KWARA STATE UNIVERSITY, MALETE, NIGERIA
SCHOOL OF POSTGRADUATE STUDIES (SPGS)

PHYSICO-CHEMICAL AND HEAVY METAL ASSESSMENT OF ASA AND MALETE RIVERS

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PHYSICO-CHEMICAL AND HEAVY METAL ASSESSMENT OF ASA AND MALETE RIVERS

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DECLARATION

I hereby declare that this thesis (Physicochemical and Heavy Metal Assessment of Asa and Malete Rivers) is a record of my research. It has neither been presented nor accepted in any previous application for higher degree.

Tawakalitu AHMED　　　　Signature/date

APPROVAL PAGE

This is to certify that this thesis by Tawakalitu AHMED has been read and approved as meeting the requirement of the Department of Plant and Environmental Biology and for the award of the degree of Master of Science (M.Sc.) in Plant and Environmental Biology.

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DEDICATION

This project is dedicated to my late aunt**, Alhaja Salimat Ayuba Abdullah**, may Almighty Allah grant her Jannatul-Fridaus (Ameen).

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All praises and adoration belongs to Almighty Allah, the Lord of all that exists. I thank Him for all He has done by giving me the grace to make this work a successful one.

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ABSTRACT

Water pollution has caused several health and environmental challenges especially in Nigeria. The rate of water pollution over the years is very alarming. Evaluating the physicochemical and heavy metal constituents of water will provide insight into their safety level. This study investigates the physicochemical and heavy metal constituents of Asa and Malete Rivers in Kwara State, Nigeria. Water samples and soil samples of the two Rivers were randomly collected at three different locations along the course of the two Rivers totaling six locations. The three different locations of Malete River were labeled as point A, B and C while Asa River was labeled as D, E, and F. The physicochemical and heavy metal constituents of the samples from these points were assessed using standard laboratory methods. The pH, dissolve oxygen, electrical conductivity, biochemical oxygen demand (BOD), chemical oxygen demand (COD), Total Solids (TS), Total Suspended Solids (TSS), Total Dissolve Solids (TDS), Total alkalinity, total acidity; total hardness, sulphate ion, chloride ion, phosphate ion and turbidity level of the water samples of the two Rivers varied significantly ($p<0.05$) across the sampling sites and ranged from 6.73±0.05 to 7.25±0.05; 3.60±0.80 to 5.95±0.20 mg/L; 60.41±0.23 to 86.21±0.10 Us/cm; 2.10 mg/L to 3.75 mg/L ; 1.40mg/L to 3.30 mg/L; 5.17 to 9.39 mg/L; 2.55 to 4. 56 mg/L; 3.56 to 5.52 mg/L; 2.40 to 4.00mg/L; 1.26 to 1.58mg/L; 1.14 mg/L to 1.64 mg/L; 21.49mg/L to 33.23mg/L; 12.76mg/L to 21.98mg/L; 0.4mg/L to 1.35mg/L and 1.63mg/L to 3.51mg/L respectively. Lead was not detected in all the water samples except site D and E (0.20 mg/L and 0.21mg/L respectively). Cadmium and Chromium level ranged from 0.01 to 0.02 and 0.01 to 0.05mg/L respectively for the two Rivers samples. The physicochemical and heavy metal constituents of the soil sample of the Rivers also varied significantly ($p<0.05$) across the sampling sites. The Pearson's correlation of the water and soil sample of the Rivers physicochemical revealed a strong relationship among all the parameters. Based on the findings of this study, the study concluded that; water from Asa River is more polluted compared to that of Malete, this may be attributed to activities that take place along the River Bank. The study concluded that the physicochemical parameters and heavy metal of water from Asa River is high compared to that of Malete but soil from Malete River is suitable and can support agricultural activities based on the result obtained. Also, the high level of the parameters at Asa are favourable for the growth of *Eichhornia crassipes* (water hyacinth) hence the plant population is higher at Asa compare to Malete.

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Water is an essential composition of the universe and a major constituent of the human body. It occupies about 70% of the Earth. It is an important element of survival for all living organisms especially plants and animals though it has been observed that it has always been faced with the issue of pollution especially as human populations grow (United Nations Environment on Programme Global Environment Monitoring System/ Water Programme, 2000). Ogunkunle *et al.* (2016) described water as a dynamic system that contains both living and non-living components made up of organic and inorganic soluble as well as insoluble substances that constitute the life support systems. Water is considered the most fundamental and indispensable of all natural resources globally (Ashto *et al.*, 2007) and it is of immense importance to all categories of living things as it contributes to the healthy growth of humans, animals and plants (Abulude *et al*., 2007).Water, an essential material used for various processes such as agricultural, manufacturing, transportation, milling, and many other day to day human activities (Ajadi *et al.,* 2016) has been variously polluted.

