

**KWAME NKRUMAH UNIVERSITY OF SCIENCE AND
TECHNOLOGY, KUMASI**



**ASSESSMENT OF SEDIMENT AND WATER QUALITY IN THE
OWABI RESERVOIR**

**By
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Kwame Nkrumah University of Science and Technology in partial
fulfillment of the requirements of**

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DECLARATION

I hereby declare that this submission is my own work towards the Msc and that, to the best of my knowledge, it contains no material previously published by another person or material which has been accepted for the award of any other degree of the university, except where acknowledgement has been made in the text.

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Date

DEDICATION

This work is dedicated to my parents, Mr. and Mrs. Abankwa, my siblings Seth Abankwa and Anita Abankwa, my love Osei Lawrencina and my friends whose encouragement and prayers made the completion of this work a success.

KNUST



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The almighty God deserves the first thanks for providing me with strength, wisdom and understanding through my education and bringing me this far both in life and my education.

My sincere and deepest appreciation goes to my project supervisor for his support, constructive criticism, patience and intellectual guidance, which were indispensable to the achievement of my research objectives.

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ABSTRACT

The Owabi reservoir is one of the major sources of drinking water for the Kumasi metropolis and its surrounding communities. The streams serving the Owabi reservoir have been encroached upon with various human activities due to high population increase within the catchment area of the reservoir, resulting in the pollution of the water. This study sought to assess the extent of pollution of sediment and water from the Owabi reservoir, measure the chemical forms or speciation of the heavy metals and determine their bioavailability. Ten water and sediment samples were collected from ten different sites within the Owabi reservoir. The water samples were analyzed for pollution indicators using standard methods from the American Public Health Association (APHA). Parameters such as temperature, pH, conductivity, hardness and nutrients were all within the acceptable limits of the World Health Organization (WHO). Levels of lead, arsenic, colour, turbidity, total suspended solids, faecal coliform and *E. coli* were above the acceptable limits of the World Health Organization (WHO). These make the water in the reservoir unsafe for domestic use without prior treatment or purification. Correlation analysis showed that arsenic correlated significantly with calcium, pH and conductivity, zinc also correlated significantly with fluoride, lead correlated significantly with magnesium and copper also correlated significantly with zinc. Factor analysis showed that agricultural discharge, domestic waste water discharge and the presence of decaying plant and other materials all contributed to the pollution of the water. The sediments were found to be acidic. The total metal content of Fe, Pb, Cu and Zn were also determined. The geoaccumulation index (I_{geo}) was also used to assess metal pollution in sediments. The sediment was found to be moderately polluted with respect to Pb and Zn and unpolluted with respect to Cu and Fe. Canonical correlation was carried out to establish the importance of pH, organic matter content (OMC), cation exchange capacity (CEC), and electrical conductivity (EC) in co precipitation and release of metals. pH was more important in co precipitating soluble Zn. Co precipitating lead and iron will more likely be associated with EC while co precipitating Zn and Cu will more likely be associated with CEC.

Factor analysis was carried out on the heavy metals to identify the sites that were significantly polluted by the heavy metals. Sites S₁, S₂ and S₃ were found to be significantly polluted. Samples from these sites were subjected to a five step sequential extraction and the results showed that Zn and Pb were potentially bioavailable in the sediments.

To understand the risk of the metals to the sediment dwelling organisms the data were compared with the Sediment Quality Values (SQV) using screening quick reference tables (SQUIRT). The comparison showed that Pb and Zn were above the probable effects level (PEL).

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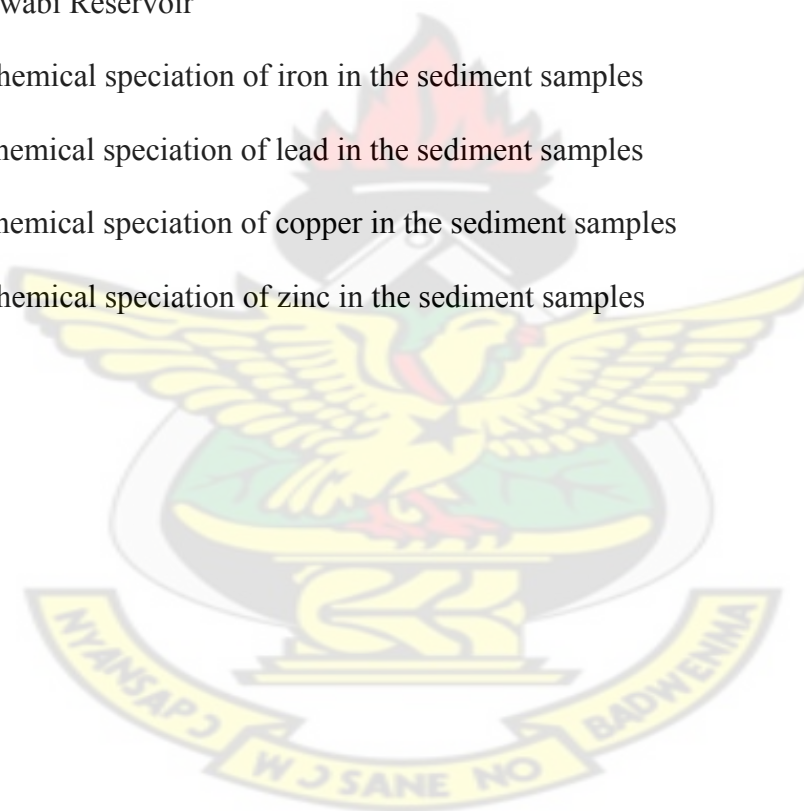
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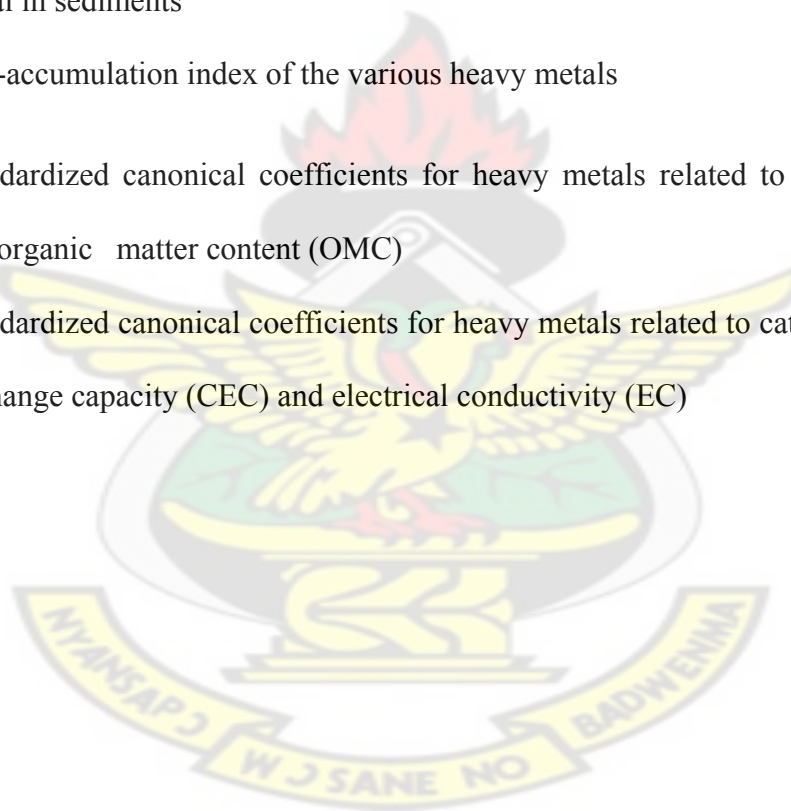
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CHAPTER ONE

1.0 Introduction

1.1 Background

Ghana's water resources have been under increasing threat of pollution in recent years. This threat can be attributed to improper planning of human settlements which lack the appropriate sanitary infrastructure and other human activities such as farming very close to water bodies. These activities are very common in peri-urban areas, which surround the larger metropolitan towns. Many such settlements are developing around the Kumasi metropolis (Ghana Statistical Service, 2002).

The Owabi reservoir is one of the major sources of drinking water for the Kumasi metropolis and its surrounding communities. It provides about twenty percent (20%) of the total water requirement of the metropolis. This reservoir is served by several streams which drain through rapidly urbanizing and agricultural towns (McGregor *et al.*, 2000). Prominent among them are the River Owabi, River Sukobri, River Akyeampomene and River Pumpunase. These streams serving the Owabi reservoir have been encroached upon with various human activities due to high population increase within the catchment area of the reservoir. This has resulted in the water being polluted (Akoto *et al.*, 2008).

The present state of the reservoir is of concern to many people and organizations, especially the Ghana Water Company (GWC) which is tasked with maintaining the reservoir and treating constantly deteriorating water for human consumption (Frimpong, 1997). Although the water flowing from these streams and tributaries may be filtered naturally the severity of the pollution

and the deteriorating state of the catchment adversely affects the quality of the raw water for the treatment plant and pollutant concentrations may increase due to changing conditions.

When a river carrying sediments and associated pollutants enters a reservoir, the flow velocity decreases and the suspended and bed load sediments start settling down. Reservoirs generally act as depositories for the sediments because of their high sediment trap efficiency (Di Toro *et al.*, 1987). Due to their high adsorption capacity, reservoir sediments act as sinks for contaminants in the reservoirs and may contain heavy metals, coliform bacteria, or mutagenic substances. Sediment environment is very complex, consisting of a quasi-stable physical system in which numerous physicochemical and microbiological gradients exist and interact. Inorganic and organic substances, both of natural (e.g., carbonates, oxyhydroxides, humics, low-molecular-weight fatty acids) and anthropogenic (e.g., metals, polycyclic aromatic hydrocarbons, biphenyls, dibenzodioxins, pesticides) origin, partition between sediments, interstitial water, overlying water, and resident biota (Burton *et al.*, 1990).

1.2 Problem statement

Global concern regarding the steadily deteriorating state of the natural resources has emphasized the need to pay attention to our natural resources. The increasing vulnerability of natural resources and the environment is one of the grand challenges to humanity in recent times. Reports from the Global environmental outlook indicates that about 20% of the worlds population lack access to safe drinking water and 50% are without safe sanitation system (JMP, 2006). A world population report indicates that 1.1 billion people lack access to safe drinking water (WHO/UNICEF, 2000). The situation in Africa is particularly bleak. In 27

African countries, including Côte d'Ivoire, Mozambique, Senegal, Uganda and Sudan, more than 30% of the population does not have access to safe water. In nine of those countries, more than 50% of the total population lack access to safe water. There are 36 African countries including Côte d'Ivoire, Mozambique and Zimbabwe where more than 50% of the population lacks access to safe sanitation systems (UNEP, 2008). This problem compounds when people tend to use surface water as a source of drinking water under the poor sanitary conditions. In Africa most peri-urban and rural communities depend on surface water for their water supply (WHO/UNICEF, 2000) which results in the spread of water borne diseases.

The functions of the Owabi catchment, which include maintenance of water quality, water storage, reproduction area for fish and other aquatic organisms and climate control, are being impaired as a result of high population growth, and associated increased human activities within the catchment area. According to Akoto *et al.* (2008), water flowing to the reservoir is contaminated by both organic and inorganic substances, including heavy metals. The authors also concluded that the streams within the catchment do not have the capacity to cleanse themselves because of the increasing level of pollution. These pollutants are therefore carried to the reservoir pool where they impact negatively on the water quality. Particulate matter and suspended particles settle to the bottom of the pool due to reduced flow rate. The bottom sediment can accumulate large amounts of pollutants and create a great danger in the aquatic environment. Such dangers can be observed well when conditions in the reservoir changes. Changes in environmental parameters, such as conductivity, salinity and pH can cause heavy metals adsorbed to the sediment to desorb back into water column (Elder, 1988). Information on

the extent to which the reservoir's water quality has been affected by the streams and the ability of the sediment to act as sink for the pollutants is therefore very important.

1.3 Justification

Monitoring and assessment of water quality in reservoirs are essential because reservoirs often serve as the main sources of water for human consumption and for irrigation. It is therefore necessary to assess the quality of water in the Owabi reservoir to ascertain the levels of contamination of some pollutants in the reservoirs. This will provide basic scientific information for finding appropriate solutions to problems that may arise as a result of pollution within the reservoir which may affect the humans that depend on the reservoir and other ecosystem services that the reservoir provides.

The reservoir is very strategic in the supply of water to the inhabitants of the metropolis and its growing environs. The functions of the catchment are being impaired as a result of high population growth and associated with it increased human activities. The industrial and commercial activities along the banks of the streams and rivers serving the reservoir pollute them (Waide, 1986). Again since the natural conditions around the catchment is also destroyed, its ability to self purify is also deteriorated. This makes the water in the reservoir more polluted. The mechanism and extent of pollution of reservoir are better understood when the chemical, physical and biochemical parameters of the water are studied (Ellis, 1989). It is thus important to establish the levels of physicochemical and biological parameters of the water in the reservoir

Sediments of a reservoir can act as a sink for pollutants such as metals of anthropogenic origin transported by rivers and atmospheric precipitation (Sigg, 1985). Heavy metals are accumulated in the sediments in different forms which affect their recycling between solution and sediment. The stability of compounds formed during the sedimentation is affected by some water quality parameters such as pH and salinity (Waide, 1986). Changes in these parameters may cause the metal ions to dissolve back into solution and can impact negatively on human health and the health of aquatic organisms.

Heavy metals cycle between the bottom sediments and the overlying water. This makes the general characteristics of the sediment an important factor in the availability of these heavy metals. Sediment characteristics such as organic matter, pH, texture and cation exchange capacity determine the amount of the heavy metals that can be present in the overlying water (Waide, 1986)..

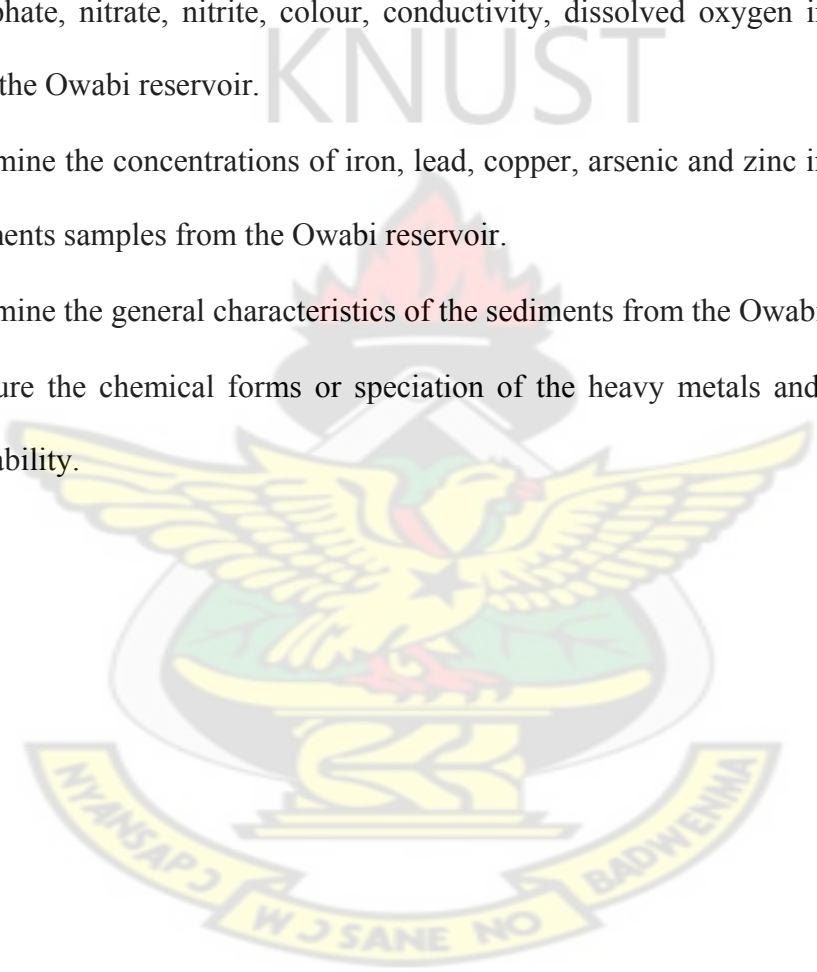
As a sink and source of metal ions, sediments contribute most of the reservoir's bioavailable heavy metals and play an important role in geobiochemical cycle (Hart, 1982). The mobility and bioavailability of metals in sediments strongly depend on the chemical forms in which they occur (Baeyens *et al.*, 2003). Therefore it is necessary to measure different forms in which these metals occur in addition to the total metal content. This will provide information on the bioavailability and the chemical forms of these heavy metals.

1.4 Objectives of the study

The main objective of the study was to assess the extent of pollution of sediment and water from the Owabi reservoir.

The specific objectives were to:

- determine some physicochemical parameters such as hardness of water, Cl^- , F^- phosphate, nitrate, nitrite, colour, conductivity, dissolved oxygen in water samples from the Owabi reservoir.
- determine the concentrations of iron, lead, copper, arsenic and zinc in both water and sediments samples from the Owabi reservoir.
- determine the general characteristics of the sediments from the Owabi reservoir, and
- measure the chemical forms or speciation of the heavy metals and determine their availability.



CHAPTER TWO

2.0 Literature review

2.1 Importance of reservoirs

Reservoirs, which are man-made lakes, are vital aquatic ecosystems that serve important environmental and economic purposes, including supply of potable water, generation of hydroelectric power, irrigation agriculture and fisheries (Smith, 2006).

Water supply reservoirs (including the Owabi Reservoir) in several parts of Ghana ensure adequate and sustainable supply of raw water throughout the year for treatment for human consumption in major cities and towns and also for irrigation. Reservoirs and streams are major source of drinking water for the earth's population. The reservoirs have special characteristics which make them vulnerable to pollution and degradation (Kira, 1993).

2.2 Factors that affect the quality of reservoir water

The quality of reservoir water is never constant because it is constantly changing in response to daily, seasonal and climatic conditions. The physical, chemical and biological characteristics of the surrounding environment also affect the water quality. The nature of soil and rocks on which the water flows into the reservoir also affect the water quality. For example, water flowing on soil overlying limestone will be alkaline with hardness depending on the amount of dissolved calcium and bicarbonate ions it contains (Hesterberg, 1992). The type of vegetation of a watershed, to some extent, affects the water quality since the products of plant decay find their way into the reservoir pool. Seasonal rise in the level of the water also drown vegetation and their decay also makes the water acidic (Svobodova *et al.*, 1993).

2.3 Reservoir pollution and water quality deterioration

2.3.1 Sources and complexities of reservoir pollution

Water pollution is any physical, chemical and biological change in the quality of water that has a harmful effect on any living organism that drinks or uses or lives in the water. According to Klein *et al.* (1962), pollution of water involves the introduction of substances which adversely and unreasonably impairs the beneficial use of water.

Reservoir water pollution types are not different from those found in other waters, however, the realization and consequences of pollution can differ between reservoirs, rivers and lakes. The greatest challenge facing solutions to water pollution is not merely the steady increase, but also the escalating diversity of water quality problems. The time span between the appearances of new problems is rapidly decreasing, yet before mankind can solve one problem, new problems appear. Prior to heavy industrialization, organic pollutants from small towns did not progress beyond the stream closest to the source (Dennison and Abal, 1999). With the onset of stream channelization the disruption of the natural return cycle of matter from nature to humans and back to nature begun, and presently matter is returned in quantities that exceed the natural digestive and homeostatic capacity of the system (Dennison and Abal, 1999).

Water quality problems can be classified according to the sources and causes of pollution. Sources are generally divided into point sources and non-point or diffuse sources (Fish, 1995) with the latter being difficult to manage. The environmental health of a reservoir is affected by the kind of human activities in the catchment. These include disposal of domestic waste water, and concentrated seepage from refuse dumps, runoffs of toxic organic compounds such as

pesticides that are used in agriculture and forestry and runoff contaminated by xenobiotics, persistent organic compounds used as industrial solvents, and traces of pharmaceutical compounds resulting from industrial activities and hospital waste (Bernhardt *et al.*, 2005). All these activities result in water quality deterioration, loss of biodiversity and loss of water resources. The extent to which pollutant can affect water quality is greatly influenced by urbanization, industrialization and large scale agricultural development (Kira, 1993). As a reservoir evolves and multiple uses arise, sources of pollution and deterioration diversify, and render existing problems enormously complex (Belize, 2004).

