Barbosa *et al.*, 2001). Mercury exits in nature as elemental mercury (Hg^0), and as both inorganic and organic mercury compounds (O'Driscoll *et al.*, 2005).

Mercury by natural emissions includes degassing from soils and oceans and volcanic releases (Lindqvist *et al.*, 1991). Forest fires also contribute to these natural emissions (Jiang *et al.*, 2006). Major sources of mercury (Hg) to aquatic systems include mining and chemical industry discharges and coal burning emissions (Wang *et al.*, 2004).

Atmospheric mercury (Hg) is dispersed across the globe by winds and returns to the earth in rainfall, accumulating in aquatic food chains and fish in lakes and rivers (Mathews, 1997).

Atmospheric elemental mercury settles in water, where it is converted into organic (methyl or ethyl) mercury by microorganisms, and is ingested by smaller creatures which are eventually consumed by larger fish. Fish at the top of the food chain (e.g., tuna, swordfish, or shark) may concentrate considerable mercury in their tissues. Methyl mercury is readily absorbed or ingested by organisms, and it is transported to all organs, particularly affecting the nervous system. Since methyl mercury bio accumulates in organisms, levels of mercury in fish tissue can be in orders of magnitude higher than mercury levels found in water. Methyl mercury and metallic mercury vapours are more harmful than other forms, because more mercury in these forms reaches the brain. Effects on brain functioning may result in irritability, shyness, tremors, changes in vision or hearing, and memory problems (ATSDR, 1999). Mercury is believed to interfere with DNA transcription and protein synthesis (Gruenwedel and Lu, 1970), including protein synthesis in the developing brain, with destruction of endoplasmic reticulum and the disappearance of ribosomes (Herman *et al*., 1973). Mercury is also possibly associated with disruption of DNA repair (Berlin *et al*., 2007; Crespo-Lopez *et al*., 2009).

Mercury's importance as an environmental problem has been recognized for decades, after thousands of residents were poisoned in Minamata (Japan) caused by release of methyl mercury (MeHg) from a chemical factory to the local bay in 1956 (Harada, 1995). Methyl mercury levels in fish could reach very high levels as a result of the methylation of inorganic mercury in the sediment and subsequent bioaccumulation of MeHg in the food chain (Bravo *et al*., 2010).

2.4.2 Selenium

Selenium ($^{79}{}_{34}Se$) is a metalloid of the same family as oxygen and sulphur (S). The atomic weight of selenium is 78.96 g/mole. It has five naturally occurring cold isotopes and two beta particles emitting radioactive isotopes, ^{75}Se and ^{79}Se (Sargent-Welch, 1979). When found in its elemental form, it is a red amorphous or black crystalline solid (Lyman *et al.*, 1988). Selenium can be combined with many elements (hydrogen, fluorine, chlorine, bromine, phosphorus, etc.). It thus forms compounds with a close analogy to those of sulphur (Simonoff *et al*., 1991; Burk *et al*., 1994; Bonnard *et al.*, 2011).

Selenium is present in nature and in organisms as organic and/or inorganic forms. The main organic forms are selenomethionine and selenocysteine while the inorganic forms are selenite (SeO_3^{-2}), selenide (Se^{2-}), selenate (SeO_4^{-2}) and the selenium element (Se) (Graham, 1991). Selenium is a solid substance at ordinary temperature (Bonnard *et al.*, 2011). Like sulphur, selenium takes various physical forms (Burk *et al*., 1994; Maroc, 1990).

Selenium is concentrated in the tissues when it is taken up by organisms faster than it can be excreted and in excess of metabolic needs. It is incorporated in small amounts into the animal's enzyme glutathione peroxidase, which protects the cell from damage from molecular oxygen, as well as into several cytochromes, myoglobulin, and hemoglobin (Eisler, 1985). Excess selenium may be incorporated into amino acids and proteins by methylation (Eisler, 1985, Coyer, 1993).

Hamilton *et al.*, (1990), Saiki, (1990), Skorupa and Ohlendorf, (1991), Besser *et al*., (1993) and Coyle *et al.*, (1993) also suggest that bioaccumulation from food items results in higher toxicity than that from aqueous exposure.

Selenium concentrations in dietary items of aquatic birds are greatly increased compared to that in water due to the bioaccumulation of selenium through the aquatic food chain. Thus, fish and birds that consume prey that have high selenium levels in their tissues are exposed to the greatest risks of bioaccumulation (Lemly and Smith, 1987; Saiki and Lowe, 1987; Hothem and Ohlendorf, 1989).

2.4.2.1 Selenium and Mercury interactions and their mechanisms in aquatic ecosystems

Ullrich *et al.*, (2001) report that the methylation process that converts inorganic Hg (Hg^{2+}) into MeHg (CH_3Hg^+) occurs primarily in aquatic ecosystems and wetlands systems. That selenium can inhibit the toxicity and enrichment of MeHg in aquatic organisms has provided a potential approach to solving the problem of mercury levels in water in recent years (Yang *et al.*, 2008). Research suggests that adding selenium to lake sediments can significantly reduce the formation of MeHg in these sediments. Jin *et al*., (1997, 1999) have added Na_2SeO_3 in various concentrations (0–12.5l g/g of wet weight) and $HgCl_2$ at a fixed concentration (50 l g/g) to lake sediments and placed these sediments in an anaerobic environment for 25–70 days at 20–37 ^{0}C.

The results show that selenium can also significantly reduce the generation of MeHg, even at low levels (0.25 l g/g), and the more selenium is added, the less MeHg is generated. Cheng *et al.*, (2001) and Belzile *et al.*, (2006), have also found, in field studies, that the total mercury and MeHg levels in lakes and in the organisms of the lakes were inversely correlated with the dissolved Se in the lake water and the total Se in the organisms.

Many studies of aquatic ecosystems conducted earlier have also indicated that selenium could inhibit the enrichment of Hg in the food chain (Jin *et al*., 1999; Paulsson and Lundbergh, 1989; Southworth *et al.*, 2000). Yang *et al*., (2008), have summarized three possible mechanisms for these phenomena as follows:

(i) Non-biological processes (with no bacterial reduction involved) directly generate an insoluble inert gel compound, HgSe, which causes sedimentation and thereby inhibits Hg methylation; the formulae for the reaction are as follows:

$Hg^{2+} + Se^{2-} = HgSe$ and $Hg^0 + Se^0 = HgSe$.

(ii) Formation of the $(CH_3Hg)_2Se$ complex to facilitate the demethylation of CH_3Hg^+; the reaction is as follows:

$HSe^- + 2CH_3Hg^+ = CH_3Hg–Se–HgCH_3 = CH_3–Hg–CH_3 + HgSe$.

(iii) Higher absorption of Se by organisms leads to stronger ‘‘repulsion’’ against MeHg absorption.

Although the results of laboratory studies of certain animal tissues indicate that the simultaneous application of Hg^{2+} and SeO_3^{2-} can increase Hg absorption, the field and laboratory studies of bacteria (Pseudomonas fluorescens) conducted by both Belzile *et al.*, (2006) and Chen *et al.*,

(2001) have clearly shown that Se and Hg are inversely correlated namely, the higher the Se content in the blood plasma of aquatic organisms or unicellular bacteria, the lower are the levels of total Hg and MeHg.

2.4.3 Manganese

Manganese is one of the abundant elements in the earth's crust and is widely distributed in soils, sediments, rocks, water, and biological materials (NCSU, 2006).

Manganese is an essential plant nutrient, and its deficiencies have been observed primarily in arid regions (Xiang and Banin, 1996). The major sources of man-made environmental pollution by manganese arise in the manufacturing of alloys, steel, and iron products. Over 90% of the manganese produced in the world is used in the making of steel, either as ferromanganese or silicomanganese (NCSU, 2006). Mining operations, the production and use of fertilizers and fungicides, and the production of synthetic manganese oxide and dry-cell batteries are other sources of manganese (Abbasi *et al.*, 1998). Manganese pollution may also arise from the incineration of refuse containing manganese (WHO, 1981).

2.4.4 Cadmium

Cadmium is widely distributed in the Earth's crust at an average concentration of about 0.2 mg/kg in rocks, sediments and soils (Manson and Moore, 1982) and is commonly found in association with zinc (WHO, 1992). Fertilizers produced from phosphate ores constitute a major source of diffuse cadmium pollution. The solubility of cadmium in water is influenced to a large degree by its acidity; suspended or sediment-bound cadmium may dissolve when there is an increase in acidity (Ros and Slooff, 1987). In natural waters, cadmium is found mainly in bottom sediments and suspended particles (Friberg *et al*., 1986). Non-ferrous metal mines represent a major source of cadmium to the aquatic environment.

Cadmium is emitted into the air by mines, metal smelters and industries using cadmium compounds for alloys, batteries, pigments and in plastics, although many countries have stringent controls in place on such emissions (Harrison, 2001). Cadmium compounds are used in electric batteries, electronic components and nuclear reactors (Friberg *et al.*, 1986; Ros and Slooff, 1987). Cadmium accumulates in the human body affecting negatively several organs (liver, kidney, lung, bones, placenta, brain and the central nervous system) (Castro-González and Méndez- Armenta, 2008). Apostoli and Catalani (2011) and ATSDR (2008) also observe other damages which include reproductive and development toxicity, hepatic, haematological and immunological effects.

2.4.5 Lead

Lead, as a toxicologically important element has been introduced into the environment by man in extreme amounts, despite its low geochemical mobility (Oehlenschläger, 2002). In the environment, most of the lead occurs in the inorganic form and in several oxidized states (Jackson *et al.*, 2005).

Lead enters the aquatic system through releases (directly or through atmospheric deposition) from the smelting and refining of lead, the burning of petroleum fuels containing lead additives etc. According to Kinder (2011), some old homes could still have lead water pipes, which can then contaminate drinking water. In the aquatic environment, lead is immobile and tends to accumulate in sediments close to its point of entry (NCSU, 1996) and also bio-accumulate in benthic bacteria, freshwater plants, invertebrates and fish (DWAF, 1996). The kidney, liver, nervous system, blood vessels and other tissues could be damaged due to high consumption of lead (Denton *et al*., 1997).

2.4.6 Iron

Iron is a non-conservative trace element found in significant concentrations in drinking water because of its abundance in the earth's crust (Ghulman *et al*., 2008). Metallic iron is found in the free state (Antonovics *et al.*, 1971). It is essential to most life forms and to normal human physiology. A human activity such as burning of coke and coal, acid mine drainage, mineral processing, sewage and landfill leachates also contribute to excessive iron concentrations in water bodies (NCSU, 2006). The chemical behaviour of iron in the aquatic environment is, however, determined by oxidation - reduction reactions, pH and the presence of coexisting inorganic and organic complexing agents (Anon, 1996). The shortage of iron causes anaemia and prolonged consumption of drinking water with high concentration of iron may lead to liver diseases (Rajappa *et al*., 2010).

CHAPTER THREE

3. METHODOLOGY

3.1 Study area

The Weija dam is situated in Accra, the capital of the Greater Accra Region of Ghana. The Weija dam is 14 km long, 2.2 km wide and has total surface area of 38 km^2 with mean depth of 5 m (Vanden, 1990). The dam, located between 0^o 20’ W 0^o 25’ W and 5^o 30’ N 5^o 45’ N, was created in 1977 as a replacement for an earlier one which was washed away in 1968 by the Ghana Water Company Limited through damming the River Densu mainly to satisfy the demand for a potable water supply (Asante, 2005). Weija dam, located about 17 km west of Accra, is almost at the mouth of the 116 km long river Densu which lies between latitude 5^o 301N and 6^o 201N and between longitudes 0^{o}101 and 0^o 351W. The current reservoir provides water to western parts of Accra, supports irrigation projects, as well as fisheries. The normal surface elevation is estimated at 14.37 km with maximum of 15.24 km (Nukunya and Boateng, 1979).

The 54.32 km^2 restricted zone demarcated under Executive Instrument 130 of 1977 for the Weija Lake has been seriously encroached upon according to the recent government committee report (Akuffo, 2003). These activities have reduced the vegetative cover, making soils more vulnerable to erosion into the river, which has serious implications on channel morphology, aquatic life and sedimentation of the Weija Dam. The river channel, especially the middle and lower courses are experiencing serious erosion and siltation which is threatening the existence of the Weija Dam. Anthropogenic activities thus introduce both organic and inorganic pollutants in the form of pesticides and heavy metals (e.g. selenium, mercury) respectively into the water, sediment and biota of the basin (Kusimi, 2009).

The dam area is low lying with undulating topography and isolated ridges. About 95% the basin is underlain by granite and granodiorite of middle precambrian origin, except for the sources and toward the mouth (Akpabli, 2001) where the basin is underlain by the birimian and the Togo series respectively. The catchment of the dam lies in the coastal savanna zone where rainfall is seasonal, with two rainfall peaks in June and September, while dry periods span between December and March.

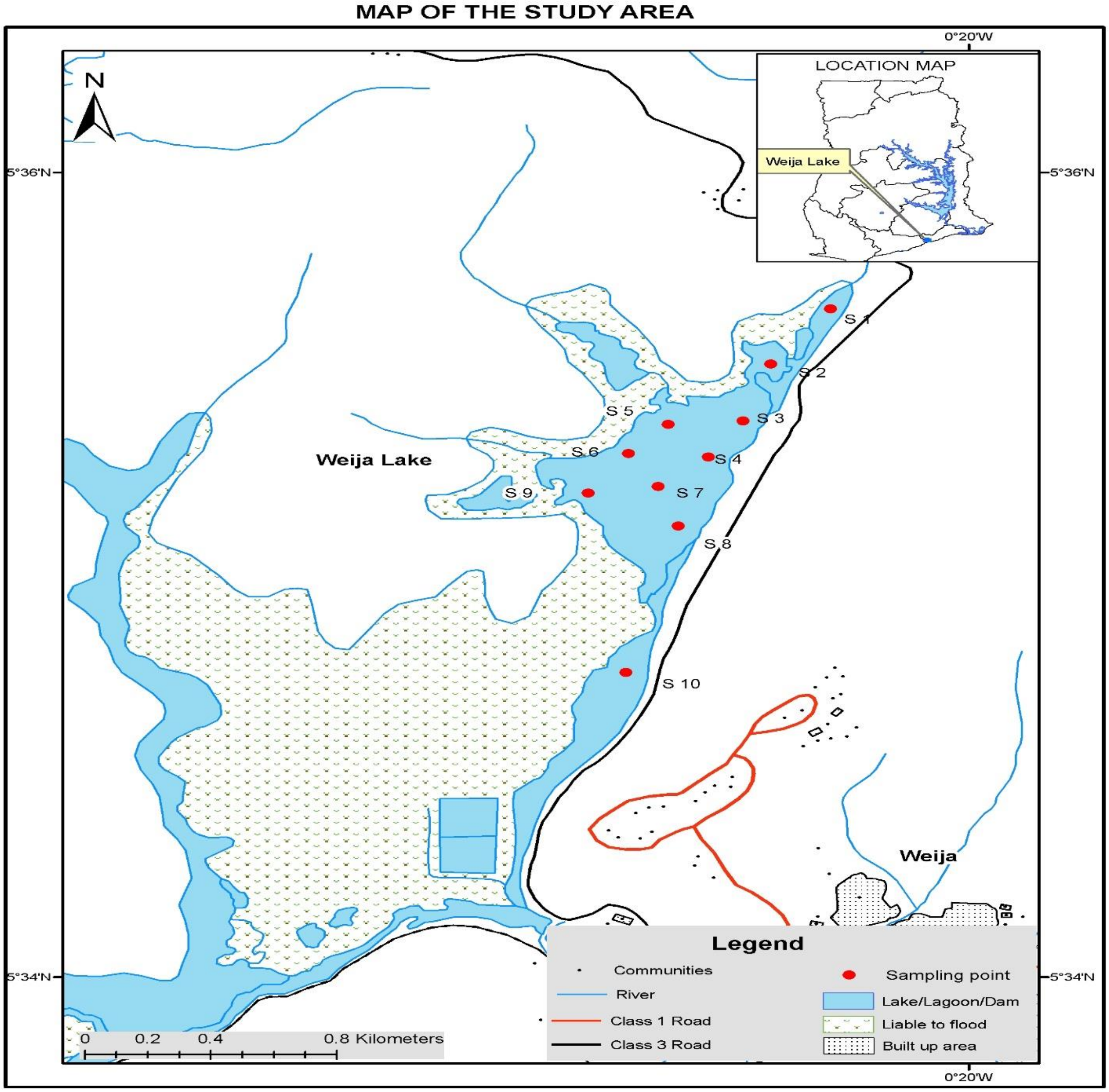


Figure 3.1: Map of the study area indicating the sampling sites

3.2 Preparation of sample containers

All the glassware and high density plastic containers were thoroughly washed with detergent and rinsed with distilled water and later soaked in analytical grade HNO_3 for three days and then rinsed with deionized water.

3.3 Samples and Sampling procedure

Sampling was done in the month of March, 2014 representing the dry season and August, 2014 for the wet season. Fifty water samples, fifty sediments and twelve fish samples comprising of three species namely *Tilapia Zilli*, *Tilapia mariae* and *Chrysichthys nigrodigitatus* were collected from the dam at ten different sites each season. For each sampling site, five water and sediments samples were collected across the dam at about 25 m intervals.

Water samples were collected at about 30 cm into acid pre-cleaned Teflon-bottles. Water samples for physicochemical determination were collected into 1.5 L plastic bottles while those for dissolved oxygen (DO) were collected into 300 ml bottles and azide modification of the Winkler method was used to fix oxygen on site for dissolved oxygen (DO) analysis. All the sample containers and corks used in the sampling were rinsed three times with the sample water before being filled to the brim and then covered with cork and labelled. The measurement of temperature, pH, electrical conductivity and total dissolved solids were done on site. Sediment samples were collected from the bottom of the Lake at each sampling point with pre-cleaned polyethylene bags, sealed and labelled.

Fresh fish samples, (3) species, were obtained from natives around the dam. Water, sediments and fish samples collected were all kept in an ice chest at a temperature of about 4 ℃ and transported to the Chemistry Laboratory of the Ghana Atomic Energy Commission (GAEC) for analyses.

3.4 Water sample analysis

3.4.1 Temperature

The temperatures of water samples were recorded on site with a thermometer. About 100 ml of the water sample was measured and transferred into a 250 ml beaker. The thermometer was immersed in the water. The reading on the thermometer was recorded after some minutes.

3.4.2 pH

Buffer solutions of pH 4.01 and 7.00 were used to calibrate the pH meter. About 100 ml of sample water was poured into a beaker and the tip of the electrode was dipped into it the sample water. The pH readings were recorded after the readings were stable. The electrode was removed and rinsed with distilled water before other samples were determined.

3.4.3 Conductivity

Conductivity was measured using Hanna instruments HI 9032 microcomputer conductivity meter. The conductivity meter was calibrated using a reference 12880 µS/cm. The electrode of the meter was rinsed and placed in distilled water. Water sample was placed in a beaker and the electrode rinsed with distilled water and was lowered into the sample water in the beaker. The measured conductivity in µS/cm was recorded.

3.4.4 Total hardness

A 100 ml of sample water was put into a 250 ml conical flask and 2 ml of NH_4Cl- NH_4OH buffer solutions were added to maintain the pH around 10.0. Two drops of the Erichrome Black T indicator was added to form a wine- red solution which was later titrated against a 0.01 M standard EDTA titrant with continuous swirling till the colour changed through purple to pure blue at the end point. Titration was repeated until a consistent titre was obtained and the average titre calculated (APHA, 1998).

$$\text{Total hardness (as } CaCO_3\text{), mg/L} = \frac{\text{mL of EDTA used} \times 1000}{\text{mL of sample}}$$

3.4.5 Total dissolved solids

TDS was measured using Hanna instruments HI 9032 microcomputer conductivity meter. The conductivity meter was calibrated using a reference buffer 12880 µS/cm. The electrode of the meter was rinsed and placed in distilled water. Sample water was placed in a beaker and the electrode rinsed with distilled water was lowered into the sample water in the beaker. The measured TDS reading in mg/L is shown on the screen and recorded.

3.4.6 Total alkalinity

A volume of 50 ml sample water was pipetted into a conical flask. Two to three drops of methyl orange indicator was added and the resulting mixture was titrated against a standard, 0.02 N H_2SO_4 solutions to a pale pink colour end point.

$$\text{Total Alkalinity (mg/L)} = \frac{a \times N \times 1000 \times 50}{\text{mL of sample}}$$

Where, a= Volume of standard H_2SO_4 consumed in titration

N= Normality of H_2SO_4 used

50 = equivalent of $CaCO_3$

3.4.7 Dissolved Oxygen (Winkler's Method)

Dissolved oxygen was measured by using the APHA, (1998) method. The sample was collected in a 300 ml BOD bottle, carefully, avoiding any kinds of bubbling and trapping of air bubbles in the bottle after placing the stopper. To the 50 ml sample taken in the conical flask 2 ml of manganese sulphate ($MnSO_4$) and 2 ml of the Sodium azide solution was added well below the surface from the wall of the bottle and a precipitate appeared. Then the stopper was placed tightly and the bottle was shaken by inverting the bottle repeatedly to ensure proper mixing of the contents. The bottle was kept for some time to settle down the precipitate: 2 ml of conc. H_2SO_4 was added to it and shaken well to dissolve all the precipitate. Then 50 ml of sample was taken in a conical flask and titrated against sodium thiosulphate ($Na_2S_2O_3$) of 0.025 N using starch as an indicator. At the end point the initial blue colour changed to colourless.