This Pollution also affects Rivers, thereby causing various damages to life found in it as well as other life that depends on it. Rivers are a crucial component of the biosphere, providing less than one percent of the world's fresh water with its greater ecological and social significance. It is however, contaminated by the indiscriminate dumping of sewage, industrial waste and excess human activities that influence their physicochemical characteristics and lead to various deleterious effects on aquatic species (Murhekar, 2011; Annalakshmi *et al*., 2012). According to World Health Organisation (2010) the quality of drinking water serves as a source of a powerful environmental determinant of humans health and as such all humans have the right to access a good quality water to carry out their basic needs. Despite the numerous benefits that is been derived from water, it still remains the most poorly managed resource in the world (Molobela *et al.,* 2011). The occurrence of heavy metal pollution from both natural and anthropogenic sources, particularly people living in urban environments who are more likely to be exposed to this hazard, has increased concern about the health impact of chronic exposures to polluted water. There is the need for man to interact with his environment, especially during his search for his basic needs (food, shelter and clothing). In the process of doing so, man subconsciously contaminates the water bodies such that it becomes unhealthy for human consumption (Ajibade, 2004) and organisms found in such environment especially aquatic plants.

Aquatic plants are very important in their ecosystems as they serve as the major producer of food to aquatic animals which interact and influence the hydrological, geomorphological and physico-chemical environments as well as other organisms found there, thereby providing habitat and food (Engelhardt and Ritchie, 2001; Wood *et al.,* 2017). These groups of plants are diverse group of macrophytic plants which include angiosperms, ferns, mosses, liverworts, and some freshwater macroalgae (Freedman, 2006). Most hydrophytes are known to accumulate metals from their environment (Rai *et al*., 2009) thereby affecting the ecosystems metal balancing (Kara *et al.*, 2005). Phytoplankton are essential and important species in any aquatic environment that function as producers i.e., the primary food supply. They are the initial biological elements from which energy is passed across the food chain to higher species (Tiwari *et al*., 2006; Saifullah *et al.,* 2014). The physicochemical parameters are the key factors that govern the aquatic ecosystem dynamics and structure of phytoplankton (Hulyal *et al*., 2009). Any slight changes in the physico-chemical parameters can affect the primary production in such ecosystems (Sharma *et al.,* 2007) and these changes could have a huge effect on the organisms living within them. All plants have the capacity to absorb heavy metals from water, which are necessary for their development and growth (Kara *et al.*, 2003), they uptake most of these pollutants with the aid of their root and shoot structures due to their fast growth and high biomass (Bonanno *et al.,* 2010; Matache *et al.,* 2013).

Heavy metals are known to be non-biodegradable and as such occur for a very long period of time in aquatic and terrestrial environments (Yusuf *et al.,* 2019). These metals can be transported from soil to ground waters and at times they might be taken up by plants. Accumulation of metals can pile up to reach unacceptable levels and thus pose a serious problem to human health and the society at large (Stigliani *et al.,* 2008). Sediments have been commonly used in the marine environment as environmental measures for measuring metal toxicity in natural water (Islam *et al.,* 2015). These sediments may experience frequent changes during the transport of heavy metals in the Riverine system due to dissolution, precipitation and sorption phenomena (Abdel-Ghani *et al*., 2007), which impact their efficiency and bioavailability (Nicolau *et al.,* 2006; Nouri *et al.,* 2011). The measurement of heavy metal concentrations in water and sediments in any polluted Riverine environment is therefore significant. Various studies have shown that nearness to industrial areas and urbanization has greatly increased soil and agricultural land pollution (WanNgah *et al*., 2007; Mmolawa *et al.,* 2011; Omotoso *et al*., 2011). They indicated that the main cause of these heavy metals is the use of agricultural waste from refuse dump sites.

Wetlands are known as the transitional zone between terrestrial and aquatic ecosystem (Singh *et al.,* 2008) which play a very important role in purifying the contaminated water bodies for many decades though their ability for this natural cleansing capacity have been tampered with as a result of presence of various pollutants such as heavy metals, pesticides, agricultural residues (Joyce, 2012). Wetland soils are formed as a result of periodic to continuous inundation and soil saturation that leads to anaerobic soil conditions which reduced decomposition thereby resulting in the buildup of organic matter (Yusuf *et al.,* 2019). Most of the heavy metals present in soils today occur from anthropogenic sources such as industrial activities, urban development, transport activities, migration etc. (Charlesworth *et al.*, 2003; Strivastava *et al.*, 2007).

Soil, which is the top most layer of earth's crust, is very important especially in the aspect of supporting plant growth. Soil forms a very important, unique and essential part of the Riverine basin, which form a variation of habitats and environments (Morillo *et al.*, 2004). Determination of heavy metals in water and sediments could be used to assess the anthropogenic and industrial impacts and risks posed by waste discharges on such ecosystems (Zheng *et al.*, 2008; Yi *et al.*, 2011; Saleem *et al.*, 2015). Thus, it becomes necessary to identify and measure the concentrations of heavy metals in water and as well as sediments of any contaminated Riverine ecosystem.