2.3.2 Water pollutants

Water pollutants that occur in reservoirs include physical, chemical and biological inputs. Many of the chemical pollutants found in the water are very toxic to both humans and aquatic life. The biological inputs which include pathogens also cause waterborne diseases in both human and other animals. The physical and chemical properties of the water such as colour temperature, acidity, conductivity and eutrophication can easily alter the quality of reservoir waters (Scanes *et al.*, 2007).

2.3.3 Physical indicators of water quality

Measurements of a reservoirs physical quality can serve as indicators of some forms of pollution. Some physical properties that can affect the water quality in a reservoir are discussed below.

2.3.3.1 Temperature

This is a measurement of hotness or coldness of water. Surface water temperatures naturally range from 0 °C under ice cover to 40 °C in hot springs. Natural sources of heat include solar radiation, transfer from air and condensation of water vapour at the water surface. Temperature affects the solubility of many chemical compounds and can therefore influence the effect of pollutants on aquatic life in the reservoir system (Ward *et al.*, 1998). Increased temperatures elevate the metabolic oxygen demand, by increasing microbial activities which reduces dissolved oxygen concentration (Haines *et al.*, 2001). Vertical stratification patterns that naturally occur in lakes and reservoirs affect the distribution of dissolved and suspended compounds (Haines *et al.*, 2001).

2.3.3.2 Turbidity

The measure of clarity of water is known as its turbidity. Turbidity can also be said to be a measurement of the suspended particulate matter in a water body which interferes with the passage of a beam of light through the water (ANZECC/ARMCANZ, 2000). Materials that contribute to turbidity are silt, clay, organic material, or micro-organisms. Turbidity values are generally reported in Nephelometric Turbidity Units (NTU). Pure distilled water would have non-detectable turbidity (0 NTU). High levels of turbidity increase the total available surface area of solids in suspension upon which bacteria can grow, reduces light penetration and therefore, it impairs photosynthesis of submerged vegetation and algae. In turn, the reduced plant growth may suppress fish productivity. Turbidity interferes with the disinfection of drinking water and is aesthetically unpleasant (DWAF, 1989).

2.3.3.3 Colour

This is a measure of the dissolved colouring compounds in water. The colour of water is attributed to the presence of organic and inorganic materials such as metallic ions of iron and manganese (Karikari and Ansa-Asare, 2006). A reddish brown colour is an indication of precipitated iron, yellowish tints also indicates the presence of humic acids. True colour of water is the colour due to natural minerals such as ferric hydroxides and dissolved organic substances such as fulvic and humic acids. Colour is expressed as Pt-Co units according to the platinum-cobalt scale (USEPA, 1997). Water colour can naturally range from 0-300 Pt-Co. Higher values are associated with swamps and bogs (ANZECC/ARMCANZ, 2000). Colour is regarded as a pollution problem in terms of aesthetics, but is not generally considered a detriment to aquatic life. Increased colour may however, interfere with the passage of light, thereby impeding photosynthesis.

2.3.3.4 Electrical conductivity (EC)

This is the measurement of the ability of water to conduct an electric current. The greater the content of ions in the water, the more current the water can carry. It is a useful indicator of the mineralization in water samples (Jain *et al.*, 2005). The ions are dissolved metals and other dissolved materials. Conductivity is reported in terms of microsiemens per centimetre ($\mu\text{S}/\text{cm}$). Conductivity may be used to estimate the total ion concentration of the water, and is often used as an alternative measure of dissolved solids. Health effects in humans for consuming water with high EC may include disturbances of salt and water balance; and adverse effect on certain myocardic patients and individuals with high blood pressure (Fatoki and Awofolu, 2003).

2.3.3.5 Total dissolved solids

This is a measure of the amount of dissolved material in the water column. It is reported in mgL^{-1} with values in fresh water naturally ranging from 0-1000 mgL^{-1} . Dissolved salts such as sodium, chloride, magnesium and sulphate contribute to elevated total dissolved solids values (WHO, 2003c). The total dissolved solids do not include gases, colloids or sediments. High concentrations of TDS above 500 mgL^{-1} limit the suitability of water as a drinking source and irrigation supply. High TDS waters may interfere with the clarity, colour and taste of manufactured products (WHO, 2003 c).

2.3.3.6 Total suspended solids

This is a measure of the particulate matter that is suspended within the water column. It is a common indicator of polluted waters (Karikari *et. al.*, 2004). High concentrations of total suspended solids increases turbidity, thereby restricting light penetration and hindering photosynthetic activity (McComb and Lukatelich, 1995). Suspended material can result in damage to fish gills. Settling suspended solids can cause impairment to spawning habitat by smothering fish eggs. Suspended solids can also interfere with water treatment processes.

2.3.4 Chemical indicators of water quality

Assessment of chemical indicators in a reservoir and other surface waters can be used to detect imbalances within the ecosystem. Such imbalances may indicate the presence of other pollutants. For example increased levels of metals like iron affect physical parameters like colour and elevated levels of acidity may indicate the presence of acid mine drainage (Akabzaa *et al.*, 2005). Commonly measured chemical indicators include pH, alkalinity, hardness, dissolved oxygen,

chloride, fluoride, nitrite, nitrate, ammonia, phosphate, sulphate and biochemical oxygen demand (APHA, 1998).

2.3.4.1 pH

This is the measurement of the hydrogen-ion concentration in the water. A pH below 7 is acidic and a pH above 7 is basic. Natural fresh waters have a pH range from 4.0 to 10.0. pH in reservoir systems may decrease because of the degradation of drowned vegetation and other organic matter causing the release of methane gas which is accompanied by the release of hydrogen sulphide (H_2S) (Connell and Miller, 1984) thereby decreasing the pH of the overlying water. Associated to acidification are changes in leaching of heavy metals and toxic form of aluminium from sediment to the overlying waters (Schlinder, 1991).

2.3.4.2 Alkalinity

Alkalinity measures the ability of water to neutralize acids. It usually indicates the presence of carbonate, bicarbonates, or hydroxides. Natural waters rarely have alkalinity levels that exceed 500 mgL^{-1} . According to Chapman (1996), alkalinity levels of $20 - 200 \text{ mgL}^{-1}$ are common in fresh water systems. Waters that have high alkalinity values are considered undesirable because of excessive hardness and high concentrations of sodium salts. Water with low alkalinity, below 10 mgL^{-1} , have little capacity to buffer acidic pollutants and are susceptible to acidification (USEPA, 1997).

2.3.4.3 Hardness

The hardness of water is generally due to the presence of calcium and magnesium in the water. Other metallic ions including Fe and Mn also contribute to hardness (USEPA, 1997). Hardness is reported in terms of calcium and magnesium carbonates and in units of mgL^{-1} . Reservoir water hardness reflects the geology of the catchment and also provides a measure of the influence of human activities on the catchment area. These reasons make hardness a useful water quality indicator (Akpabli and Drah, 2001). Harder water also has the effect of reducing the toxicity of some metals including copper, lead and zinc. Soft water may have corrosive effect on metal plumbing, while hard water may result in scale deposits in the pipes.

2.3.4.4 Dissolved Oxygen (DO)

This is a measure of the amount of DO in water. Generally the concentration of dissolved oxygen in surface water is less than 10 mgL^{-1} . The DO concentration is subject to diurnal and seasonal fluctuations that are due to variations in temperature, photosynthetic activity and river discharge (Connell and Miller, 1984). The maximum solubility of oxygen (fully saturated) ranges from approximately 8 mgL^{-1} at 25°C to 25 mgL^{-1} at 25°C (at sea level). Natural sources of dissolved oxygen are derived from the atmosphere or through photosynthetic production by aquatic plants. Natural re-aeration of streams can take place in areas of waterfalls and rapids. DO is essential to the respiratory metabolism of most aquatic organisms. It affects the solubility and availability of nutrients, and therefore the productivity of aquatic ecosystems (Best *et al.*, 2007). Low levels of DO in reservoirs facilitate the release of nutrients from the sediments since they contribute to the decay of organic matter. These low levels are common in reservoirs and results from

decomposition of organic matter in the reservoir system. This decreases the populations of fish and other aquatic organisms (Best *et al.*, 2007).

2.3.4.5 Chloride

Among the halides, chloride appears in the highest concentrations in natural fresh water systems. It is reported as mgL^{-1} dissolved chloride. The average chloride concentration in natural fresh waters is approximately 8.3 mgL^{-1} . Halide concentrations are generally greater in lakes and reservoirs that are in proximity to marine regions. Since almost all chloride salts are soluble in water the chloride content range from $10 - 100 \text{ mgL}^{-1}$ (Nkansah, 2005). Chloride is important in terms of metabolic processes, as it influences osmotic salinity balance and ion exchange. Higher chloride concentrations can reduce the toxicity of nitrite to aquatic life.

2.3.4.6 Fluoride

Fluoride may be present as a result of natural decomposition of rocks but some can enter water bodies through water treatment systems. Fluoride prevents tooth decay. Excessive amounts of fluoride can result in mottled tooth enamel. The maximum acceptable concentration in drinking water is 1.5 mgL^{-1} (WHO, 2004).

2.3.4.7 Nitrite (NO_2^-)

This is a measure of a form of nitrogen that occurs as an intermediate in the nitrogen cycle. It is an unstable form that is either rapidly oxidized to nitrate (nitrification) or reduced to nitrogen gas (de-nitrification). This form of nitrogen can also be used as a source of nutrients for plants (FAO/WHO, 2003). Since nitrite is also a source of nutrients for plants its presence encourages

plant proliferation. Nitrite is toxic to aquatic life at relatively low concentrations. Nitrite oxidizes haemoglobin in the blood stream to methemoglobin thus limiting the ability of blood to carry oxygen and as a result anoxia and death may occur (FAO/WHO, 2003).

2.3.4.8 Nitrate (NO_3^-)

Nitrate is the principle form of combined nitrogen found in natural waters. It results from the complete oxidation of nitrogen compounds. Nitrate is the primary form of nitrogen used by plants as a nutrient to stimulate growth. Excessive amounts of nitrate may result in phytoplankton proliferations. At high levels it is toxic to infants and could develop blue baby syndrome also known as methemoglobinemia (Spalding and Exner, 1992). Nitrates also come into water through the nitrogen cycle although most of that occur in drinking water are as a result of contamination by septic systems, and agricultural fertilizers (Hubbard and Sheridan, 1989).

2.3.4.9 Total Ammonia

This is a measure of the most reduced inorganic form of nitrogen in water and includes dissolved ammonia (NH_3) and ammonium ion (NH_4^+). Nitrogen is an essential plant nutrient and although ammonia is only a small component of the nitrogen cycle, it contributes to the trophic status of a body of water (Millero, 1996). Ammonia contributes to eutrophication of water bodies. This results in prolific algal growths that have deleterious impacts on other aquatic life, drinking water supplies, and recreation (SDWF, 2007). Ammonia at high concentrations is toxic to aquatic life. The criteria set for ammonia to protect aquatic life are dependent on the temperature and pH of the water (Nordin and Pommen, 1986). As an example, at pH 7.0 and a water

temperature of 15°C, the maximum concentration should not exceed 19.7 mgL⁻¹, and the average over 30-days should not exceed 1.77 mgL⁻¹ since they become harmful to the organisms.

2.3.4.10 Total phosphate

This is a measure of both inorganic and organic forms of phosphorus. Phosphorus can be present in water as dissolved or particulate matter. It is an essential plant nutrient and is often the most limiting nutrient to plant growth in fresh water (Ansa-Asare and Asante, 2000). Since phosphorus is generally the most limiting nutrient, its input to fresh water systems can cause extreme proliferations of algal growth. Anthropogenic sources include agriculture, domestic (particularly from detergents), and industrial effluents (Froelich, 1988).

2.3.4.11 Sulphate

Sulphate occurs in almost all natural waters. Most sulphate originates from the oxidation of sulphite ores, the presence of shale and the existence of industrial wastes. Sulphate is one of the major dissolved constituents in rain (WHO, 2003 a). High concentration of Sulphate in drinking water cause a laxative effect when combined with calcium and magnesium, the two most common ions responsible for water hardness. Sulphates can be reduced by bacteria in water to produce hydrogen sulphide. This tends to increase the acidity of water in a reservoir (Connell and Miller, 1984).

2.3.4.12 Copper

Copper is measured either as total or dissolved Copper in a water sample. Increased quantities of copper make water distasteful to drink. Copper is acutely toxic to most forms of aquatic life at

relatively low concentrations (IPCS, 1998). Copper is an essential micro-nutrient required for the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. In plants, copper is especially important in seed production, disease resistance and regulation of water. Copper is indeed essential, but in high doses it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation (IPCS, 1998). Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth. While copper's interaction with the environment is complex, research shows that most copper introduced into the environment is, or rapidly becomes, stable and results in a form which does not pose a risk to the environment (WHO, 2003 b). In fact, unlike some man-made materials, copper is not magnified in the body nor bio-accumulated in the food chain (IPCS, 1998).

2.3.4.13 Zinc

Zinc is an essential element for plants and animals as it is necessary for the functioning of certain enzymes. Zinc is relatively non-toxic to terrestrial organisms. Zinc toxicity decreases with increasing hardness, increases with increasing temperature, and increases with decreasing dissolved oxygen. Zinc occurs naturally in air, water and soil, but zinc concentrations in rivers and reservoirs are rising unnaturally, due to addition of zinc through human activities. Industrial sources may cause the zinc concentration in drinking water to reach levels that can cause health problems. Zinc is a trace element that is essential for human health but shortages can cause birth defects (WHO, 2003d).

2.3.4.14 Iron

Iron is the most abundant metal, and is believed to be the tenth most abundant element in the universe (WHO, 2003e). Iron is a metal extracted from iron ore. It can also be found in the free (elemental) state. Iron is essential to all organisms, except for a few bacteria. It is mostly stably incorporated in the inside of metalloproteins, because in exposed or in free form it causes production of free radicals that are generally toxic to cells (USGS, 1970). Iron binds avidly to virtually all bio molecules so it will adhere non-specifically to cell membranes, nucleic acids, proteins etc. Iron distribution is heavily regulated in mammals. Excess iron in the body causes liver and kidney damage (haemochromatosis) (ICPS, 2000).

2.3.4.16 Lead

Lead occurs naturally in the environment. However, most lead compounds that are found in the environment are as a result of human activities. Lead is among the most recycled non-ferrous metals. Its physical and chemical properties are applied in the manufacturing, construction and chemical industries. Lead is most common in batteries and was previously used as petrol additives in the EU and some other countries (WHO, 2003f). Exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Lead is toxic to both the central and peripheral nervous systems, inducing subencephalopathic neurological and behavioral effects (WHO, 2003f). There is electrophysiological evidence of effects on the nervous system in children with blood lead levels well below 30 mg L⁻¹ (WHO, 2003f). Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains (WHO, 2003f).

2.3.4.17 Arsenic

Arsenic is found widely in the earth's crust in oxidation states of -3, 0, +3 and +5, often as sulfides, metal arsenides or arsenates. In water, it is mostly present as arsenate (+5), but in anaerobic conditions, it is likely to be present as arsenite (+3) (WHO, 2003g). It is usually present in natural waters at concentrations of less than 1–2 mg/litre. However, in waters, particularly groundwaters, where there are sulfide mineral deposits and sedimentary deposits deriving from volcanic rocks, the concentrations can be significantly elevated (WHO, 2003g). Apart from occupational exposure, the most important routes of exposure to lead are through food and drinking-water, including beverages that are made from drinking-water. IPCS (2001) concluded that long-term exposure to arsenic in drinking water is causally related to increased risks of cancer in the skin, lungs, bladder and kidney, as well as other skin diseases, such as hyperkeratosis and pigmentation changes. Inorganic arsenic compounds are carcinogenic to humans (IARC, 1987).

2.3.5 Bacteriological indicators

2.3.5.1 Faecal coliform

Coliform bacteria have traditionally been used as indicators of water quality. Presence of the indicator bacteria signify the presence of pathogenic micro organisms associated with faecal contamination and waterborne diseases (Niemi, *et al.*, 1997). In rural watersheds, faecal coliforms are closely associated with agricultural activities and leakage from septic tanks. Faecal contamination from livestock production and the heavy use of manure as a fertilizer is an important source of bacterial pollution in streams finally ending in reservoirs (Farrel Poe *et. al.*, 1997). In most urban communities, human waste is identified as the primary source of faecal-

coliform contamination of surface water (Ong *et al.*, 1996). Health risks associated with faecal coliform contamination include common diarrhoea, ear infections and deadly diseases such as cholera, hepatitis and typhoid fever. It is therefore suggested that total body contact with water containing total coliform greater than 200 colonies per 100 mL of water should be avoided (WHO, 2004).

2.3.5.2 *Escherichia coli*

This parameter is used as an indicator for the suitability of water bodies for recreational purposes. *Escherichia coli* are thus used to indicate the possible presence of pathogens (Hirschinger, 2002). *E. coli* occurs only in the faeces of warm blooded animals. An EPA study in 1994 established that the presence of *Escherichia coli* in fresh water has a much higher correlation with the presence of human pathogens. USEPA therefore recommends *Escherichia coli* as the best indicator of health risk for recreational freshwater.

2.3.6 Sedimentation in reservoirs

Natural sediments are complex mixtures of various phases, namely residues of weathering and erosion of materials such as clays and aluminosilicates, iron and aluminium oxyhydroxides, sulphides, substances produced by biological activity, both organic (living micro organisms, biological detritus and humic substances) and inorganic (carbonates, phosphates and silica) (Tessier, 1992). Sediment from anthropogenic sources includes atmospheric precipitation, settling of suspended solids, decaying organic matter and erosion. Sediment loads delivered to reservoirs dramatically increases in response to waterborne erosion in catchments in which large tracts of native vegetation have been cleared and replaced with intensive agriculture (Hodgkin

and Hesp, 1998) and urban areas (Hancock and Hunter, 1999; McLaughlin, 2000; Marston *et al.*, 2001). Turbidity levels and the amount of sediment-bound nutrients such as total phosphorus, total nitrogen and total organic carbon, trace elements such as Fe, Zn, Pb and other toxicants entering reservoirs from catchments also tend to increase sedimentation (McComb and Lukatelich, 1995; Chenhall, 1995). Greater nutrient loads can lead to eutrophication which can further enhance sedimentation rates because the amount of organic matter being deposited also increases (Nixon, 1995).

2.3.7 Effects of reservoir sediments on water quality

Sedimentation affects both the useful life of a reservoir for such important purposes as flood control and water supply as well as its aesthetic quality. Sediment quality is an important environmental concern because sediment may act as a sink for water-quality constituents and as a source of constituents to the overlying water column and biota (Casey *et al.*, 2007). Once in the food chain, sediment-derived constituents may pose an even greater concern due to bioaccumulation because their concentrations increase as they reach the top of the food chain. Increased sedimentation rates allow more organic matter to be degraded by anoxic processes (e.g. sulphate reduction) because the exposure time of organic matter to dissolved oxygen in the water column is shortened (Chenchall, 1995). Denitrification efficiencies are lowered under anoxic conditions, and more dissolved nutrients are recycled to the water column.

2.3.8 Metals in sediments

Natural background levels of heavy metals exist in the majority of sediments due to mineral weathering and natural soil erosion. It is when man's activities accelerate or antagonize these

processes that the background levels are increased to levels that have detrimental effects on the environment. Sediments with low heavy metal concentrations are not necessarily “natural” just because the levels are low. They may represent a mixture of small quantity of pollutants diluted by a large amount of natural sediment with low heavy metal content (Herut *et al.*, 1993).

The introduction of metallic pollutants into a reservoir, whether it is natural or artificial (anthropogenic), can occur in dissolved and particulate form. Depending on physico-chemical conditions of the water, the pollutants in dissolved form can later precipitate. They can also be adsorbed by the iron or manganese oxides and hydroxides or co-precipitated with these, or form dissolved organic or inorganic complexes (Salomons and Forstner, 1984; Drever, 1988).

Metals are partitioned amongst soluble phases, suspended and bottom sediments and biota in aquatic systems (Elder, 1988). The major pathways of metal partitioning include adsorption, complexation, precipitation and biological uptake. Adsorption is usually the predominant process because metals have strong affinities for iron and manganese oxyhydroxides, particulate organic matter, and to a lesser extent clay minerals (Elder, 1988). Consequently, metals tend to accumulate in bottom sediments. The soluble phase represents the principal source of bioavailable metals. The dissolved fraction is favoured under conditions of low pH, low particulate loads and high concentrations of dissolved organic matter. More metals may also enter solution as water hardness increases, because cations (especially Ca^{2+} and Mg^{2+}) also compete with metals for binding sites. However, increasing salinity usually results in reduced dissolved metal concentrations because clay-organic particles form flocs with a high settling velocity (Elder, 1988).