3.4.8 Chloride

Chloride was measured by the titration method. 50 ml of sample in a conical flask was taken.2 ml of potassium chromate indicator was added to the sample solution. It was titrated against 0.02 N silver nitrate until a persistent brick red colour was appeared, which was the end point of the titration. The volume of the titre was recorded (APHA, 1998). A blank by placing 50 mL of chloride free distilled sample water was also conducted.

Calculation

$$\text{Chloride (mg/L)} = \frac{(a-b)\times 35.5 \times 1000}{V}$$

Where, a = Volume of titrant (silver nitrate) for sample

b = Volume of titrant (silver nitrate) for blank

V = Volume of the sample in mL

N = normality of silver nitrate

3.4.9 Phosphate

KH_2PO_4 was used to prepare standard solutions of 0.1, 1 and 10 ppm of phosphate. From each standard and sample, 50 mg/L was taken and placed in a beaker. 5 ml of a mixed solution containing 50 cm^3 of 0.0016 M ammonium molybdate, 125 cm^3 of 0.2 M sulphuric acid, 50 cm^3 of 0.02 M ascorbic acid and 125 cm^3 of 0.0001 M potassium antimonyl - tartrate was added to the beakers. A blue colour appears and was allowed to develop for thirty minutes. UV-Visible spectrophotometer was used to measure the absorbance at 885 nm against the corresponding reagent blank. The concentration was determined with the help of a standard curve obtained by plotting standard values against absorbance (Strickland and Parsons, 1988).

3.4.10 Nitrate

Sample solution of about10 ml was pipette into a beaker; 2 g of Zn / NaCl granular mixture and 5 ml of Conc. HCl was added and allowed to stand for thirty minutes while stirring occasionally to form a nitrite. Whatman No. 41 filter paper was used to filter the solution into a 100 ml standard flask and diluted to the mark. Aliquots of stock solution containing 0.2 - 10.0 µgm/L of reduced nitrite were transferred into a series of 10 ml flasks. 1 ml of sulfanilic acid and 1 ml of 2 M HCl solution were added and shaken thoroughly for about five minutes for the diazotization reaction to go to completion. Afterwards, 1 ml of 5 % methyl anthranilate and 2 ml of 2 M sodium hydroxide solution were added to form an azo dye and the mixture was then diluted to 10 ml with water. The absorbance of the resulting red coloured dye was measured with UV - Visible spectrophotometer at 493 nm. The calibration curve was constructed and concentrations of the samples determined from the calibration curve (Ensafi *et al*., 2004).

3.4.11 Fluoride

Direct measurement using a mettler Toledo sevenGo pH/mV meter was used to determine the fluoride. Standards solutions of 0.1, 1, 10, 100 ppm of fluoride ion were used to calibrate the mettler Toledo sevenGo pH/mV meter. Standard solutions were treated with 50 ml of TISAB 1 and the mV readings recorded and a calibration curve constructed. 5o ml of sample was added to 50 ml of TISAB 1 in a clean dry 150 ml plastic beaker. The beaker was placed on a magnetic stirrer and stirred. The electrode was rinsed with distilled water, dried and lowered into the solution. The stable mV reading was recorded. Fluoride concentration in the sample was determined using the calibration curve (Fucsko *et al*., 1987).

3.5 Preparation of water samples

A weight of 5.0 g of water sample was weighed into an already acid washed labelled 100 ml polytetrafluoroethylene (PTFE) Teflon bombs. A volume of 6 ml of concentrated nitric acid (HNO_3, 65 %); 3ml of concentrated hydrochloric acid (HCl, 35 %) and 0.25 ml of hydrogen peroxide (H_2O_2, 30 %) were added to each sample in a fume chamber. The samples were then loaded on the microwave carousel. The vessel caps were secured tightly using a wrench. The complete assembly was microwave irradiated for 26 minutes using the milestone microwave labstation ETHOS 900, INSTR: MLS-1200 MEGA using the microwave programme. The Teflon bombs mounted on the microwave carousel were cooled after digestions in a water bath to reduce internal pressure and allow the volatilized material to re-stabilize. This was also applied to sediment and fish samples as well as to the Standard Reference Material used for the metals of interest, blanks and samples duplicates. Distilled water was added to digestate up to the 20 ml make and then used to determine the metals.

3.6 Preparation of sediment

Sediment samples were air dried in the laboratory and any crumbs found in the sediments were removed. Porcelain mortar and pestle were used to ground the dried samples and these were sieved through a mesh of 325 μm to produce a fine powder for analyses in laboratory. About 1.5 g of the sample was weighed into an already acid washed labelled 100 ml polytetrafluoroethylene (PTFE) Teflon bomb. 6 ml volume of concentrated nitric acid (HNO_3, 65 %), 3 ml of concentrated hydrochloric acid (HCl, 35 %) and 0.25 ml of hydrogen peroxide (H_2O_2, 30 %) were added to each sample in a fume chamber. The samples were then loaded on the microwave carousel. The vessel caps were secured tightly using a wrench. The complete assembly was microwave irradiated for 26 minutes using the milestone microwave labstation ETHOS 900, INSTR: MLS-1200 MEGA using the microwave programme.

3.7 Preparation of Fish Samples

The fish samples kept in the freezer were defrost and washed with distilled water. The length and weight were then recorded. The fish samples were milled into powdered form after freeze drying using CHRIST BETA 1-16 for two days. 0.5 g of the sample was weighed into already acid washed labelled 100ml polytetrafluoroethylene (PTFE) Teflon bombs. A volume of 6 ml of concentrated nitric acid (HNO_3, 65 %) and 1.0 ml of hydrogen peroxide (H_2O_2, 30 %) were added to each sample in a fume chamber using a wrench. The complete assembly was microwave irradiated for 22 minutes using a milestone microwave labstation ETHOS 900, INSTR: MLS-1200 MEGA microwave programme.

3.8 Determination of heavy metals

Trace metals Hg, Se, Pb, Mn, Fe and Cd were measured with Varian spectra AA 240 FS Atomic Absorption spectrophotometer equipped with a multi element hollow cathode lamp and also a H_2 hollow cathode lamp as background corrector. However, the AAS was equipped with a cold vapour facility and a hydride generator for the determination of Hg and Se.

The digested samples were aspirated onto the burner head of the AAS using an acytelin-air mixture and argon as the inert carrier gas. Calibration of the instrument with the standards prepared for the elements to be analysed and then the absorbance of each element were measured after setting their wavelengths.

The wave length of Hg, Se, Mn, Pb, Cd, and Fe were set at 253.7 nm, 279.5 nm, 217.0 nm, 228.8 nm and 248.3 nm respectively.

3.9 Quality assurance

Quality assurance guidelines were followed to ensure accuracy of results. Reagents used where all of analytical reagent grade and deionized water was also used in all the preparations in the laboratory. Sampling protocols were followed to prevent contamination of the samples. Samples were prepared and analysed in triplicates for accurate results. Standard Reference Materials (SRM) used was treated as the samples for analysis. The SRM used are 1643e Trace Elements in water by National Institute of Standard Technology (NIST), IAEA –SRM 1646a (Estuarine sediment) and IAEA-350 for the fish samples to validate the analytical techniques and procedures employed.

3.10 Statistical analysis

The data obtained in this study were subjected to statistical analysis using Microsoft Excel 2010 (Microsoft Corp.) and Statistical Package for Social Sciences (SPSS) (v 21.0, SPSS Inc., Chicago, IL, USA). Statistical models such as descriptive and one-way ANOVA, Pearson correlation and regression analysis were applied to the results to determine the relationship between parameters, heavy metals concentration in the water, sediment and fish. The coefficient of variation was also used for the measurement of dispersion of a probability or frequency distribution of parameters. The contamination factor (C_f), Geo-accumulation Index and Pollution Load Index are indices used to determine the contamination status of sediment in the Weija dam.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1 Introduction

The results obtained from the sampling site and laboratory analyses are showed in the form of tables and figures in this chapter. Trace metals and physicochemical parameters determined were assessed using relevant criteria such WHO acceptable limits. The interpretation and discussion of results were grouped into two seasons, thus dry and wet seasons to ascertain the seasonal variation in the concentrations of metals and physicochemical indicators

4.2 Coefficient of variation

A coefficient of variation is used to determine the frequency of distribution and dispersion pattern of the studied parameters. It is the ratio of standard deviation to the mean.

$$\text{Coefficient of variation Co. V \%} = \frac{\text{Standard Deviation} \times 100\%}{\text{Mean}}$$

A parameter is considered to be uniformly, closely or narrowly distributed when the coefficient of variation is less than 50% and when the coefficient of variation is 50% and above, the parameter is considered to be scattered, widely distributed or highly dispersed (Affum *et al*., 2008).

4.3 One Way ANOVA (Heavy metals versus pH)

Analysis of variance is a technique used to compare the means of multiple unrelated groups. One way ANOVA was used to find out whether pH had significant effect on the linear variation of heavy metals along the watercourse. The sites pH was set as factor variable while heavy metals were set as dependent variables with significance level set at 95 %. Variations are significant if ($P < 0.05$) and not significant if ($P > 0.05$).

There were no significant variations ($P > 0.05$) between the group means of Fe ($P = 0.403$), Cd ($P = 0.247$), Pb ($P = 0.900$) and Mn ($P = 0.896$) with pH ($0.247 \leq P \leq 0.900$) for lake water in the wet season.

In the dry season, there were significant variations ($P < 0.05$) between group means of Mn ($P = 0.001$) with site pH ($0.000 \leq P \leq 0.001$). No significant variations ($P > 0.05$) was observed for Fe ($P = 0.405$), Cd ($P = 0.412$) and Pb ($P = 0.833$). From the results obtained in this study, the pH affected the distribution patterns and mobility of manganese in water along the sampling sites in the dry season.

4.4 Paired sample T- Test

To compare the means of the physicochemical and nutrients values for the dry and wet seasons, a paired sample t-test was applied to the data. Physicochemical and nutrients results for the dry and wet seasons were set as paired variables with the confidence interval set at 95%. The hypothesis was:

Ho: Physicochemical and nutrients parameters varies significantly with seasonal variation.

Ha: Physicochemical and nutrients parameters did not vary significantly with seasonal variation.

From the results obtained, it was observed that all the physicochemical parameters had paired values which were significant ($0.000 \leq P \leq 0.008$) hence the null hypothesis is rejected by all the physicochemical parameters.

Results obtained for the nutrients indicated that nitrate ($P = 0.119$) had paired value above the significance level ($P > 0.05$) hence not significant. Phosphate, chloride and fluoride had their paired values in the range ($0.00 \leq P \leq 0.002$) and were significant at $P < 0.05$. The nitrate accepted the null hypothesis but the other nutrients rejected it.

4.5 Contamination Factor (C_f)

The level of heavy metal contamination of sediments from the Weija Dam is expressed in terms of a contamination factor (C_f).

The contamination factor is expressed by equation 1

$C_f = C_m$ Sample / C_m Background Equation 1

Where C_m Sample represents the concentration of the given metal in the sediment and C_m Background is the value of the metal represents mean shale concentration given by Martin and Meybeck, (1979). Contamination factor values for describing the ascribed levels of contamination are indicated in Table 4.1.

Table 4.1: Contamination Factor and Level of Contamination (Hakanson, 1980)

Contamination Factor (C_f)	Level of Contamination
$C_f < 1$	Low contamination
$1 \leq C_f < 3$	Moderate contamination
$3 \leq C_f < 6$	Considerable contamination
$C_f > 6$	Very high contamination

4.6 Geo-accumulation Index (I_{geo})

The Geo-accumulation Index (I_{geo}) was calculated to determine the contamination of heavy metals in sediments from the Weija Dam. The Geo-accumulation Index was proposed by Muller, (1979) and later classified by Muller, (1981). It evaluates pollution in terms of seven classes based on the increasing numerical values of the index. The seven contamination classes are indicated in Table 4.2.

Table 4.2: Muller's Classification for the Geo-accumulation Index

I-Geo Value	Value Class	Sediment Quality
≤ 0	0	Unpolluted
0-1	1	From Unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
> 6	6	Extremely polluted

The geo-accumulation Index is expressed by the following equation 2

: $I_{geo} = \text{Log}_2 (C_n / (1.5 * B_n)$ Equation 2

Where C_n is the measured concentration of the sediments for metal (n), B_n is the geochemical background value for metal (n). 1.5 represents rock average given by Martin and Meybeck, (1979). The factor 1.5 is incorporated in the relationship to account for possible variation in background data due to terrigenous effects.

4.7 Pollution Load Index (PLI)

The Pollution Load Index (PLI) is used to determine the contamination status of the sediments found in the Weija Dam. The PLI for the Weija Dam was evaluated based on the following equation 3: $PLI = (C_F1*C_F2*C_F3*C_F4)^{1/n}$ Equation 3

Where n represents the number of metals. The PLI value > 1 is an indication of pollution whereas PLI value < 1 indicates no pollution (Seshan *et al*., 2010). The results of the Pollution Load Index (PLI) are shown in Table 7 and 8. The values for all the sites for both the dry and wet seasons are less than 1 which indicates that the dam is not polluted with respect to the heavy metals measured.

Table 4.3: Mean, standard deviation and coefficient of variation of physico-chemical parameters of water samples in the dry season

Parameter	Mean	St. D	Co. V%
pH	6.93	0.24	3.46
Temp. (℃)	27.34	0.59	2.16
Cond. (µS/cm)	215.41	59.22	27.49
TDS (mg/L)	47.52	12.86	27.07
DO	3.52	0.56	15.91
Alkalinity (mg/L)	98.18	6.06	6.17
T. Hardness (mg/L)	82.59	9.19	11.13
Chloride (mg/L)	53.33	7.98	14.97
Fluoride (mg/L)	0.07	0.02	28.57
Phosphate (mg/L)	0.27	0.09	33.33
Nitrate (mg/L)	0.32	0.09	28.13
Mercury (mg/L)	0.00	0.00	0.00
Selenium (mg/L)	0.00	0.00	0.00
Iron (mg/L)	0.03	0.02	66.67
Cadmium (mg/L)	0.02	0.02	100.00
Lead (mg/L)	0.02	0.02	100.00
Manganese (mg/L)	0.03	0.03	100.00

DO: Dissolved Oxygen, TDS: Total Dissolved Solids

Table 4.4: Mean, standard deviation and coefficient of variation of physico-chemical parameters of water samples in the wet season

Parameter	Mean	St. D	Co. V%
pH	7.36	5.82	79.08
Temp. (℃)	26.26	2.21	8.42
Cond. (µS/cm)	156.08	49.63	31.80
TDS (mg/L)	41.50	8.89	21.42
DO	5.22	0.44	8.43
Alkalinity (mg/L)	94.68	5.96	6.29
T. Hardness (mg/L)	50.04	10.84	21.66
Chloride (mg/L)	50.04	8.40	16.79
Fluoride (mg/L)	0.07	0.02	28.57
Phosphate (mg/L)	0.06	0.03	50.00
Nitrate (mg/L)	0.31	0.07	22.58
Mercury (mg/L)	0.00	0.00	0.00
Selenium (mg/L)	0.00	0.00	0.00
Iron (mg/L)	0.28	0.16	57.14
Cadmium (mg/L)	0.02	0.01	50.00
Lead (mg/L)	0.00	0.00	100.00
Manganese (mg/L)	0.03	0.03	100.00

DO: Dissolved Oxygen, TDS: Total Dissolved Solids

Table 4.5: Mean values of physico-chemical parameters of water in the dry season

Parameter	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
pH	6.93	7.03	7.01	7.02	6.94	7.03	7.16	6.62	6.84	6.77
Temp. (℃)	27.06	26.57	26.99	28.19	26.52	27.72	27.44	28.10	27.63	27.20
Con.(µS/cm)	207.60	178.60	222.50	164.57	231.53	246.46	285.61	188.78	229.73	198.72
DO	3.70	2.90	3.90	4.10	3.10	3.60	2.70	4.00	3.20	4.00
TDS (mg/L)	55.09	73.45	44.66	30.73	48.73	28.60	46.26	51.62	44.86	51.16
Alkalinity (mg/L)	93.55	105.68	92.22	99.61	101.76	94.36	101.60	90.43	99.63	103.00
T. Hardness (mg/L)	75.86	68.94	83.47	71.15	91.07	94.54	79.94	90.73	89.94	80.28

Table 4.6: Mean values of physico-chemical parameters of water in the wet season

Parameter	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
pH	7.40	7.38	8.00	7.20	8.00	6.75	7.20	6.95	7.30	7.38
Temp. (℃)	26.41	26.38	25.81	26.10	26.72	25.95	25.82	26.69	25.67	27.01
Con.(µS/cm)	110.26	114.00	203.43	165.48	100.05	189.78	187.12	94.95	205.19	190.58
DO	5.84	5.28	5.40	5.40	5.12	4.56	5.14	5.00	5.56	4.94
TDS (mg/L)	39.00	36.00	58.00	36.00	40.00	30.00	51.00	34.00	52.00	39.00
Alkalinity (mg/L)	98.90	102.00	86.82	97.24	100.05	91.84	99.52	90.42	86.21	93.77
T. Hardness (mg/L)	64.67	49.18	55.25	62.22	71.51	65.75	58.20	54.27	58.60	62.60

Table 4.7: Anions, trace metals and nutrient concentrations in the dry season (mg/L)

Parameter	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Chloride	51.66	46.12	53.50	68.98	57.18	51.94	55.80	44.18	48.74	55.22
Fluoride	0.08	0.09	0.07	0.09	0.07	0.08	0.07	0.06	0.05	0.07
Phosphate	0.38	0.98	0.24	0.30	0.82	0.22	0.19	0.22	0.15	0.40
Nitrate	0.38	0.29	0.24	0.30	0.28	0.18	0.29	0.36	0.39	0.47
Mercury	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Selenium	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Iron	0.03	0.04	0.02	0.03	0.03	0.03	0.03	0.03	0.04	0.04
cadmium	0.02	0.03	0.03	0.04	0.01	0.01	0.02	0.03	0.03	0.02
Lead	0.015	0.004	0.021	0.060	0.028	0.024	0.014	0.007	0.004	0.008
Manganese	0.03	0.06	0.04	0.03	0.03	0.07	0.02	0.02	0.03	0.02

BDL: Below detection limit

Table 4.8: Anions, heavy metals and nutrient concentrations in the wet season (mg/L)

Parameter	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
Chloride	48.108	50.648	50.636	67.132	47.644	49.238	43.564	43.544	39.534	60.336
Fluoride	0.070	0.060	0.068	0.640	0.074	0.056	0.034	0.04	0.058	0.070
Phosphate	0.057	0.050	0.057	0.046	0.126	0.072	0.033	0.063	0.054	0.047
Nitrite	0.014	0.020	0.013	0.011	0.014	0.019	0.014	0.017	0.019	0.016
Nitrate	0.360	0.290	0.230	0.290	0.278	0.2068	0.290	0.338	0.380	0.410
Mercury	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Selenium	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Iron	0.198	0.108	0.204	0.406	0.238	0.170	0.644	0.378	0.300	0.142
Cadmium	0.029	0.031	0.022	0.010	0.038	0.012	0.012	0.012	0.007	0.006
Lead	0.001	0.001	0.000	0.001	0.000	0.002	0.001	0.001	0.001	0.001
Manganesse	0.018	0.058	0.022	0.020	0.006	0.038	0.088	0.016	0.004	0.004

BDL: Below detection limit

Table 4.9: Mean values of parameters of water for both dry and wet seasons over the entire sampling period compared with WHO guidelines.

Parameter	Dry season	Wet season	Mean	WHO
pH	6.93	7.36	7.15	6.5-8.5
Temp. (℃)	27.34	26.26	26.8	25.00
Cond. (µS/cm)	215.41	156.08	185.75	1000
TDS (mg/L)	47.51	41.5	44.51	1000
DO	3.52	5.22	4.37	5.00
Alkalinity (mg/L)	98.18	94.68	96.43	400
T. Hardness (mg/L)	82.59	50.04	71.4	500
Chloride (mg/L)	53.33	50.04	51.69	250
Fluoride (mg/L)	0.11	0.07	0.09	1.50
Phosphate (mg/L)	0.27	0.06	0.16	0.30
Nitrate (mg/L)	0.32	0.31	0.31	10.00
Mercury (mg/L)	0.00	0.00	0.00	0.00
Selenium (mg/L)	0.00	0.00	0.00	
Iron (mg/L)	0.03	0.28	0.16	0.30
Cadmium (mg/L)	0.02	0.02	0.02	0.01
Lead (mg/L)	0.02	0.00	0.01	0.05
Manganese (mg/L)	0.03	0.03	0.03	0.50

Table 4.10: Mean, standard deviation and coefficient of variation of heavy metals in sediment samples from various sampling points in the dry season (mg/kg)

Parameter	Mean	St.d	Co. V%
Mercury	0.00	0.00	0.00
Selenium	0.00	0.00	0.00
Iron	30.54	12.09	39.59
Cadmium	0.07	0.04	57.14
Lead	1.70	0.48	28.24
Manganese	19.99	3.44	17.21

Table 4.11: Mean, standard deviation and coefficient of variation of heavy metals in sediment samples from various sampling points in the wet season (mg/kg)

Parameter	Mean	St.d	Co.V%
Mercury	0.00	0.00	0.00
Selenium	0.00	0.00	0.00
Iron	26.22	3.87	14.76
Cadmium	0.10	0.09	90.00
Lead	1.48	0.66	44.59
Manganese	20.83	2.11	10.13

Table 4.12: Mean values of heavy metal concentrations in sediments in the dry season (mg/kg)

Parameter	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Mercury	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Selenium	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Iron	29.47	29.21	25.87	20.45	24.29	28.48	27.94	22.29	25.00	29.20
Cadmium	0.14	0.09	0.16	0.16	0.16	0.10	0.06	0.03	0.09	0.06
Lead	1.77	1.64	2.37	1.25	1.11	1.25	1.12	0.84	2.01	1.48
Manganese	21.92	20.79	20.95	18.02	23.03	19.70	21.79	21.28	20.94	19.89

Table 4.13: Mean values of heavy metal concentrations in sediments in the wet season (mg/kg)

Parameter	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Mercury	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Selenium	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Iron	22.52	18.97	45.35	20.45	21.29	27.16	12.09	36.99	34.06	43.17
Cadmium	0.10	0.06	0.08	0.14	0.04	0.03	0.05	0.04	0.10	0.03
Lead	1.92	1.92	1.75	1.65	1.49	1.81	1.74	1.44	1.456	1.85
Manganese	21.05	21.58	19.02	20.18	21.88	20.11	19.97	17.86	19.38	18.84

Table 4.14: Mean values of sediments for both dry and wet seasons over the entire period compared with WHO threshold.