1.2 Statement of Research Problem

Asa and Malete Rivers serve as the major source of water in which the two communities of Ilorin and Malete depend on for their domestic and agricultural purposes. There is however, the need to investigate the physicochemical parameters of these water bodies to ascertain their quality because of the activities going on in and around the Rivers. Thus, the study was designed to assess the physicochemical properties and heavy metal content of Asa and Malete Rivers so as to reliably inform the residents of the two areas, about the safety of the water from these two Rivers.

1.3Aim and Objectives of the Study

1.3.1 Aim

- The aim of the study was to assess physicochemical properties and heavy metal contents of Asa and Malete Rivers.

1.3.2 Objectives

The objectives of the study were to:

- determine and compare the physicochemical properties of Asa and Malete Rivers;
- determine the presence of selected heavy metals in water, plant and soil found in both Rivers;
- compare the values of the physicochemical parameters with WHO standards

CHAPTER TWO

LITERATURE REVIEW

2.1 River Ecosystem

Water is an essential natural resource for the sustainability of life on earth (Olubanjo and Adeleke, 2020). Man depends on inland waters, especially freshwater, for domestic and industrial use. Water is a vital commodity and its sources include Rivers, streams, lakes, wells, boreholes, springs, etc. Rivers are among the oldest water bodies in the world (Higler, 2012). The quality of any body of surface or groundwater is a function of either or both natural influences and human activities (Stark *et al*., 2001; Kolawole *et al*., 2008). It is now generally accepted that aquatic environments cannot be perceived simply as holding tanks that supply water for human activities but are rather complex matrices that require careful use to ensure sustainable ecosystems function well into the future (UNEP, 2000). In recent decades, population growth, runoff of sewage from urban areas, and agricultural practices have increased nutrient inputs to Rivers above the level of their natural occurrence, causing accelerated eutrophication (Choudhary *et al*., 2010; Zanf *et al*., 2010; Kuffour and Benjamin, 2014). The monitoring of water quality is needed to provide an overview of water quality and to keep track of trends for the long-range of the selected water quality parameters.

2.2 Physicochemical Properties of Water

The quality of water can be described as a network of variables such as pH, temperature, biological oxygen demand, oxygen concentration; total dissolve solids etc. and any changes in these physical as well as chemical variables can have different forms of effect on life in water (Kolawole *et al.,* 2011). In other words, it gives information about the level of various solutes at a given place and time and this gives the basic knowledge for judging the condition of water for its designated uses and to improve existing conditions (Ali *et al.*, 2004; Patil, 2012).

2.2.1 Atmospheric Temperature

Atmospheric temperature is mostly responsible for cooling and warming of aquatic ecosystems (Patil *et al*., 2012). Thus, Pooja (2017) describes temperature as the measure of the average kinetic energy of water molecules that is measured on a linear scale of degrees Celsius. It is a basic water quality variable that determines the suitability of water for various forms of aquatic life (Pooja, 2017) and other purposes. Patil *et al.* (2016) reported that the minimum variation in temperature between temperature of the atmosphere and water bodies plays a vital role in the production of biological processes in shallow water bodies. Also, the growth rates of terrestrial and aquatic plants are temperature-dependent, with species having optimal growth and competitive ability at particular temperature, that is, differences in temperature-dependent growth could lead to different plant species to be specialized on different portions at different seasons, period of time (Patil *et al*., 2012). Temperature does not only affect distribution of organisms but also affects numerous water quality parameters which include the amount of dissolved oxygen present in the water bodies (Pooja, 2017). Temperature is one of the parameters that is determined on site with the aid of different kind of thermometer although Gebreyohannes *et al.* (2015) reported that temperature, pH and dissolved oxygen could be determined on site using HQ40d multimeter (HACH LANGE, NV). Hameed *et al.* (2015) used thermometer while Oyedeji *et al.* (2013) and Abdolmajid *et al.* (2014) in their reports made use of mercury in glass thermometer for determining temperature of water.

2.2.2 Water Colour

Another physical parameter of water is colour. This parameter is very important to most water users, be it domestic or industrial, because usually colourless water is of greater preference. Colour has been used for quantitative assessment of the presence of potentially hazardous or toxic organic materials present in water, for instance, presence of algae or other humic substances can be detected with the colour of the water (Pooja, 2017). Colour is also primarily used for aesthetic concern and more so coloured water gives the appearance of being unfit to drink, even though the water may be perfectly safe for other public use (Pooja, 2017).