2.3.9 Factors that influence the quality and behaviour of reservoir sediment

Comparison of total heavy metal content in sediments in different areas may be a convenient way of expressing some measure of pollution, but this method has its limitations. Sediment metal concentrations are influenced by a range of factors. They include physical and hydrological characteristics of the region and its benthos, atmospheric conditions, productivity, pH, soil texture, redox potential and cation exchange capacity among others (Belize *et al.*, 2004).

All sediments contain some amount of heavy metals from natural sources. However, these background levels can vary widely depending on a number of factors such as parent material and sedimentation processes in water bodies. It is usually through human activities that levels of heavy metals increase. Due to this, pollution in sediments can rise to the point where they represent a potential health or ecological risk (Chen and Lin, 2001).

Heavy metals that are soluble in water are highly mobile and are also readily available for plant and animal uptake. Exchangeable metals, however, are those that rather than existing in the water column, are primarily bound to soil surfaces by cation exchange processes. Metals that are found in this form are considered to be bonded very weakly and may be displaced easily to the water-soluble form. Together, the metals in the soluble and exchangeable form are considered readily mobilized. When changes occur in the oxidation status of soils and sediments, transformations of metals between chemical forms, soluble and insoluble, may occur. This affects the mobility and plant availability of metals (Chuan *et al.*, 1996).

The quantity of heavy metals retained in sediments is also affected by the characteristics of the sediment into which they are adsorbed. Grain size, cation exchange capacity, organic matter content and mineral constituents are some of the factors that influence the uptake of heavy metals in the aquatic environment (CSIRO, 2000). However elevated concentrations of metals do not necessarily pose a threat as they may never be released from the sediments and therefore may not be available for excessive plants and animals' uptake (Elder, 1998).

2.3.9.1 Soil texture

Particle size is one of the most significant parameters influencing heavy metal speciations in sediments. Bioavailable metals in sediment depend, to a significant extent, on the particle size fraction with which a metal is associated. The decrease of flow velocity in the reservoir pool causes sedimentation of suspended solids. Sand particles being heavier than silt and clay particles settle at the bottom and the finer silt and clay particles settle on top. These finer sediments cover the majority of the reservoir bottom and they are mainly generated by sedimentation of suspended solids (Dojlido and Taboryska, 1991). Tam and Wong (2000) established that the highest percentage of heavy metals were bound to the fine-grained fraction of size $<63\mu\text{m}$. They suggested that the concentrations of organic matter in the fine-grained fraction of sediment were often higher than that in the sand sized fraction. Chakrapani and Subramanian (1993) also reported that Cu, Zn, Mn and Fe increased in concentration with finer size. Haque and Subramanian (1982) reported that metal absorption capacity was in the order of sand $<$ silt $<$ clay, due to increases in surface area, minerals and organic matter as particle size decreased from sand to clay. However, this trend of more metal being accumulated in the fine-grained of the sediment may not be universal for all metals and may be varied between metal species.

2.3.9.2 Cation exchange capacity

Soil cation exchange capacity (CEC) is the total of the exchangeable cations that a soil can hold at a specified pH. Soil components known to contribute to soil CEC are clay and organic matter, and to a lesser extent, silt (Manrique *et al.*, 1991). The exchange sites can be either permanent or pH-dependent. Mineral soils have an exchange capacity that is a combination of permanent and pH-dependent charge sites, while that of organic soils is predominantly pH-dependent. In any given soil, the number of exchange sites is dependent on the soil pH; type, size and amount of clay; and amount and source of the organic material (Parfitt *et al.*, 1995).

Reservoir sediments are predominantly clayey and the ability to hold cations strongly depends on pH and organic matter content. Heavy metals are positively charged and since they have affinity for negatively charged surfaces they are easily attached to the negative charges present at the sediment surface. High CEC means that the possibility of binding to negative charges increases implying that the metals will be firmly bound to the sediment and have longer residence time on the sediment (Tessier and Campbell, 1987).

2.3.9.3 Organic matter content

Sediment organic matter is derived from plant and animal detritus, bacteria or plankton formed in situ, or derived from natural and anthropogenic sources in catchments. Organic matter in sediment consists of carbon and nutrients in the form of carbohydrates, proteins, fats and nucleic acids (CSIRO, 2000). Sewage and effluent from homes and industry such as food processing factories are examples of organic-rich wastes of human origin. Organic matter has a high affinity for fine-grained sediment because it adsorbs onto mineral surfaces (CSIRO, 2000). Sediment

organic matter can be a source of water column nutrients when it degrades (Twilley *et al.*, 1999). This release of nutrients during degradation can also release metals including heavy metals that are bound to their surfaces. Dissolved oxygen concentrations are usually lowered when organic matter is degraded by aerobic bacteria, and anoxic and hypoxic conditions may develop under stratified conditions and this raises the acidity of the reservoir system (Enriquez *et al.*, 1993).

High organic matter content in sediments also implies immobilization of the metals that are bound to the fulvic or humic acids. On the other hand, binding on smaller organic molecules may increase metal mobility and bioavailability (Kabata-Pendias and Pendias, 1992). Angehrn-Bettinazzi *et al.* (1989) reported high ability of Pb to form complexes with insoluble humic substances, while Cd and Zn form complexes with mobile organic substances of low molecular weight.

2.3.9.4 Acidity

This is the measure of the hydrogen ion concentration in the sediment. This parameter also greatly affects metal availability. A higher acidity (implying a lower pH) increases metal availability since H^+ has a higher affinity for the negative charges on the colloidal surfaces. This affinity for negative charges thus leads to competition between the metals and the H^+ ions thereby releasing the metals (Koning and Kroos, 1999). A lower pH is a common phenomenon since degradation of organic matter and detritus in the sediment produces acids that tend to decrease the pH. Soil oxidation conditions also influence soil pH, a major factor influencing metal chemistry (Gambrell, 1994). The pH value of the solution is the master variable that oversees the adsorption of metal ions at surfaces (Schlinder, 1991). High pH values promote

adsorption whereas low pH actually prevents the retention of metals by sediment (Belize *et al.*, 2004). The pH can not only markedly affect the type of surface sites, but also the speciation of the metal ion in solution adsorbed out of solution (Stumm and Morgan, 1981). The results of Gambrell (1994) support this idea and indicate that permanently flooded sediment becomes strongly acidic upon drainage, the process which retains metals tends to be intensified.

2.4 Work done by other authors

Although extensive work has not been conducted on the Owabi reservoir and within its catchment, work done by Frimpong (1997) revealed that the concentration of lead, iron and mercury were above the WHO standards for drinking water. He reported that nitrates were not found in any of the samples analyzed. However concentrations of sulphate, phosphate were found to be within their acceptable limits. He therefore concluded that the tributaries of River Sukobri were generally loaded with organic matter and heavy metals. He asserted that most of the pollution might have come from Suame and surrounding areas.

Other studies performed by McGregor *et al.* in 2000 were focused on the assessment of the consequences of land use practices within peri-urban watersheds around Kumasi. According to McGregor *et al.* (2000), water resources in the peri-urban areas around Kumasi are being compromised by a variety of activities. Untreated sewerage and untreated domestic waste, hospital waste, industrial waste, including assortment of chemicals and heavy metals, oil from informal motor repair businesses, urban and rural run-off including agricultural chemicals and residues and leachate from ground water into the river system being the main cause of the pollution.

Akoto *et al.* (2008), conducted studies on the rivers serving the Owabi reservoir and found that all physicochemical parameters for the serving rivers were within acceptable limits with the exception of colour and turbidity which were found to be above the WHO acceptable limits. Heavy metals that were analyzed in the study generally were above the acceptable levels with lead, copper, arsenic and manganese being the most abundant pollutant. The study also established that the catchments ability to self purify is impaired as a result of the intensity of the pollutants.

Work done on other reservoirs in Ghana includes the study by Kpekata and Biney (1979) that looked at the chemistry of the Densu Lake between November 1976 and March 1978. They found the pH and temperature to be within ranges suitable for biological processes and, therefore, congenial to fish life. They reported that the Densu was richer in nutrients, had higher salt content and could be biologically very productive. They, therefore, predicted it would undergo eutrophication faster and become extinct earlier than the Volta Lake which had low conductivity. The study concluded that being eutrophic the Densu Lake could support mainly the coarse species of fish, especially those which prefer slightly polluted waters.

Bosque-Hamilton *et al.* (2004) compared Weija, Brimsu and Inchaban reservoirs in Ghana and found that the Weija Reservoir was well mixed and aerated but less transparent with high phytoplankton abundance. The water chemistry showed that cationic pattern of the reservoir waters were similar to sea water due to its proximity to the sea but anionic pattern was intermediate between fresh water and sea water, a trend observed in the present study. The

reservoir had more aquatic weeds as evidenced by nutrient dominance with higher nutrient recorded in the wet season. Land use and human activities were identified as principal sources of pollution that greatly influenced the quality of the three reservoirs.

KNUST



CHAPTER THREE

3.0 Materials and methods

3.1 Study area

The Owabi reservoir where the study was conducted is located within the Kumasi metropolis in the Ashanti region of Ghana. The Kumasi metropolis has a semi-humid tropical climate, with a total average annual rainfall of 1340 mm and a mean temperature of 26 °C. The rainfall distribution is weakly bimodal, with a main peak between March and June, and a secondary peak in September to October. The Kumasi metropolis itself lies across the top of a local watershed at approximately 280 m above sea level. The terrain is moderately dissected (amplitude of relief up to 30 m) with slopes commonly of 5° to 15° (Cornish *et al.*, 1999). The soils in the catchment are clayey or silt loams and are described as forest oxysols because of their sharp or acidic nature (Adu, 1992).

The reservoir is about 10 km northwest of Kumasi with a catchment area of about 69 km². The catchment is primarily forest (Owabi forest reserve) facing problems with encroachment. Commissioned in 1926, the reservoir has a depth of 7.4 m along the spillway and 11.5 m along the embankment with an approximate volume of 2.6 million cubic meters. The reservoir was refurbished in 1960 where the spillway crest was raised by 0.56 m. The dam is a composite dam with a central concrete gravity spillway and earth filled embankments (GWSRP, 2004).

3.2 Sampling sites

Ten sampling sites were selected using the global positioning system, GPS (table 1). A map of the sampling sites is shown in fig 1.

Table 1: Location of the various sampling sites

SAMPLING SITE	SAMPLE CODE	LOCATION
SITE 1	S ₁	6°44'46.58"N 1°42'8.00"W
SITE 2	S ₂	6°44'30.88"N 1°42'8.40"W
SITE 3	S ₃	6°44'36.69"N 1°42'4.11"W
SITE 4	S ₄	6°44'37.59"N 1°41'59.90"W
SITE 5	S ₅	6°44'36.24"N 1°41'42.53"W
SITE 6	S ₆	6°44'33.04"N 1°41'35.01"W
SITE 7	S ₇	6°44'25.21"N 1°41'25.71"W
SITE 8	S ₈	6°44'19.80"N 1°41'28.47"W
SITE 9	S ₉	6°44'32.27"N 1°41'26.68"W
SITE 10	S ₁₀	6°44'27.64"N 1°41'20.41"W

Ten water samples and ten sediment samples were collected from the reservoir. Samples were collected in February, 2009.

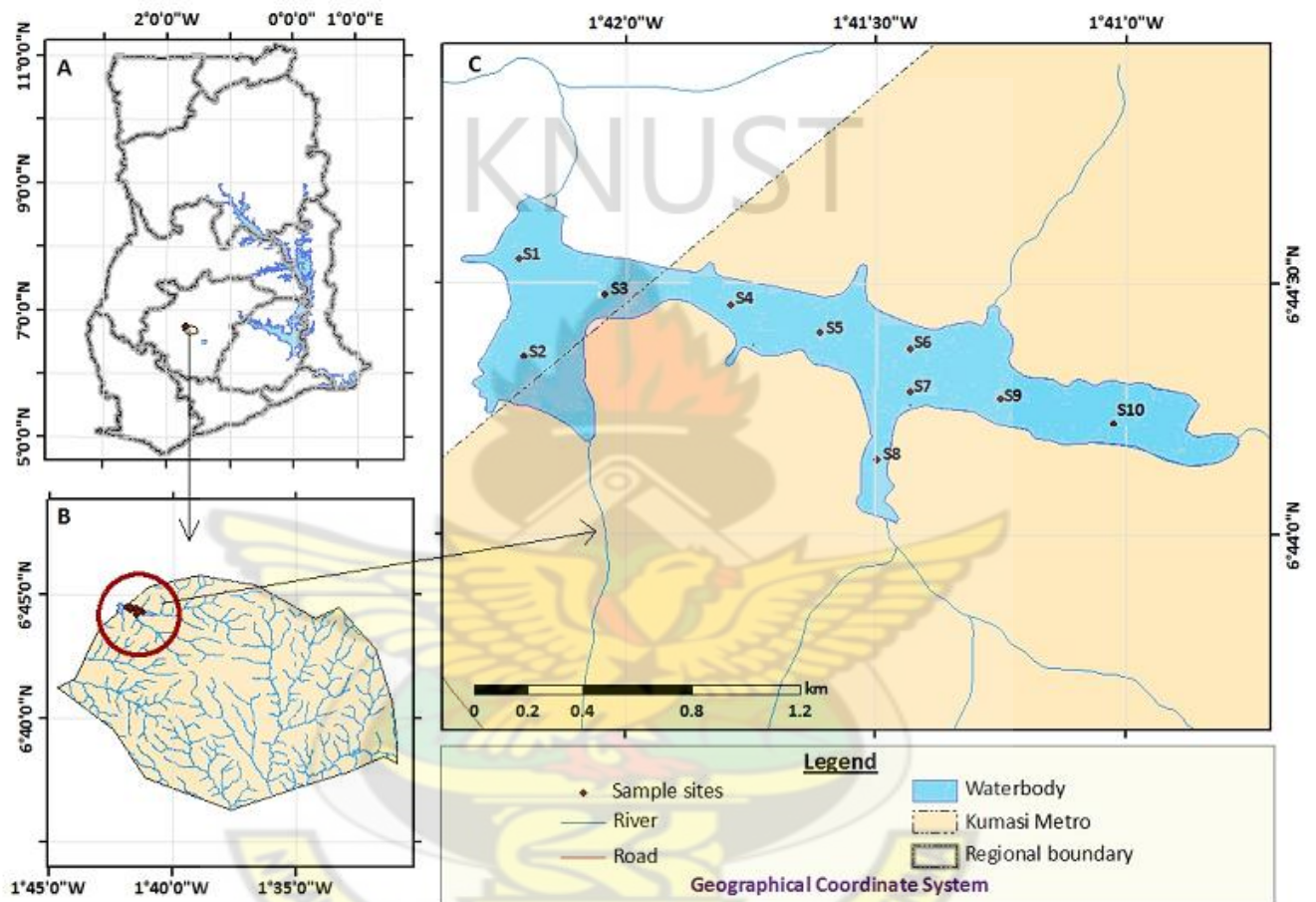


Fig 1: Map of the Owabi reservoir showing all sampling sites.

3.3.2 Sample collection

Sample containers were thoroughly washed with water and detergent. They were then left in concentrated nitric acid overnight and finally rinsed with distilled water and left to dry. Glass-wares used were soaked in aqua regia followed by a thorough wash with distilled water.

Water samples were collected using spot sampling equipment. Samples in duplicates were collected into sterile 500 ml plastic for microbial analysis. All sample containers and corks were rinsed three times with the sample water and then filled to capacity and covered immediately with the lid and properly sealed and labelled. For the determinations of the physicochemical parameters, samples were collected in 1.5 L plastic containers and placed in an ice chest at a temperature of about 4 °C and immediately transported to the lab for analysis. Bottom sediment samples were collected using dept sampler and placed in polythene bags, labelled, sealed, and placed in the ice chest.

Temperature, pH, turbidity, dissolved oxygen and conductivity of the water samples were determined on site and recorded. The physicochemical analysis of water samples was done at the Quality Assurance Laboratory of the Ghana Water Company Limited in Kumasi. Heavy metal determination was done at the environmental laboratory, AngloGold Ashanti, Obuasi. Microbiological analyses were also done in the microbiological laboratory of the department of theoretical and applied biology, KNUST, Kumasi. Physicochemical properties of the sediment samples were done at the Soil Chemistry Laboratory of the Faculty of Agriculture, KNUST.

3.4 Analyses of water samples

3.4.1 Temperature determination

The temperatures of the water samples were determined on site. An aliquot of about 100 mL was measured and transferred into a 500 mL beaker. A thermometer (0 °C – 60 °C) was immersed in the water. The reading on the thermometer was recorded after two minutes.

3.4.2 Determination of conductivity, pH, dissolved oxygen, total dissolved solids (TDS) and turbidity

These quantities were also determined on site. Turbidity values were taken using cybercan IR TB 100 Turbidimeter. The Turbidimeter was calibrated using the 1000 NTU, 100 NTU, 10 NTU and 0.02 NTU calibration standards. The cuvette was rinsed three times with the sample to be analyzed. The light shield cap was replaced and all outside surfaces were cleaned and made dry. The cuvette was pushed firmly into the optical well and index to the lowest reading. The NTU values were measured by pressing and releasing the arrow button and value was recorded after the display has stopped flashing.

For pH reading, a Mettler Toledo MP220 pH meter was used in the measurements. The pH meter was calibrated with two buffer solutions of pH 4.01 and 7.00. The water sample was placed in a beaker and the electrode was rinsed with distilled water and placed in the sample in the beaker. The readings were recorded after the reading was stable.

Conductivity and TDS were measured using Hanna instruments HI 9032 micro computer conductivity meter. The conductivity meter was calibrated using a reference buffer of 12,880

$\mu\text{S}/\text{cm}$. when the "buf" sign was displayed on the screen and blinking. The reading was not stable until "CON" appeared on the screen. The "CON" key was then pressed to confirm the reading on the equipment. The equipment was returned to the operation mode for measurement. The electrode of the meter was rinsed and placed in storage distilled water. The water sample was put in a beaker and the electrode rinsed with distilled water was lowered into the sample in the beaker. The conductivity in $\mu\text{S}/\text{cm}$ of the sample was displayed on the screen and recorded.

TDS was recorded by selecting the TDS key of the Hanna instrument while the electrode remained in the water sample that was used to measure the conductivity. The TDS value in mg/L displayed on the screen was recorded.

Dissolved oxygen was measured using Hanna instruments dissolved oxygen meter. The electrode was immersed and the reading taken after the readings became stable.

3.4.3 Total hardness determination

A 100 mL portion of the water sample was put into a 250 mL conical flask and 10 mL of $\text{NH}_4 / \text{NH}_3$ buffer was added to it. Two drops of Erichrome Black T indicator was added. The content of the conical flask was titrated against 0.02 M EDTA solution until the colour changed from the wine-red to the blue end point. Titration was repeated until a consistent titre was obtained and the average titre calculated (APHA, 1998). Total hardness was calculated using the relation below

$$\text{Total hardness (mgL}^{-1}\text{)} = \text{average titre} \times 20$$

3.4.4 Calcium hardness determination

A 100 mL portion of the water sample was put into a 250 mL conical flask. Four mL sodium hydroxide solution was added to the contents of the flask, followed by the addition of about 0.2 g of murexide indicator. The content of the conical flask was titrated against 0.02 M EDTA to the pink end point. Titration was repeated until a consistent titre was obtained and the average titre calculated (APHA, 1998). Calcium hardness was calculated using the relation below

$$\text{Calcium hardness as mg CaCO}_3 / \text{L} = \text{Average titre value} \times 20$$

3.4.5 Magnesium hardness determination

The magnesium hardness of a sample was calculated as a difference between the total hardness and calcium hardness values obtained from analysis of the sample (APHA, 1998).

$$\text{Mg hardness} = \text{total hardness} - \text{calcium hardness}$$

3.4.6 Alkalinity determination

A 50 mL sample was put into a conical flask. 2 drops of methyl orange indicator was added and the resulting mixture was titrated against a standard 0.1 M HCl solution to the first permanent pink colour at pH 4.5 (APHA, 1998). The alkalinity was calculated using the relation below

$$\text{Alkalinity (mgL}^{-1}\text{)} = \frac{A \times M \times 50000}{T}$$

Where:

A = Volume of acid used (mL).

T = volume of sample (mL).

M = Molarity of standard acid used.