Parameters	Dry season	Wet season	Mean
Mercury	0.00	0.00	0.00
Selenium	0.00	0.00	0.00
Iron	30.54	26.22	28.38
Cadmium	0.07	0.10	0.09
Lead	1.70	1.48	1.59
Manganese	19.99	20.83	20.41

Table 4.15: Geo-accumulation Index, Contamination factor and Pollution Load Index for heavy metal concentrations in sediments of Weija dam in the dry season

Parameter	Overall Concentration (mg/kg)				Geo-accumulation Index (Geo-I)				Contamination factor (C_f)				Pollution Load Index (PLI)
	Fe	Cd	Pb	Mn	Fe	Cd	Pb	Mn	Fe	Cd	Pb	Mn	
Site 1	29.47	0.14	1.77	21.92	2.06	-1.68	-4.08	-5.94	6.27	0.47	0.11	0.03	2.09E-03
Site 2	29.21	0.09	1.64	20.79	2.05	-2.32	-4.19	-6.02	6.21	0.30	0.10	0.02	1.17E-03
Site 3	25.87	0.16	2.37	20.95	1.88	-1.49	-3.66	-6.01	5.50	0.53	0.15	0.02	2.68E-03
Site 4	20.45	0.16	1.25	18.02	1.54	-1.49	-4.58	-6.23	4.35	0.53	0.08	0.02	9.61E-04
Site 5	24.29	0.16	1.11	23.03	1.78	-1.49	-4.76	-5.87	5.17	0.53	0.07	0.03	1.30E-03
Site 6	28.48	0.10	1.25	19.70	2.01	-2.17	-4.58	-6.10	6.06	0.33	0.08	0.02	9.14E-04
Site 7	27.94	0.06	1.12	21.79	1.99	-2.91	-4.74	-5.95	5.94	0.20	0.07	0.03	5.33E-04
Site 8	22.29	0.03	0.84	21.28	1.66	-3.91	-5.16	-5.99	4.74	0.10	0.05	0.03	1.56E-04
Site 9	25.00	0.09	2.01	20.94	1.83	-2.32	-3.90	-6.01	5.32	0.30	0.13	0.02	1.23E-03
Site 10	29.20	0.06	1.48	19.89	2.05	-2.91	-4.34	-6.08	6.21	0.20	0.09	0.02	6.72E-04
Mean	26.22	0.11	1.48	20.83	1.88	(2.27)	(4.40)	(6.02)	5.58	0.35	0.09	0.02	1.11E-03

Table 4.16: Geo-accumulation Index, Contamination factor and Pollution Load Index for heavy metal concentrations in sediments of Weija dam in the wet season

Parameter	Overall Concentration (mg/kg)				Geo-accumulation Index (Geo-I)				Contamination factor (C$_f$)				Pollution Load Index (PLI)
	Fe	Cd	Pb	Mn	Fe	Cd	Pb	Mn	Fe	Cd	Pb	Mn	
Site 1	22.52	0.10	1.92	21.05	1.68	-2.17	-3.97	-6.00	4.79	0.33	0.10	0.02	6.42E-02
Site 2	18.97	0.06	1.92	21.58	1.43	-2.91	-3.97	-5.97	4.04	0.20	0.10	0.02	2.77E-02
Site 3	45.35	0.08	1.75	19.02	2.69	-2.49	-4.10	-6.15	9.65	0.27	0.09	0.02	1.51E-01
Site 4	43.82	0.14	1.65	20.18	2.64	-1.68	-4.18	-6.06	9.32	0.47	0.08	0.02	2.37E-01
Site 5	21.29	0.04	1.49	21.88	1.59	-3.49	-4.33	-5.95	4.53	0.13	0.07	0.02	1.79E-02
Site 6	27.16	0.03	1.81	20.11	1.95	-3.91	-4.05	-6.07	5.78	0.10	0.09	0.02	2.54E-02
Site 7	12.09	0.05	1.74	19.97	0.78	-3.17	-4.11	-6.08	2.57	0.17	0.09	0.02	7.26E-03
Site 8	36.99	0.04	1.44	17.86	2.39	-3.49	-4.38	-6.24	7.87	0.13	0.07	0.02	4.52E-02
Site 9	34.00	0.10	1.46	19.38	2.27	-2.17	-4.36	-6.12	7.23	0.33	0.07	0.02	9.99E-02
Site 10	43.17	0.03	1.85	18.84	2.61	-3.91	-4.02	-6.16	9.19	0.10	0.09	0.02	5.55E-02
Mean	30.54	0.07	1.70	19.99	2.00	-2.94	-4.15	-6.08	6.50	0.22	0.09	0.02	6.18E-02

4.8 Physicochemical parameters of water

4.8.1 pH

Though most lakes are basic (alkaline) when they are first formed, they however become more acidic with time due to the build-up of organic materials. When organic substances decay, carbon dioxide (CO_2) forms and combines with water to produce carbonic acid, a weak acid, which lowers water's pH (Akan *et al*., 2012).

As shown in tables 4.3 and 4.4, the coefficient of variation values of pH were 3.46 % for the dry season and 79.08 % for the wet season. These coefficients of variation values were all far less and more than 50 % indicating narrowness and scattered distributions of pH within the sampling sites for dry and wet seasons respectively. The mean pH values ranged from 6.62 at site 8 to 7.16 at site 7 in the dry season (Table 4.5) and ranged from 6.75 at site 6 in the wet season to 8.00 at site 5 (Table 4.6) with seasonal mean values of 6.93 and 7.36 as indicated in Tables 4.3 and 4.4 respectively. The mean pH value of 7.36 in the wet season was higher than that of the dry season. All the pH values were within the (WHO, 2006) stipulated range of 6.5 – 8.5 for drinking water hence; the parameter does not give cause for concern in this river.

The waters in the lake could be described as slightly acidic to neutral based on the pH values obtained. The moderately acidic nature of the water in the dam could be attributed to the increased human activities and rapidly growing population and urbanizing towns (Asante and Ansa-Asare, 2005) where degradation of drowned vegetation and other organic matter cause the release of methane pas which is accompanied by the release of hydrogen sulphide (H_2S) (Connell *et al*., 1984) thereby decreasing the pH of the overlying water. Numerous effects which can harm aquatic life, thereby reducing fish population and lower biodiversity within the dam, can be caused by this slightly acidic nature of the lake.

4.8.2 Temperature

From Tables 4.5 and 4.6, the mean temperature ranged from 26.52 ℃ at site 5 to 28.19 ℃ at site 4 in the dry season with the mean value of 27.34 ℃ (Table 4.3) and from 25.67 ℃ at site 9 to 27.01 ℃ at site 10 with the mean value of 26.26 ℃ (Table 4.4) in the wet season. The levels of temperature in the dry season were relatively high; this could be attributed to the high temperature during the sampling period. High temperature reduces the amount of dissolved oxygen in water thereby affecting aquatic lives (Akan *et al*., 2012). The rise in temperature of water accelerates chemical reactions, reduces solubility of gases, amplifies taste and odour and elevates metabolic activity of organisms.

The coefficient of variation for the dry season and wet season are 2.16 % (Table 4.3) and 8.42 % (Table 4.4) respectively indicating uniform and very close temperature distribution throughout the sampling site within the dam.

4.8.3 Electrical conductivity

The conductivity values varied from 164.57 µS/cm to 285.61 µS/cm (Table 4.5) in the dry season with site 7 recording the highest mean conductivity value of 285.61 µS/cm, while the lowest conductivity value of 164.57 µS/cm at site 4 and ranged from 94.95 µS/cm at site 8 in the wet season to 190.58 µS/cm (Table 4.6) at site 10.

The mean values of 215.41 µS/cm (Table 4.3) and 156.08 µS/cm (Table 4.4) were obtained for the dry season and the wet season respectively.

The dry season's high conductivity mean values may be due to a reduction in the lake volume as a result of evaporation at the water surface resulting in concentration of ions and dissolved organic matter (Coke, 2001), which gets into the dam through runoffs. The nature of the rocks within the study area may also contribute to the high mean conductivity values. However, the wet season's low conductivity might be due to high rainfall which reduces the level of dissolved solids by a dilution of the water in the lake through runoffs which end up increasing the water volumes (FAO, 1993).

As shown in tables 4.3 and 4.4, the dry season obtained 27.49 % while 31.80 % was obtained for the wet season. These low values indicate that the mean conductivity values are closely distributed.

WHO (2004), recommends 1000 µS/cm as acceptable limit for fresh water. The average value of typical, unpolluted water body is approximately 350 µS/cm (Koning and Roos, 1999). This indicates that the electrical conductivity of the lake falls within the acceptable limit. The ionic content measured by conductivity was higher in the Weija Reservoir (mean value of 408 µS/cm) compared to a study on the Volta lake (mean value of 79 µS/cm) (Ofori-Danson and Ntow, 2005).

4.8.4 Total dissolved solids

The dry season recorded the highest mean value of 47.52 mg/L and ranged from 28.59 mg/L at site 6 to 73.45 mg/L at site 2, while the wet season recorded the lowest mean value of 41.50 mg/L and ranged from 30.00 mg/L at site 6 to 52.00 mg/L at site 9, from Tables 4.5 and 4.6.

Tables 4.3 and 4.4 show the Coefficient of variations of total dissolved solids in both the wet and dry seasons. The dry season and wet season recorded 27.07 % and 21.42 % respectively indicating close distribution in both season. A decrease in the volume of water due to the evaporation on the surface of the water might be the reason for the high TDS values in the dry season. The high temperatures recorded in the dry season were relatively higher than that of the wet season; this was in line with the observation made by Ayibotele and Nerquaye-Tetteh (1989) and can be attributed to ionic, nutrient enrichment from agricultural runoff and leaching of soil contaminant (Asante *et al*., 2005; Gampson e*t al.*, 2013).

Water containing more than 500 mg/L of TDS is not considered desirable for drinking water supplies, but in unavoidable cases 1500 mg/L is also allowed (Shrinivasa Rao, 2000). According to McCutheon *et al.,* (1983), the palatability of water with TDS level less than 600 mg/L is generally considered to be good whereas water with TDS greater than 1200 mg/L becomes increasingly unpalatable**.** The total dissolved solids consist mainly of carbonates, bicarbonates, chlorides, sulphates, phosphates and possibly nitrates of calcium, magnesium, sodium, potassium, with traces of iron, manganese and other substances. The chemical content of water may be lowered artificially by dilution or raised by the addition of chemical wastes, dissolved salts, acids, alkalis, gas or oil-well brines or drainage waters from irrigated land. Excessive TDS can reduce water clarity, hinder photosynthesis, and lead to increased water temperatures (USEPA, 1999). However, the TDS levels recorded in the entire sample points were below the WHO guideline of 1000 mg/L for the protection of fisheries and aquatic life and for domestic water supply.

4.8.5 Dissolved Oxygen (DO)

The dissolved oxygen refers to the amount of oxygen dissolved in the water and it is particularly important in limnology (aquatic ecology) (Weiss, 1970). The value of DO is of critical importance because low DO causes reduction in specific fish species and the loss of aquatic ecosystems. The major factors controlling dissolved oxygen concentration are photosynthesis producing oxygen while respiration and nitrification consume oxygen (Best *et al.*, 2007).

According to Todd (1970), DO concentrations of 5 ml and above are recommended for maintaining life in a dam.

The coefficients of variation of DO recorded in both the dry and wet seasons are 15.91 % and 8.43 % in tables 4.5 and 4.6 respectively. These values are less than 50 % hence the distributions were uniform. The results shown in Table 4.6 and 4.5 show that the wet season recorded mean DO values varying from 4.56 mg/L to 5.84 mg/L at sites 6 and site 1 respectively and ranged from 2.70 mg/L at site 7 to 4.10 mg/L at site 4 in the dry season. Relatively higher DO levels were registered in the wet season than those of the dry season (Tale 4.5). This relatively higher DO levels in the waters of Weija dam could be ascribed to mixing and aeration due to wind action (Straskaba and Tundisi, 1999) as well as photosynthetic activity. Thus, the oxygen levels in the Weija dam were slightly above the 5 mg/L threshold needed to support fish life (Hynes, 1970). They may also be due to the inflow of cool oxygenated flood waters from the catchment area. The inflow is an annual event that normally occurs from May to August, a phenomenon which was also reported by Ameka *et al.*, (2000). In general, DO levels less than 3 mg/L are stressful to most aquatic organisms. Most fish die at DO level of 1 - 2 mg/L. However, fish can move away from low DO areas. Water with low DO from 0.2 - 0.5 mg/L are considered hypoxic; waters with less than 0.5 mg/L are anoxic. The standard for sustaining aquatic life is stipulated at

5 mg/L a concentration below this value adversely affects aquatic biological life, while concentration below 2 mg/L may lead to death for most fish (Chapman, 1993). The ranges of DO in all the ten sampling sites thus 4.56 to 5.84 mg/L were above the (USEPA, 1999 and WHO, 2002) permissible limit of 4 mg/L and 5 mg/L during the wet season. Hence, the parameter does give cause for concern within the Weija Lake.

4.8.6 Alkalinity

The levels of alkalinity fluctuate between 90.43 to 105.56 mg/L (Table 4.5) in the dry season with site 2 recording the highest and site 8 the lowest while it varies in the wet season from 86.21 to 102.00 mg/L (Table 4.6) at site 9 and site 2 being the lowest and highest respectively. The mean alkalinity for the respective seasons was 98.18 mg/L (Table 4.3) dry and 94.68 mg/L (Table 4.4) wet as well as the reduction in the water volume due to evaporation might increase the constituents of alkalinity. The activities of vegetables farmers within the catchment area of the dam may have resulted in the relatively high values in the dry season. The alkalinity values recorded were all below the WHO (2003) permissible limits for drinking water and hence gives the water the ability to neutralize acids.

The coefficients of variation values were low in both seasons. The dry season obtained 6.17 % while the wet season obtained 6.29 % as shown in Tables 4.3 and 4.4 respectively. The low values indicated that the mean alkalinity values are narrowly distributed. Levels of 20-200 mg/L are common in fresh water systems according to Chapman, (1996). Therefore the recorded means of 98.18 mg/L (Table 4.3) in the dry season and 94.68 mg/L (Table 4.4) in the wet season makes the water acceptable.

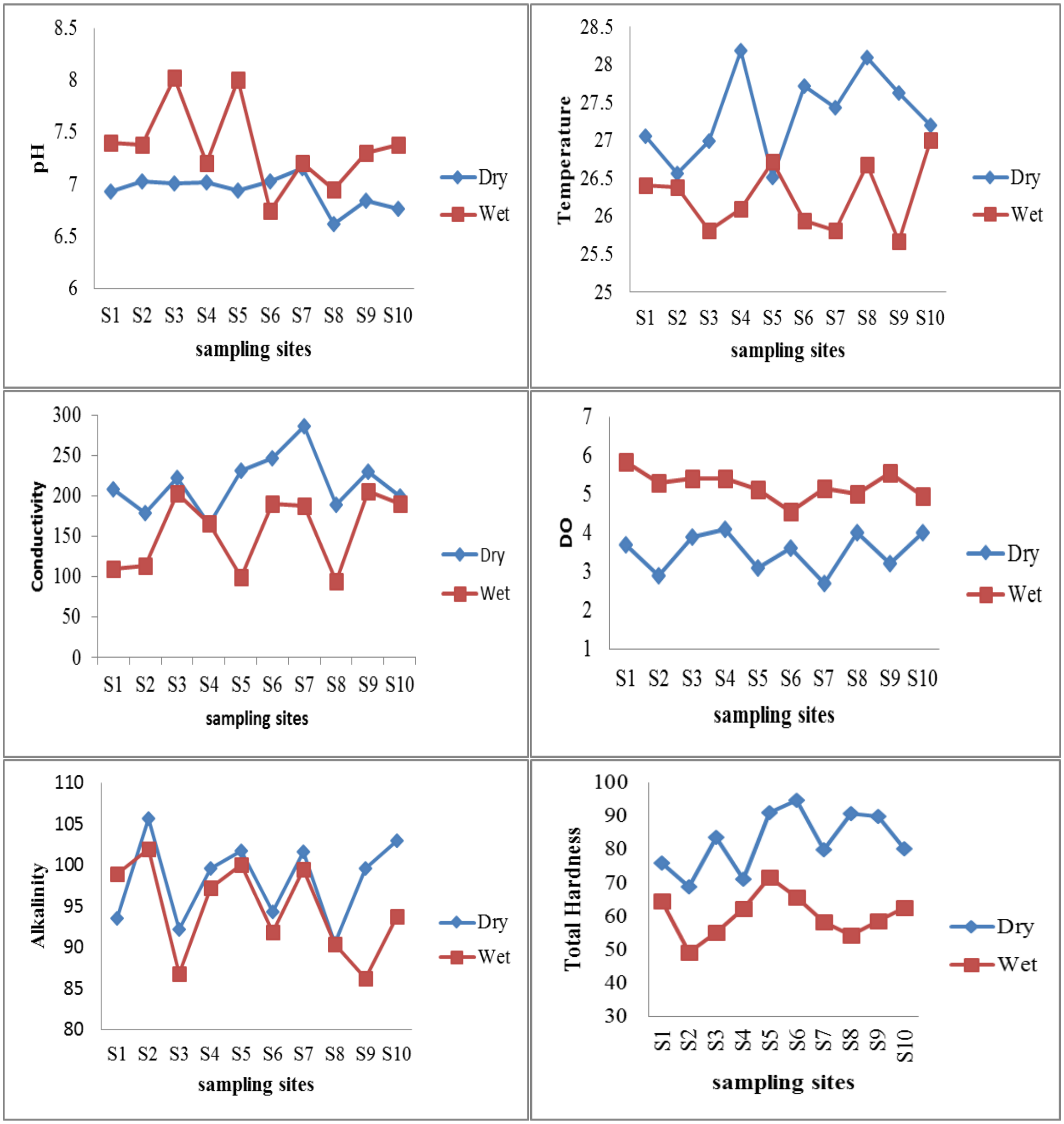
4.8.7 Total Hardness

The levels of total hardness within the ten sampling sites varied from 68.94 mg/L to 94.54 mg/L (Table 4.5) in the dry season, the highest value of Total hardness was observed at site 6, while site 2 shows the least value. The wet season ranged from 49.18 mg/L to 71.51 mg/L (Table 4.6) with the highest level recorded at site 5and the least value detected at site 2. The mean values of the dry season were generally higher than those of the wet season (Tables 4.5 and 4.6). The hardness of water from the dam could be as a result of the nature of rocks in the area with which the surface water is associated (Karikari and Ansa-Asare, 2006). All the total hardness values obtained in both seasons were found to be within the permissible limit of WHO.

From tables 4.3 and 4.4, the coefficients of variations are 11.13 % in the dry season and 21.66 % in the wet season. Though the wet season value is higher than that of the dry season, they were both narrowly distributed.

According to some classifications, water having hardness up to 75 mg/L is classified as soft, 76-150 mg/L is moderately soft, 151-300 mg/L as hard and more than 300 mg/L as very hard **(**Saravanakumar *et al.*, 2011). Hence, water samples from the Weija dam can be considered as moderately soft based on this classification.

Figure 4. 1 indicates the mean concentration distribution of the various physicochemical parameters in both dry and wet seasons for the sampling sites



4.8.8 Chloride

Chloride concentration in the dry season varied from 44.18 mg/L to 68.98 mg/L (Table 4.7) at site 8 and site 4 respectively, while the mean concentration in the wet season varied from 39.53 mg/L to 67.13 mg/L (Table 4.8) respectively at sites 9 and 4. There was a difference in chloride concentrations between both seasons, with the dry season showing relatively higher values (mean 53.33 mg/L) than the wet season (mean 50.04 mg/L) probably due to evapotranspiration (Asante *et al.*, 2005).

The dry and wet seasons recorded coefficients of variation of 14.97 % (Table 4.3) and 16.79 % (Table 4.4) for mean chloride concentrations respectively. These low values show that the mean chloride concentration values are relatively narrowly distributed. All the water samples were found below the threshold of 250 mg/L prescribed by WHO.