2.2.3 pH

Pooja, (2017) defined pH as the negative log of hydrogen ion concentration i.e., it is a logarithmic scale which ranges from 0 (very acidic) to 14 (very alkaline). It gives an insight into the type and extent of water pollution (Patil *et al*., 2012). The presence of organic acids, biological processes such as photosynthesis, respiration etc. as well as physical processes like turbulence and aeration, which has the capacity to affect the concentration of dissolved carbon dioxide could change the pH level in the sea (Sunday *et al.,* 2011). Lower numbers on the pH scale indicate acidity, the lower the pH, the more the acidity while the higher the number, the higher the alkalinity. The pH does have an effect on soil as well as plant growth. The range of natural pH in fresh water ranges from 4.5, for acid, peaty upland waters, to over 10.0 in waters where there is high photosynthetic activity by algae. The pH of drinking water does not have an instant direct effect on human health though it could lead to some indirect health effects by bringing about changes in other water quality parameters such as solubility of metals and survival of pathogens (Zabed *et al.,* 2014). In other words, changes in pH could lead to alteration of other substances in water, for instance, ammonia toxicity, chlorine disinfection efficiency, and metal solubility are all subjective to changes in pH value (Pooja, 2017). The pH of less than 6.5 affects the production of vitamins and minerals in the human body while range of more than 8.5 values bring about change in the taste of water to become saltier thereby bringing about irritation of the eye as well as skin disorder (Carolin *et al.,* 2017).

2.2.4 Turbidity

Turbidity is a measurement of ability of the light to penetrate water and is comprised of suspended and colloidal material. It gives an inexpensive or a simple estimate of total suspended solids (TSS) concentration present in a body of water. There are a number of factors that could affect the turbid level of water and this include the size, shape, and refractive index of the clay, colloidal particles and presence of micro-organisms (Asadullah *et al.,*2013). Increase of turbidity of water results in interference of the penetration of light (Gupta *et al.,* 2003) and this will damage the aquatic life as well as also deteriorate the quality of surface water. Transparency and turbidity play a very important role in the energy of an aquatic ecosystem (Patil *et al*., 2012) and they are of utmost important for health and aesthetic reasons. Transparency of natural water bodies is also affected by human activity, decaying plant matter, algal blooms, suspended sediments, and plant nutrients. The consumption of high turbid water could be a serious health risk due to presence of microorganism that it contains (Asadullah *et al.,*2013). Hameed *et al.* (2015) and Oyedeji *et al.* (2013) reported that turbidity of water sample can be directly determined by the portable turbidometer (Jenway 6035) at room temperature.

2.2.5 Total Dissolved Solids

Total dissolved solids (TDS) describes the presence of inorganic salts and small amounts of organic matter available in water bodies (Pooja., 2017) i.e it helps in the determination of the amount of solid materials dissolved in the water (Gupta *et al.*, 2003). The main constituents are calcium, magnesium, sodium, potassium, hydrogen carbonate, chloride, sulfate, nitrate ion and others. Presence of synthetic organic chemicals could bring about offensive tastes, odors and colours to fish and aquatic plants (Chang, 2005). High level of TDS can be toxic to aquatic life as a result of increases in salinity or changes in the composition of the water (Ftsum *et al.*, 2015). Primary sources of higher TDS in the River water might be as a result of agricultural runoff, discharge of domestic waste from the town and other human activities like washing of different vehicles at and around the River (Annalakshmi and Amsath, 2012). This high content of TDS values could also lead to harmful effect especially to the public health such as the central nervous system, provoking paralysis of the tongue, lips, and, face, irritability, dizziness (Gupta *et al.*, 2003).

Solids can generally be grouped into three classes, i.e

- Settleable solids: These are solids which settle or sinks under the influence of gravitation e.g silt, heavy organic substances etc.
- Suspendable solids
- Filterable solids.

Both Suspend able and filterable solids are grouped based on particle size and the availability of suspended solids on standard glass-fibre filters. Therefore, the total solids content of water is simply described as the residue remaining after evaporation of the water and drying the residue to a constant weight at a temperature range of 103°C to 105°C (Pooja., 2017).

The importance of suspended solids in water bodies is of great significance because the solids sometimes might consist of algal growths thereby leading to severe eutrophic conditions in any water body. These will bring about reduction in the rate at which light penetrates the surface waters thereby interfering with aquatic plant life. Deposition of these solids in water gives rise to septic and offensive odor or conditions; thereby indicating the presence of unsatisfactory sewage effluent discharge. The decay of aquatic plants due to combined effect of high-water temperature, low dissolved oxygen and high turbidity might create an imbalance for the aquatic life (Patil *et al*., 2012). Also, high values of TDS could change the taste, hardness and corrosive properties of the water (EPA, 1976).