3.4.7 Chloride determination.

A 100 mL water sample was put into a conical flask and 3 drops of potassium chromate indicator was added to the contents of the flask. The content of the flask was titrated against standard silver nitrate solution, while stirring constantly, to the permanent red colour end point. The volume of the titre was recorded (APHA, 1998). Chloride concentration was calculated using the relation below

$$\text{Chloride (mgL}^{-1}\text{)} = \text{titre value} \times 10$$

3.4.8 Determination of nitrite

Aliquots of standard solutions containing 0.2 8.0 μgL^{-1} of nitrite were transferred in to series of 10 mL flask. To each flask, 1 mL of 0.5% sulfanilic acid and 1 mL of 2 M hydrochloric acid solution were added and the solution was shaken thoroughly for 5 minutes to allow the diazotization reaction to go to completion. Then, 1 mL of 0.5% methyl anthranilate and 2 mL of 2 M sodium hydroxide solution were added to form an azo dye. The contents were diluted to 10 mL using distilled water. After the dilution, the absorbance of the red colored dye was measured at 493 nm against the corresponding reagent blank using a Shimadzu UV-2550 UV-Visible spectrophotometer and a calibration curve was constructed. The samples were treated similarly and the concentrations were determined from the calibration curve (Ensafi *et al.*, 2004).

3.4.9 Determination of nitrate

10 mL of sample solution was Pipetted into a beaker, 5 mL of Conc. HCl and 2 g of Zn / NaCl granular mixture was added, and allowed to stand for 30 minutes with occasionally stirring to form nitrite. The solution was then filtered into a 100 mL standard flask using Whatman No 41 filter paper and diluted up to the mark. Aliquots of stock solution containing 0.2- 10.0 $\mu\text{g mL}^{-1}$ of reduced nitrate were transferred into a series of 10 mL flask. 1 mL of 0.5% sulfanilic acid and 1 mL of 2 M HCl solution was added and shaken thoroughly for 5 minutes for the diazotization reaction to go to completion. Then, 1 mL of 0.5% methyl anthranilate and 2 mL of 2 M sodium hydroxide solution were added to form an azo dye and the contents were diluted to 10 mL with water. After dilution to 10 mL with water, the absorbance of the red colored dye was measured at 493 nm against the corresponding reagent blank using a Shimadzu UV-2550 UV-Visible spectrophotometer and a calibration curve was constructed. The concentrations of the samples were determined from calibration curve (Ensafi *et al.*, 2004).

3.4.10 Determination of fluoride

Fluoride was determined by Direct Measurement using a mettler Toledo sevenGo pH/mV meter. The mettler Toledo sevenGo pH/mV meter was calibrated with Standard solutions of 0.1, 1, 10, 100 ppm of fluoride ion. Standard solutions were treated with 50 mL of TISAB 1 and the mV readings taken. A calibration curve was constructed. To a clean, dry, 150 ml plastic beaker, 50 ml of sample was added to 50 ml of TISAB 1. The beaker was placed on a magnetic stirrer and stirred. The electrode was rinsed with distilled water, dried and lowered into the solution. The mV reading was recorded when the reading was stable. The concentrations of fluoride in the samples were determined using the calibration curve (Fucsko *et al.*, 1987).

3.4.11 Determination of phosphate

Standard solutions of 0.1, 1 and 10 ppm solutions of phosphate were prepared using KH_2PO_4 . 50 mL each of the standards and the samples were taken and placed in beakers. 5 mL of a mixed solution containing 50 cm³ of 0.0016 M ammonium molybdate, 125 cm³ of 0.2 M sulfuric acid, 50 cm³ of 0.02 M ascorbic acid, and 25 cm³ of 0.0001 M potassium antimonyl - tartrate was added to the beakers. A blue colour developed and was allowed to develop for thirty minutes. The absorbances were measured at 885 nm against the corresponding reagent blank using a Shimadzu UV-2550 UV-Visible spectrophotometer. A calibration curve was constructed using the standards and the concentration of phosphate in the samples were determined from the calibration curve (Strickland and Parsons, 1988).

3.4.12 Determination of sulphate

A crucible was ignited to constant weight while completing the following steps.

100 ml aliquot of sample was taken into a 250 mL beaker the pH was adjusted to about 4.5 and then 2 ml of 50% HCl added. The solution was heated to boiling while a 50 ml beaker containing 25 ml 0.4 M BaCl_2 solution was warming. The warm BaCl_2 solution was slowly added to the sample solution and stirred slowly until precipitate stopped forming. 2 mL of 0.4 M BaCl_2 was added to confirm completeness of the precipitation. The walls of the beaker was rinsed with distilled water and covered with a watch glass. The resulting solution was then heated at 80 ± 5 °C for about two hours. The beaker was then removed from the heat and the precipitate allowed to settle. The precipitate was then filtered through a 9 cm ashless filter paper. The precipitate was washed with hot distilled water, decanting through the filter paper. The precipitate and the filter

paper were dried and ignited at 800 °C for one hour in the crucible. The crucible was then cooled in a dessicator and weighed. (APHA, 1975)

Calculation

$$mgL^{-1} SO_4 = \frac{mg BaSO_4 \times 411.5}{100}$$

3.4.14 Determination of total suspended solids

A cellulose nitrate membrane filter with pore size 0.45 µm was placed on a Teflon faced glass filter holder and wetted by filtering about 20 mL distilled water using the Millipore vacuum filtration. This was done to open the pores of the filter paper. The wet paper was removed carefully using a pair of forceps and placed on a watch glass. The watch glass and the wet paper were placed in an oven at 103 °C to 105 °C for 15 minutes to dry. The filter paper together with the watch glass were removed from the oven and placed in desiccators to cool to a constant weight. The filter paper was marked and weighed and the weight recorded as W₁. The water sample was shaken to obtain a homogenous mixture and thereafter a known volume was taken in a graduated glass cylinder. The volume was recorded as V mL. The test sample was put into the funnel and vacuum filtration applied. The contents of the measuring cylinder were rinsed with distilled water and emptied into the funnel while the vacuum filtration continued. The filtration continued until the last drop of the filtrate was seen. The filter paper together with the solids was carefully removed using a pair of forceps and placed on a clean watch glass. The watch glass together with its contents was oven dried at 104 °C to 107 °C for, at least, 30 minutes to dry. The watch glass with the paper was removed and placed in a desiccator to cool. The filter paper and

its contents were weighed and the weight recorded as W_2 (APHA, 1998). TSS was calculated using the relation below

$$\text{TSS (mgL}^{-1}\text{)} = \frac{W_2 - W_1}{V} \times 10^6$$

Where:

W_2 = weight of filter paper and solids in grams.

W_1 = weight of filter paper only in grams.

V = volume of water sample in mL

3.4.15 Determination of colour

Apparent and true colour were determined using HACH DR/2010 Portable Data Logging Spectrophotometer. The water samples were filtered and their pH adjusted to 7.6. Water samples with pH less than 7 were adjusted with 1.0 N NaOH and those with pH greater than 7 adjusted with 1.0 N HCl. The wavelength used for the determination was 465 nm. The stored program was calibrated in colour units based on APHA recommended standard of one colour unit equal to 1 mgL⁻¹ platinum as the chloroplatinate ion. By filtering out suspended particles, the samples true colour were measured but for the apparent colour the samples were not filtered.

3.4.16 Enumeration of faecal coliform and *Escherichia coli*

Faecal coliform were estimated using a three tube most probable number (MPN) method. Dilutions of 10⁻¹ to 10⁻¹⁰ were prepared in 0.1 % buffered peptone water (BPW) (Oxoid CM 509) and 1 mL of each solution inoculated into three tubes 5 mL of minerals of modified glutamate medium (Oxoid CM 607). The three tubes from the dilution were incubated at 44 °C. Tubes showing acid gas after 24 hours were confirmed as faecal coliform. By plating on Mac Conkey

no. 3 agar (Oxoid CM 115) and examining for typical colonies. Counts per 100 mL were calculated from MPN tables.

Escherichia coli was confirmed by further inoculating tubes showing acid gas in tryptone broth and incubated for 24 hours at 35 °C. 0.3 mL Kovac's reagent was added to test for indole ring. Appearance of distinct red colour in the upper layer gives a positive test. Count per 100 mL was calculated from MPN tables (Feng *et al.*, 2002).

3.5.0 Analysis of sediment samples

3.5.1 Sample preparation

Sediment samples were air dried and sieved through No 75 sieve.

3.5.2 Determination of cation exchange capacity, CEC

Cation exchange capacity was determined as the sum of all exchangeable cations (potassium, sodium, calcium, magnesium, aluminium and hydrogen). A ten gram portion of the sediment sample was placed in an extraction bottle. The sediment was extracted with 100 mL of 1.0 N of ammonium acetate. The bottle and the contents were shaken on an orbital shaker for one hour. The supernatant was then filtered through No 42 whatman filter paper.

For the determination of exchangeable calcium, 10 mL aliquot of the supernatant was taken and 10 mL of 10% KOH was added and followed by 1 mL of 30% triethanolamine. Three drops of 10% KCN was added followed by a few drops of cal-red indicator. The resultant solution was shaken vigorously to form a uniform mixture. The mixture was then titrated with 0.02 N EDTA

solution from a red to blue end point (Yuan, 1959). Exchangeable calcium was calculated as follows

$$\text{Ca} = \text{titre value of Ca} \times 2 \text{ in me/100 g of sediment}$$

For the determination of exchangeable calcium and magnesium (Ca+Mg), 10 mL aliquot of the filtered solution was placed in a 100 mL conical flask and 5 mL of ammonium chloride – ammonium hydroxide buffer solution followed by 1 mL of triethanolamine. Three drops of 10% KCN solution and a few drops of erichrome black T indicator was also added. The solution was shaken vigorously to form a uniform mixture. The mixture was then titrated with 0.02 N EDTA solution from red to blue end point (Yuan, 1959). Exchangeable calcium and magnesium (Ca+Mg) was calculated as follows

$$\text{Mg} = (\text{titre value of Ca+Mg} - \text{titre value of Ca}) \times 2 \text{ in me/100g sediment}$$

Flame photometry was used for the determination of exchangeable sodium and potassium. Standard solutions of 0, 2, 4, 6, 8, 10 ppm (K+Na) were run on the flame photometer and the readings used to construct a calibrating curve. 10 mL of the ammonium acetate extract was taken and analyzed on the flame photometer for Na and K after calibrating of photometer with prepared standards. Using the photometer reading and the standard curve, the concentrations of K and Na in the sediment were determined using the relation below

$$\text{Exchangeable K or Na (ppm)} = \frac{\text{graph reading} \times 100 \times \text{aliquot} \times \text{dilution factor}}{\text{Weight of sample}}$$

For the determination of hydrogen and aluminium ions, 5.0 g of sediment sample was weighed into a 50 mL bottle and extracted with 100mL of 1.0 N KCl for two hours on a mechanical shaker. A 50 mL aliquot of the KCl extract was placed in an Erlenmeyer flask and diluted with 100 mL of distilled water. Three drops of phenolphthalein indicator was added and titrated against 0.05 N NaOH to a permanent pink end point and the end point recorded. To the same flask 2 drops of 0.05 N HCl was added to bring the solution back to its original colourless condition. 10 mL of 1.0 N NaF solution was added to change colour to pink again. The resulting solution was then titrated against 0.05 N HCl with constant swirling until the colour of the solution disappeared completely (Schollenberger and Simon, 1945).

Calculations:

The value for the titration with 0.05N NaOH gives the amount of exchangeable ($Al^{+} + H^{+}$) and the value of the titration for HCl give the amount of exchangeable Al. Hence subtracting this value from the titre value for titration with 0.05 N NaOH gave the value for exchangeable H^{+} . these values were then expressed in meq per 100 g of sample using the relations below.

$$\text{Meq total acidity (Al + H)} = \frac{\text{NaOH end point} \times \text{Normality of NaOH} \times 100}{\text{Weight of sample}}$$

$$\text{Meq of exchangeable Al} = \frac{\text{HCl end point} \times \text{Normality of HCl} \times 100}{\text{Weight of sample}}$$

$$\text{Meq H} = \text{Meq total acidity (Al + H)} - \text{Meq of exchangeable Al}$$

3.5.3 Particle size analysis

The Bouyoucos Hydrometer Method was used for particle size analysis. A 51 g portion of the sediment sample was weighed into a 'milkshake' mix cup. To this 50 mL of 10 % sodiumhexametaphosphate along with 100 mL distilled water were added. The mixture was shaken for 15 minutes after which the suspension was transferred from the cup into a 1000 mL measuring cylinder and distilled water was added to reach the 1000 mL mark. The mixture was inverted several times until all soil particles were in suspension. The cylinder was placed on a flat surface and the time noted immediately a soil hydrometer was placed into the suspension. The first reading on the hydrometer was taken after 40 seconds. The temperature of the solution was also recorded with a thermometer. After the first reading the suspension was allowed to stand for 3 hours and the second hydrometer and temperature readings were taken. The first readings indicate the percentage of sand and the second reading percentage clay. Percentage of silt was determined by difference (Page *et al.*, 1982; Milford, 1997). The respective percentages were calculated as follows:

$$\% \text{ Sand} = 100 - [H_1 + 0.2 (T_1 - 20) - 2.0] \times 2$$

$$\% \text{ Clay} = [H_2 + 0.2 (T_2 - 20) - 2.0] \times 2$$

$$\% \text{ Silt} = 100 - (\% \text{ Sand} + \% \text{ Clay})$$

Where:

H_1 = hydrometer reading at 40 seconds.

T_1 = temperature at 40 seconds.

H_2 = hydrometer reading at three hours.

T_2 = temperature reading at three hours.

$0.2 (T - 20)$ = temperature correction to be added to hydrometer reading.

-2.0 = salt correction to be added to hydrometer reading.

3.5.4 Determination of pH and conductivity

A 10 g portion of air dried sediment sample was weighed and 25 ml of distilled water added. The resulting suspension was stirred intermittently for 30 minutes. The pH was measured using a Mettler Toledo MP220 pH meter after calibrating with 4.01, 7.00, and 10.00 standards. The conductivity was measured using Hanna instruments HI 9032 micro computer conductivity meter (Page *et al.*, 1982).

3.5.5 Determination of organic matter content

Crucibles were washed with water and placed in an oven at 105 °C to dry to a constant weight and the weight recorded as W_1 . Air dried sediment were also dried at 105 °C to remove moisture. The oven dried sediment samples were then weighed into the crucibles and their weights recorded as W_2 . The crucibles were then placed in a furnace operating at a temperature of about 495 ± 5 °C for 24 hours. The crucibles were removed with the help of a pair of tongs and place in a desiccator and allowed to cool. The crucible and its contents were weighed and the weight recorded as W_3 (Page *et al.*, 1982). The percentage of organic matter was calculated as follows

$$\% \text{ organic matter content} = \frac{W_3 - W_1}{W_2 - W_1} \times 100$$

Where

W_1 = Weight of crucible only

W_2 = Weight of sample + crucible before heating

W_3 = Weight of sample + crucible after heating

3.5.6 Determination of total heavy metal concentration in sediment samples

One gram of the sediment sample was weighed in 250 ml beakers and digested with 20 ml of aqua regia on a hot plate for about 2 hours. The beakers were then removed from the hot plate and allowed to cool to room temperature. The contents of the beakers were then filtered into 50 ml volumetric flasks through 0.45 μ m whatman filter paper and topped to the mark with distilled water. The resulting solution was then aspirated onto an atomic absorption spectrophotometer SpectraAA 220 using oxy - acetylene after running standards on the spectrophotometer (Lin, 2002). The cathode lamps used were copper (wavelength nm 324.7), lead (wavelength nm 217.0), zinc (wavelength nm 213.9) arsenic (wavelength 193.7 nm) and iron (wavelength nm 248.3 nm).

3.5.7 Measurement of chemical forms of heavy metals

A five step sequential extraction procedure as described by Tessier *et al.* (1979) was adopted. The method establishes metal concentration in five different phases namely; Exchangeable metal fraction, Carbonate-bound metal fraction, Fe-Mn oxide metal fraction, Organic and Sulphide metal fraction, Residual metal fraction.

3.5.7.1 Exchangeable metal fraction

One gram of sediment sample was weighed into a 40 mL centrifuge tubes, eight millilitres of 1 M $MgCl_2$ solution was added and agitated frequently at room temperature for 1 hour. The

resultant solution was centrifuged at 2500 rpm for ten minutes and decanted. The residue was washed with 10 mL distilled water and used for the extraction in the next stage. Four millilitres aqua regia was added to the extract and added to the wash water and diluted to 50 mL for metal analysis.

3.5.7.2 Carbonate-bound metal fraction

To the residue from the previous step 1 M sodium acetate solution adjusted to pH 5.0 with acetic acid was added and agitated periodically at room temperature for 5 hours. The resulting solution was centrifuged at 2500 rpm for 10 minutes, decanted and 4mL of aqua regia added. The residue was washed again with distilled water and centrifuged at 2500 rpm. The filtrate was added to the initial filtrate and the resultant solution was diluted to 50 mL with distilled water and used for metal analysis. The washed residue was used for the next step in the extraction process.

3.5.7.3 Fe-Mn oxide metal fraction

To the residue from the previous leach, 20 mL of 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) acetic acid was added and the mixture agitated periodically in boiling water bath for 5 hours. The resulting solution was centrifuged at 2500 rpm for 10 minutes, decanted and 4 mL of aqua regia added. The residue was washed again with 10 mL distilled water and centrifuged at 2500 rpm. The filtrate was added to the initial filtrate and the resultant solution was diluted to 50mL with distilled water and used for metal analysis. The washed residue was used for the next step in the extraction process.

3.5.7.4 Organic and Sulphide metal fraction

To the residue from the previous leach, 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 which has been adjusted to pH 2 with HNO_3 was added and agitate periodically at 85 °C for 2 hours. To the resultant mixture, 3 mL of 30% H_2O_2 (pH 2) was added and agitated periodically at 85 °C for 3 hours and cooled to room temperature. A five millilitres portion of 3.2 M ammonium acetate in 20% v/v HNO_3 was added and agitated periodically at room temperature for 30 minutes. The resulting solution was centrifuged at 2500 rpm for 10 minutes, decanted and 4 mL of aqua regia added to the extract. The residue was washed again with 10 mL distilled water and centrifuged at 2500 rpm. The filtrate was added to the initial filtrate and the resultant solution was diluted to 50 mL with distilled water and used for metal analysis. The washed residue was used for the next step in the extraction process.

3.5.7.5 Residual metal fraction

To the residue from the previous leach, 16 mL of aqua regia was added and heated in a hot water bath for 2 hours. The resulting solution was centrifuged at 2500 rpm for 10 minutes, decanted and 4mL of aqua regia added. The residue was washed again with distilled water and centrifuged at 2500 rpm. The filtrate was added to the initial filtrate and the resultant solution was diluted to 50 mL with distilled water and used for metal analysis.

3.6 Extent of pollution of sediment by heavy metals

The geoaccumulation index (I_{geo}) introduced by Muller (1979) was also used to assess metal pollution in sediments to quantify the degree of anthropogenic contamination in the reservoir sediments. Geoaccumulation index is expressed as follows:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right)$$

Where C_n = measured concentration of heavy metal n in the reservoir sediment,

B_n = geochemical background value of metal n in average shale

(Turekian and Wedepohl, 1961), 1.5 is the background matrix correction in factor due to lithogenic effects.

3.7 Statistical analysis

Statistical analysis was carried out using the Statistical Package for Social Science (SPSS) version 15 and Microsoft office excel 2007 edition. Correlation analysis was carried out on both the water and sediment quality parameters. Factor analysis was carried out on the water quality parameters to establish the relationship between the parameters and their sources. Similarly factor analysis was also carried out on the heavy metals in the sediment samples to establish sites significantly polluted with heavy metals. Canonical correlation was carried out on the sediment samples using pH, organic matter content, electrical conductivity and cation exchange capacity as dependent variables and the heavy metals as predictor variables.

CHAPTER FOUR

4.0 Results

4.1 Water quality results

A statistical analysis of the physic - chemical parameters of water from the reservoir is presented in table 2.1 and 2.2. The mean concentration of heavy metals in the water samples from the reservoir are also presented in table 3. The untreated data of physicochemical parameters and that of heavy metals are presented in appendix 1A, 1B, 1C, and 1D.