4.8.9 Phosphate

Though the natural background levels of phosphate in inland waters usually range from 0.01 to 0.05 mg/L (Dunne and Leopold, 1978), the mean phosphate concentrations at all the ten sites in the Weija dam were in excess of 0.1 mg/L (Table 4.7 and 4.8) in the dry season with site 5 recording the highest (0.82 mg/L) and site 9 recording the least (0.15 mg/L) with a mean value of 0.27 mg/L (Table 4.3) while the wet season values were all below the 0.1 mg/L with the exception of site 5 which recorded the highest value of 0.13 mg/L and site 7 recording the least value of 0.03 mg/L (Table 4.4) with the mean value of 0.06 mg/L. The huge agricultural activities together with the use of fertilizers, pesticides and other agrochemical as well as washing of cars, clothing and bathing within the study area might have been responsible for the high levels of phosphate in the water samples (Asante *et al.*, 2005). Tables 4.3 and 4.4 give the coefficients of variation of mean phosphate concentrations through the entire sampling sites. The phosphate concentration recorded 33.33 % and 50.00 % coefficients of variation respectively, in both the dry and the wet seasons.

Phosphates is not harmful to people or animals unless they are present at very high levels (Akan *et al.*, 2005). Digestive problems could occur from extremely high levels of phosphate (Morrison *et al.*, 2001). The concentrations of phosphate in almost the entire water sampling sites were below the WHO maximum permissible limit of 0.3 mg/L and 5 mg/L set as standard in South Africa (Morrison *et al.*, 2001).

4.8.10 Nitrate

Nitrate concentrations ranged from 0.18 to 0.47 mg/L (Table 4.7), while the mean was 0.32 mg/L (Table 4.3). The lowest and highest concentrations were recorded at sampling sites 6 (0.18 mg/L) and 10 (0.47 mg/L), respectively in the dry season while in the wet season, the highest nitrate value was observed at site 10 (0.41 mg/L), while site 6 shows the least value (0.21 mg/L) (Table 4.8) with the mean value of 0.31 mg/L (Table 4.4).

These concentrations highly exceeded the global average of 0.1 mg/L for nitrate in fresh water (Meybeck and Helmer, 1989). This might be as a result of runoff from fertilized farm lands and domestic wastes (Asante *et al.*, 2005). According to Adedokum *et al.*, (2008), significant nitrate contamination of surface water is found in areas of high population pressure and agricultural development. Also, many nitrogenous fertilizers are converted into mobile nitrates by natural processes which contaminate nearby water bodies more profusely (Freeze and Cherry, 1979, Walter *et. al.*, 1975).

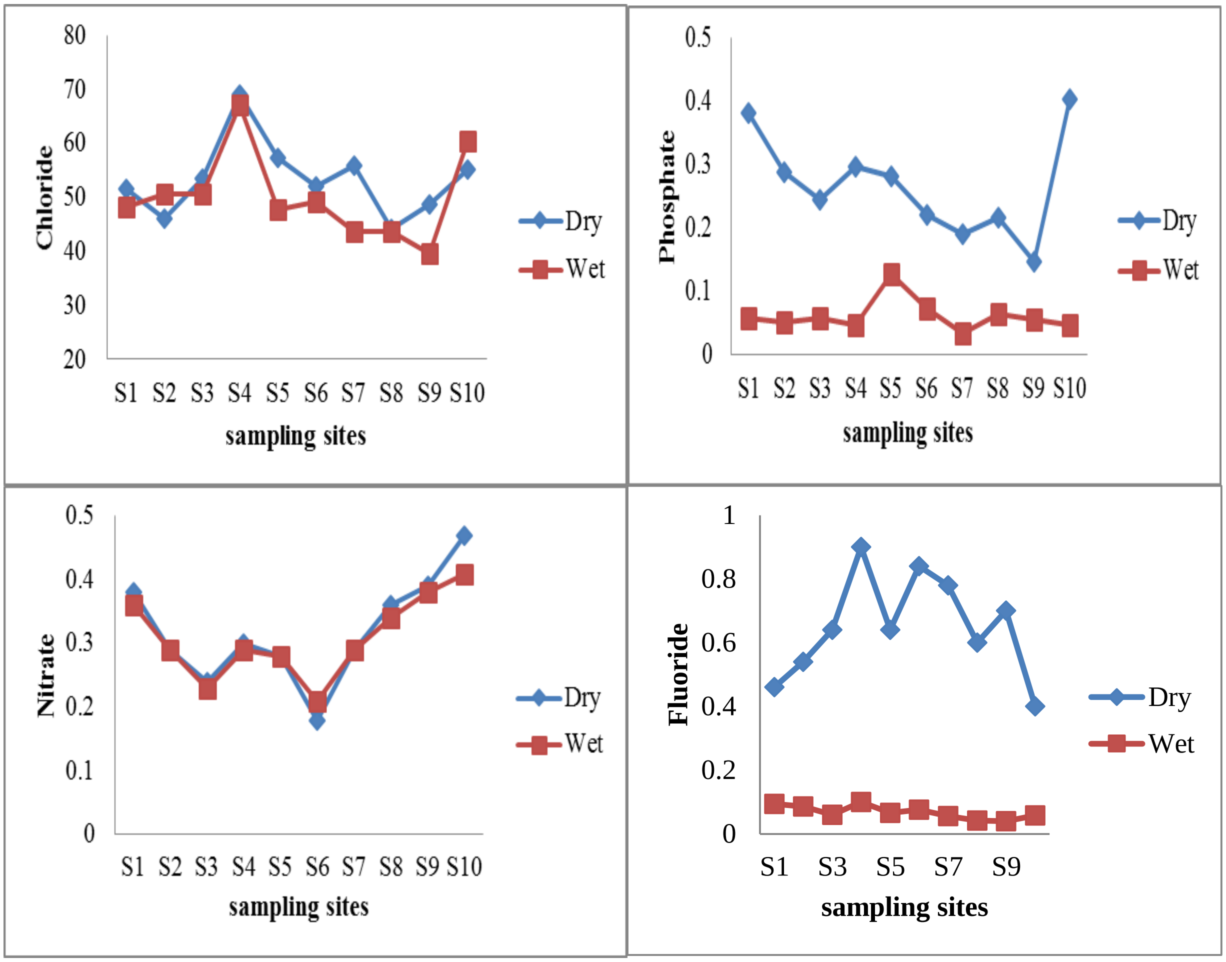
From tables 4.3 and 4.4, the coefficients of variation are 28.13 % in the dry season and 22.58 % in the wet season. These values were both narrowly distributed. Levels of nitrate reported in the present study also corroborates with the mean values of 0.04 mg/L recorded by the water quality assessment of south western and coastal river systems by CSIR/WRI for the Water Resources Commission (WRC, 2003). The overall nitrate levels obtained in all the sampling sites were below the WHO limit of 10 mg/L.

4.8.11 Fluoride

The mean fluoride concentrations ranged from 0.09 mg/L at site 2 to 0.05 mg/L at site 9 in the dry season, while the mean concentrations in the wet ranged from 0.03 mg/L at site 8 to 0.07 mg/L at site 6. The mean value of 0.07 mg/L for the dry season is slightly higher than the 0.06 mg/L of the wet season. Presence of fluoride may be due to the natural decomposition of rocks within the catchment area. From tables 4.3 and 4.4, the coefficients of variation are 28.57 % in the dry season and 28.57 % in the wet season. The recorded values were below 50 %, which indicates closely dispersed fluoride concentration. Tables 4.7 and 4.8 indicate the range of fluoride concentrations in both dry and wet seasons.

The WHO (2003), report showed that low levels of fluoride are medically good for healthy teeth but a high levels can result in a disease called skeletal fluorosis. Fluoride levels within the dam in both seasons were generally below WHO recommended levels for drinking water of 1.5 mg/L.

The mean concentration distribution of nutrients in both dry and wet seasons for sampling sites as shown in figure 4.2



4.9 Heavy metal concentrations in water

4.9.1 Iron

The highest concentration of Fe (0.04 mg/L) in the water samples was detected at site 10, while the least value of 0.02 mg/L (Table 4.7) was observed at site 3 in the dry season with a mean concentration of 0.03 mg/L (Table 4.3). For the wet season, site 7 shows the highest concentration of 0.64 mg/L (Table 4.8), and the least value of 0.11 mg/L was detected at site 2 with a mean value of 0.28 mg/L (Table 4.4). Though, iron is one of the essential elements in human nutrition, however, their presence at elevated concentration in aquatic ecosystems, poses serious pollution and health problems hence only a concentration of 0.3 mg/L in water is the acceptable value (Akan, 2012). The levels of Fe obtained in this study exceeded the iron average of 0.01 mg/L for fresh water (Meybeck and Helmer, 1989). All the results obtained from this study also indicated that the Fe concentrations in both seasons were below WHO guideline value of 0.3 mg/L except at sites 4, 7 and 8 all in the wet season. This may be due to the fact that the Weija Lake is basically granite and analyses of rocks in Ghana by Kerbyson and Schandorf, (1966) have shown that Fe_2O_3 composition in granite is about 2.8 % and may primarily be the source of iron in surface waters. Langanegger (1987) and Pelig-Ba (1989) have also shown in their studies that corrosive materials contribute significantly to the level of iron in the waters. Runoff from domestic activities may also cause these high iron concentrations. From Tables 4.3 and 4.4, the coefficient of variation was 66.67 % in the dry season, while that of the wet season was 57.14 %. Both values were widely distributed in the catchment area of the study during the wet and the dry seasons.

According to Osborn and Hem (1962), iron levels in lakes could generally be influenced by the vegetation of the aquatic environment which included both rooted and free floating forms.

Toxicity of iron in humans has been found to bring about vomiting, cardiovascular collapse and diarrhoea, while iron deficiency may lead to failure of blood clotting (Akan, 2005).

4.9.2 Cadmium

The concentrations of cadmium in the water samples fluctuate between 0.01 mg/L at site 6 and 0.04 mg/L at site 4 (Table 4.7) with the mean value of 0.02 mg/L (Table 4.3) in the dry season, and those of the wet season did ranged between 0.01 mg/L at site 10 and 0.04 mg/L (Table 4.8) at site 5 with a mean value of 0.02 mg/L (Table 4.4). Cadmium concentrations in the dry season were relatively higher than those of the wet season. This could be due to factors such as runoff from agricultural soils where phosphate fertilizers are used (Stoeppler, 1991), leaching from Nickel-Cadmium based batteries (Hutton *et. al.*, 1999) and other metals from wastes (Gampson, 2013; Akan, 2012). Coefficients of variation indicate that the distribution of cadmium was scattered, since it recorded coefficients of variation of 100.00 % (Table 4.3) and 50.00 % (Table 4.4) in both the dry and wet seasons.

The levels of cadmium in the water samples in both seasons were above the (WHO, 2004) standard values of 0.01 mg/L for the survival of aquatic organism, however, they were within the Ghana's target water quality range of 0-5 mg/L.

4.9.3 Lead

The concentrations of lead in the water samples ranged between 0.004 mg/L and 0.060 mg/L (Table 4.7) at sites 9 and 4 respectively with a mean value of 0.02 mg/L (Table 4.3) in the dry season, while, those of the wet season ranged from 0.000 mg/L at site 3 and 0.002 mg/L at site 6

(Table 4.8) with a mean value of 0.001 mg/L (Table 4.4). The levels of lead in the dry season were relatively higher than those of the wet season. These results clearly indicate that lead which is used in paints, batteries, pesticides, herbicides might have been introduced into the water body due to anthropogenic activities in the catchment area (Gampson, 2013). Lead in drinking water can be toxic.

Tables 4.3 and 4.4, indicate a wide distribution of lead with 100.00 % and 100.00 % coefficient of variations in the dry and wet seasons respectively.

The concentration of lead in the water samples from all the sampling sites within the dam in both seasons were all below the permissible limit of 0.05 mg/L set by (WHO, 2004 and USEPA, 2002) except in site 4 in the dry season.

According to U.S. Environmental Protection Agency (1999), the health effect of too much lead in humans can cause serious damage to the brain, kidneys, nervous system, and red blood cells. High lead levels could also cause high blood pressure in adults and paralysis of the wrists and ankles (Gampson, 2013). Hence, the lead levels observed within the dam, especially at site 4 in the dry season, will need to be treated so that the lead levels meet these standards before the water is safe for drinking and for domestic activities.

4.9.4 Manganese

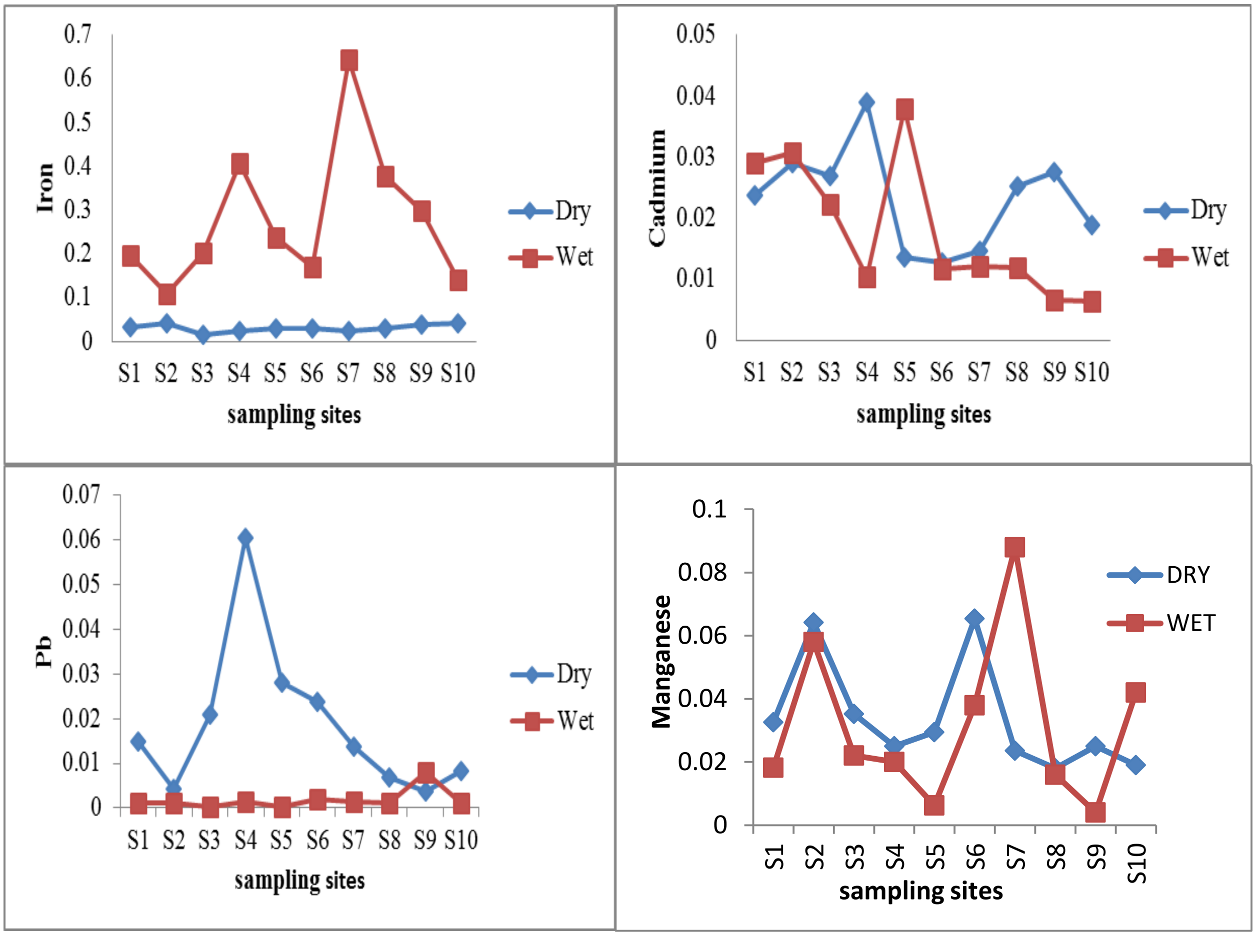
Manganese concentrations in the dry season ranged between 0.02 mg/L and 0.07 mg/L. Site 8 showed the lowest concentration, while the highest level was observed at site 6 (Table 4.7) with a mean value of 0.03 mg/L (Table 4.3). The wet season levels ranged from 0.004 mg/L at site 9 and 0.088 mg/L at site 7 (Table 4.8) with the mean value of 0.03 mg/L (Table 4.4).

The coefficients of variation of manganese shown in tables 4.3 and 4.4 gave a scattered distribution, which includes 100.00 % in the dry season and in the wet season 100.00 %.

Manganese is a common problem element in natural waters. In drinking waters, this element may cause unsightly stains and produce a brown/black precipitate. Although it is an essential element, the chronic ingestion of manganese in drinking water is associated with neurological damage (Kondakis *et al*., 1989).

In this study, the mean manganese concentrations in the dry season (0.034 mg/L) were relatively higher than in the wet season (0.028 mg/L) and this might probably be as a result of weathering from rocks in the lake, domestic and waste from activities of industries located upstream (Karikari and Ansa-Asare, 2006). The levels of manganese in both seasons were all lower in relation to the WHO guideline value of 0.40 mg/L for Mn in drinking water (WHO, 2004) but most of the sites had values in excess of the average of 0.01 mg/L for fresh water (Meybeck and Helmer, 1989).

The mean concentration distribution of heavy metals (in water) in both dry and wet seasons for sampling sites as shown in figure 4.3



4.10 Heavy metal concentrations in sediments

4.10.1 Iron

The concentrations of iron in the sediment samples ranged between 20.45 mg/kg and 29.47 mg/kg (Table 4.12) at sites 4 and 1 respectively with a mean value of 30.54 mg/kg (Table 4.10) in the dry season while, those of the wet season ranged from 12.09 mg/kg at site 4 and 45.35 mg/kg at site 3 (Table 4.13) with a mean value of 26.22 mg/kg (Table 4.11). The sources of these high levels of iron could be the rocks found in the study area and human activities such as the use of agricultural inputs which find their way into the lake through runoffs as well as dumping of chemicals such as paints and ceramics into the lake (Hagan *et al.*, 2011). From tables 4.10 and 4.11, the coefficients of variation of iron in both the dry and the wet seasons are 39.59 % and 14.76 % respectively indicating narrow distribution of Iron (Fe). The mean Contamination factor of Fe was 5.58 and ranged from 4.35 (Site 4) to 6.27 (Site 1) during the dry season and the mean during the wet season was 6.56 with ranges between 2.57 (Site 7) and 9.65 (Site 3). All the C_f values were more than one suggesting moderate contamination by Fe. The Geo-accumulation Index values ($I\text{-}_{Geo}$) during the dry season, had a mean value of 1.88 and ranged from 1.54 to 2.06 (Site 1). In the wet season, the mean was 2.00 and ranged from 0.78 (Site 7) to 2.69 (Site 4). This, from the Muller's classification, falls into category 2 indicating moderate pollution by Iron (Fe).

4.10.2 Cadmium

Cadmium levels in the ten sampling sites fluctuated between 0.03 mg/kg at site 8 and 0.16 mg/kg at sites 4 and 5 (Table 4.12) in the dry season, while those of the wet season ranged between 0.03

mg/kg and 0.14 mg/kg (Table 4.13). The highest cadmium value in the wet season was observed at site 4, while sites 6 and 10 show the least values. From tables 4.10 and 4.11, the seasonal variation recorded a higher mean value of 0.10 mg/kg in the wet season while 0.07 mg/kg occurred in the dry season.

The high cadmium levels might be due to dumping of domestic wastes, agricultural runoff, fertilizers, pesticides and other agrochemicals which possibly release sediment bound metals (Akan *et al*., 2012), urban storm-water runoffs like car batteries, leaching of metals from waste dump and weathering of parent rocks in the study area as well as atmospheric sources (Dankwah, 2011). Cadmium gave 57.14 % coefficients of variation in the dry season while 90.00 % was in the wet season indicating scattered distributions as shown in tables 4.10 and 4.11 respectively. The mean Contamination factor (C_f) was 0.22 and ranged from 0.10 (Site 6) to 0.47 (Site 4) during the dry season. The mean for the wet season was 0.35 and ranged from 0.10 (Site 8) to 0.53 (Site 3, 4 and 5). All the C_f values were less than one suggesting low contamination by Cd. The Geo-accumulation Index values ($I\text{-}_{Geo}$) in the wet season had a mean of -2.94 and ranged between -3.49 (Site 6 and 10) to -1.68 (Site 4). During the dry season, the mean of -2.27 was recorded and ranges from -3.91 (Site 8) to -1.49 (Site 3, 4 and 5). The Geo-accumulation values for all the sampling Sites were negative. From the Muller classification this falls into category 0 indicating no pollution by Cadmium (Cd).