2.2.6 Electrical Conductivity

Electrical Conductivity is a valuable indicator that shows the range of hardness, alkalinity and the level of dissolved solids content in water. It is the measure of the ability of an aqueous solution to convert an electric current which is used as an indicator of total concentration of ions or electrolytes in water solution (Hameed *et al.,* 2015) i.e. its capability to conduct an electric current due to the breakdown of dissolved solids into positively ((Na^+, Ca^{2+}, k^+ and Mg^{2+}) and negatively charged ions (Cl^-, SO_4^{2-}, $CO_3^{2-}$and HCO_3^-)., although Nitrates (NO_3^{-2}) and phosphates (PO_4^{-3}) are minor contributors to conductivity, but they are very important biologically (Pooja , 2017). Conductivity varies with water source therefore it can indicate groundwater seepage or sewage leak. There is a high degree of correlation between electrical conductivity and TDS because both signifies the presence of dissolved solid in water samples (Mihir *et al.,* 2014). Conductivity of water and soil could be determined through the use of conductivity meter (Model 103 Jencose). This has to be calibrated using 0.1M solution of KCl before it could be used in water and soil samples (Hameed *et al.,* 2015). Asadullah *et al.* (2013) reported that conductivity and TDS could be carried out at temperature of 25°C using conductivity meter (Jenway 470) after calibration with calibration solution (HI7031, Henna instrument Hungry). Furthermore, Oyedeji *et al.* (2013) measured electrical conductivity with the use of HACH Wilson Grimes conductivity meter calibrated with 0.001 M KCl. While Zubia *et al.* (2015) also reported that chemical parameters such as TDS, conductivity and pH are analyzed in laboratory.

2.2.7 Alkalinity

Alkalinity is the capacity of the water to be able to neutralize acids thereby giving reflection of its *buffer capacity*. Alkalinity is not a pollutant but rather it is a total measure of the substances in water that have acid neutralizing ability or effects (Abdolmajid *et al.,* 2014). The alkalinity level in natural water bodies is as a result of the presence of bicarbonates that is formed in reactions in the soils through which the water percolates (Pooja, 2017). It could also be attributed to the presence of carbonates and hydroxides. This parameter is important especially for fish and aquatic life because it gives protection or buffers against rapid pH changes that could occur. Changes in alkalinity levels in water is brought about by rocks, soils, salts, specific plant activities, and certain industrial wastewater discharges: low nutrient level condition (oligotrophic) in water tends to have lower alkalinity while higher nutrient (eutrophic) waters have a tendency of high alkalinity (Pooja, 2017). The normal pH range for living organisms, especially aquatic life is between 6.0 to 9.0 and higher alkalinity levels in surface waters could buffer the acidic rain and other acid wastes. Total alkalinity can be measured by acid titration method which involves the titration of 0.01N hydrochloric acid and methyl orange as indicator according to standard methods (Abdolmajid *et al.,* 2014)

2.2.8 Total Hardness

Hardness is ability of water to form lather with soap easily. It occurs as a result of the presence of bicarbonates of calcium and magnesium ions (Patil *et al*., 2012), thus hardness is grouped into two via:

- Calcium Hardness.
- Magnesium Hardness

Hardness could also be divided into two parts: temporary (carbonate) and permanent (noncarbonate) hardness, though the temporary hardness of water can easily be removed by boiling the water. Excessive hardness of water could cause massive build-up of salt on the roots as well as in the medium which could prevent plants nutrient uptake i.e. the plant could stop getting major nutrients required for normal growth which will eventually cause the plant to die. Measurement of hardness range (expressed in mg/l as $CaCO_3$) as reported by Pooja (2017) is shown below:

Soft: 0 - 100 mg/l as $CaCO_3$

Moderate: 100 - 200 mg/l as $CaCO_3$

Hard: 200 - 300 mg/l as $CaCO_3$

Very hard: 300 - 500 mg/l as $CaCO_3$

Extremely hard: 500 - 1,000 mg/l as $CaCO_3$.

2.2.9 Nitrates and Nitrites

Both nitrate (NO_3) and nitrites (NO_2) are found naturally in water (Jordao *et al., 2002*) and the toxicology of nitrate to humans is as a result of its reduction to nitrite while the major biological effect of nitrite is its involvement in the oxidation of normal hemoglobin to methahemoglobin, which lacks the capacity is to transport oxygen to the tissues (Abdolmajid *et al.*, 2014). Nitrates serve as a source of nutrients to plants especially algae. Algae make use of water oxygen present and this leads to reduction in the oxygen level available thereby affecting the growth of the aquatic plant. Increase in concentration of nitrates is harmful because it promotes the growth rate of blue green algae which is unsuitable for use (Patil *et al*., 2012). The dominant human health risk associated with nitrate consumption is considered to be of methaemoglobin anemia by nitrate-derived nitrite (Van Busse *et al.,* 2012).