Table 2.1: The ranges, means and standard deviations of physicochemical parameters of the Owabi reservoir compared with their natural background and WHO acceptable limits (n = 10)

Parameter	Range	Mean \pm Std. Dev.	Natural background	WHO (2006)
pH	6.30 – 7.30	6.97 \pm 0.32	7	6.6-8.5
Apparent Colour (PtCo)	93.03 - 375.10	130.60 \pm 86.75	-	15
True Colour(PtCo)	29.10 - 50.02	37.40 \pm 7.09	-	-
Turbidity (mgL ⁻¹)	29.01 - 37.03	32.63 \pm 2.75	5	5
Conductivity (μ scm ⁻¹)	254.04 - 407.10	308.00 \pm 53.35	50-300	700
TSS (mgL ⁻¹)	110.01 - 143.00	128.60 \pm 10.56	-	1000
TDS (mgL ⁻¹)	30.21 - 58.03	43.11 \pm 12.63	-	20
Temperature (°C)	29.50 - 31.50	30.65 \pm 0.63	22-29	-
Alkalinity (mgL ⁻¹)	139.00 - 205.00	178.90 \pm 33.65	-	400

Table 2.2: The ranges, means and standard deviations of physicochemical and bacteriological parameters of the Owabi reservoir compared with their natural background and WHO acceptable limits (n = 10)

Parameter	Range	Mean \pm Std. Dev.	Natural background	WHO (2006)
Dissolved Oxygen (mgL^{-1})	2.80 - 4.07	3.58 ± 0.51	7	-
Total Hardness (mgL^{-1})	64.00 - 74.00	69.67 ± 2.76	-	500
Ca – Hardness (mgL^{-1})	37.33 - 50.00	41.6 ± 3.88	12	75
Mg – Hardness (mgL^{-1})	24.00 - 30.00	28.07 ± 2.07	1-99	30
Nitrite (mgL^{-1})	0.004 - 0.006	0.005 ± 0.001	-	3
Nitrate (mgL^{-1})	0.180 - 0.280	0.24 ± 0.04	0.23	50
Phosphate (mgL^{-1})	0.280 - 1.200	0.65 ± 0.28	0.02	< 0.3
Ammonium (mgL^{-1})	0.000 - 0.010	0.005 ± 0.005	-	1.5
Sulphate (mgL^{-1})	8.11 - 15.02	10.90 ± 2.28	0.1-10	250
Chloride (mgL^{-1})	60.00 - 73.00	65.53 ± 4.07	7.8	250
Fluoride (mgL^{-1})	0.60 - 1.10	0.88 ± 0.19	-	1.5
Faecal coliform (counts per 100 mL)	10.18 - 12.62	11.68 ± 0.77	0	0
<i>E. Coli</i> (counts per 100 mL)	8.86 - 11.86	9.69 ± 0.92		0

Graph illustrating the levels of water quality parameters with significantly high values in the water samples are shown in figure 2.

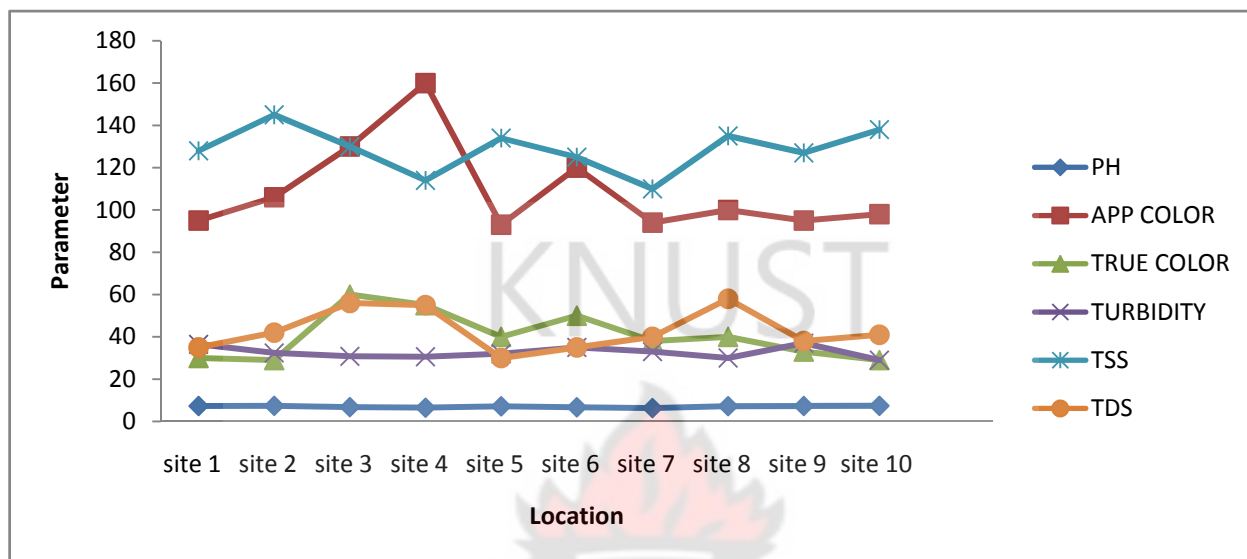


Fig. 2 Graph of physicochemical parameters of water samples from the reservoir

4.1.1 Physicochemical parameters of water samples from the reservoir

The apparent and true colours recorded for each site in the reservoir was above the WHO standards. Site S₄ recorded the maximum value of 160 PtCo while site S₃ recording the minimum of 93 PtCo for apparent colour. Site S₁₀ recorded the minimum value of 29 PtCo and site S₃ recorded the maximum value of 60 PtCo for true colour.

Turbidity values for all the sites were above the WHO standards (table 2.1). Site S₉ recorded highest value of 37 NTU and site S₁₀ recorded the lowest of 29 NTU. Site S₂ recorded the highest value for TSS with a value of 142 mgL⁻¹ while site S₇ recorded the lowest value of 127 mgL⁻¹. All the recorded values for TSS were above WHO standards for drinking water.

For TDS site S₈ recorded the maximum value of 58 mgL⁻¹ while site S₅ recorded a minimum of 30 mgL⁻¹. All the sites recorded values higher than the WHO standards for drinking water.

Temperature of the water in the reservoir ranged from a minimum of 29.5 °C recorded at site S₁₀ to a maximum of 31.5 °C at site S₉. These were above the natural background of 22 - 29 °C for fresh water. Alkalinity values recorded ranged from a minimum of 139.00 mgL⁻¹ recorded at site S₆ to a maximum of 205.00 mgL⁻¹ recorded at site S₁₀. These recorded values were below the WHO standards (table 2.1).

Dissolved oxygen levels in the water ranged from a minimum of 2.80 mgL⁻¹ at sites S₄ and S₉ while site S₇ recorded a maximum of 4.07 mgL⁻¹. These values were below the natural background level of 7 mgL⁻¹.

Calcium and magnesium ions in the water samples from the reservoir were below the WHO levels for drinking water of 75 mgL⁻¹ and 30 mgL⁻¹ respectively. For calcium site S₄ recorded a maximum of 43.67 mgL⁻¹ while site S₁ recorded a minimum of 37.33 mgL⁻¹. Magnesium values recorded ranged from a minimum 24 mgL⁻¹ recorded at site S₄ to a maximum of 30 mgL⁻¹ at sites S₉ and S₁₀.

Concentrations of nitrite in the reservoir were below the WHO levels of 3 mgL⁻¹ for drinking water. Site S₁₀ recorded a minimum of 0.004 mgL⁻¹ while sites S₃, S₄, S₆, S₇, S₉ recorded the maximum value of 0.006 mgL⁻¹. Nitrates in the reservoir were below the WHO level for drinking

water. They ranged from a minimum of 0.18 mgL^{-1} recorded at sites S_3 and S_6 to a maximum of 0.28 mgL^{-1} recorded at sites S_1 and S_9 .

Site S_8 recorded the maximum value of 0.91 mgL^{-1} for phosphate while site S_1 recorded the minimum of 0.28 mgL^{-1} . Nine out of the ten sites recorded values above the WHO levels of $< 0.03 \text{ mgL}^{-1}$.

Recorded values of ammonium in the water from the reservoir ranged from below detection to 0.01 mgL^{-1} . All the recorded values were below the WHO levels of 1.5 mgL^{-1} for drinking water.

The concentrations of sulphate recorded in samples from the reservoir were below the WHO levels of 250 mgL^{-1} for drinking water. Sites S_1 and S_7 recorded a minimum concentration of 8.11 mgL^{-1} while site S_2 recorded a maximum of 15.02 mgL^{-1} .

Chloride concentration of the water in the reservoir ranged from a minimum of 60.00 mgL^{-1} recorded at site S_6 to a maximum of 73 recorded at site S_7 . All the recorded values were below the WHO levels of 250 mgL^{-1} for drinking water.

Fluoride concentrations recorded were below the WHO levels of 1.5 mgL^{-1} for drinking water. Sites S_1 , S_4 , and S_8 recorded the maximum concentration of 1.1 mgL^{-1} while sites S_9 recorded the minimum concentration of 0.6 mgL^{-1} .

Table 3: The ranges, means and standard deviations of heavy metals of water from the Owabi reservoir compared with their natural background and WHO acceptable limits for drinking water

Heavy metal	Range /mgL ⁻¹	Mean \pm Std. dev.	Natural background	WHO (2006)
Fe	0.010 - 0.035	0.016 \pm 0.008	0.670	1.00
Pb	0.010 - 0.022	0.015 \pm 0.005	0.005	0.01
Zn	0.001 - 0.012	0.009 \pm 0.003	0.030	3.00
As	0.196 - 0.412	0.299 \pm 0.067	-	0.01
Cu	0.008 - 0.013	0.011 \pm 0.002	0.005	1.00

4.1.2 Heavy metal concentration in the water samples

Iron levels in the water ranged from a minimum of 0.01 mgL⁻¹ recorded at sites S₃, S₅, and S₈ to a maximum of 0.35 mgL⁻¹ recorded at site S₁₀. These values were below the WHO levels of 1.0 mgL⁻¹ recommended for drinking water.

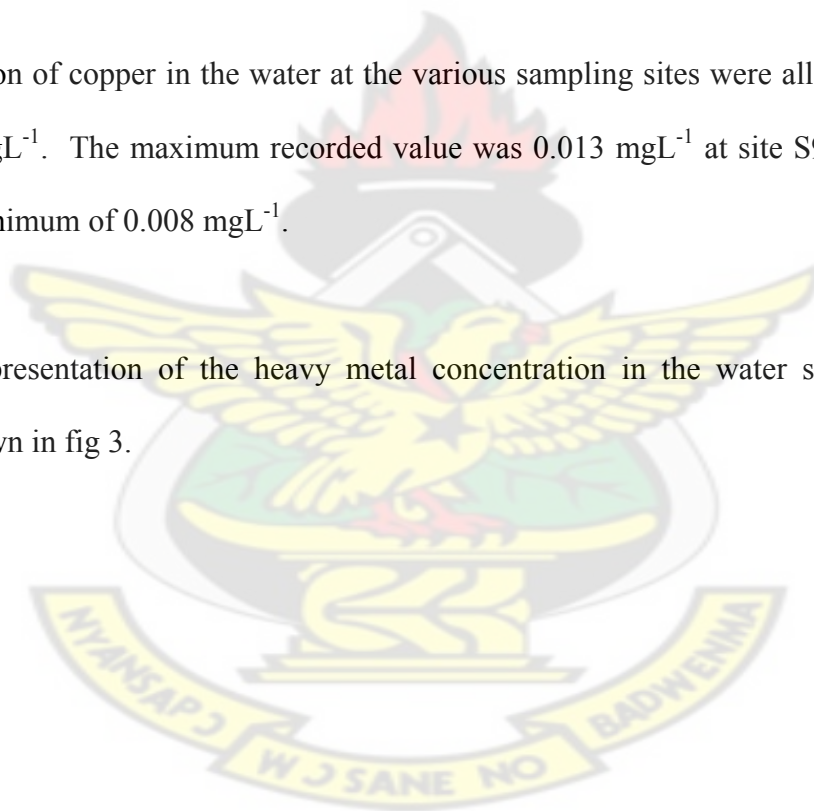
The concentration of lead in the water samples were all above the WHO standards of 0.01 mgL⁻¹ for drinking water. The maximum recorded value of 0.095 mgL⁻¹ was recorded at site S₅ and a minimum of 0.075 mgL⁻¹ recorded at site S₈.

The concentration of zinc in water samples from the reservoir were all below the WHO limits of 3.0 mgL^{-1} for drinking water. A minimum value of 0.001 mgL^{-1} was recorded at site S₉ while site S₅ recorded a maximum value of 0.012 mgL^{-1} .

The concentration of arsenic at the various sampling sites were all above the WHO standards of 0.01 mgL^{-1} for drinking water. The maximum recorded value was 0.412 mgL^{-1} at site S₄ and a minimum of 0.196 mgL^{-1} at site S₃.

The concentration of copper in the water at the various sampling sites were all below the WHO levels of 1.0 mgL^{-1} . The maximum recorded value was 0.013 mgL^{-1} at site S₉ while site S₁₀ recorded the minimum of 0.008 mgL^{-1} .

A graphical representation of the heavy metal concentration in the water samples from the reservoir is shown in fig 3.



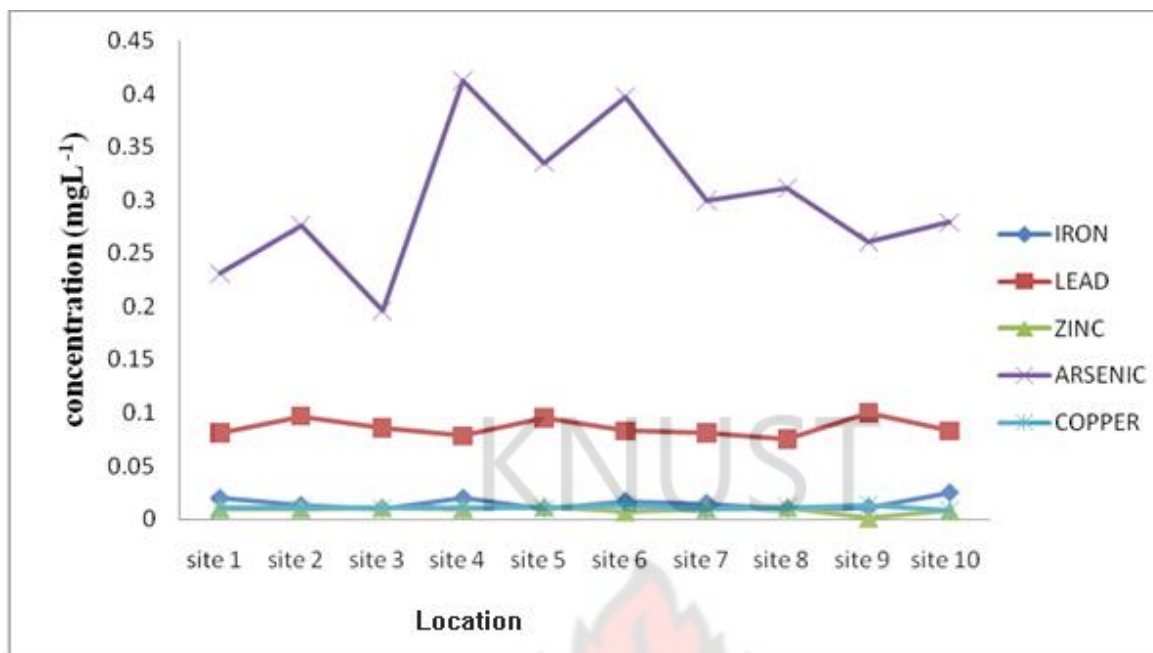


Fig 3: Graph of heavy metal concentration in the water samples at the various sampling sites in the reservoir

4.1.3 Bacteriological indicators

The levels of both faecal coliforms and *E. Coli* established within the reservoir were above the WHO levels of zero for drinking water. For faecal coliform, sites S₇ and S₃ recorded a maximum value of 12.60 counts per 100 mL while site S₁ recorded a minimum of 10.18 counts per 100 mL. For *E. coli*, site S₇ recorded a maximum value of 11.86 counts per 100 mL while sites S₄ and S₁₀ recorded a minimum value of 8.86 counts per 100 mL. A graphical representation of the bacteriological concentrations is shown in fig 4.

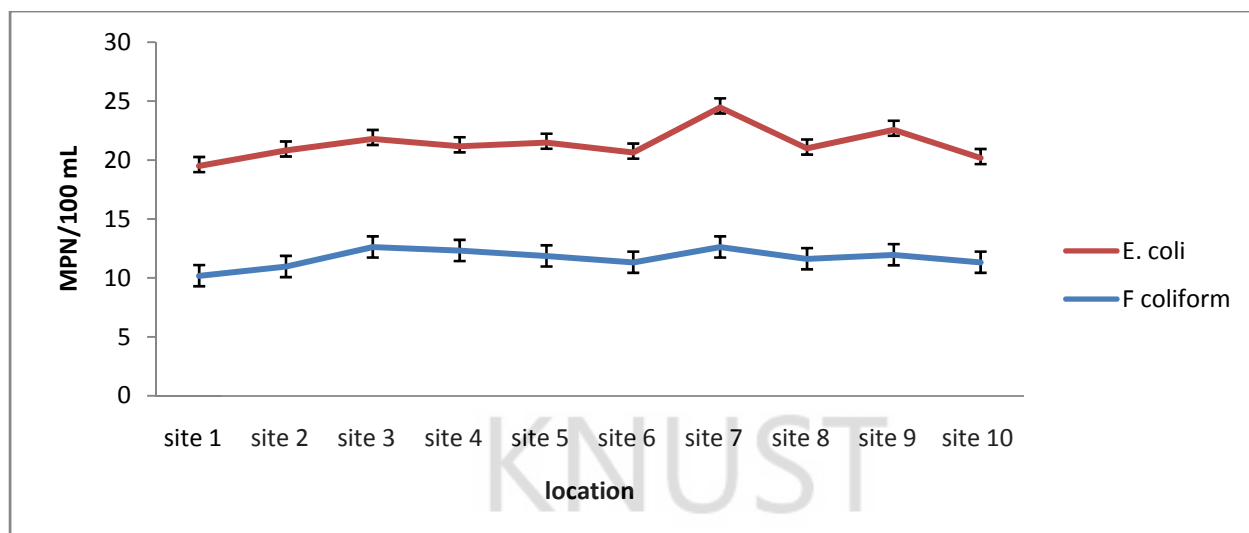


Fig. 4: Graph of bacteriological concentrations of the various sampling sites in the reservoir

4.1.4 Correlation analysis

Correlation analysis was carried out between pH, electrical conductivity, Ca^{2+} , Mg^{2+} , PO_4^{2-} , SO_4^{2-} , Cl^- , F^- , Fe^{2+} , Pb^{2+} , Zn^{2+} , As^+ , and Cu^{2+} . The results are presented in table 4.

Table 4: Correlation between pH, electrical conductivity, Ca^{2+} , Mg^{2+} , PO_4^{2-} , SO_4^{2-} , Cl^- , F^- , Fe^{2+} , Pb^{2+} , Zn^{2+} , As^+ , and Cu^{2+} .

Parameter	pH	EC	Ca^{2+}	Mg^{2+}	Cl^-	F^-	Fe^{2+}	Pb^{2+}	Zn^{2+}	As^+	Cu^{2+}
pH	1										
EC	-0.626*	1									
Ca^{2+}	-0.714*	0.726**	1								
Mg^{2+}	0.100	-0.143	-0.396	1							
Cl^-	-0.119	0.402	0.503	-0.583*	1						
F^-	-0.373	0.373	0.330	-0.627*	0.544	1					
Fe^{2+}	0.043	-0.030	0.154	0.142	-0.291	-0.118	1				
Pb^{2+}	0.326	0.096	-0.307	0.639*	-0.180	-0.379	0.245	1			
Zn^{2+}	-0.173	0.045	0.202	-0.292	0.336	0.673*	-0.086	-0.543	1		
As^+	-0.595*	0.623*	0.762**	0.046	0.237	0.101	0.103	0.136	0.039	1	
Cu^{2+}	-0.109	-0.018	-0.064	0.137	-0.092	-0.335	-0.505	0.251	-0.601*	0.238	1

* Correlation is significant at the 0.05 level

** Correlation is significant at the 0.01 level

4.1.5 Factor Analysis

Factor analysis was carried out on the water quality parameters that were above the natural background values. The result of the factor analysis is shown in tables 5 and 6.