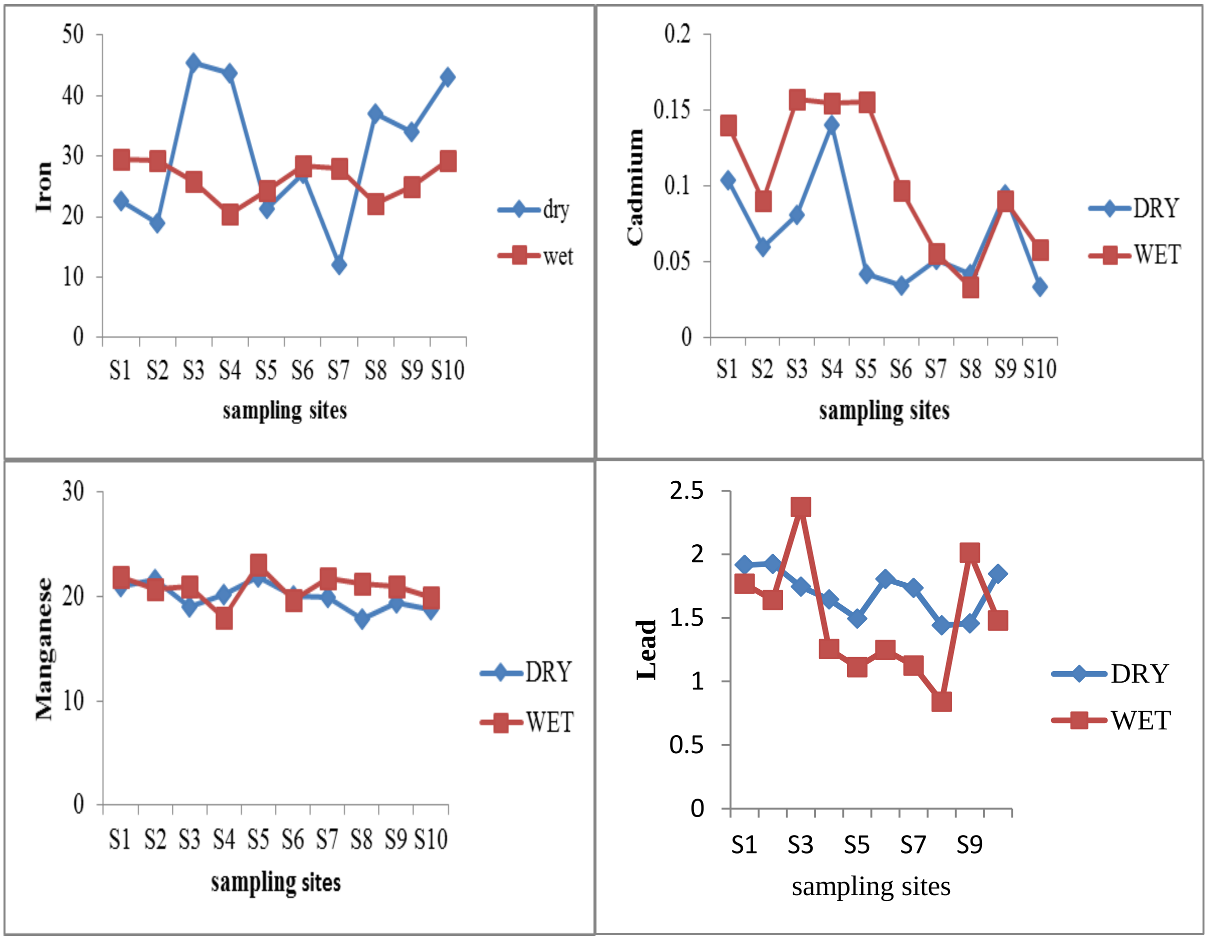
4.10.3 Manganese

The highest concentration of manganese occurred in the wet season with the mean value of 20.83 mg/kg while 19.99 mg/kg occurred in the dry season (Table 4.10) and ranged from 18.02 mg/kg at Site 4 to 23.03 mg/kg at Site 5 in the dry season. The manganese concentration in the wet season ranged from 17.86 mg/kg to 21.58 mg/kg at site 8 and site 2 respectively. The high concentrations of the manganese may be due to the nature of the rocks in the catchment area and runoffs from dump sites along the lake. Manganese can be adsorbed into soil; the extent of adsorption depends on the organic content and cation exchange capacity of the soil. It can also bioaccumulate in lower organisms (e.g., phytoplankton, algae, molluscs and some fish) but not in higher organisms; biomagnifications in food chains is not expected to be very significant (Abbasi *et al.*, 1998). Rubio and Rauret (1996) report that the mobility and transport of metals in aquatic media make them bioavailable and this was found to be in agreement with the high concentration of manganese obtained in this study. Manganese recorded a coefficient of variation of 17.21 % (Table 4.10) and 10.13 % (Table 4.11) in both the dry and the wet seasons. A uniform distribution was observed along the Weija dam. The mean Contamination factor (C_f) was 0.02 which remains constant throughout all the Sites during the dry season and the mean during the wet season is 0.02 and ranges from 0.02 (Site1, 2, 3, 4, 6, 7, 8, 9, 10) to 0.03 (Site5). C_f values below 1 indicates no pollution. This means the dam is not polluted with respect to Mn. The Geo-accumulation Index value ($I\text{-}_{Geo}$) during the dry season was -6.02 and ranged between -6.23 (Site 4) and -5.87 (Site 5). The mean $I\text{-}_{Geo}$ value in the wet season was -6.08 and ranged from -6.24 (Site 8) to -5.95 (Site 5). From the Muller classification this falls into category 0 indicating no pollution by Manganese (Mn).

4.10.4 Lead

In the dry season, lead gave 28.24 % coefficients of variation while 44.59 % was recorded in the wet season; both indicate a uniform distribution as shown in tables 4.10 and 4.11 respectively. Lead concentration ranged from 0.84 at site 8 to 2.37 mg/kg at site 3 (Table 4.12) while the mean was 1.70 mg/kg (Table 4.10) in the dry season. In the wet season, the highest lead value was observed at sites 1 and 2 (1.92 mg/kg), while site 8 shows the least value (1.44 mg/kg) (Table 4.13) with the mean value of 1.48 mg/kg (Table 4.11). The levels of lead obtained in this study showed that the limiting value set by USEPA 10 μg/g was exceeded. The concentration of lead in the sediment samples from the ten sampling sites of the Weija Lake might be attributed to heavy agricultural run-off which contains fertilizers, agrochemicals and pesticides (Banat *et al.*, 1998) and also dumping of lead acid batteries waste into the Lake by artisans within the catchment area of this study. The mean Contamination factor (C_f) for Pb in the sediments was 0.07 and ranged from 0.04 (Site 8) to 0.1 (Site 9) in the dry season and a mean of 0.9 ranging from 0.7 (Site 8 and 9) to 0.1 (Site 1 and 2) in the wet season. All the C_f values were less than one suggesting low contamination by Pb. The Geo-accumulation Index values ($I\text{-}_{Geo}$) for Pb ranged from -3.66 (Site 3) to -4.74 (Site 7) in the dry season with a mean of -4.15 and ranging from -3.97 (Site 1) to -4.38 in the wet season. The Geo-accumulation values for all the sampling Sites were negative. This from the Muller classification falls into category 0 indicating no pollution by Lead (Pb).

The mean concentration distribution of heavy metals (in sediment) in both dry and wet seasons for the sampling sites as shown in figure 4.4



4.11 Heavy metals concentrations in fish

Fish are considered as one of the most indicative factors, in freshwater ecosystems, for the estimation of metals pollution in aquatic ecosystems (Rashed, 2001, Mendil and Uluozlu, 2007, Yousafzai and Shakoori, 2008; Yousafzai *et al.*, 2010, Bhuvaneshwari *et al.*, 2012) because they are easy to obtain in large quantities as well as they occupy high trophic level in the aquatic food chain (Buikena *et al.*, 1982).

According to Karadede *et al.,* (2004), metals have the tendency to accumulate in several organs of the aquatic organisms, especially in fish which in turn may enter into the human metabolism through consumption causing serious health hazards (Puel *et al.*, 1987 and USEPA, 1991).

High amounts of heavy metals are accumulated comparatively by fish located at the high trophic level in the food web. However, this amount is quite high in some cases (Dick and Dixon, 1985; Larsson *et al.,* 1985, Hilmy *et al.,* 1987, Tort and Torres, 1988; Kalay and Erdem, 1995, Canli, 1995).

Tables 4.17 and 4.18 indicate the mean values of the metals, and the weight and length of the fish during both the dry and the wet seasons respectively. Six trace metals Hg, Se, Cd, Fe, Mn and Pb were determined in the fish species. The metals determined were ranked in a decreasing order of Fe>Mn>Pb>Se>Hg with the exception of TZ where the Mn was the highest during the wet season. The Cd and Se were below the detection limit in all the fish species and CN respectively while Hg was present in the lowest concentration, Fe and Mn were high while Se and Hg recorded the lowest concentration and ranked as Fe >Mn>Pb>Se > Hg with the exception of TZ during the wet season. For the dry season, the metals level were ranked in the order of Mn>Fe>Pb>Se>Hg>Cd in all the fish species except in TM in which Fe obtained the highest concentration followed by Mn, Pb, Cd, Se and Hg during the dry season.

T-Hg levels in the edible muscle tissue of fish ranged from 0.099 - 0.014 mg/kg in the dry season while ranging from 0.224 - 0.466 mg/kg in the wet season. All fish samples studied showed T-Hg levels below the World Health Organization (WHO/FAO) limit of 0.5 mg/kg wet weight. The level of T-Hg in fish is based on the fish species and the concentrations also varied with factors such as total length of fish and fresh weight of fish. The highest Hg concentration of 0.466 mg/kg was recorded in *Tilapia zilli* in the wet season and minimum concentration of 0.014 mg/kg in *Chrysichthys nigrodigitatus* in the dry season.

The presence of mercury in the fish species could be as a result of add-on due to the handling of the fish species by fishermen and retailers from whom the fish species where obtained. The migration of the fish from upstream where there might be possible mercury pollution could also be a factor.

Results of mercury concentrations obtained indicated that in the same environment, fish of the same species have significantly different concentrations of mercury within the same aquatic system based on the results of mercury levels obtained. This may be due to physiological factors such as sex, age, size, growth rate, or metabolic rate since these are vital variables that determine concentration of mercury accumulation in fish according to Huckabee *et al*., (1979). In the food chain, the maximum levels of Hg is observed in the secondary and tertiary tropic levels (Dix, 1891; Hamilton, 1971) and at these concentrations, toxicity of mercury is much felt.

Mercury content in fish is considered to be a good indicator of human exposure to organic or methyl mercury. Humans' health concerns arise when fish and wildlife from aquatic ecosystems are consumed by humans since fish accumulate high concentrations of methyl mercury (Uchida *et al*., 1961) which can affect the nervous system, cause blurred vision, coma and ultimately death (Harada, 1995; Takeuchi and Eto, 1999). Hence, diet consisting particularly of fish, may be the main source of human exposure to methyl mercury. Mean mercury concentrations vary widely between species, which can be explained by trophic positions or food chain length in the food web according to studies conducted by Cabana *et al*., (1994) on fish from Ontario Lake in Canada and Kidd *et al*., (1995) on fish from Lango Manso, a reservoir in Brazil. Moreover in aquatic environments, mercury is converted to methyl mercury which is taken up by biota and accumulated in the food chain, sometimes to concentrations that are many thousands of times greater than concentrations in the surrounding water (UNEP, 2010).

Relatively low mercury levels found in the fish species analysed in this study may be as a result of unsuitable organic matter, pH, seasonal changes, regional variations and hydrologic conditions which are thought to be the most significant factors that control accumulation of mercury in fresh water fish as reported by Lindqvist *et al*., (1991). From the study, it is observed that Fe, Mn, Cd and Pb were highly bioaccumulated in the muscles of the fish sample while Hg and Se were the least accumulated in both dry and wet seasons. Any contamination from toxic substances in the muscle (main edible parts) of fish can adversely affect human health (Agah *et al.*, 2009).

All the trace metals observed in this study were all above guideline limits of WHO, 2003. This indicates significant level of trace metal contamination of the edible parts of the three fish species consumed in the study area as reported by Anim-Gyampo *et al.,* (2013). High concentrations of Lead (Pb), Magnesium (Mg) and Cadmium (Cd) in the muscles of the fish species might be due to chemicals from agricultural activities (Anim-Gyampo, 2013). According to Rashed (2001), Pb and Cd levels can increase in fish tissues collected in freshwater ecosystem impacted by agriculture activities. Within the study area, Pb and Cd are some of the common heavy metals found in the chemical fertilizers used therefore, the likelihood of these trace metals coming from the chemical fertilizers, weedicides and all forms of pesticides being used on farms may be carried-out by surface run-off into the dam as pollutants (Anim-Gyampo, 2013).

Table 4.17: Mean metal concentration in some species of fresh water fish from Weija in the wet season

Fish species	**Weight (g)**	**Length (cm)**	**Hg (mg/kg)**	**Se (mg/kg)**	**Fe (mg/kg)**	**Cd (mg/kg)**	**Pb (mg/kg)**	**Mn (mg/kg)**
Tilapia zilli	70.850	15.390	0.466	0.133	0.557	0.000	0.163	1.284
Tilapia mariae	81.450	14.870	0.224	0.081	0.626	0.000	0.103	0.541
Chrysichthys nigrodigitatus	75.830	12.270	0.294	BDL	0.343	0.000	0.000	0.089

BDL: Below detection limit

Table 4.18: Mean metal concentration in some species of fresh water fish from Weija in the dry season

Fish species	Weight (g)	Length (cm)	Hg (mg/kg)	Se (mg/kg)	Fe (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Mn (mg/kg)
Tilapia zilli	75.287	15.857	0.099	0.061	0.847	0.011	0.206	1.357
Tilapia mariae	75.477	14.514	0.047	0.081	0.694	0.023	0.089	0.611
Chrysichthys nigrodigitatus	66.060	14.214	0.014	0.011	0.423	0.000	0.011	0.943

4.12 Bioaccumulation Factor (BF) in Fish Species

The bioaccumulation factor in fish tissues from the aquatic ecosystem, which include water and sediments, was calculated according to Kalfakakour and Akrida-Demertzi (2000) and Rashed (2001) as follows:

$$BF=\frac{\text{Metal concentration in fish tissue}}{\text{Metal concentration in sediment or water}}$$

The muscle tissues of *Tilapia Zilli*, *Tilapia mariae* and *Chrysichthys nigrodigitatus* were analysed to ascertain the level of heavy metals bioaccumulation. Hg, Se and Cd were not detected in the tissue of *Tilapia Zilli*, *Tilapia mariae* and *Chrysichthys nigrodigitatus*.

Pb was also not detected in the tissues of *Chrysichthys nigrodigitatus* in the wet season. Results obtained indicated that Fe, Mn and Pb were bioacumulated maximumly in TM and TZ respectively. The BF of heavy metals detected for all fish samples were ranked in a decreasing order of:

Tilapia Zilli (TZ);

Pb (210.272) > Mn (67.411) > Fe (2.730) > Hg (0.000) ≈ Cd (0.000)≈ Se (0.000)

Tilapia mariae (TM);

Pb (113.469) > Mn (31.008) > Fe (3.040) > Hg (0.000) ≈ Cd (0.000)≈ Se (0.000)

Chrysichthys nigrodigitatus (CN);

Mn (58.194) > Fe (1.613) >Pb (0.000) ≈ Hg (0.000) ≈ Cd (0.000)≈ Se (0.000)

The high values of Pb, Mn and Fe bioaccumulated in fish samples might be due to the disposal of industrial and domestic wastes from surrounding areas which may contain higher levels of these metals (Enuneku *et al.,* 2013). The accumulation difference in metal levels obtained in the muscles of the fish samples might be attributed to differences in their physiological roles (Asante *et al.,* 2013). It has been reported that different organisms have different metabolic rates and different food requirements and amounts. Organisms with high food intake tend to accumulate more metals (Ademoroti, 1996).

Table 4.19: Mean metal concentration in some species of fresh water fish from Weija in the dry season (mg/kg)

Sample	Hg	Se	Fe	Cd	Mn	Pb
Tilapia zilli	0.00	0.00	2.73	0.00	67.41	210.27
Tilapia mariae	0.00	0.00	3.01	0.00	31.01	113.47
Chrysichthys Nigrodigitatus	0.00	0.00	1.61	0.00	58.19	0.00

Table 4.20: Mean metal concentration in some species of fresh water fish from Weija in the wet season (mg/kg)

Sample	Hg	Se	Fe	Cd	Mn	Pb
Tilapia zilli	0.00	0.00	30.79	0.84	39.30	15.97
Tilapia mariae	0.00	0.00	25.42	0.82	18.04	5.77
Chrysichthys nigrodigitatus	0.00	0.00	15.98	0.00	28.06	0.55

4.13 Mercury and Selenium molar ratios

Ralston and others (Ralston, 2008; Peterson *et al.*, 2009) have suggested that selenium: mercury molar ratios above 1 protect against mercury toxicity, although the actual ratio that is protective is unclear. Ralston (2008, 2009) and others (Kaneko and Ralston, 2007; Raymond and Ralston, 2004, 2009; Peterson *et al.*, 2009; Ralston and Raymond, 2010) have argued strongly for the molar ratio being an important value for risk assessment, rather than relying only on the level of methyl mercury, although, the practical implications of the modification of mercury toxicity by selenium are unclear (Watanabe, 2002) because of the variability in toxic kinetics. Koerman *et al.*, (1975) however, reported a 1:1 molar ratio between Se and Hg in organs (mainly liver) of some mammals. The threshold levels of selenium need to be attained especially in fish parts inorder to identify a protective effect of selenium in the detoxification of mercury. The selenium/mercury (Se/Hg) molar ratio was obtained by dividing the mean selenium concentration (mg/g) by 78.96 and the mean mercury concentration (mg/g) by 200.59,

Mean Se/Hg molar ratio in TM (0.9091) recorded the highest compared to TZ (0.739) and CN (O) (Table 4.21) in the wet season. In the dry season, the mean (Hg/Se) molar ratio in TM (47) was the highest compared to TZ (0.625) and CN (0.1643) while the mean Se/Hg molar ratio in TZ (1.600) was higher than in TM (0.0213) and CN (0.609) (Table 4.22).

The mean Se:Hg ratio obtained in this study showed a clear difference among fish species due to the variation in Hg levels in the fish species. Selenium usually varies less because it is an essential trace element (i.e. a deficiency state has been identified) known to regulate the body, and is toxic at high levels (Eisler, 2000). Mercury, on the other hand, has no known essential role (Burger and Gochfeld, 2012). Mercury levels are usually correlated with fish size (weight or length), both within and among species (Penedo de Pinho *et al.,* 2002; Green and Knutzen, 2003; Storelli *et al*., 2002; Simonin *et al*., 2008) and was hence correlated in this present study.

There are many reasons for the variability in selenium: mercury ratios within the fish species in the Weija dam. Since the ratio is a function of both mercury and selenium levels, it should reflect differences in mercury levels (since selenium have some regulation and therefore more consistent levels within the fish species) (Eisler, 2000).

Other reasons for variation within the species include (1) mercury levels are not physiologically regulated; levels reflect bioaccumulation with age, and biomagnification up the food chain (Downs *et al.,* 1998; Swanson *et al.,* 2003); (2) mercury levels increase with age, while selenium levels do not (McIntyre and Beauchamp, 2007; Burger and Gochfeld, 2011), (3) differences in trophic level and for aging location (locally or geographically) affect mercury uptake (Power *et al.*, 2002), (4) mercury levels in prey foods vary, even if the prey are at the same trophic level, due to feeding in different habitats (Snodgrass *et al.,* 2000), and (5) fish have different migratory paths and time in residence in contaminated waters, which result in different mercury uptake and levels within a species (Burger, 2009).

Table 4.21: Total Mercury-Selenium molar ratios in fish species

Codes	Hg (mg/kg)	Se (mg/kg)	Hg:Se	Se:Hg
Tilapia zilli	0.002	0.002	1.365	0.739
Tilapia mariae	0.001	0.001	1.100	0.909
Chrysichthys nigrodigitatus	0.001	0.000	0.000	0.000

Table 4.22: Total Mercury-Selenium molar ratios in fish species

Codes	Hg (mg/kg)	Se (mg/kg)	Hg:Se	Se:Hg
Tilapia zilli	0.001	0.001	0.625	1.600
Tilapia mariae	0.047	0.001	47.000	0.021
Chrysichthys nigrodigitatus	0.000	0.000	0.164	0.609

4.14 Relationship between Total mercury and selenium in fish species

Figures 4.5 A-C and 4.6 D-F indicate the relationship between mercury and selenium levels in the fish samples in this study. There was a relatively strong direct relationship in *Tilapia zilli*, weak correlation in *Tilapia mariae* and no correlation in *Chrysichthys nigrodigitatus* as indicated by the regression analysis for T-Hg and Se in the fish samples.

Mercury was positively correlated with selenium in *Tilapia Zilli* (r^2 = 0.707) and *Tilapia mariae* (r^2 = 0.1736) in the wet season while in the dry season, a positive correlation in *Tilapia mariae* (r = 0.533) and *Tilapia zilli* (r = 0.259). A weak correlation was also observed in *Chrysichthys nigrodigitatus* (r = 0.0667). In *Tilapia zilli*, the mean levels of T-Hg and selenium were 0.017 mg/kg and 0.00 mg/kg in the dry season and 0.023 mg/kg and 0.00 mg/kg in the wet season. All the fish species recorded a similar trend of T-Hg and selenium level in both seasons with the exception of *Chrysichthys nigrodigitatus* in which T-Hg levels were higher than selenium levels within the two seasons (Table 4.19 and 4.20).