2.2.10 Sulphate ion

Sulphates are mostly related to their ability to form strong acids and this could bring about changes in the pH level. Sulfate ions also are involved in complexion and precipitation reactions which affect solubility of metals and other substances (Patil *et al*., 2012). The presence of high sulphate level may be as a result of various human activities along the River bank, leaching from fertilized and irrigated agricultural land. Sulfates at low concentrations are not considered toxic to plants or animals but could be very poisonous at higher concentrations (Patil *et al*., 2012).

2.2.11 Chloride

Chloride ion is mainly obtained from the dissolution of salts of hydrochloric acid as table salt (NaCl), $NaCO_2$ and added through industrial waste, sewage, sea water etc. (Abdolmajid *et al.,* 2014). Surface water bodies often have low concentration of chlorides as compare to ground water. Phosphate ion (PO_4^{3-}) both industrial and sewage waste leads to pollution due to the presence of phosphates ion which aids the growth of nuisance for micro-organisms (Gupta *et al.,* 2003). Also, the continual use of fertilizer is another main source of phosphate which comes from agricultural or residentially cultivated land into surface waters during erosion or flooding; the increase in this in the Rivers could leads to eutrophication and depletion of dissolved oxygen concentrations in the water bodies (Davie, 2003). High level of phosphate could damage the muscle, bring about difficulty with breathing as well as kidney failure (Nyamangara *et al.,* 2013).

2.2.12 Chemical Oxygen Demand

Chemical oxygen demand COD is the amount of oxygen needed to degrade all pollution chemically (Patil *et al*., 2012). It helps to determine the quantity of oxygen required to oxidize the organic matter available in water body under specific conditions of oxidizing agent, temperature and time (Pooja, 2016). It is an important water quality parameter as it provides an index to assess the effect of discharged wastewater will have on the surrounding environment. High COD levels indicates the presence of numerous amount of oxidizeable organic material in the water samples and the degradation of such which will again lead to hypoxic conditions (lack of oxygen) in the water body (Pooja, 2016).

2.2.13 Biochemical Oxygen Demand

Biochemical oxygen demand BOD is used for the determination of oxygen required for stabilizing waste discharged from household and industrial (De, 2003). It is used for indicating the pollution level in water bodies, i.e it shows the amount of dissolved oxygen required by biologically aerobic organisms to degrade the organic material present in a water body at certain temperature over a specific time period (Pooja, 2017). BOD is used in assessing the contamination level of the effluents deposited both domestically and industrially into water bodies. It is most commonly expressed in milligrams of oxygen consumed per liter of sample during 5 days (BOD_5) of incubation at 20°C. When organic matter decomposes, microorganisms (such as bacteria and fungi) feed upon this decaying material and eventually the matter becomes oxidized. The harder the microorganisms work, the more oxygen will be used up giving a high measure of BOD, leaving less oxygen for other life in the water. The ratio of BOD to COD indicates the percentage of organic material in water that can be degraded by natural microorganism in that environment (Pooja, 2017).

2.2.14 Dissolved Oxygen

Dissolved oxygen is needed by most aquatic organisms for survive as well as growth. It is thus defined as the amount of dissolved gaseous oxygen (O_2) present in an aqueous solution which gets into water through diffusion from the surrounding air, aeration, and as a waste product of photosynthesis. The hypoxic condition (lack of oxygen) in water body ($DO< 3mg/L$) causes reduction in cell functioning and disrupts circulatory fluid balance in aquatic system, eventually leading to death (Pooja, 2017). Decomposition of organic matter, dissolved gases, industrial waste, mineral waste and runoff from agricultural land result into a lower DO levels (Srivastava *et al.,* 2011; Addo *et al.,* 2013).

2.3 Water Quality

Water quality gives information on the concentration of various solutes at a given place over a given period of time (Ftsum *et al.,* 2015). These quality parameters provide the basis for judging or assessing the suitability of water for its designated uses and to contribute to the improvement of existing conditions (Ali *et al.*, 2004). There is no single method for determining the quality of water, thus, some characteristics or numerous natural substances and contaminants of water might be determined depending on their needs (Ftsum *et al.,* 2015). Several physical, chemical and biological parameters determine the nature and extent of water pollution. Also, increased anthropogenic activities as a result of industrialization have contributed to the decline in water quality including climate factors such as precipitation, soil type, vegetation, and groundwater and flow conditions. The nature of Rivers and lakes changes with the seasons and geographic regions even when there are no contaminants present (Chitmanat and Traichaiyaporn, 2010).