Table 5: The Varimax rotated factor loadings for water quality parameters

Parameter	Factor					Communality
	1	2	3	4	5	
pH	0.4079	-0.4560	-0.6505	-0.1989	0.3700	0.9379
Apparent colour	-0.2334	0.7165	0.3530	0.1270	-0.4700	0.9296
True colour	-0.2814	-0.1591	0.7562	0.3220	-0.1370	0.7989
Turbidity	-0.3945	-0.2717	-0.3795	0.5740	0.3630	0.8348
Conductivity	-0.3694	0.7894	0.3145	0.0579	0.3140	0.9603
TDS	0.7424	-0.3330	-0.4481	-0.0352	-0.3200	0.9667
DO	-0.1296	-0.4096	-0.1325	-0.8027	0.0670	0.8510
phosphate	0.9316	-0.0025	-0.2100	0.1048	0.0920	0.9316
sulphate	0.8208	-0.0481	0.0636	-0.1230	0.0080	0.6593
chloride	0.1492	0.7609	-0.1976	-0.1583	-0.0610	0.6691
E - Coli	-0.0841	0.0634	0.0504	-0.0870	0.9420	0.9090
Faecal coliform	0.0452	0.1961	0.8731	-0.1686	0.2690	0.9037
Lead	0.0411	-0.1266	0.0102	0.2255	0.6580	0.5021
arsenic	-0.1625	0.5708	0.3026	0.4538	-0.1260	0.6658
copper	-0.0562	-0.1461	0.0381	0.9122	0.1420	0.8783
Variance	4.8060	2.5850	2.0080	1.7270	1.3440	12.4700
% total variance	32.0400	17.2330	13.3890	11.5130	8.9630	83.1380

Extraction Method: Principal Component Analysis.

Table 6: Factor scores of water quality parameters of the Owabi reservoir

Sampling site	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Site 1	-1.7354	-0.6335	-1.9745	-0.3393	-0.5975
Site 2	1.7480	0.6226	-0.9928	0.0525	-0.0403
Site 3	0.1883	-1.3606	1.4660	-0.7986	-0.8205
Site 4	-0.7041	2.2097	0.7937	0.2889	-1.1878
Site 5	0.3738	-0.3755	0.2973	-0.2386	-0.3965
Site 6	-0.6061	-0.8029	0.6818	1.9180	-0.1324
Site 7	-0.9145	0.4554	0.6825	-1.1694	2.1497
Site 8	0.3061	0.5098	-0.4079	-0.2235	0.0617
Site 9	0.4972	-0.1943	-0.3010	1.4545	1.2858
Site 10	0.8465	-0.4309	-0.2451	-0.9444	-0.3221

4.2 Results of sediment analysis

A statistical analysis of the physicochemical parameters of sediment from the reservoir is presented in tables 7 and 8. The raw data on physicochemical parameters of the sediments are presented in appendix 2A and 2B.

Table 7: The ranges, means and standard deviations of physicochemical properties of sediments from the Owabi reservoir

PARAMETER	RANGE	MEAN \pm STD. DEVIATION
OMC (%)	13.84 - 19.53	16.35 \pm 2.05
pH	4.29 -6.61	5.32 \pm 0.82
CONDUCTIVITY (μ S/cm)	474.11 -1728.02	1249.70 \pm 394.11
CEC (cmol/kg)	16.21 -22.42	19.83 \pm 2.01
SAND (%)	15.60 -31.60	25.51 \pm 4.63
SILT (%)	60.80 -70.80	64.64 \pm 3.75
CLAY (%)	5.60 -14.10	9.85 \pm 2.69

4.2.1 Physicochemical properties of sediments from the Owabi reservoir

The pH values recorded ranged from a minimum of 4.29 recorded at site S₈ to a maximum of 6.61 at site S₁. The average pH of 5.32 \pm 0.82 makes the sediment acidic. Site S₁₀ recorded the maximum CEC of 22.42 cmol/kg with site S₆ recording the minimum if 16.21 cmol/kg.

The organic matter content of the sediment samples ranged from a minimum of 13.84% recorded at site 6 to a maximum of 19.53% recorded at site 10. A graphical representation of the OMC, pH and CEC of the sediment samples is shown in fig 5.

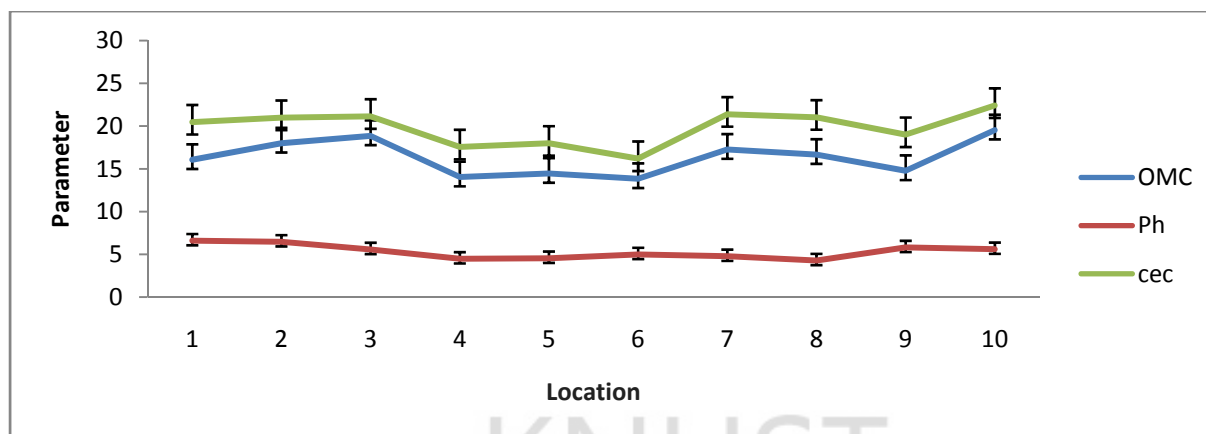


Fig 5: Graph of pH, OMC, and CEC of the sediment samples.

Results of the particle size distribution showed that all the sediment samples contained silt as the largest fraction ranging from 60.8 % - 70.8 % followed by sand which ranged from 15.6% - 31.6 %. Clay recorded the least of the fractions which ranged from 5.6 % - 14 %. This makes all the sediment samples clay samples using the soil texture triangle. A graphical representation of the particle size distribution of the various sediment samples is shown in fig 6.

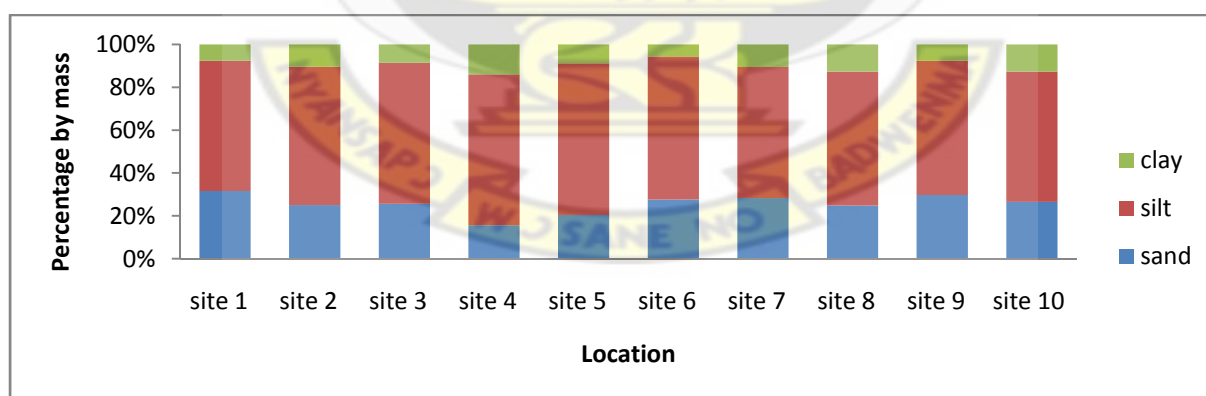


Fig 6: Graph of particle size distribution of the various sediment samples.

Table 8: The ranges, means and standard deviations of selected heavy metals in sediments from the Owabi reservoir compared with threshold effect level (TEL) and continental average shale (CAS) levels

PARAMETER	RANGE	MEAN \pm STD. DEV	TEL standard	CAS standard
Fe (g/kg)	3.52 - 5.43	4.03 \pm 0.56	-	47.2
Pb (g/kg)	0.08- 0.12	0.098 \pm 0.01	0.0059	0.02
Zn (g/kg)	0.14- 0.67	0.40 \pm 0.16	0.123	0.095
Cu (g/kg)	0.0023 - 0.05	0.03 \pm 0.01	0.0357	0.045

The readings for zinc showed the highest of 0.67 g/kg recorded at site S₃ and a minimum of 0.14 g/kg recorded at site S₉ with an average of 0.403 \pm 0.16 g/kg. All the recorded values were above the threshold effect level (TEL) of 0.123 g/kg (Buchnan, 2008) and the average continental shale of 0.095 g/kg (Turekian and Wedepohl, 1961).

The recorded values for lead ranged from a minimum of 0.08 g/kg recorded at site S₉ and a maximum of 0.12 g/kg recorded at site S₁. The average concentration was 0.098 \pm 0.01 g/kg. All the recorded values were above the threshold effect level (TEL) of 0.035 g/kg (Buchman, 2008) and the continental average shale of 0.02 g/kg (Turekian and Wedepohl, 1961).

Copper recorded a maximum of 0.0500 g/kg at site S₁ and a minimum 0.0191 g/kg at site S₁₀. Sites S₁, S₂ and S₇ recorded values above the threshold effect level (TEL) of 0.0357 g/kg (Buchman, 2008) while the others falling below the TEL. The average of 0.0310 \pm 0.01 g/kg

fell below the TEL value and the continental average shale of 0.045 g/kg (Turekian and Wedepohl, 1961).

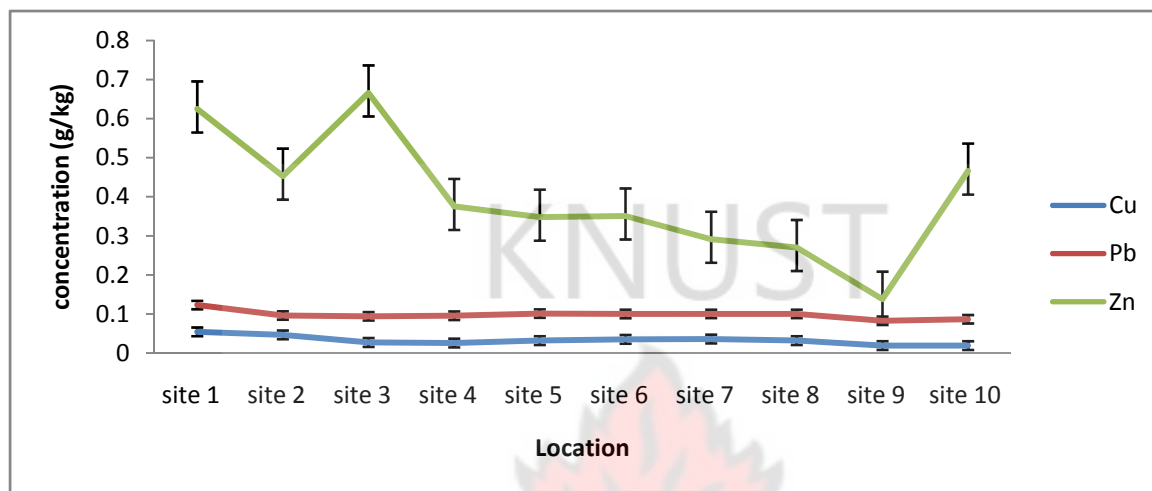


Fig 7: Graph of heavy metal concentration of the various sampling sites in the reservoir.

Iron levels in the sediment samples ranged from a minimum of 3.52 g/kg recorded at site S₉ to a maximum of 5.43 at site S₃. All the recorded values were below the average continental shale of 47.20 g/kg (Turekian and Wedepohl, 1961).

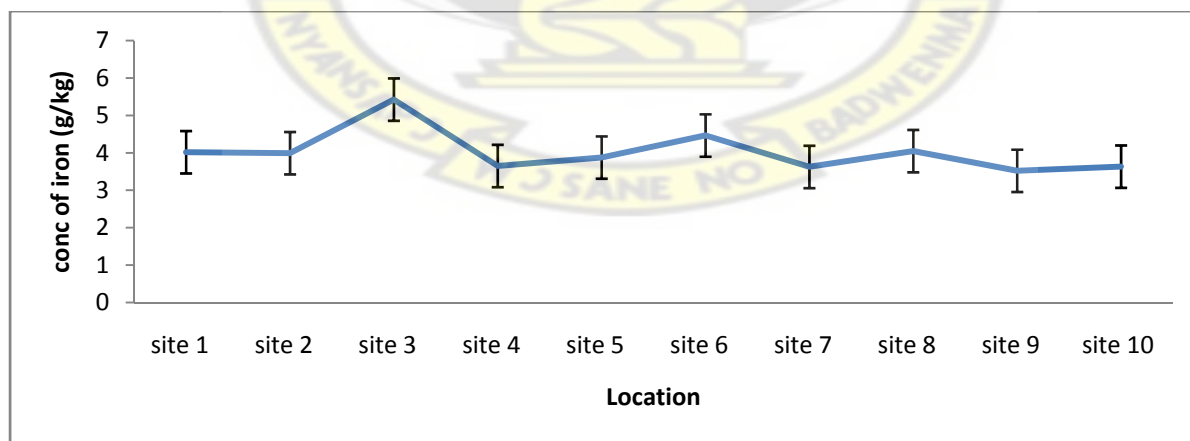


Fig 8: Graph of Fe concentration at the various sampling sites in the reservoir.

4.2.2 Results of the factor analysis on heavy metals in the sediment of the Owabi reservoir

Factor analysis was carried out on the heavy metal concentration to establish the sites most polluted by the heavy metals. The result of the factor analysis is shown in tables 9 and 10.

Table 9: Factor loadings for selected heavy metals in the Owabi reservoir sediment

Factor Matrix for heavy metals in the Owabi reservoir				
Heavy metal	Factor 1	Factor 2	Factor 3	Communality
Iron	0.481	0.632	0.233	0.685
lead	0.889	-0.403	-0.193	0.989
zinc	0.698	0.537	-0.214	0.822
Copper	0.781	-0.411	0.2683	0.851
Variance	2.249	1.22	0.406	3.875
% Total variance	56.232	30.511	10.149	96.892

Table 10: Factor scores of selected heavy metals in the Owabi reservoir sediment

Factor Scores Of The Selected Heavy Metals In The Owabi Reservoir			
Location	Factor 1	Factor 2	Factor 3
Site 1	2.04382	-0.76408	-0.91956
Site 2	0.18896	0.14433	1.23114
Site 3	0.67048	2.16514	0.45853
Site 4	-0.38766	-0.11981	-0.37022
Site 5	0.05253	-0.48072	-0.22198
Site 6	0.26517	-0.0882	0.45581
Site 7	-0.1206	-0.84605	0.10278
Site 8	-0.0419	-0.64497	0.07862
Site 9	-1.59599	-0.34657	0.64875
Site 10	-1.07482	0.98091	-1.46389

4.2.3 Results of sequential extraction of metals in sediments

The results of the sequential extraction are presented in table 11. The raw data on sequential extraction of metals in sediments is presented in appendix 3A, 3B, 3C and 3D.

TABLE 11: Mean concentrations of selected heavy metals in the different phases of sediments from the Owabi reservoir after sequential extraction

LEACHATE	HEAVY METAL CONCENTRATION (g/kg)			
	Fe (mean \pm std dev)	Pb (mean \pm std dev)	Cu (mean \pm std dev)	Zn (mean \pm std dev)
Exchangeable	< 0.0050	0.0052 \pm 0.00	< 0.0050	0.0050 \pm 0.00
Carbonate	< 0.0050	0.0051 \pm 0.00	< 0.0050	0.0893 \pm 0.01
Mn – Fe oxide	0.9584 \pm 0.18	0.0350 \pm 0.01	0.0173 \pm 0.01	0.2510 \pm 0.05
Organic bound	0.0557 \pm 0.01	0.0240 \pm 0.01	0.0052 \pm 0.01	0.0893 \pm 0.02
Residual	3.4037 \pm 0.62	0.0323 \pm 0.01	0.0109 \pm 0.01	0.1348 \pm 0.03

The concentrations of iron in both the exchangeable and carbonate fractions were less than 0.005 g/kg. An average value of 0.9584 \pm 0.18 g/kg was present in the Mn – Fe oxide fraction with site S₃ recording the maximum value of 1.161 g/kg while site S₁ recording a minimum value of 0.854 g/kg. An average of 0.0557 \pm 0.01 g/kg was found to be organic bound with site S₃ recording a maximum value of 0.0711 g/kg while site S₁ recording a minimum value of 0.0432 g/kg. The amount of iron present in the residual fraction ranged from a minimum of 3.011 g/kg recorded at site S₁ to a maximum of 4.1139 g/kg recorded at site S₃. The recorded average value was 3.4037 \pm 0.62 g/kg.

Lead present in the exchangeable fraction ranged from a minimum of 0.005 g/kg recorded at site S₃ to a maximum of 0.0055 g/kg recorded at site S₂. The exchangeable fraction recorded an

average value of 0.0052 ± 0.001 g/kg. The levels of lead present in the carbonate fraction ranged from a minimum of 0.005 g/kg recorded at site S₂ to a maximum of 0.0052 g/kg recorded at sites S₁ and S₃ with an average of 0.0051 ± 0.001 g/kg. In the Mn – Fe oxide fraction lead concentration ranged from a minimum of 0.0312 g/kg recorded at site S₃ to a maximum of 0.0415 g/kg recorded at site S₁ with an average of value of 0.0350 ± 0.01 g/kg. In the organic bound fraction, lead ranged from a minimum of 0.0186 g/kg recorded at site S₂ to a maximum of 0.0290 g/kg recorded at site S₃ with an average of 0.0240 ± 0.01 g/kg. The amount of lead present in the residual fraction ranged from a minimum of 0.0291 g/kg recorded at site S₃ to a maximum of 0.0375 g/kg recorded at site S₁. The recorded average value was 0.0323 ± 0.01 g/kg.

The concentrations of copper in both the exchangeable and carbonate fractions were less than 0.005 g/kg. An average value of 0.0173 ± 0.01 g/kg was present in the Mn – Fe oxide fraction with site S₁ recording the maximum value of 0.0211 g/kg while site S₃ recorded a minimum value of 0.0121 g/kg. An average of 0.005 ± 0.01 g/kg was found to be organic bound with site S₁ recording a maximum value of 0.0067 g/kg while site S₃ recorded a minimum value of 0.004 g/kg. The amount of copper present in the residual fraction ranged from a minimum of 0.0083 g/kg recorded at site S₃ to a maximum of 0.0143 g/kg recorded at site S₁. The recorded average value was 0.0109 g/kg.

All three sites recorded the same amount of zinc in the exchangeable fraction with a value of 0.005 g/kg. The levels of zinc present in the carbonate fraction ranged from a minimum of 0.0799 g/kg recorded at site S₂ to a maximum of 0.0981 g/kg recorded at site S₃ with an average of 0.0893 ± 0.01 g/kg. In the Mn – Fe oxide fraction zinc concentration ranged from a minimum

of 0.2024 g/kg recorded at site S₂ to a maximum of 0.2915 g/kg recorded at site S₃ with an average of value of 0.2510 ± 0.05 g/kg. Zinc in the organic bound fraction ranged from a minimum of 0.0705 g/kg recorded at site S₂ to a maximum of 0.1003 g/kg recorded at site S₃ with an average of 0.0240 ± 0.01 g/kg. In the residual fraction zinc ranged from a minimum of 0.1103 g/kg to a maximum of 0.1621 g/kg with an average of 0.1348 ± 0.03 g/kg.

4.2.4 Correlation analysis

The result of correlation analysis between the physicochemical parameters and the heavy metals in the sediment is presented in table 12. The result of the Correlations analysis between physicochemical parameters and bioavailable metal in sediments is presented in table 13.

Table 12: Correlation between the physicochemical parameters and total heavy metal concentrations of the sediment samples

Parameter	OMC	pH	EC	CEC	Fe	Pb	Zn	Cu
OMC	1							
pH	0.375	1						
EC	-0.332	-0.341	1					
CEC	0.921**	0.351	-0.407	1				
Fe	0.256	0.101	0.371	0.011	1			
Pb	-0.162	0.134	-0.216	-0.052	-0.001	1		
Zn	0.487	0.484	-0.089	0.324	0.621*	0.426	1	
Cu	-0.22	0.298	-0.27	-0.124	0.18	0.774**	0.258	1

* Correlation is significant at the 0.05 level.