In the food chain, selenium can be bioaccumulated and biomagnified (Lemly, 1999; Muscatell *et al*, 2002) and cause severe effect in the aquatic environment. Parˇizek and Oštˇadalova, (1967) and Lindh and Johansson, (1987) indicate in their studies that selenium could protect against mercury toxicity and also suggest that mercury could protect against selenium toxicity. Although most mercury toxicity has been attributed to its binding to sulphur, mercury also binds to selenium with a high affinity. Selenium of low concentrations is associated with increased coronary heart disease (Seppanen *et al.,* 2004), while higher (but subtoxic) concentrations of selenium are associated with lower levels of nonfatal heart attacks (Mozaffarian, 2009). Hence, the relatively high selenium levels obtained in this study could be as a result of selenium being able to bioaccumulate and biomagnify in large aquatic organisms (fish). According to Parizek and Ostadalova (1967), the detoxification of mercury in the presence of selenium indicates its antagonistic effect. Therefore, the high levels of selenium obtained corroborates with the report by Suzuki *et al.*, (1998), that the high levels of selenium is responsible for the detoxification of mercury due to the formation of an equimolar Hg - Se complex which is biologically inert. Hansen (1988), suggest that a threshold level of selenium must be attained before an antagonistic effect can take place within organisms, but, there is a limit to the protection of selenium on mercury toxicity, and selenium itself can be highly toxic (Klimstra *et al.*, 2011).Results obtained from this study corroborate the fact that an important role is played by selenium in the protection and limiting the toxicity of mercury and methyl mercury pollution in aquatic system though there is no previous work done on the mercury and selenium interaction in the Weija dam to compare with.

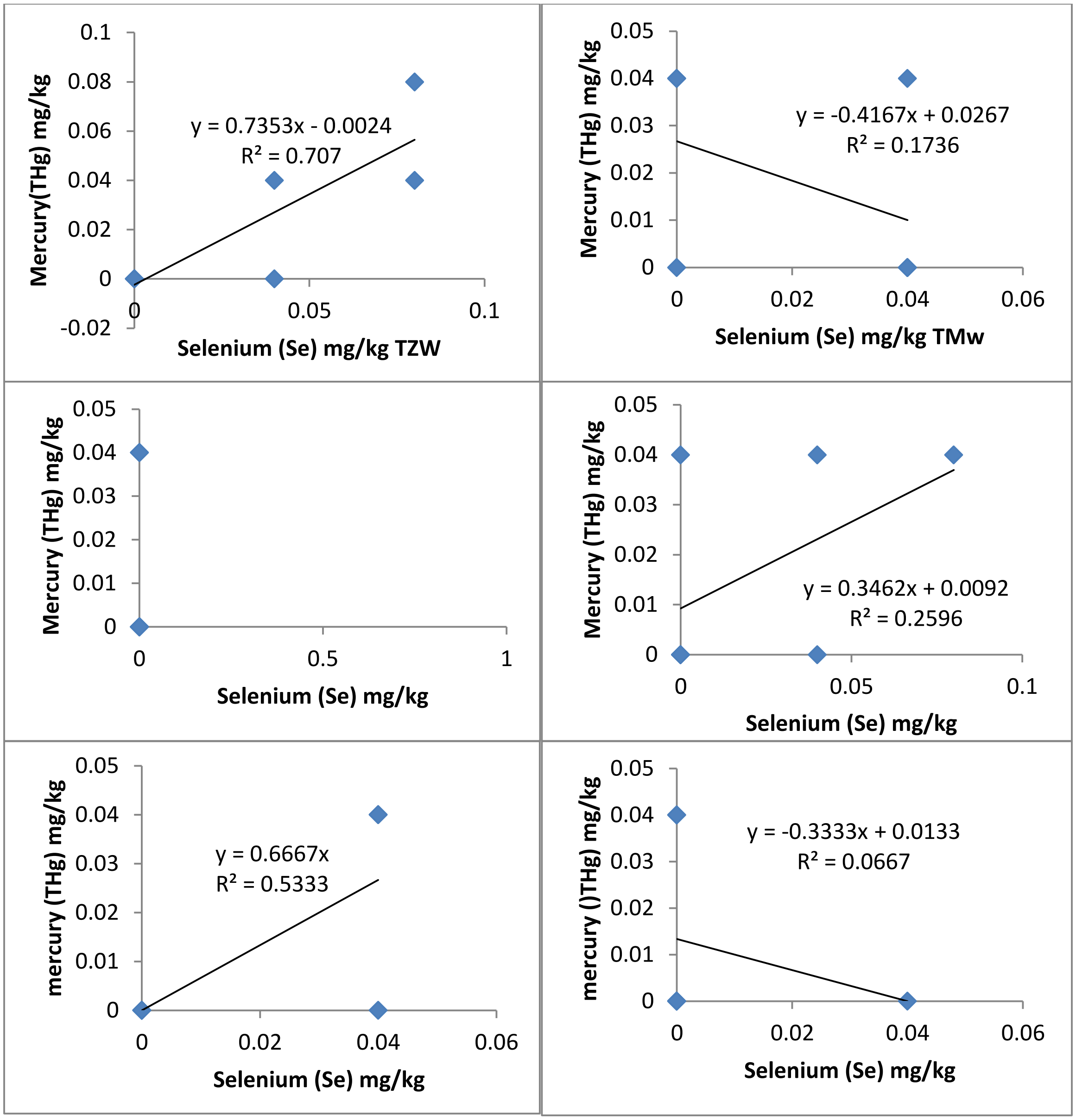


Figure 4.5: A-C: Scattered diagram showing the relationship between Hg and selenium concentrations for *Tilapia zilli* (TZ), *Tilapia mariae* (TM) and *Chrysicthys nigrodigitatus* (CN) respectively in the wet season. Figure 4.6: D-F: Scattered diagram showing the relationship between Hg and selenium concentrations for *Tilapia zilli* (TZ), *Tilapia mariae* (TM) and *Chrysicthys nigrodigitatus* (CN) respectively in the dry season.

Table 4.23: Correlations between Temp, pH and Conductivity in *Tilapia zilli* (dry season)

Dry Season		**Temp (℃)**	**pH**	**Conductivity (µS/cm)**
Hg (mg/kg)	Pearson Correlation	0.088	-0.604	-0.531
	Sig. (2-tailed)	0.851	0.151	0.220
	N	7	7	7

Table 4.24: Correlations between Temp, pH and Conductivity in *Tilapia zilli* (wet season)

Wet Season		**Temp (℃)**	**pH**	**Conductivity (µS/cm)**
Hg (mg/kg)	Pearson Correlation	-0.524	-0.516	-0.620
	Sig. (2-tailed)	0.227	0.236	0.137
	N	7	7	7

Table 4.25: Correlations between Temp, pH and Conductivity in *Tilapia mariae* (dry season)

Dry Season		Temp (℃)	pH	Conductivity (µS/cm)
Hg (mg/kg)	Pearson Correlation	-0.215	0.471	0.460
	Sig. (2-tailed)	0.644	0.286	0.299
	N	7	7	7

Table 4.26: Correlations between Temp, pH and Conductivity in *Tilapia mariae* (wet season)

Dry Season		Temp (℃)	pH	Conductivity (µS/cm)
Hg (mg/kg)	Pearson Correlation	0.113	0.412	-0.161
	Sig. (2-tailed)	0.809	0.359	0.730
	N	7	7	7

Table 4.27: Correlations between Temp, pH and Conductivity in *Chrysicthys nigrodigitatus* (dry season)

Dry Season		**Temp (℃)**	**pH**	**Conductivity (µS/cm)**
	Pearson Correlation	0.335	0.326	-0.016
Hg (mg/kg)	Sig. (2-tailed)	0.462	0.476	0.973
	N	7	7	7

Table 4.28: Correlations between Temp, pH and Conductivity in *Chrysicthys nigrodigitatus* (wet season)

Dry Season		**Temp (℃)**	**pH**	**Conductivity (µS/cm)**
	Pearson Correlation	0.494	0.463	-0.589
Hg (mg/kg)	Sig. (2-tailed)	0.259	0.296	0.164
	N	7	7	7

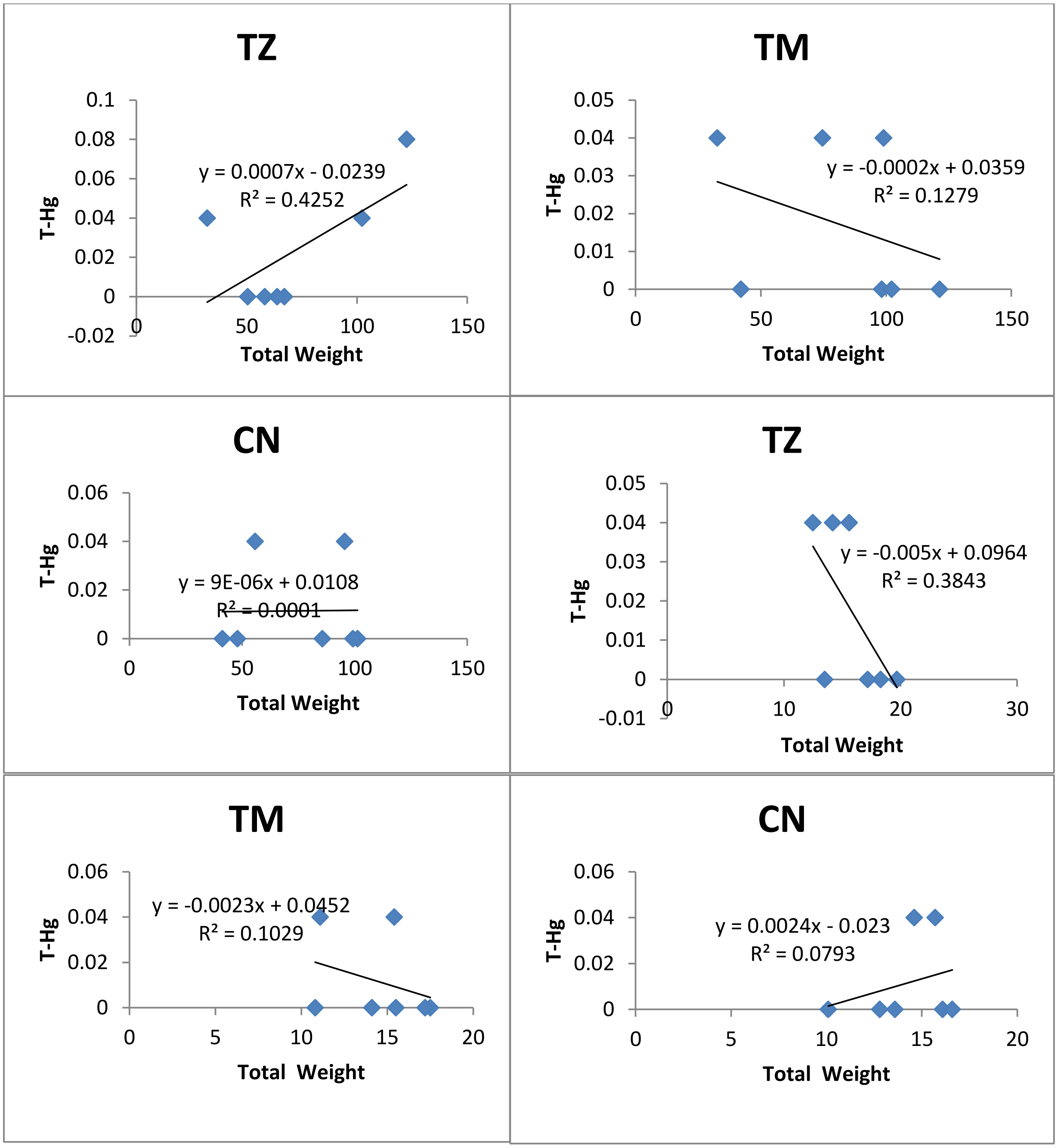


Figure 4.7: A-C: Scatter diagrams showing the relationship between T-Hg and total weight for *Tilapia zilli* (TZ), *Tilapia mariae* (TM) and *Chrysicthys nigrodigitatus* (CN) respectively in the wet season. Figures 4.8: D-F: Scatter diagrams showing the relationship between T-Hg and total weight for *Tilapia zilli* (TZ), *Tilapia mariae* (TM) and *Chrysicthys nigrodigitatus* (CN) respectively in the dry season.

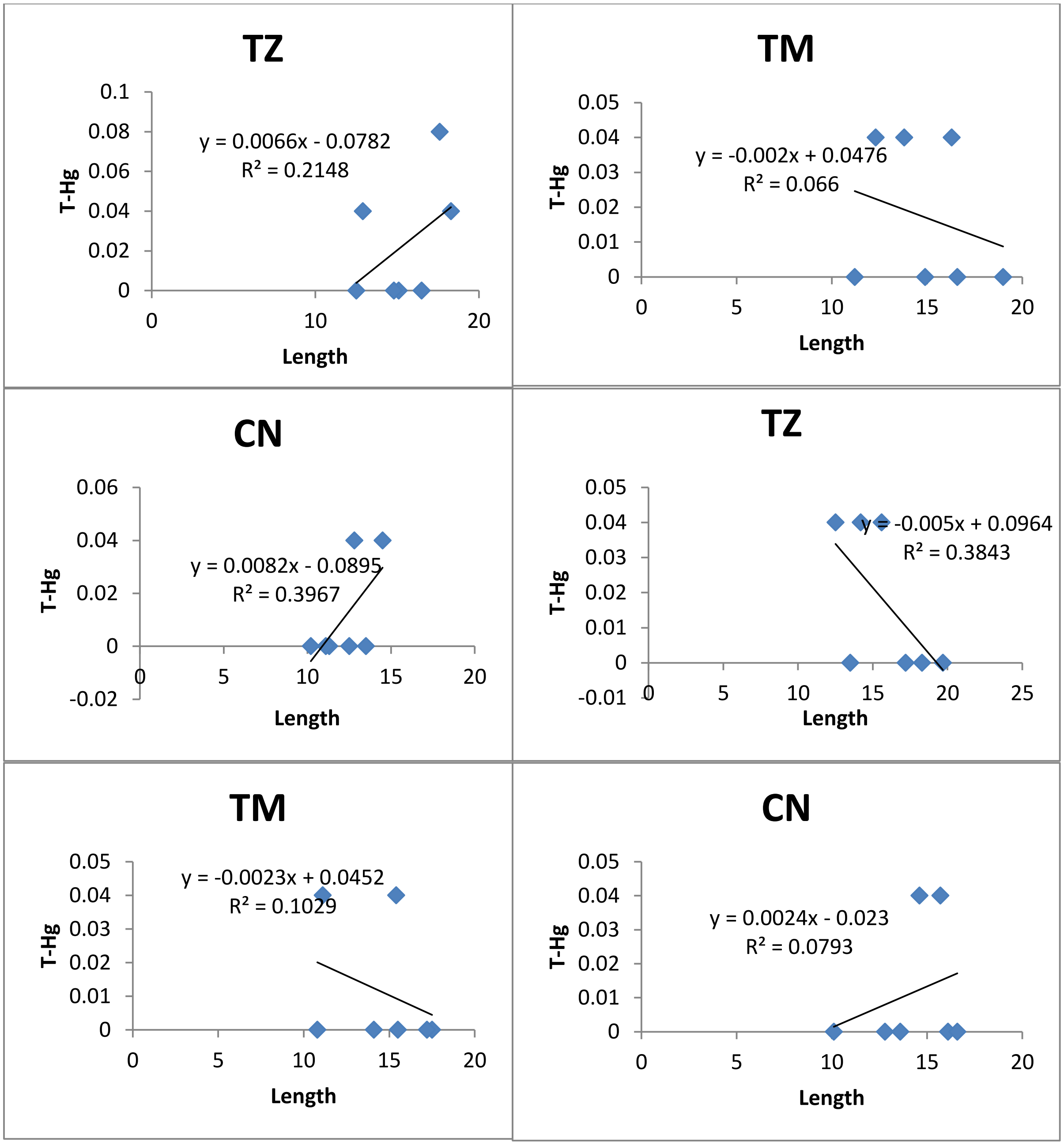


Figure 4.9: A-C: Scatter diagrams showing the relationship between T-Hg and length for *Tilapia zilli* (TZ), *Tilapia mariae* (TM) and *Chrysicthys nigrodigitatus* (CN) respectively in the wet season. Figure 4.10: D-F: Scatter diagrams showing the relationship between T-Hg and length for *Tilapia zilli* (TZ), *Tilapia mariae* (TM) and *Chrysicthys nigrodigitatus* (CN) respectively in the dry season.

4.15 Relationship between T-Hg and Weight and Length in various Fish species

The relationship between mercury levels, weight and length in fish samples are indicated in figures 4.7 A-C and 4.8 D-F. From tables 4.17 and 4.18, the mean T-Hg level in the fish samples ranged from 0.10 to 0.47 mg/kg in the *Tilapia zilli*, 0.05 to 0.22 mg/kg in the *Tilapia mariae*, and 0.01 to 0.30 mg/kg in *Chrysichthys nigrodigitatus*. In both seasons (dry and wet), all the fish samples analysed indicated that the levels of T-Hg were below the WHO acceptable limit of 0.5 mg/kg and were also within the range of mercury concentrations reported by Bodaly *et al.*, (1999). The T-Hg level obtained showed that the fish species have different mercury levels within the same aquatic system. This may be attributed to factors such as sex, age, size, growth rate well as different metabolic and excretion rate (Ntow and Khwaja, 1988). The T-Hg levels were influenced by the length and weight of the fish samples in both seasons.

Tilapia zilli with the highest length had the maximum T-Hg content in its tissues, higher than that of the *Tilapia marae* and *Chrysichthys nigrodigitatus* (Table 4.17 and 4.18) in both seasons. These findings corroborate with the results obtained by Lathrop *et al*., (1991) who reported that length and age of fish species have been shown to be important factors determining mercury level in fish. Huckabee *et al*., (1979) also suggest that beside trophic level and diet, differences in longevity, growth rate and other physiological and ecological factors could also lead to differences in mercury levels among species.

There was a poor correlation between mercury concentration and total weight of *Tilapia zilli* ($r^2 = 0.4252$), *Tilapia mariae* ($r^2 = 0.1279$) and *Chrysichthys nigrodigitatus* ($r^2 = 0.0001$) in the wet season and *Tilapia zilli* ($r^2 = 0.3843$), *Tilapia mariae* ($r^2 = 0.1029$) and *Chrysichthys nigrodigitatus* ($r^2 = 0.0793$) in the dry season.

There was also a poor correlation between mercury concentration and length of *Tilapia zilli* ($r^2 = 0.2148$), *Tilapia mariae* ($r^2 = 0.066$) and *Chrysichthys nigrodigitatus* ($r^2 = 0.3967$) in the wet season and *Tilapia zilli* ($r^2 = 0.3843$), *Tilapia mariae,* ($r^2 = 0.1029$) and *Chrysichthys nigrodigitatus* ($r^2 = 0.0793$) in the dry season. This observation can be due to the fact that the rate of accumulation differs for every fish species as various fish species have different migratory and feeding habits (Ntow and Khwaja, 1988). Lange *et al.*, (1994) indicate that mercury levels differ with fresh weight of fish and total length.

There was no correlation between total length and mercury level for several fish species distributed along the Tasmanian continental shelf, Thompson (1985). The results obtained in this study is in accordance with studies conducted by Thompson (1985), who suggest that without proper knowledge of the biology and particularities of environment inhabited by each species, the use of correlation to estimate mercury content and define human consumption limit for a given species cannot be done.

4.16 Relationship between T-Hg and Physical Parameters

The relationship between mercury and temperature in *Tilapia zilli* as shown in tables 4.23 and 4.24, indicate a weak correlation coefficient of $r = 0.088$ in the dry season and a strong negative correlation coefficient $r = -0.524$ which is not significant at $p < 0.05$ in the wet season. *Chrysicthys nigrodigitatus* showed a weak positive correlation in both seasons but not significant at $p < 0.05$ as shown in tables 4.27 and 4.28. In *Tilapia mariae*, a weak negative correlation coefficient of $r = -0.215$ (Table 4.25) was recorded in dry season but the reverse in which $r = 0.113$ (Table 4.26) was obtained in the wet season was insignificant at $p < 0.05$ in both seasons. As temperature decreases in *Tilapia zilli*, T-Hg concentration increases.

The relationship between pH and T-Hg recorded both strong negative correlations r = -0.604 (Table 4.19) in the dry season and r = -0.516 (Table 4.20) in the wet season. These correlations were not significant at $p < 0.05$. *Tilapia mariae* recorded a weak strong correlation coefficient r = 0.471 (Table 4.25) at $p < 0.05$ insignificant in the dry season and recorded r = 0.412 in the wet season (Table 4.26). Tables 4.26 and 4.28 indicate weak positive correlations between pH and mercury in *Chrysicthys nigrodigitatus* for both seasons. Though weak positive, they were not significant at $p < 0.05$. The positive correlations between pH and mercury which were observed in *Tilapia mariae* and *Chrysicthys nigrodigitatus* in both dry and wet seasons showed that the T-Hg levels increase with an increasing pH although their relationships are not significant at $p < 0.05$. However, the inverse of these positive correlations was observed in *Tilapia zilli* in both seasons, indicating that total mercury levels are indirectly proportional to the pH (Table 4.23 and 4.24).