The deterioration of water quality has numerous effects which include destruction of ecosystem balance, contamination and pollution of ground and surface water resources (Ftsum *et al.,* 2015). Degradation of water quality world-wide is due to many anthropogenic activities that release pollutants into the environment thereby having an adverse effect upon aquatic ecosystems. Quality of water can be regarded as a network of variables such as pH, oxygen concentration, temperature, Biological oxygen demand, chemical oxygen demand etc. and any changes in these physical and chemical variables can affect aquatic ecosystem in different ways (Kolawole *et al*., 2011). The quality of water is directly related to health and as such, it is very important to determine water utility to ascertain its essentiality by testing the quality of the water before it is used for drinking, domestic, agricultural or even industrial purposes (Singh *et al.*, 2012). These utilities of River water for various purposes are governed by physicochemical and biological quality of such water (Singh *et al*., 2012).

2.4 Water and Pollution

Water is one of the most important and abundant compounds of the ecosystem. All living organisms on the earth need water for their survival and growth. As of now, only earth is the planet having about 70% of water but due to increased human population, industrialization, use of fertilizers in the agriculture and man-made activity it is highly polluted with different harmful contaminants (WHO and UNICEF, 2006; Enyoh *et al.,* 2018). Therefore, water pollution is primarily caused by industrial wastes, sewage disposal, petroleum contamination, and some agricultural activities (Tariq *et al.,* 2006). These contaminants (both organic and inorganic) are not easy to destroy biologically but can be reduced to a very low toxic form (Zhang *et al*., 2017; Jiang *et al*., 2018). Therefore, it is necessary that the quality of drinking water should be checked at regular time intervals because due to the continual use of contaminated drinking water, human population could suffer from water borne diseases. It is difficult to understand the biological phenomenon fully because the chemistry of water reveals much about the metabolism of the ecosystem and explain the general hydro biological relationship (Basavaraja *et al*., 2011).

2.5 Soil and Pollution

Soil pollution is mainly as a result of disposal of industrial and urban wastes as well as usage of agrochemicals (Demirezen *et al.,* 2006). Different studies have shown that some plants have the capacity of accruing high heavy metals levels from contaminated water or soil (Sahu *et al.,* 2016). Consumption of heavy metal contaminated plants in any quantity could lead to various health challenges; for example, exposure to Cadmium might lead to pulmonary effects like emphysema, bronchiolitis, and alveolitis (Duruibe *et al.,* 2007), while short-term exposure of Cadmium can cause renal effects (Young, 2005). The continual buildup of heavy metals in the liver and kidney of humans results in disruption of many biochemical processes in the body thereby resulting in nervous, kidney, cardiovascular, and bone diseases (Jarup, 2003). Toxicity as a result of lead could cause dysfunction of kidney, reproductive and cardiovascular systems, joints problems, reduction in haemoglobin formation, and enduring impairment to the central and peripheral nervous systems (Ogwuegbu *et al.*, 2005).

Contamination of soil by heavy metals is of utmost importance in the industrialized world because it does not only result in adverse effects on various parameters relating to plant quality or yield but also cause changes in the size, composition and activity of the microbial community (Hinojosa *et al.*, 2004). It indirectly affects soil enzymatic activities through the change brought about in the microbial community that synthesizes enzymes (Shun-hong *et al.,* 2009). Heavy metals exhibit toxic effects towards soil biota by affecting key microbial processes and decrease the number and activity of soil microorganisms. Furthermore, long-term heavy metal effects can increase bacterial community tolerance as well as the tolerance of fungi like Arbuscular mycorrhizal (AM) fungi, which helps in the restoration of contaminated ecosystems. Generally, increase in metal concentration has a great effect on soil physicochemical properties e.g. respiration rate, enzymatic activities etc. (Singh *et al.,* 2010). Accumulation of heavy metals in plants depends upon plant species and the efficiency of plants to absorb metals is evaluated by either plant uptake or soil to transfer metals to the plant's factors (Khan *et al.,* 2008).

High percentage of Pb in soils might reduce soil productivity while a minute quantity of Pb level may inhibit some vital plant processes, such as photosynthesis, mitosis and water absorption resulting into toxic symptoms of dark green leaves, wilting of older leaves, stunted foliage and brown short roots (Bhattacharyya *et al.*, 2008). These further lead to phytotoxicity for plants resulting in chlorosis, weak plant growth, yield reduction, low nutrient uptake, disorders in plant metabolism and reduced ability to fixate molecular nitrogen in leguminous plants (Guala *et al.,* 2010). Seed germination could gradually get delayed in the presence of increasing concentration of lead (Pb) as a result of prolong incubation of the seeds that must have bring about a neutral effect of lead by some mechanisms e. g. leaching, chelation, metal binding or/and accumulation by microorganisms (Ashraf *et al.,* 2007).