** Correlation is significant at the 0.01 level.

TABLE 13: Correlations between physicochemical parameters and bioavailable metal in sediments

Parameter	OMC	pH	COND	CEC	Sand	Silt	Clay	Fe	Pb	Cu	Zn
OMC	1										
pH	-0.811	1									
COND	0.117	-0.675	1								
CEC	0.996*	-0.755	0.027	1							
Sand	-0.926	0.53	0.267	-0.956	1						
Silt	0.997*	-0.766	0.044	1.000**	-0.951	1					
Clay	0.546	0.046	-0.768	0.620	-0.823	0.607	1				
Fe	0.727	-0.991*	0.767	0.662	-0.413	0.674	-0.178	1			
Pb	-0.985	0.699	0.056	-0.997*	0.977	-0.995*	-0.683	-0.597	1		
Cu	-0.881	.991*	-0.573	-0.834	0.636	-0.844	-0.085	-0.965	0.786	1	
Zn	0.164	-0.71	0.999*	0.074	0.221	0.091	-0.736	0.797	0.008	-0.612	1

4.2.5 Extent of pollution of sediment by heavy metals

The extent of pollution of the sediment by the heavy metals was calculated as the geoaccumulation index and the result is presented in table 14. Lead recorded the maximum value of 1.71 with iron recording the minimum of -4.13. Copper and zinc recorded -1.16 and 1.48 respectively.

Table 14: Geo-accumulation index of the various heavy metals

Heavy Metal	Geo-accumulation index (I_{geo})	Pollution Intensity
Copper	-1.16	Unpolluted
Iron	-4.13	Unpolluted
Zinc	1.48	Moderately polluted
Lead	1.71	Moderately polluted

4.2.6 Canonical correlation analysis

Canonical correlation was carried out on the physicochemical parameters and the heavy metal concentration. The first step, OMC and pH were considered as dependent variables while other heavy metals were reserved for the covariates. The results are presented in table 15.

Table 15: Standardized canonical coefficients for heavy metals related to pH and organic matter content (OMC)

COVARIATES	V_1	DEPENDENT VARIABLES	W_1
IRON	-1.0437	pH	0.8599
LEAD	-1.5259		
ZINC	1.6378	OMC	0.2813
COPPER	1.1273		

In the next step, CEC and electrical conductivity were considered as the dependent variables and the heavy metals as covariates. The results are presented in table 16

Table 16: Standardized canonical coefficients for heavy metals related to cation exchange capacity (CEC) and electrical conductivity (EC)

COVARIATES	V_1	DEPENDENT VARIABLES	W_1
IRON	1.4894	CEC	0.0245
LEAD	1.1952		
ZINC	-1.2207	EC	1.0097
COPPER	-1.2471		



CHAPTER FIVE

5.0 Discussion

5.1 Water Quality

5.1.1 Physicochemical characteristics of the Water

The average pH (6.97 ± 0.32) of samples collected from the reservoir indicates that the water is slightly acidic with site S₇ recording a minimum pH value of 6.3. This is below the WHO standards for drinking water. The maximum and the minimum recorded were above and below the natural background levels of fresh water respectively. The slightly acidic nature of the water in the reservoir may be attributed to the fact that the streams serving the reservoir flows through rapidly growing urbanizing towns (Akoto *et al.* 2008) where degradation of drowned vegetation and other organic matter cause the release of methane gas which is accompanied by the release of hydrogen sulphide (H₂S) (Connell *et al.* 1984) thereby decreasing the pH of the overlying water. The slightly acidic nature can cause a cascade of effects that can harm or kill individual fish, thereby reducing fish population and decrease biodiversity within the reservoir. The variation in pH due to change in sampling location was not statistically significant ($p < 0.05$).

The apparent and true colour recorded for each site in the reservoir was above the WHO standards for drinking water. Site S₄ recorded the maximum value of 160.10 PtCo while site S₃ recording a minimum of 93.03 PtCo. This shows that colour is not aesthetically acceptable. These high readings can be attributed to the presence of decaying organic material (Ansa-Asare, 1992) and dissolved organic materials which are present within the reservoir. The presence of iron and other metals either as impurity or products of corrosion may have also influenced these values.

The readings for turbidity ranged from a highest of 37.03 NTU at site S₉ to a lowest of 29.01 NTU at site S₁₀. These readings were above the WHO standard for drinking water. When compared to the natural background of 5 NTU the water in the Owabi reservoir can be said to be polluted with respect to turbidity. The high levels of turbidity in the reservoir can be attributed to high biological pollution, soil erosion and decay of dead organic matter from improper waste disposal along the streams serving the reservoir (Akoto *et al.*, 2008). The variations of turbidity among the sampling sites were statistically significant ($p < 0.05$).

Electrical conductivity of the samples ranged from 254.04 – 407.10 $\mu\text{S}/\text{cm}$ with an average of $308 \pm 53.35 \mu\text{S}/\text{cm}$. The average value of a typical unpolluted water body is approximately 350 $\mu\text{S}/\text{cm}$ (Koning and Kroos, 1999) which falls within the range stated above. The levels of electrical conductivity in the Owabi reservoir when compared with the conductivity of the Volta Lake at Kpong (range 62.0-77.5 $\mu\text{S}/\text{cm}$), (Antwi and Ofori-Danson, 1993) were found to be higher. Electrical conductivity also correlated positively with pH, Ca^{2+} and As^+ . The variations of conductivity among the sampling sites were statistically significant ($p < 0.05$).

According to Tay, 2007, total dissolved solids (TDS) can be used as a common indicator for polluted waters. Values of TDS ranged from a maximum value of 58.03 mgL^{-1} at site S₈ to a minimum of 30.21 mg L^{-1} at site S₅. All recorded values were higher than the WHO standards. However long term effects of TDS may arise as the TDS values increases (Kempster *et al.* 1997). McCutcheon *et al.*, (1983) established that water with TDS level less than 600 mgL^{-1} generally considered palatable and levels above 1200 mgL^{-1} are considered not palatable. In view

of this the water in the reservoir can be said to be palatable since it recorded an average TDS of $43.11 \pm 12.63 \text{ mgL}^{-1}$.

Concentration of TSS in all the samples were above WHO standards for drinking water. This implies that the water is not suitable for domestic use in the raw state. These readings can be attributed to the fact that as water enters a reservoir and the flow rates decreases the amount of trapped suspended particles also increases. If these particles are not heavy enough to settle then their concentration increases. Activities within the catchment such as land use practices such as farming, sewage discharge, and runoffs tend to bring silt to the reservoir and thereby increasing the TSS concentration within the reservoir (Cloern, 1987).

Temperature ranged from a minimum of 29.5°C to a maximum of 30.5°C . These values were slightly above the natural background level of temperature which is $22\text{-}29^{\circ}\text{C}$. The temperature range is a reflection of the tropical status of the water and is influenced by the atmospheric ambient temperature of 27°C at the time of sampling. High readings for turbidity and TSS might be responsible for the slight increase in temperature (DWAf, 1998). This is because suspended solids and substances that increase the turbidity also increase the heat holding capacity of water.

Alkalinity values were below the WHO recommended limits for drinking water. Based on the WHO guidelines one can say that water from the reservoir can be used for domestic purposes. These levels of alkalinity gives the water the ability to neutralize acids. According to Chapman, (1996) levels of $20 - 200 \text{ mgL}^{-1}$ are common in fresh water systems. This makes the recorded average of $183.6 \pm 26.41 \text{ mgL}^{-1}$ acceptable.

5.1.2 Dissolved oxygen (DO) and nutrient characteristics

DO affects chemical and biological processes occurring in the reservoir. Its optimum level is therefore important for the maintenance of life within the reservoir. According to Todd (1970) DO concentrations of 5 mgL^{-1} and above are recommended for maintaining life in a reservoir. The maximum recorded value of dissolved oxygen was 4.07 mgL^{-1} and a minimum of 2.8 mgL^{-1} . These values compared with the background value of 7 mgL^{-1} suggest some amount of pollution in the reservoir possibly from decaying organic material. This measurement of DO is a broad indicator of water quality (DFID, 1999). DO concentrations in unpolluted water are normally about $8\text{-}10 \text{ mgL}^{-1}$ at 25°C . The concentration of DO in water in the reservoir is lower than 5 mgL^{-1} implying that the water is not suitable for supporting all forms of aquatic life.

High concentrations of nutrients (phosphate and nitrate) in waters accelerate growth of algae, which affects the quality of water in terms of colour and odour (Anderson *et al.*, 2002). The amount of nitrate, nitrite and ammonia present in natural waters in the form of nitrogen are of great interest because they can be toxic to human and aquatic life (Dallas and Day, 1993). High levels of nitrite and nitrate in water imposes great health risks particularly in infants and pregnant women (Kempster *et al.*, 1997; Kelter *et al.*, 1997). Ammonia is present naturally in both surface and ground water and can be produced from deamination of nitrogen containing compounds and hydrolysis of urea.

Nitrate, nitrite and ammonia concentration in the water samples were all below the WHO limit of 10 mgL^{-1} , 3.0 mgL^{-1} and 1.5 mgL^{-1} respectively (WHO, 2006). According to Akoto *et al.* (2008) nitrate concentration increase along the course of the stream towards the Owabi reservoir. These

observations might account for the presence of nitrate and nitrite within the reservoir. The concentration of ammonia in the reservoir was established to be very low ranging from below detection to 0.01 mgL^{-1} .

Average phosphate levels within the reservoir was alarming compared to the natural background of 0.02 mgL^{-1} and the WHO recommended levels of less than 0.3 mgL^{-1} . The maximum recorded value was 0.91 mgL^{-1} at site S_8 while the minimum value 0.28 mgL^{-1} was recorded at site S_1 . A higher level of phosphate is an indication of pollution which may cause eutrophication (McCutcheon *et al.*, 1983) and may account for the growth of weeds within the reservoir. Phosphates in water bodies may arise from agricultural runoffs from numerous small scale farming activities along the banks of rivers that serve the Owabi reservoir.

The concentrations of nutrients within the reservoir were generally low. This might be due to the fact that the sampling was done during the dry season (Ansa-Asare and Asante, 2000). The low levels of nutrients can be attributed to the fact that these nutrients are used up by plants and the volatile ones are lost to the atmosphere as the temperatures rise during the dry seasons.

5.1.3 Total Hardness and Dissolved ions characteristics

The levels of total hardness of the water from the various sampling sites were much lower than the WHO recommended levels for drinking water of 500 mgL^{-1} . Calcium levels ranged from a minimum value of 38 mgL^{-1} at site S_3 to a maximum value of 50 mgL^{-1} at S_5 . Although these levels are lower than the WHO recommended levels of 75 mgL^{-1} for drinking water they were higher than the natural background level of 12 mgL^{-1} . Magnesium levels in the water ranged

from 24 mgL^{-1} at site S_4 to 30 mgL^{-1} at sites S_9 and S_{10} . with the exception of sites S_9 and S_{10} , all the readings were lower than the WHO recommended level of 30 mgL^{-1} for drinking water and also within the natural background levels of $1 - 99 \text{ mgL}^{-1}$ for freshwater systems. The water can therefore be said to be fit for domestic use since hardness was within acceptable WHO limits for drinking water.

The pattern of ionic dominance of the water within the reservoir was established to be of the order chloride > calcium > magnesium > sulphate. This was not in accordance with the ionic dominance pattern of freshwater of the order calcium > magnesium > sulphate > chloride (Burton and Liss 1976; Stumm and Morgan, 1981). The high position of chloride in the ionic dominance pattern of water samples from the reservoir can be attributed to fertilizer application untreated domestic waste as well as those from anthropogenic sources (Karikari and Ansa-Asare, 2006). Chloride levels were above their natural background of 7.8 mgL^{-1} indicating that large amounts of domestic waste are being discharged into the reservoir (Karikari and Ansa-Asare, 2006). The dominance of calcium over magnesium and sulphate is characteristic of tropical freshwater (Karikari and Bosque-Hamilton, 2004). The sulphate levels were slightly above the natural background levels of $0.1-10 \text{ mgL}^{-1}$ but were within the WHO recommended levels of 250 mgL^{-1} for drinking water.

Fluoride may be present as the result of the natural decomposition of rocks. It prevents tooth decay but excessive amounts of fluoride can result in mottled tooth enamel. Fluoride levels within the reservoir were generally low ranging from $0.6 - 1.01 \text{ mgL}^{-1}$. These concentrations fell within the WHO recommended levels for drinking water of 1.5 mgL^{-1} .

5.1.4 Total heavy metal concentration in water samples from the Owabi reservoir

The results of heavy metal analysis in the water samples are presented in table 4. These metals are widely distributed in the environment with sources from weathering of minerals and soils (O'Neil, 1993). The streams serving the Owabi reservoir flows through rapidly urbanizing towns and hence erodes the polluted urban soils and increases the heavy metal concentrations. Heavy metals in urban soils have been shown to be very useful tracers of environmental pollution (Bacon *et al.*, 1992; Kelly *et al.*, 1996). Although metals may occur naturally their levels can be elevated as a result of pollution.

The concentration of iron in the water samples ranged from 0.01- 0.04 mgL⁻¹. These levels did not exceed the natural background level of 0.67 mgL⁻¹ and also fell within the WHO recommended levels for drinking water of 1.0 mgL⁻¹. The lower levels of iron in the reservoir might be due to the fact that pathogenic organisms utilize these ions for normal growth (Campbell, 1995). Also iron may be attached to surfaces of suspended solids and settle as sediments. They can also be adsorbed by the iron or manganese oxides and hydroxides or co-precipitated with them (Salomons and Forstner, 1984; Drever, 1988). The variations of iron in the water among the sampling sites were statistically significant ($p < 0.05$). This could be as a result of the variations in the sediment character of the various sampling sites.

Levels of lead in the analysed water samples analyzed ranged from 0.075-0.095 mgL⁻¹. These values are above the natural background value of 0.005 mgL⁻¹. This is an indication of pollution. The concentrations were above the WHO limits for drinking water of 0.01 mgL⁻¹. These levels may pose serious health threat due to the toxic and cumulative nature of lead, the water could be

used for other domestic purposes except for drinking. The levels of lead within the reservoir must be looked at with all seriousness because the reservoir is constantly fed with water from streams with high levels of lead. Lead concentration may also change if physical and chemical conditions, such as temperature and pH, of the water change since lead can be adsorbed on organic and inorganic complexes and settle with sediments and desorbed back into solution when conditions are favourable (Waide, 1986). The variations of lead in water among the sampling sites were statistically significant ($p < 0.05$).

The levels of zinc in the water samples were not alarming since they were below the natural background of 0.03 mgL^{-1} . The recorded concentrations which ranged from $0.001 - 0.012 \text{ mgL}^{-1}$ were far below the WHO recommended levels of 3 mgL^{-1} for drinking water (WHO, 2004). The variations of zinc in water among the sampling sites were statistically insignificant at the 5% level. The mean concentration zinc established within the reservoir shows that the water that does not pose any immediate health threat to humans and other aquatic organisms. The low concentration of Zinc is probably due the fact that metals can easily be absorbed and utilized by organisms in the aquatic environment since it is a micronutrient (Campbell 1995).

Copper concentrations established within the reservoir were higher than their natural background levels of 0.005 mgL^{-1} indicating some extent of pollution. Although they were above the natural background the copper concentrations were below the WHO acceptable limits of 1 mgL^{-1} for drinking water (WHO, 2006). In view of the levels of copper in the water, the water can be said to be useful for domestic purposes and does not pose any health threat to the aquatic ecosystem.

The variations of copper in water among the sampling sites were statistically significant ($p < 0.05$).

The levels of arsenic ranged from $0.1960 - 0.4120 \text{ mgL}^{-1}$. However this result when compared with the WHO acceptable limits of 0.01 mgL^{-1} for drinking water gives cause for concern. Due to the health effects of arsenic above trace concentrations water from the reservoir should be subjected to some form of treatment before being used by human beings and other animals. An increased level of arsenic in humans and other organisms can cause carcinogenic and teratogenic symptoms (Weis and Weis 1991; Abedin *et al.*, 2002; Urminská *et al.*, 2002; Saha, 2003). The arsenic levels within the reservoir should be constantly monitored in order to avert any health related problems that may arise due to an increase in the concentration of arsenic.

Heavy metal concentrations were generally low with the exception of lead and arsenic. This gives an indication of minimal effect of industrial and agricultural activities within the catchment.

5.1.5 Bacteriological indicators

Water can be said to be free of risk to human health if the faecal coliform count in the water is zero and *E. Coli* is absent (WHO, 2004). The recorded values for faecal coliform range from $10.18 - 12.62 \text{ MPN/100 mL}$ and the *E. Coli* levels ranged from $8.86 - 11.86 \text{ MPN/100 mL}$. The high faecal coliform and *E. Coli* counts is an indication of the water being polluted by pathogenic organisms. This makes the water unsuitable for human consumption and for

recreational purposes such as swimming and fishing (WHO, 2004). These levels could be attributed to the poor sanitary conditions within the catchment.

5.1.6 Factor Analysis

Factor analysis was carried out on the water quality parameters that were above the natural background values. The results of the analysis yielded the extraction of five factors which accounted for 83.13% of total variance. The results of the factor analysis are presented in tables 5 and 6.

Factor 1 which accounted for 32.040% of total variance showed strong loadings for phosphate, sulphate and total dissolved solids. These high loadings represent a relative high correlation between each other. This finding reflects a negative influence on the water quality by agricultural discharges and hence could be considered as inorganic contamination. The high scores for factor 1 are observed for sites 2 and 10, indicating inorganic pollution risk.

Factor 2 on the other hand accounted for 17.233% of total variance and showed high loadings for conductivity, chloride and apparent colour. These findings also buttress the effect on the water quality by agricultural activities since the conductivity, chloride and apparent colour could be aggravated by those activities. The high score for factor 2 were observed for site 4 which represent the risk for pollution.

Factor 3 also accounted for 13.389% of total variance and registered high loadings for colour and faecal coliform. These results suggest domestic waste water discharge and the presence of

decaying plant and other materials, which have adverse consequences on the water quality. Sites 3, 4, 6 and 7 had high factor scores for the third factor. This indicates the risk of pollution from improper domestic wastewater discharge.

Factors 4 and 5 which accounted for 11.513% and 8.963% respectively showed high loadings for copper, lead, turbidity, and *E. coli*. This is an indication of both organic and inorganic pollution since high turbidity levels are often associated with the microbial pollution (DWAF, 1998). The presence of lead and copper could be attributed to the improper discharge of garage waste by artisans within the catchment of the reservoir. Sites S₆, S₇ and S₉ had high factor scores for these factors indicating the risk of pollution from both organic and inorganic sources.

5.2 Physicochemical analysis of sediment from the Owabi reservoir

The range, means and standard deviation of physicochemical parameters that were measured in the sediment are presented in tables 7 and 8. Correlation analysis was carried out on the physicochemical parameters and the total metal concentration. The results are shown in table 12. Correlation analysis was also carried out on the physicochemical parameters and the bioavailable metal fractions. The results are also presented in table 13.

5.2.1 nature and properties of sediments

5.2.1.1 pH

The pH levels of the sediments showed acidity. Accumulation of methane gas accompanied by accumulation of H₂S in the hypolimnion due to the decomposition of drowned plant materials and other organic matter may have decreased the pH of the water in the reservoir. pH of a

sediment system can also be attributed to oxidation of sulfide phases (Kerner and Wallmann, 1992) and oxidation of organic matter (Forstner and Patchineelam, 1980). pH correlated significantly ($P < 0.05$) with iron and copper in the sum of the bioavailable fractions. An increase in pH will increase the bioavailability of copper since the correlation is positive and a decrease in the bioavailability of iron since the correlation was negative.

5.2.1.2 Particle size distribution

All sediment samples were established as clayey using the soil texture triangle. This indicates that the particulate nature of the sediments will be favourable for attachment of heavy metals. Heavy metal concentrations in sediments are affected by particle size and composition of sediments (Krumlgalz, 1989). Silt levels being high can be attributed to runoff from agricultural fields and other places enter the reservoir these particles become suspended and settle later thereby staying at the top of the reservoir bed. Silt also negatively correlated significantly with sand, organic matter content (OMC) and cation exchange capacity (CEC). This shows an inverse relationship with between particle size and OMC and CEC. Silt also correlated significantly ($P < 0.05$) with lead in the sum of bioavailable fractions.