Tilapia mariae recorded a weak positive correlation between conductivity and T-Hg with r = 0.460 (Table 4.25) but insignificant at $p < 0.05$ in the dry season. A weak negative correlation coefficient r = -0.161 (Table 4.26) insignificant at $p < 0.05$ was recorded in the wet season. *Tilapia zilli* and *Chrysicthys nigrodigitatus* recorded negative correlations in both dry and the wet seasons. However, none of these values were significant at $p < 0.05$. Based on the negative results obtained in the correlation, conductivity is not directly proportional the levels of total mercury in the fish samples. This can be ascribed to the fact that the ionic influence in the fish samples turn to suppress the level of total mercury as a result of chemicals which get into to lake water from anthropogenic activities within the catchment area of the study.

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Based on the results of analysis carried out on the water, sediments and fish from the Weija dam, the following conclusions are derived.

The concentration of total mercury in the edible muscle tissue of all the fish species analysed from the dam did not exceed the World Health Organization (WHO) limit 0.5 mg/kg. However, the total mercury concentrations in sediment and water were all below the detection limit in both the dry and wet seasons. This indicated that the fish species from the Weija dam are not likely to constitute a significant level of Hg exposed to the public through the consumption of fish. A strong association, positive correlation and a weak association were observed between T-Hg and Se in *Tilapia zilli, Tilapia mariae* and *Chrysichthys nigrodigitatus* respectively but an antagonism effect of Se on T-Hg was not clearly established.

The results obtained for all the physicochemical parameters of water from the Weija dam were all below the WHO threshold values except for phosphate which obtained a mean value of 0.27 mg/L in the dry season. Moreover, the results recorded for the physicochemical parameters in the dry season were generally higher than those of the wet season.

The results of this study indicate the presence of heavy metals in the water and sediments from the Weija dam. However, these levels were not high enough to pose danger to consumers. All the heavy metal levels in the water were below the WHO maximum permissible limits. The levels of the heavy metals were generally higher in the dry season compared to the wet season with a exception of a few. Heavy metal levels in the sediment were higher in the dry season than in the wet season except for iron, which was higher in the wet season than in the dry season. The contamination factors and Geo-accumulation Index for all the elements show that there is no contamination of the Weija dam. The Pollution Load Index (PLI) of all sampling sites in the Dam suggest no overall pollution of the Dam. With regards to the measured heavy metals in sediment, water and fish species, a relatively clean aquatic ecosystem is assumed.

5.2 Recommendations

Further studies on heavy metals, especially mercury and selenium interactions, should be carried out, since data on such are not readily available. There should be constant education on proper handling of fish species, as from the study mercury might have been introduced through handling. Though, the concentrations of heavy metals in the Weija dam are largely below the recommended limit, the bioaccumulation effect might be of great concern in the future, hence interventions and constant monitoring of the dam and management in order to reduce anthropogenic discharges in the lake; otherwise, high levels of heavy metal pollution will pose some problems to health and aquatic lives.

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APPENDICES

APPENDIX A

TABLES OF PHYSICOCHEMICAL PARAMETERS OF WATER SHOWING THE MEAN AND STANDARD DEVIATIONS

Temperature (℃)

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
August	27.10	26.10	25.50	26.00	26.66	26.41	25.56	27.22	25.02	26.25
	26.80	26.20	25.50	26.10	26.06	25.55	25.70	26.81	25.30	27.70
	25.90	26.70	26.55	26.20	27.00	26.01	25.62	27.11	26.11	27.10
	26.10	25.90	25.80	26.10	27.10	25.77	26.01	26.23	25.94	27.20
	26.15	27.00	25.70	26.10	26.80	26.00	26.21	26.10	26.00	26.80
Mean	26.41	26.38	25.81	26.10	26.72	25.95	25.82	26.69	25.67	27.01
Std	±0.51	±0.46	±0.43	±0.07	±0.41	±0.32	±0.28	±0.51	±0.48	±0.53
March	27.10	26.80	27.00	28.35	26.55	27.75	27.45	28.10	27.55	27.20
	27.10	25.55	27.00	28.32	26.55	27.80	27.50	28.15	28.10	27.21
	27.10	26.90	27.10	28.32	26.55	27.75	27.45	28.12	27.50	27.18
	27.00	26.80	26.75	27.98	26.40	27.80	27.50	28.05	27.50	27.20
	27.00	26.80	27.10	28.00	26.55	27.50	27.30	28.10	27.50	27.22
Mean	27.06	26.57	26.99	28.194	26.52	27.72	27.44	28.10	27.63	27.20
Std	±0.06	±0.57	±0.14	±0.19	±0.07	±0.13	±0.08	±0.04	±0.26	±0.02

pH

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
August	7.75	7.70	8.21	7.16	7.88	6.63	7.26	6.85	7.29	7.71
	7.29	7.02	8.11	7.25	8.21	6.76	7.31	6.91	7.40	6.97
	7.12	7.76	7.89	7.19	8.02	6.81	7.07	7.01	7.24	7.11
	7.69	7.13	8.07	7.11	7.79	6.92	7.20	6.89	7.27	7.85
	7.17	7.30	7.81	7.30	8.11	6.63	7.16	7.07	7.32	7.26
Mean	7.40	7.38	8.02	7.20	8.00	6.75	7.20	6.95	7.30	7.38
Std	±0.30	±0.33	±0.16	±0.08	±0.17	±0.12	±0.09	±0.09	±0.06	±0.38
	6.76	6.92	6.98	7.11	6.81	7.20	7.21	6.66	6.66	6.81
	6.65	7.22	7.16	7.12	7.20	7.16	7.13	6.66	6.80	6.84
	7.06	7.09	6.94	7.30	6.82	6.77	7.19	6.00	6.88	6.80
	7.11	7.02	7.00	6.83	6.74	7.31	7.42	7.10	6.85	6.75
	7.05	6.91	6.97	6.75	7.11	6.69	6.84	6.68	7.00	6.66
Mean	6.93	7.03	7.01	7.02	6.94	7.03	7.16	6.62	6.84	6.77
Std	±0.21	±0.13	±0.09	±0.23	±0.20	±0.28	±0.21	±0.39	±0.12	±0.07

Conductivity (µS/cm)

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
August	100.11	105.08	198.36	96.69	101.22	189.55	179.43	94.45	185.09	188.60
	96.70	143.11	156.35	105.23	101.00	200.09	207.77	94.05	192.34	189.36
	101.00	121.00	198.24	222.01	98.23	188.16	182.01	93.55	207.22	189.41
	98.23	100.37	261.20	199.89	100.02	179.87	177.27	96.51	240.71	206.66
	155.25	100.42	203.01	203.57	99.80	191.21	189.11	96.20	200.60	178.88
Mean	110.26	114.00	203.43	165.48	100.05	189.78	187.12	94.95	205.19	190.58
Std	±25.21	±18.34	±37.44	±59.57	±1.19	±7.23	±12.38	±1.32	±21.54	±10.03
	171.21	188.01	194.66	151.12	288.72	292.10	307.62	106.21	262.19	199.00
	199.21	194.30	189.92	164.37	192.82	302.29	299.11	206.10	185.42	101.00
	281.16	198.11	259.97	204.21	290.82	197.02	310.49	311.27	211.10	297.67
	217.39	212.37	276.19	102.46	189.12	224.81	298.48	209.84	297.04	195.91
	169.01	100.21	191.77	200.67	196.17	216.09	212.34	110.47	192.89	200.00
Mean	207.60	178.60	222.50	164.57	231.53	246.46	285.61	188.78	229.73	198.72
Std	±45.80	±44.72	±42.03	±41.57	±53.23	±47.53	±41.29	±84.70	±48.09	±69.55

Total Dissolved Solids mg/L

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
August	39.00	35.00	61.00	36.00	40.00	31.00	52.00	29.00	53.00	37.00
	41.00	36.00	57.00	35.00	40.00	30.00	51.00	37.00	49.00	40.00
	39.00	36.00	58.00	40.00	40.00	32.00	48.00	36.00	50.00	36.00
	39.00	39.00	59.00	32.00	40.00	28.00	54.00	34.00	55.00	42.00
	37.00	34.00	55.00	37.00	40.00	29.00	50.00	34.00	53.00	40.00
Mean	39.00	36.00	58.00	36.00	40.00	30.00	51.00	34.00	52.00	39.00
Std	±1.41	±1.87	±2.24	±2.92	±0.00	±1.58	±2.24	±3.08	±2.45	±2.45
	60.20	70.66	46.90	22.99	44.21	38.10	47.31	47.52	32.85	47.21
	52.92	78.21	43.85	30.21	54.10	28.80	47.12	49.27	49.79	52.92
	57.27	67.47	43.66	27.47	50.20	28.10	45.75	51.72	52.72	55.60
	49.85	81.01	45.10	32.87	47.87	20.22	51.29	55.64	49.21	49.81
	55.21	69.90	43.79	40.10	47.29	27.75	39.82	53.94	39.72	50.27
Mean	55.09	73.45	44.66	30.73	48.73	28.59	46.26	51.62	44.86	51.16
Std	±3.97	±5.83	±1.38	±6.39	±3.68	±6.35	±4.15	±3.31	±8.30	±3.20

Dissolved Oxygen mg/L

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
August	6.10	5.50	5.10	4.80	5.10	4.90	5.00	4.80	5.50	5.00
	5.80	4.90	5.60	5.80	5.10	3.90	5.00	5.30	5.30	5.00
	5.70	4.90	5.60	5.40	5.30	4.70	5.10	5.10	5.70	4.90
	5.70	5.60	5.80	6.00	5.00	4.30	5.30	5.00	5.30	4.80
	5.90	5.50	4.90	5.00	5.10	5.00	5.30	4.80	6.00	5.00
Mean	5.84	5.28	5.40	5.40	5.12	4.56	5.14	5.00	5.56	4.94
Std	±0.17	±0.35	±0.38	±0.51	±0.11	±0.46	±0.15	±0.21	±0.30	±0.09
	4.10	3.10	4.20	4.20	3.20	3.50	3.40	3.90	3.40	4.00
	3.70	2.80	3.90	3.70	3.00	3.10	2.90	4.30	3.00	4.00
	3.90	2.50	3.50	3.90	3.40	4.20	2.20	3.90	2.90	3.90
	3.40	3.20	3.70	4.40	2.80	3.20	2.50	4.20	3.20	4.10
	3.40	2.90	4.20	4.30	3.10	4.00	2.50	3.70	3.50	4.00
Mean	3.70	2.90	3.90	4.10	3.10	3.60	2.70	4.00	3.20	4.00
Std	±0.31	±0.27	±0.31	±0.29	±0.22	±0.48	±0.46	±0.24	±0.25	±0.07

Alkalinity mg/L

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
August	100.11	105.08	89.06	96.69	101.22	93.05	100.30	90.50	80.71	96.55
	96.70	103.11	86.32	95.76	101.00	91.01	100.11	92.27	81.13	90.35
	101.00	101.00	82.25	97.06	98.23	95.21	98.20	90.38	90.09	90.27
	98.23	100.37	85.25	98.28	100.02	90.19	97.00	92.25	91.05	94.33
	98.47	100.42	91.20	98.40	99.80	89.76	102.01	86.70	88.07	97.36
Mean	98.90	101.99	86.82	97.24	100.05	91.84	99.52	90.42	86.21	93.77
Std	±1.68	±2.05	±3.46	±1.11	±1.19	±2.27	±1.95	±2.27	±4.95	±3.35
	90.42	104.36	91.40	98.61	100.72	90.02	103.00	84.50	97.24	101.21
	96.11	107.21	93.21	98.57	104.44	94.55	98.66	88.67	102.19	113.29
	94.31	106.16	93.11	111.42	104.10	96.31	101.11	96.00	98.41	100.33
	92.62	106.20	91.37	89.21	99.87	94.35	100.00	94.25	102.27	98.85
	94.31	104.47	92.00	100.22	99.65	96.55	105.21	88.71	98.02	101.34
Mean	93.55	105.68	92.22	99.61	101.76	94.36	101.60	90.43	99.63	103.00
Std	±2.14	±1.23	±0.90	±7.91	±2.33	±2.62	±2.57	±4.66	±2.41	±5.84

Total hardness mg/L

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
August	67.15	48.10	50.62	62.14	70.00	64.11	57.33	65.29	58.21	62.37
	62.31	51.39	58.41	61.24	74.20	62.10	60.41	0.24	56.19	62.00
	65.42	48.56	58.32	62.11	73.22	68.30	55.67	70.17	60.02	68.01
	65.29	45.65	56.40	61.55	71.07	68.09	57.36	67.31	61.22	59.33
	63.16	52.20	52.52	64.07	69.07	66.13	60.25	68.34	57.38	61.28
Mean	64.67	49.18	55.25	62.22	71.51	65.75	58.20	54.27	58.60	62.60
Std	±1.93	±2.65	±3.52	±1.10	±2.16	±2.65	±2.06	±30.26	±2.02	±3.24
	82.14	68.66	81.44	72.82	91.07	92.27	85.10	90.01	89.11	81.10
	78.27	70.62	80.10	69.69	91.64	100.01	77.61	90.21	90.01	80.09
	84.07	70.55	87.41	74.24	91.31	95.09	79.22	97.01	89.21	80.11
	67.61	66.81	78.37	68.91	91.09	97.05	75.31	89.15	91.31	80.04
	67.20	68.08	90.01	70.09	90.22	88.28	82.44	87.26	90.05	80.06
Mean	75.86	68.94	83.47	71.15	91.07	94.54	79.94	90.73	89.94	80.28
Std	±8.00	±1.64	±4.99	±2.27	±0.53	±4.50	±3.88	±3.70	±0.88	±0.46

Phosphate mg/L

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
August	0.410	0.320	0.220	0.290	0.230	0.180	0.200	0.210	0.120	0.470
	0.400	0.320	0.220	0.290	0.280	0.190	0.160	0.230	0.150	0.470
	0.450	0.260	0.260	0.300	0.320	0.230	0.200	0.250	0.090	0.390
	0.320	0.240	0.270	0.330	0.300	0.250	0.200	0.190	0.220	0.330
	0.330	0.300	0.250	0.270	0.280	0.250	0.190	0.200	0.150	0.360
Mean	0.382	0.288	0.244	0.296	0.282	0.220	0.190	0.216	0.146	0.404
Std	±0.055	±0.036	±0.023	±0.022	±0.033	±0.033	±0.017	±0.024	±0.048	±0.064
March	0.056	0.057	0.059	0.042	0.110	0.075	0.034	0.061	0.053	0.048
	0.048	0.050	0.052	0.055	0.127	0.068	0.030	0.069	0.057	0.046
	0.054	0.050	0.055	0.048	0.130	0.071	0.031	0.067	0.052	0.047
	0.064	0.032	0.060	0.044	0.134	0.077	0.038	0.059	0.050	0.047
	0.062	0.058	0.060	0.040	0.128	0.066	0.029	0.060	0.057	0.043
Mean	0.057	0.050	0.057	0.046	0.126	0.072	0.033	0.063	0.054	0.047
Std	±0.006	±0.010	±0.003	±0.006	±0.009	±0.003	±0.004	±0.005	±0.003	±0.002

Nitrate mg/L

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
August	0.35	0.30	0.21	0.30	0.27	0.24	0.31	0.31	0.36	0.39
	0.34	0.30	0.22	0.30	0.27	0.02	0.30	0.32	0.37	0.40
	0.36	0.28	0.23	0.29	0.28	0.25	0.27	0.35	0.38	0.41
	0.37	0.28	0.24	0.29	0.28	0.25	0.28	0.35	0.39	0.42
	0.38	0.29	0.25	0.27	0.29	0.27	0.29	0.36	0.40	0.43
Mean	0.36	0.29	0.23	0.29	0.28	0.21	0.29	0.34	0.38	0.41
Std	±0.02	±0.01	±0.02	±0.01	±0.01	±0.10	±0.02	±0.02	±0.02	±0.02
March	0.41	0.32	0.22	0.29	0.23	0.20	0.35	0.30	0.29	0.51
	0.40	0.32	0.22	0.29	0.28	0.16	0.27	0.35	0.40	0.48
	0.45	0.26	0.25	0.30	0.32	0.17	0.31	0.39	0.39	0.45
	0.31	0.24	0.27	0.33	0.30	0.13	0.26	0.42	0.50	0.41
	0.33	0.30	0.25	0.27	0.28	0.25	0.26	0.36	0.38	0.50
Mean	0.38	0.29	0.24	0.30	0.28	0.18	0.29	0.36	0.39	0.47
Std	±0.06	±0.04	±0.02	±0.02	±0.03	±0.05	±0.04	±0.05	±0.08	±0.04

Chloride mg/L

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
August	46.70	58.10	50.40	70.12	51.61	50.50	43.70	43.20	38.62	61.60
	50.20	44.60	51.66	62.42	42.44	48.90	38.10	42.41	38.70	61.60
	50.12	51.21	53.12	66.10	47.24	46.82	47.20	44.50	42.10	63.34
	48.62	49.00	49.20	70.80	46.72	52.32	38.81	47.81	39.50	60.13
	44.90	50.33	48.80	66.22	50.21	47.65	50.01	39.80	38.75	55.01
Mean	48.11	50.65	50.64	67.13	47.64	49.24	43.56	43.54	39.53	60.34
Std	±2.29	±4.88	±1.78	±3.41	±3.55	±2.21	±5.18	±2.94	±1.48	±3.19
March	48.30	54.20	62.40	70.60	53.50	45.00	54.20	45.00	47.70	54.70
	51.70	52.10	50.60	67.70	50.70	51.00	52.10	43.90	49.60	56.40
	54.90	41.80	53.30	71.20	67.70	50.60	57.60	46.20	50.20	57.10
	54.90	52.10	49.10	69.10	56.30	62.40	54.80	43.60	49.80	54.40
	48.50	30.40	52.10	66.30	57.70	50.70	60.30	42.20	46.40	53.50
Mean	51.66	46.12	53.50	68.98	57.18	51.94	55.80	44.18	48.74	55.22
Std	±3.25	±10.03	±5.22	±2.02	±6.47	±6.36	±3.19	±1.51	±1.62	±1.49

Fluoride mg/L

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
August	0.080	0.080	0.050	0.060	0.070	0.070	0.060	0.020	0.040	0.080
	0.080	0.080	0.050	0.080	0.080	0.070	0.070	0.020	0.040	0.060
	0.070	0.070	0.070	0.060	0.070	0.080	0.060	0.060	0.050	0.060
	0.050	0.070	0.060	0.080	0.050	0.070	0.050	0.030	0.040	0.050
	0.070	0.050	0.070	0.060	0.050	0.080	0.040	0.040	0.030	0.040
Mean	0.070	0.070	0.060	0.068	0.064	0.074	0.056	0.034	0.040	0.058
Std	±0.012	±0.012	±0.010	±0.011	±0.013	±0.005	±0.011	±0.017	±0.007	±0.015
March	0.090	0.090	0.070	0.100	0.080	0.100	0.060	0.030	0.060	0.100
	0.090	0.090	0.060	0.100	0.100	0.070	0.080	0.050	0.070	0.090
	0.080	0.080	0.100	0.100	0.060	0.090	0.080	0.070	0.030	0.060
	0.090	0.080	0.050	0.080	0.060	0.080	0.050	0.090	0.030	0.040
	0.070	0.090	0.080	0.070	0.070	0.080	0.100	0.060	0.050	0.040
Mean	0.084	0.086	0.072	0.090	0.074	0.084	0.074	0.060	0.048	0.066
Std	±0.009	±0.005	±0.019	±0.014	±0.017	±0.011	±0.019	±0.022	±0.018	±0.028

APPENDIX B

MEAN CONCENTRATIONS OF HEAVY METALS

Iron (Fe) levels in water mg/L

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
August	0.150	0.110	0.200	0.040	0.000	0.030	0.000	0.150	0.020	0.000
	0.200	0.130	0.000	0.030	0.000	0.020	0.000	0.140	0.030	0.000
	0.150	0.090	0.150	0.000	0.040	0.020	0.040	0.140	0.030	0.000
	0.000	0.100	0.240	0.020	0.040	0.030	0.040	0.200	0.000	0.030
	0.190	0.110	0.250	0.030	0.030	0.000	0.000	0.050	0.000	0.030
Mean	0.140	0.110	0.170	0.020	0.020	0.020	0.020	0.140	0.020	0.010
Std	±0.080	±0.010	±0.100	±0.010	±0.020	±0.010	±0.020	±0.050	±0.010	±0.010
March	0.070	0.050	0.070	0.040	0.020	0.040	0.010	0.050	0.060	0.070
	0.040	0.070	0.000	0.030	0.050	0.030	0.030	0.030	0.050	0.030
	0.020	0.050	0.000	0.030	0.024	0.010	0.010	0.060	0.040	0.060
	0.010	0.029	0.001	0.020	0.020	0.070	0.050	0.000	0.030	0.040
	0.020	0.001	0.017	0.010	0.037	0.008	0.027	0.000	0.013	0.000
Mean	0.030	0.040	0.020	0.030	0.030	0.030	0.020	0.030	0.040	0.040
Std	±0.030	±0.030	±0.030	±0.010	±0.010	±0.020	±0.020	±0.029	±0.020	±0.030

Cadmium (Cd) levels in water mg/L

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
August	0.030	0.030	0.020	0.010	0.020	0.020	0.010	0.010	0.010	0.000
	0.030	0.030	0.020	0.010	0.040	0.020	0.010	0.010	0.010	0.010
	0.030	0.030	0.030	0.010	0.040	0.010	0.010	0.010	0.010	0.000
	0.030	0.030	0.030	0.010	0.050	0.010	0.010	0.010	0.010	0.010
	0.030	0.030	0.020	0.010	0.040	0.010	0.010	0.020	0.010	0.010
Mean	0.030	0.030	0.020	0.010	0.040	0.010	0.010	0.010	0.010	0.010
Std	±0.004	±0.001	±0.003	±0.001	±0.011	±0.004	±0.000	±0.002	±0.002	±0.006
March	0.016	0.006	0.013	0.004	0.017	0.004	0.017	0.009	0.018	0.008
	0.027	0.028	0.010	0.073	0.014	0.014	0.014	0.033	0.008	0.034
	0.009	0.036	0.052	0.030	0.008	0.006	0.014	0.022	0.018	0.011
	0.052	0.034	0.024	0.039	0.019	0.030	0.014	0.031	0.049	0.024
	0.015	0.041	0.036	0.049	0.010	0.010	0.014	0.031	0.045	0.017
Mean	0.024	0.029	0.027	0.039	0.014	0.013	0.015	0.025	0.028	0.019
Std	±0.017	±0.014	±0.017	±0.025	±0.005	±0.010	±0.001	±0.010	±0.018	±0.010

Lead (Pb) levels in water mg/L

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
August	0.003	0.004	0.001	0.002	0.001	0.005	0.003	0.003	0.000	0.003
	0.000	0.002	0.001	0.000	0.001	0.002	0.002	0.002	0.000	0.002
	0.001	0.000	0.000	0.001	0.000	0.002	0.001	0.000	0.002	0.000
	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.002	0.001
	0.000	0.000	0.000	0.004	0.000	0.001	0.000	0.000	0.000	0.000
Mean	0.001	0.001	0.000	0.001	0.000	0.002	0.001	0.001	0.001	0.001
Std	±0.001	±0.002	±0.001	±0.001	±0.000	±0.002	±0.001	±0.001	±0.001	±0.001
March	0.020	0.008	0.024	0.080	0.029	0.021	0.013	0.009	0.000	0.009
	0.000	0.008	0.021	0.042	0.027	0.011	0.015	0.009	0.007	0.012
	0.020	0.006	0.021	0.040	0.030	0.031	0.003	0.000	0.007	0.000
	0.017	0.000	0.018	0.060	0.030	0.022	0.020	0.016	0.002	0.013
	0.017	0.000	0.020	0.080	0.024	0.034	0.018	0.000	0.002	0.008
Mean	0.015	0.004	0.021	0.060	0.028	0.024	0.014	0.007	0.004	0.008
Std	±0.008	±0.004	±0.002	±0.020	±0.003	±0.009	±0.007	±0.007	±0.003	±0.005

Manganese (Mn) levels in water mg/L

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
August	0.009	0.060	0.030	0.010	0.007	0.020	0.110	0.010	0.004	0.004
	0.020	0.060	0.020	0.020	0.007	0.020	0.090	0.010	0.004	0.004
	0.010	0.080	0.020	0.030	0.005	0.050	0.070	0.010	0.004	0.006
	0.022	0.050	0.030	0.020	0.005	0.070	0.070	0.010	0.004	0.003
	0.030	0.040	0.010	0.020	0.007	0.030	0.100	0.040	0.004	0.004
Mean	0.018	0.058	0.022	0.020	0.006	0.038	0.088	0.016	0.004	0.004
Std	±0.009	±0.015	±0.008	±0.007	±0.001	±0.022	±0.018	±0.013	±0.000	±0.001
March	0.074	0.054	0.066	0.038	0.022	0.037	0.013	0.040	0.026	0.014
	0.043	0.066	0.030	0.028	0.046	0.031	0.027	0.028	0.030	0.020
	0.016	0.054	0.042	0.028	0.024	0.014	0.012	0.022	0.024	0.018
	0.010	0.082	0.021	0.021	0.018	0.045	0.039	0.000	0.032	0.043
	0.020	0.065	0.017	0.010	0.037	0.200	0.027	0.000	0.013	0.000
Mean	0.033	0.064	0.035	0.025	0.029	0.065	0.024	0.018	0.025	0.019
Std	±0.026	±0.011	±0.020	±0.010	±0.012	±0.076	±0.011	±0.018	±0.007	±0.016

Iron (Fe) levels in sediment mg/kg

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
August	30.14	29.35	23.86	19.00	23.57	26.78	28.37	21.20	29.83	30.04
	30.65	29.18	24.78	18.93	25.24	30.61	28.38	28.09	28.38	30.61
	29.93	30.04	26.37	20.33	26.07	30.68	29.12	19.67	29.94	29.09
	27.07	29.09	27.02	23.02	25.57	27.25	29.09	20.83	17.00	26.38
	29.55	28.38	27.32	20.99	21.03	27.07	24.72	21.66	19.86	29.88
Mean	29.47	29.21	25.87	20.45	24.29	28.48	27.94	22.29	25.00	29.20
Std	±1.40	±0.60	±1.49	±1.69	±2.05	±1.99	±1.84	±3.33	±6.12	±1.67
March	21.01	14.80	44.54	49.53	18.13	30.45	10.84	45.88	32.27	44.22
	17.45	20.89	47.71	47.22	23.25	23.36	9.86	38.88	30.37	45.02
	28.02	18.84	48.20	43.32	11.94	30.18	11.67	30.22	49.01	45.13
	22.03	21.20	44.60	39.22	25.00	31.63	14.23	37.77	30.00	41.26
	24.11	19.13	41.70	39.80	28.12	20.10	13.84	32.19	28.60	40.20
Mean	22.52	18.97	45.35	43.82	21.29	27.16	12.09	36.99	34.00	43.17
Std	±3.90	±2.55	±2.66	±4.52	±6.36	±5.07	±1.90	±6.17	±8.46	±2.27

Cadmium (Cd) levels in sediment mg/kg

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
August	0.040	0.107	0.293	0.199	0.160	0.120	0.013	0.027	0.093	0.000
	0.053	0.079	0.067	0.200	0.149	0.020	0.010	0.027	0.052	0.066
	0.530	0.082	0.066	0.053	0.160	0.147	0.080	0.041	0.088	0.065
	0.042	0.082	0.283	0.201	0.146	0.099	0.087	0.019	0.086	0.079
	0.038	0.101	0.077	0.123	0.166	0.101	0.090	0.053	0.133	0.081
Mean	0.141	0.090	0.157	0.155	0.156	0.097	0.056	0.033	0.090	0.058
Std	±0.217	±0.013	±0.120	±0.066	±0.008	±0.047	±0.041	±0.013	±0.029	±0.033
March	0.075	0.034	0.081	0.121	0.045	0.038	0.044	0.052	0.120	0.031
	0.133	0.035	0.045	0.201	0.022	0.029	0.051	0.049	0.092	0.031
	0.081	0.041	0.107	0.165	0.019	0.027	0.050	0.047	0.101	0.025
	0.107	0.121	0.082	0.107	0.064	0.032	0.051	0.029	0.081	0.037
	0.122	0.067	0.092	0.110	0.061	0.044	0.061	0.031	0.080	0.043
Mean	0.104	0.060	0.081	0.141	0.042	0.034	0.051	0.042	0.095	0.033
Std	±0.025	±0.037	±0.023	±0.041	±0.021	±0.007	±0.006	±0.011	±0.017	±0.007

Lead (Pb) levels in sediment mg/kg

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
August	2.759	1.720	4.080	1.747	1.693	1.107	1.401	0.627	1.973	2.547
	1.079	1.613	1.627	1.293	0.840	1.919	0.987	0.560	2.600	0.867
	2.001	2.314	1.821	1.121	0.853	1.221	0.998	1.002	1.652	0.880
	2.014	1.032	2.012	0.999	0.961	0.987	1.215	1.201	2.010	1.858
	0.985	1.515	2.312	1.111	1.212	1.003	1.021	0.814	1.821	1.236
Mean	1.768	1.639	2.370	1.254	1.112	1.247	1.124	0.841	2.011	1.478
Std	±0.739	±0.460	±0.989	±0.295	±0.358	±0.387	±0.180	±0.265	±0.358	±0.721
March	2.252	2.206	2.010	2.346	1.542	1.751	2.561	2.225	2.651	2.352
	2.007	1.654	1.787	1.211	1.999	2.006	1.465	1.532	1.260	3.191
	1.584	2.066	1.005	1.532	1.504	2.013	1.365	1.502	1.192	1.205
	1.992	1.694	2.234	1.445	1.222	1.261	1.717	0.982	1.006	1.232
	1.746	2.001	1.691	1.690	1.201	2.001	1.573	0.962	1.173	1.255
Mean	1.916	1.924	1.745	1.645	1.494	1.806	1.736	1.441	1.456	1.847
Std	±0.258	±0.241	±0.464	±0.429	±0.323	±0.324	±0.479	±0.516	±0.674	±0.895

Manganese (Mn) levels in sediment mg/kg

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
August	21.646	20.031	21.345	18.826	24.517	20.209	24.165	22.961	21.456	20.958
	24.112	20.316	21.456	16.376	26.462	20.316	24.115	22.352	20.316	18.625
	21.618	21.440	21.352	18.715	26.324	21.034	20.581	21.489	21.196	20.551
	21.196	21.209	20.564	19.942	16.565	17.235	20.440	18.965	21.264	20.345
	21.031	20.958	20.021	16.253	21.298	19.698	19.658	20.625	20.456	18.989
Mean	21.921	20.791	20.948	18.022	23.033	19.698	21.792	21.278	20.937	19.893
Std	±1.254	±0.597	±0.630	±1.632	±4.172	±1.457	±2.172	±1.566	±0.515	±1.024
March	20.687	19.874	17.658	15.669	23.232	19.887	18.322	21.235	11.236	22.112
	22.021	20.332	15.998	15.987	21.024	13.589	17.832	10.232	17.854	25.324
	18.987	22.200	19.365	23.654	19.354	24.024	21.366	22.369	24.214	19.215
	23.658	21.487	22.100	21.258	22.664	22.002	22.222	18.624	21.365	15.214
	19.887	24.021	19.984	24.325	23.102	21.032	20.122	16.854	22.214	12.321
Mean	21.048	21.583	19.021	20.179	21.875	20.107	19.973	17.863	19.377	18.837
Std	±1.836	±1.645	±2.320	±4.133	±1.662	±3.947	±1.893	±4.783	±5.099	±5.209

ANOVA table of heavy metals for dry season

ANOVA (Dry Season)

		Sum of Squares	df	Mean Square	F	Sig.
Fe	Between Groups	0.018	37	0.000	1.167	0.405
	Within Groups	0.005	12	0.000		
	Total	0.023	49			
Cd	Between Groups	0.009	37	0.000	1.157	0.412
	Within Groups	0.003	12	0.000		
	Total	0.011	49			
Pb	Between Groups	0.011	37	0.000	0.665	0.833
	Within Groups	0.005	12	0.000		
	Total	0.016	49			
Mn	Between Groups	0.043	37	0.001	6.666	0.001
	Within Groups	0.002	12	0.000		
	Total	0.045	49			

ANOVA table of heavy metals for wet season

ANOVA (Wet season)

		Sum of Squares	**df**	**Mean Square**	**F**	**Sig.**
Fe	Between Groups	0.226	40	0.006	1.212	0.403
	Within Groups	0.042	9	0.005		
	Total	0.268	49			
Cd	Between Groups	0.006	40	0.000	1.553	0.247
	Within Groups	0.001	9	0.000		
	Total	0.007	49			
Pb	Between Groups	0.000	40	0.000	0.557	0.900
	Within Groups	0.000	9	0.000		
	Total	0.000	49			
Mn	Between Groups	0.027	40	0.001	0.563	0.896
	Within Groups	0.011	9	0.001		
	Total	0.038	49			

Paired t-test comparing physicochemical parameters

Paired Samples Test

		Paired Difference							
					95% Confidence Interval of the Difference				
		Mean	**Std. Deviation**	**Std. Error Mean**	**Lower**	**Upper**	**t**	**df**	**Sig. (2-tailed)**
Pair 1	Dry season Temp. Wet season Temp.	1.086	0.89861	0.12708	0.83062	1.34138	8.546	49	0
Pair 2	Dry pH - Wet pH	-0.4248	0.47567	0.06727	-0.55998	-0.28962	-6.315	49	0
Pair 3	Dry season Conc. Wet season Conc.	59.3248	66.49889	9.40436	40.42602	78.22358	6.308	49	0
Pair 4	Dry season TDS Wet season TDS	6.0152	15.44499	2.18425	1.62578	10.40462	2.754	49	0.008
Pair 5	Dry season DO Wet season DO	-1.704	0.69868	0.09881	-1.90256	-1.50544	-17.246	49	0
Pair 6	Dry season Alkalinity Wet season Alkalinity	3.5046	6.60129	0.93356	1.62853	5.38067	3.754	49	0
Pair 7	Dry season T. Hardness Wet season T. Hardness	22.365	12.63324	1.78661	18.77467	25.95533	12.518	49	0

Paired t-test comparing the nutrients 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	Dry season PO_4^{3-}	0.20637	0.08800	.01244	0.18136	0.23138	16.583	49	0.000
	Wet season PO_4^{3-}								
Pair 2	Dry season NO_3^-	0.01132	0.05051	0.00714	-.00303	0.02567	1.585	49	0.119
	Wet season NO_3^-								
Pair 3	Dry season Cl^-	3.29360	7.14813	1.01090	1.26212	5.32508	3.258	49	0.002
	Wet season Cl^-								
Pair 4	Dry season Fl^-	0.01440	0.01680	0.00238	0.00963	0.01917	6.060	49	0.000
	Wet season Fl^-								

APPENDIX C

Tilapia zilli

	Sample ID	**Total Weight**	**Length**	**Hg**	**Se**	**Mn**	**Cd**	**Fe**	**Pb**	**Fe**
August	TZ	32.01	12.90	0.60	0.20	1.52	0.00	0.64	0.12	0.64
	TZ	50.42	15.10	0.20	0.08	1.30	0.00	0.64	0.16	0.64
	TZ	122.43	17.60	0.40	0.08	1.30	0.00	0.55	0.20	0.55
	TZ	66.96	16.50	0.60	0.20	1.35	0.00	0.58	0.18	0.58
	TZ	102.22	18.30	0.40	0.08	1.22	0.00	0.51	0.16	0.51
	TZ	63.82	12.50	0.60	0.20	1.10	0.00	0.50	0.18	0.50
	TZ	58.09	14.80	0.40	0.20	1.20	0.00	0.48	0.14	0.48
	Mean	70.85	15.39	0.47	0.13	1.28	0.00	0.56	0.16	0.56
	Std	±2.22	±31.09	±0.07	±0.21	±0.13	±0.00	±0.07	±0.03	±0.07
March	TZD	66.56	12.50	0.20	0.08	1.64	0.00	1.10	0.19	1.10
	TZD	62.96	15.60	0.20	0.04	1.77	0.00	1.10	0.24	1.10
	TZD	72.12	18.30	0.08	0.00	1.23	0.00	0.80	0.24	0.80
	TZD	51.47	13.50	0.00	0.04	1.34	0.00	0.70	0.19	0.70
	TZD	111.06	19.70	0.00	0.00	1.21	0.08	0.75	0.17	0.75
	TZD	72.12	14.20	0.02	0.00	1.12	0.00	0.74	0.20	0.74
	TZD	90.72	17.20	0.00	0.00	1.19	0.00	0.74	0.21	0.74
	Mean	75.29	15.86	0.10	0.06	1.36	0.01	0.85	0.21	0.85
	Std	±19.72	±2.65	±0.03	±0.02	±0.25	±0.03	±0.18	±0.03	±0.18

Chrysichthys nigrodigitatus

	Sample ID	**Total weight**	**Length**	**Hg**	**Se**	**Fe**	**Pb**	**Mn**
August	CN	41.22	11.30	0.40	0.00	0.40	0.00	1.08
	CN	47.89	13.50	0.08	0.00	0.32	0.00	1.00
	CN	55.75	12.80	0.40	0.00	0.32	0.00	1.12
	CN	95.54	14.50	0.08	0.00	0.40	0.00	1.20
	CN	85.62	12.50	0.08	0.00	0.38	0.00	1.20
	CN	101.21	10.20	0.40	0.00	0.29	0.00	1.00
	CN	99.20	11.10	0.60	0.00	0.29	0.00	0.00
	Mean	75.20	12.27	0.29	0.00	0.34	0.00	0.94
	Std	±25.99	±1.50	±0.08	±0.00	±0.05	±0.00	±0.42
March	CND	51.52	10.10	0.00	0.04	0.33	0.00	0.90
	CND	61.44	13.60	0.00	0.00	0.39	0.00	0.80
	CND	70.70	15.70	0.04	0.00	0.44	0.08	1.10
	CND	58.01	14.60	0.04	0.04	0.51	0.00	1.00
	CND	85.44	16.10	0.00	0.00	0.48	0.00	1.10
	CND	68.90	16.60	0.00	0.00	0.42	0.00	0.90
	CND	66.41	12.80	0.00	0.00	0.39	0.00	0.80
	Mean	66.06	14.21	0.01	0.01	0.42	0.01	0.94
	Std	±10.82	±2.27	±0.02	±0.02	±0.06	±0.03	±0.13

Tilapia mariae

	Sample ID	**Total weight**	**Length**	**Hg**	**Se**	**Fe**	**Pb**	**Mn**
August	TM	32.62	12.30	0.08	0.20	0.76	0.20	0.82
	TM	98.25	14.90	0.08	0.08	0.66	0.18	0.55
	TM	121.34	16.60	0.08	0.04	0.59	0.00	0.51
	TM	74.65	13.80	0.40	0.04	0.62	0.08	0.48
	TM	99.04	16.30	0.40	0.08	0.70	0.12	0.62
	TM	102.23	19.00	0.08	0.08	0.54	0.06	0.41
	TM	42.02	11.20	0.40	0.04	0.51	0.08	0.40
	Mean	81.16	17.20	0.22	0.08	0.63	0.10	0.54
	Std	±33.17	±2.69	±0.09	±0.03	±0.09	±0.07	±0.15
March	TMD	55.31	11.10	0.04	0.04	0.80	0.14	0.72
	TMD	74.49	15.40	0.00	0.08	0.78	0.07	0.74
	TMD	95.82	15.50	0.08	0.20	0.64	0.12	0.50
	TMD	101.02	17.50	0.04	0.08	0.66	0.09	0.59
	TMD	21.72	10.80	0.04	0.04	0.69	0.10	0.62
	TMD	93.82	14.10	0.08	0.08	0.71	0.10	0.49
	TMD	86.16	17.20	0.04	0.04	0.58	0.00	0.62
	Mean	75.48	14.52	0.05	0.08	0.69	0.09	0.61
	Std	±28.33	±2.69	±0.03	±0.03	±0.08	±0.05	±0.10

APPENDIX D

Water

ELEMENT	WAVELENGTH nm	LAMP CURRENT	SLIT WIDTH	FUEL	SUPPORT
		nA	nm		
Hg	253.7	4	0.5	ACETYLENE	ARGON
Se	196.0	10	1.0	ACETYLENE	ARGON
Fe	248.3	5	0.2	ACETYLENE	AIR
Pb	217.0	5	1.0	ACETYLENE	AIR
Cd	228.8	4	0.5	ACETYLENE	AIR
Mn	279.5	5	0.2	ACETYLENE	AIR

Sediment

ELEMENT	**WAVELENGTH nm**	**LAMP CURRENT** nA	**SLIT WIDTH** nm	**FUEL**	**SUPPORT**
Hg	253.7	4	0.5	ACETYLENE	ARGON
Se	196.0	10	1.0	ACETYLENE	ARGON
Fe	248.3	5	0.2	ACETYLENE	AIR
Pb	217.0	5	1.0	ACETYLENE	AIR
Cd	228.8	4	0.5	ACETYLENE	AIR
Mn	279.5	5	0.2	ACETYLENE	AIR

Fish

ELEMENT	WAVELENGTH nm	LAMP CURRENT nA	SLIT WIDTH nm	FUEL	SUPPORT
Hg (BY HYDRIDE)	253.7	4	0.5	ARGON	AIR
Se	196.0	10	1.0	ARGON	AIR
Fe	248.3	5	0.2	ACETYLENE	AIR
Pb	217.0	5	1.0	ACETYLENE	AIR
Cd	228.8	4	0.5	ACETYLENE	AIR
Mn	279.5	5	0.2	ACETYLENE	AIR

Water

STEP	TIME	POWER	PRESSURE	TEMP ℃ 1	TEMP ℃ 2
1		250	100	400	500
2		0	100	400	500
3		250	100	400	500
4		450	100	400	500
Vent:00:05:00		Rotorctrl on		Twist on	

Ref: Milestone Acid Digestion Cookbook update 1st January, 1996

Sediment

STEP	TIME	POWER	PRESSURE	TEMP ℃ 1	TEMP ℃ 2
1		250	100	400	500
2		0	100	400	500
3		250	100	400	500
4		450	100	400	500
Vent:00:05:00		Rotorctrl on		Twist on	

Ref: Milestone Acid Digestion Cookbook update 1st January, 1996

Fish

STEP	TIME	POWER	PRESSURE	TEMP ℃ 1	TEMP ℃ 2
1	0:01:00	250	100	400	500
2		0	100	400	500
3		250	100	400	500
4		400	100	400	500
5		650	100	400	500
Vent:00:05:00		Rotorctrl on		Twist on	

Ref: Milestone Acid Digestion Cookbook update 1st January, 1996