5.2.1.3 Electrical conductivity

Electrical conductivity which is a measure of the ionic content of the sediment. Although electrical conductivity did not show any significant correlation with both the heavy metals and the other physicochemical parameters, it cannot be concluded that this parameter does not affect the heavy metal concentration but could do so in combination with other parameters and

geochemical support phases. In spite of this electrical conductivity correlated significantly ($p < 0.05$) with zinc in the sum of the bioavailable fractions implying an effect on the toxicity of zinc.

5.2.1.4 Cation exchange capacity (CEC)

According to Majid and Mohsen (2008) high pH and high organic matter content implies a high CEC. However Sediments from the Owabi reservoir recorded low pH with an average of 5.32 ± 0.82 . This might have accounted for the values of CEC recorded. CEC correlated significantly ($P < 0.01$) with organic matter content (OMC) implying that an increase in OMC increases the CEC of the sediment.

5.2.2 Heavy metal concentrations in the sediments from the Owabi reservoir

Heavy metals are natural constituents of reservoir sediments. Some heavy metals are even essential for many living organisms but can be toxic at higher concentrations. Metals get transported to the reservoir either in the form of suspended matters or dissolved ions, which are subsequently removed from water and are adsorbed on to and finally incorporated into the sediments. The reservoir sediments therefore are major sinks for the metals and their concentrations are controlled by a variety of physical and chemical factors in the sediment (Binning and Baird 2001). Sediments are therefore widely used as indicators of environmental contaminants such as heavy metals (Helz *et al.*, 1975).

Iron recorded an average concentration of 4.03 ± 0.57 g/kg. All the recorded values were below the threshold effect level (the level above which toxic effects are observed) of 2% and the average continental shale of 47.2 g/kg (Turekian and Wedepohl, 1961). This gives an indication

that there is no form of pollution with respect to iron. The variations of iron in the sediment among the sampling sites were statistically insignificant ($p < 0.05$).

Zinc concentrations were above the continental average shale (CAS) of 0.095 g/kg (Turekian and Wedepohl, 1961). This indicates some form of pollution and can be attributed to the fact that zinc ions in solution can adhere to suspended particles and settle with sediment. All the recorded values were above the threshold effect level (TEL) of 0.123 g/kg (Buchman, 2008). This result suggests that toxic effects associated with zinc could be observed in the organisms and humans that depend on the water within the reservoir. The variations of zinc in the sediment among the sampling sites were statistically insignificant ($p < 0.05$).

Lead concentrations in the sediment samples had an average of 0.098 ± 0.01 g/kg. All the recorded values were above the continental average shale of 0.02 g/kg (Turekian and Wedepohl, 1961) indicating some extent of pollution. This can be attributed to the improper disposal of lead acid battery waste from the artisans within the catchment. The recorded values were also above the threshold effect level (TEL) of 0.035 g/kg (Buchman, 2008). This also suggests toxic risks associated with lead could be observed in the organisms and humans that depend on the water within the reservoir. The variations of lead in the sediment among the sampling sites were statistically insignificant ($p < 0.05$).

The average value of Cu in the sediment (0.0310g/kg) was below the TEL and the continental average shale of 0.045 g/kg (Turekian and Wedepohl, 1961). This indicates that the reservoir sediment is not polluted with copper on the average but is polluted at sites S₁ and S₂ where its

concentration is above the continental average shale of 0.045 g/kg. The variations of copper in the sediment among the sampling sites were statistically insignificant ($p < 0.05$).

5.3 Extent of pollution of sediment by heavy metals

The geoaccumulation index (I_{geo}) introduced by Muller (1979) was also used to assess metal pollution in sediments to quantify the degree of anthropogenic contamination in the reservoir sediments. The results of the geo-accumulation index of the various heavy metals as presented in table 14 indicates that the sediment is unpolluted with respect to copper and iron. However the index showed that the sediment is moderately polluted with respect to zinc and lead.

5.4 Canonical correlation

Metal release from sediments at the sediment-water interface is largely controlled by electrical conductivity and pH of a sediment system (Peters *et al.*, 1997). Metals such as copper, cadmium, lead, and zinc can be mobilized during oxidation of low pH sediments through oxidation of sulphide phases (Kerner and Wallmann, 1992) and oxidation of organic matter (Forstner and Patchineelam, 1980). So, apart from heavy metal concentrations, some other factors such as organic matter content (OMC) and pH should be mentioned to demonstrate the release of metals from the sediment to solution and vice versa.

The aim of canonical correlation was to identify pairs of new axes, called canonical variates, (i.e., W_i and V_i), with each pair resulting into two new variables, where one variable is a linear

combination of the X variables and the other variable is a linear combination of the Y variables such that:

1. The correlation between W_i and V_i is maximum, and
2. Each set of the new variables is uncorrelated with other sets of new variables.

In this case, rather than examining numerous correlations between the two sets of variables to discern the associations among them, each set is first reduced to a few linear combinations and only the correlations between a few linear combinations are interpreted (Sharma, 1996).

Considering the aforesaid discussion, canonical correlation was utilized in an attempt to investigate the importance of these parameters in the Owabi reservoir sediment. For this purpose, at the first step, OMC and pH were considered as criterion variables while other heavy metals were reserved for the predictor variables to demonstrate the importance of organic matter and acidity in displacement of the trace elements between solid and dissolve phases in the water-sediment system. The results are presented in table 15.

The standardized canonical coefficients of first canonical variate for the predictor variables suggested that Zn is more influential in forming the first canonical variate whereas that of the dependent variables implying that pH is more important. Therefore, it may be concluded that pH is of great importance in co precipitation of the soluble Zn. Generally, zinc in sediment solution is very low part of which is in stable complexes with organic matter in the solution. In this field,

the humic and fulvic acid fractions are prominent in Zn absorption (Tisdale *et al.*, 1993). This implies that the leaching of zinc is associated with pH.

In the next step, CEC and electrical conductivity were considered as the dependent variables and the heavy metals as covariates to examine the importance of these two parameters in co-precipitation reactions. The results in table 16 showed that iron and lead had high positive standardized coefficient whereas copper and zinc had the biggest negative coefficients among covariates. On the other hand, conductivity was more important in the dependent variables. In this regard it could be concluded that the co-precipitation of iron and lead will more likely be associated with conductivity whereas zinc and copper will more likely be associated with CEC as they had a low coefficient in the first variate.

5.2.8 Factor analysis of heavy metals in sediment

Because of the negative effects of heavy metals in aquatic environment their pollutant sourcing in watershed is very important. For this reason and to pick the site for the sequential extraction process, factor analysis was used to identify sites that are significantly polluted by heavy metals.

Three major factors were extracted and accounted for 96.905% of total variance as shown in table 9. With the extraction of the first factor, which accounted for 56.236% of total variance, lead, zinc and copper had high loadings of 0.889, 0.699 and 0.781 respectively. In this regard site S₁ which recorded the highest factor score of 2.0434 (table 10) in factor 1 implies that the amount of heavy metals at this site is higher than the other stations.

The second factor which accounted for 30.503% of total variance yielded high loadings for iron and zinc with values of 0.632 and 0.537 respectively. Site S₃ which had the highest factor score of 2.1654 in the second factor can be said to be the next polluted site after site 1.

The third factor which accounted for 10.166% of total variance yielded high loadings for iron and copper. Site S₂ had the highest factor score of 1.2311. This makes site S₃ the next polluted site after sites S₁ and S₂.

With reference to the results of the factor analysis it may be concluded that site 1, site 2, and site 3 are the site that contains the largest amounts of the heavy metals analyzed in this study and hence their selection for the sequential extraction analysis.

5.2.9 Metal speciation in reservoir sediment

Chemical speciation by sequential extraction procedure has helped in assessing the mobility, bioavailability and toxicity of metals and hence giving a better insight into the ultimate fate of heavy metal pollutants which are introduced into the reservoir system. The result of the heavy metal speciation is presented in table 11.

5.2.9.1 Iron

Major amount of iron was found to be present in the residual fraction with the least present in the exchangeable fraction. The amount present in the exchangeable fraction constituted about 0.11% of total mass. The amount present in the residual fraction constituted 76.87% of total mass. Large amount of Fe is available in the residual fraction, probably because this is an element basically of

natural origin and it is one of the most common elements in the earth's crust (Deepti *et al.*, 2007). An average of 0.9584 ± 0.18 g/kg of iron was also found to be present in the Mn – Fe phase. Bioavailable fractions (exchangeable, carbonate and Fe–Mn oxide bound fractions) recorded an average of 0.9684 ± 0.16 g/kg which gives an indication that a substantial amount of iron could easily be transferred from the sediment into the water column.

5.2.9.2 Copper

Substantial amount of Cu was present in the residual fraction, with an average of 0.0109 ± 0.01 g/kg, constituting 25.02 % of total mass and the Mn-Fe phase with an average of 0.0173 ± 0.01 g/kg constituting 39.91 % of total mass. The higher concentration of Cu in the residual fraction can be attributed to natural sources such as weathering of rocks and decomposition of biota detritus (Badri and Aston 1983). An amount which was less than 0.005g/kg was present in both the exchangeable and carbonate fractions. An average of 0.0052 ± 0.01 g/kg constituting 12.05 % of total mass was found bound to the organic phase. Cu forms highly stable complexes with the organics matter/sulphide (Li *et al.*, 2001). The bioavailable fractions (exchangeable, carbonate and Fe–Mn oxide bound fractions) recorded an average of 0.0273 ± 0.01 g/kg which was below the threshold effect level (TEL) of 0.0357 g/kg (Buchman, 2008). This outcome therefore suggests that copper at its present level is not toxic to the reservoir sediment.

5.2.9.3 Lead

Significant amounts of lead were bound to the Mn-Fe, organic and the residual phases. An average of 0.035 g/kg was found to be bound to the Mn-Fe phase constituting 34.45 % of total mass with the carbonate phase recording an average of 0.0051 g/kg constituting 5.05 % of total mass. The exchangeable fraction recorded an average of 0.0052 ± 0.01 g/kg. The residual

fraction recorded an average of 0.0323 ± 0.01 g/kg. This could be attributed to natural origin. An amount 0.0239 ± 0.01 g/kg was bound to the organic phase. Significant amount of lead was found to be present in the bioavailable fractions (exchangeable, carbonate and Fe–Mn oxide bound fractions). This recorded an average of 0.0454 ± 0.01 g/kg which was above the threshold effect level (TEL) of 0.0350 g/kg indicating potential bioavailability of this element but below the probable effects level (PEL) of 0.0913 g/kg (Buchman, 2008) which suggests that toxic effects would not be observed on the organisms within the reservoir.

5.2.9.4 Zinc

Like lead and Copper, significant amount of Zn was also available in the Mn-Fe fraction, with an average of 0.251 ± 0.05 g/kg. This constitutes 44.08 % of total mass. These results can be attributed to the fact that lead, zinc, and copper having similar valency will therefore have the affinity to bind to the same site. This is followed by the residual phase which recorded an average 0.1438 ± 0.03 g/kg, which constitutes 23.67 % of total mass. This amount can be attributed to natural sources such as weathering of rocks and decomposition of biota detritus (Badri and Aston 1983). Both the carbonate and organic bound fractions recorded similar average concentrations of 0.0893 ± 0.01 g/kg for the carbonate and 0.0893 ± 0.02 g/kg for the organic bound. The exchangeable phase recording the least average concentration of 0.005 ± 0.00 g/kg which constitutes 0.88% of total mass. The amount of zinc that is bioavailable recorded an average of 0.3453g/kg which constitutes 60.64 % of totals mass. The amount of zinc present in the bioavailable fractions is above the threshold effect level (TEL) of 0.123 g/kg indicating potential bioavailability of this element and the probable effects level (PEL) of 0.315 g/kg

(Buchman, 2008) which suggests that toxic effects would be observed in the organisms within the reservoir. In this regard zinc can be considered as a pollutant in the reservoir.

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CHAPTER SIX

6.0 Conclusion and Recommendations

6.1 Conclusion

Water samples collected from the Owabi reservoir as it was at the time of sampling is contaminated and not fit for human consumption and recreational purposes without treatment. This is so because with the exception of pH, electrical conductivity, TSS, total hardness, nitrite, nitrate, ammonium, sulphate, chloride, fluoride, Fe, Cu and Zn all the water quality parameters were above the WHO acceptable limits for drinking water. Thus people using water from the reservoir for domestic and agricultural activities must be warned of the imminent dangers including common diarrhoea, ear infections and deadly diseases such as cholera, hepatitis and typhoid fever.

The sediment samples are generally acidic and polluted with zinc and lead. This correlates with the number of activities including farming, automobile workshops and rapid development within the catchment.

Lead and zinc in the sediments are potentially bioavailable and this makes the sediment potentially toxic to the aquatic life and the ecosystem as a whole. The availability of metals in the sediment is also dependent on the physicochemical parameters of the sediment samples.

6.2 Recommendations

Since Both the sediment and the water in the reservoir are in one way or the other contaminated and the water is used for a variety of purposes such as drinking, fishing and irrigation without any form of treatment then for proper maintenance and management of the water resources;

- Periodic or constant monitoring of the water quality of both the reservoir pool and the streams serving the reservoir should be undertaken to ensure good water quality standards are achieved.
- Reservoir maintenance strategies should be instituted to prevent weeds from growing within the reservoir.
- Sanitation facilities should be openly constructed for inhabitants living within the catchment to discourage them from defecating in and around both the reservoir pool and the streams serving the pool.

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APPENDIX

RESULTS OF WATER QUALITY ANALYSIS

Appendix 1A: Physicochemical and bacteriological indicators of the water samples

LOCATION	pH	App colour	True colour	Turbidity	Conductivity	F coliform	<i>E. Coli</i>
site 1	7.28	95.01	30.10	36.50	272.10	10.18	9.32
site 2	7.30	106.03	29.10	32.40	300.02	10.96	9.86
site 3	6.75	130.20	60.21	30.80	254.04	12.62	9.18
site 4	6.55	160.10	55.13	30.60	407.10	12.32	8.86
site 5	7.13	93.11	40.20	32.10	275.03	11.86	9.62
site 6	6.70	120.21	50.07	35.20	315.10	11.32	9.32
site 7	6.30	94.17	38.11	33.40	397.17	12.62	11.86
site 8	7.20	100.03	40.21	30.30	305.08	11.62	9.37
site 9	7.28	95.07	33.02	37.30	295.11	11.96	10.62
site 10	7.30	98.15	29.03	29.10	260.15	11.32	8.86

Appendix 1B: Chemical and physical parameters of the water samples.

LOCATION	TSS	TDS	DO	Total hardness	Ca Hardness	Mg Hardness	Temperature	Alkalinity
site 1	128.22	35.10	4.02	64.00	37.33	26.67	30.5	156
site 2	145.10	42.03	3.40	69.33	43.67	25.66	31.0	200
site 3	130.15	56.20	4.00	68.67	39.00	29.67	30.5	205
site 4	114.03	55.10	2.80	74.00	50.00	24.00	30.5	200
site 5	134.01	30.21	3.80	68.67	40.00	28.67	31.0	210
site 6	125.10	35.03	3.10	73.33	46.00	27.33	30.0	139
site 7	110.10	40.21	4.07	70.67	41.33	29.34	30.5	156
site 8	135.05	58.03	4.00	69.33	40.00	29.33	31.5	165
site 9	126.90	38.11	2.80	68.67	38.67	30.00	31.5	200
site 10	138.10	41.07	3.80	70.00	40.00	30.00	29.5	205

Appendix 1C: Ions in the water samples from the Owabi reservoir

LOCATION	PO ₄ ²⁻	NH ₄ ⁺	Nitrite	Nitrate	SO ₄ ²⁻	Cl ⁻	F ⁻
site 1	0.28	b/d	0.006	0.28	8.11	64.00	1.10
site 2	0.90	0.01	0.004	0.24	15.02	68.67	0.70
site 3	0.60	0.01	0.006	0.18	12.10	62.00	0.90
site 4	0.35	b/d	0.006	0.26	10.10	70.67	1.10
site 5	0.85	0.01	0.005	0.23	12.21	65.00	0.90
site 6	0.55	b/d	0.006	0.18	9.05	60.00	0.70
site 7	0.40	0.01	0.006	0.26	10.11	65.00	1.00
site 8	0.91	b/d	0.005	0.23	8.12	73.00	1.10
site 9	0.80	0.01	0.006	0.28	12.21	64.67	0.60
site 10	0.75	b/d	0.004	0.24	13.10	62.33	0.70

Appendix 1D: Heavy metals in water samples from the Owabi reservoir.

LOCATION	IRON	LEAD	ZINC	ARSENIC	COPPER
site 1	0.020	0.081	0.010	0.231	0.010
site 2	0.013	0.097	0.010	0.276	0.010
site 3	0.010	0.086	0.011	0.196	0.010
site 4	0.020	0.078	0.010	0.412	0.010
site 5	0.010	0.095	0.012	0.335	0.010
site 6	0.017	0.083	0.007	0.397	0.013
site 7	0.015	0.081	0.01	0.299	0.009
site 8	0.010	0.075	0.011	0.311	0.011
site 9	0.011	0.100	0.001	0.261	0.013
site 10	0.035	0.083	0.008	0.279	0.008

Results of sediment analysis.

Appendix 2A: Heavy metals in the sediments of the Owabi reservoir.

LOCATION	Cu	Fe	Pb	Zn
site 1	0.0543	4.0185	0.1230	0.6250
site 2	0.0465	3.9925	0.0962	0.4530
site 3	0.0272	5.4255	0.0940	0.6660
site 4	0.0256	3.6500	0.0956	0.3755
site 5	0.0320	3.8750	0.1012	0.3480
site 6	0.0351	4.4650	0.1001	0.3510
site 7	0.0359	3.625	0.1003	0.2915
site 8	0.0320	4.0475	0.1004	0.2705
site 9	0.0192	3.5200	0.0827	0.1380
site 10	0.0023	3.6325	0.0866	0.4660

**Appendix 2B: Physicochemical parameters of water sediment samples from the Owabi
Reservoir**

LOCATION	conductivity	CEC	sand	clay	silt	OMC	pH
site 1	1179.10	20.48	31.60	7.60	60.80	16.07	6.61
site 2	474.11	21.00	25.00	10.40	64.60	18.00	6.48
site 3	1534.14	21.15	25.60	8.60	65.80	18.86	5.59
site 4	904.07	17.58	15.60	14.00	70.40	14.04	4.49
site 5	1696.21	18.00	20.40	8.80	70.80	14.46	4.56
site 6	1728.02	16.21	27.60	5.60	66.80	13.84	5.00
site 7	923.10	21.40	28.30	10.50	61.20	17.26	4.79
site 8	1387.03	21.04	24.80	12.70	62.50	16.67	4.29
site 9	1442.20	19.01	29.70	7.60	62.70	14.77	5.82
site 10	1230.21	22.42	26.50	12.70	60.80	19.53	5.61

Appendix 3A: Chemical speciation of iron in the sediment samples

Leachate	Fe (g/kg)		
	site 1	site 2	site 3
Exchangeable	< 0.005	< 0.005	< 0.005
Carbonate	< 0.005	< 0.005	< 0.005
Mn – Fe oxide	0.8599	0.8544	1.161
Organic bound	0.0522	0.0432	0.0711
Residual	3.011	3.0861	4.1139

Appendix 3B: Chemical speciation of lead in the sediment samples

Leachate	Pb (g/kg)		
	site 1	site 2	site 3
Exchangeable	0.0052	0.0055	0.005
Carbonate	0.0052	0.005	0.0052
Mn – Fe oxide	0.0415	0.0324	0.0312
Organic bound	0.0243	0.0186	0.029
Residual	0.0375	0.0304	0.0291

Appendix 3C: Chemical speciation of copper in the sediment samples

Leachate	Cu (g/kg)		
	site 1	site 2	site 3
Exchangeable	< 0.005	< 0.005	< 0.005
Carbonate	<0.005	< 0.005	< 0.005
Mn – Fe oxide	0.0211	0.0188	0.0121
Organic bound	0.0067	0.0055	0.0035
Residual	0.0143	0.0100	0.0083

Appendix 3D: Chemical speciation of zinc in the sediment samples

Leachate	Zn (g/kg)		
	site 1	site 2	site 3
Exchangeable	0.005	0.005	0.005
Carbonate	0.09	0.0799	0.0981
Mn – Fe oxide	0.2591	0.2024	0.2915
Organic bound	0.0972	0.0705	0.1003
Residual	0.132	0.1103	0.1621