Soil quality analysis has to do with the analysis of parameters and all the processes that affect soil effective operation as a component of a sound ecosystem (Anu *et al.,* 2010). Soil qualities include its water retention capacity, carbon sequestration, plant productivity, waste remediation ability etc. The quality of soil often depends both on its physical properties such as colour, texture, moisture contents, pH, organic matter content etc., and chemical properties e.g. cation exchange capacity CEC, organic matter contents, phosphate-phosphorous, nitrate-nitrogen, nitrite-nitrogen etc., (Sani *et al.,* 2012). These physical and chemical properties helps in the determination of soil suitability for its planned use and management needed to keep it most productive to a limited extent, soil fertility determine its possible uses and yields (Jaiswal, 2004). Soil is a unique connection between the biosphere and lithosphere which contributes a practically non-renewable natural resource for the agriculture and the environment at large (Moraetis *et al.,* 2016).

These properties also play a very vital role in determining the extent to which the heavy metals pollution of soil occurred (Sani *et al.,* 2012). Soil pollution is one of the major threats to plant, animals and people’s lives, these pollutions could be in the form of seepage from landfills, solid waste discharge, industrial waste discharge into the soil, percolation of contaminated water into the soil, rupture of underground storage tanks or excessive application of pesticides or fertilizers in to the soil (Seifi *et al.,* 2010). Sometimes, this untreated waste discharge is often released or channeled from the industries and/or households to the ground or directly into the water surface in coastal environments through which Rivers flow (Fomenky *et al.,* 2018). This could lead to a drastic change in the physicochemical properties of such water bodies thereby rendering these water undesirables to the surrounding ecosystem (Tening *et al.,* 2013). This could also bring about change in the physicochemical properties of the soils onto which the wastes are deposited.

2.6 Pollution in Aquatic Environment

Quality of water is increasingly being affected by anthropogenic activities through which natural waters are contaminated (Giwa *et al.,* 2008 and Salami *et al., 2003*) and the effect on any body of surface or ground water is a function of either or both natural influences and human activities (Olatunji *et al*., 2011). Recent studies described pollution of Asa River (Ilorin, Nigeria) especially with various industrial discharges as alarming (Adekola and Eletta, 2005). It is now generally accepted that aquatic environments cannot be perceived simply as holding tanks that supply water for human activities but rather are complex matrices that require careful use in order to ensure sustainable ecosystem functioning well into the future (Olatunji *et al*., 2011). Rivers are the most important freshwater resource for man but unfortunately, River waters are being polluted by indiscriminate disposal of sewerage, industrial waste and plethora of human activities, which affect their physico-chemical characteristics and microbiological quality (Olatunji *et al*., 2011).

Pollution of the aquatic environment is a serious and growing problem due to increasing numbers and amounts of industrial, agricultural and commercial chemicals discharged into the aquatic environment which have led to various deleterious effects on aquatic organisms. Aquatic organism such as fish and hydrophytes accumulate pollutants directly from contaminated water and indirectly *via* the food chain (Mohammed, 2009) into their body system. Owing to the large quantity of effluent discharged to the receiving waters, the natural processes of pathogen reduction are inadequate for protection of public health. In addition, this wastes disposal alters the water pH and provide excessive bacterial nutrients often compromise the ability of natural processes to inactivate and destroy pathogens (Olatunji *et al*., 2011).

Disposal of sewage wastes into a large volume of water could also bring about an increase in the biological oxygen demands to such a high level that all the available oxygen may be removed, consequently causing the death of all aerobic species, e.g., fish (Maduka, 2004). Also, the presence of ions of phosphorus and nitrogen brings about eutrophication in both fresh and marine water ecosystems (Khan and Ansari, 2005). The untreated effluents from these industries cause pollution, accumulation of heavy metals and change in colour of the water. These heavy metals are toxic even at minute quantity or concentrations and as such become a serious problem if they find their way into the food chain (Vasanthy *et al*., 2004). Colour is an easily noticed pollutant and the presence of any form of colouring substance in water makes it to become unfit or unsafe for domestic purposes as well as recreational purposes as a result of its anesthetic appearance (Vasanth Kumar *et al*., 2003). Thus, prevention of River pollution requires effective monitoring of their physico-chemical and microbiological parameters (Chandra *et al*., 2006) although in most countries, the principal risk to human health is associated with the consumption of polluted water are microbiological in nature (Olatunji *et al*., 2011). Besides microorganisms, plants are also being studied for their potential roles in environmental cleanup. Green plants, commonly belief, are not only the lungs of nature with an ability of purifying impure air during photosynthetic activities but there are some species that have the unique ability to uptake, tolerate and even hyperaccumulate heavy metals and other toxic substances from soil and water through their roots and concentrate them their roots, stems and leaves.

2.7 Heavy Metals

Heavy metals are metallic elements with relatively high density; and toxic or poisonous at low concentrations e.g. mercury (Hg), arsenic (As), chromium (Cr), thallium (Tl) and lead (Pb) (Lenntech, 2020). These include the transition metals, some metalloids, lanthanides and actinides. Heavy metals have variously been used to denote: (i) metals with atomic number 23 (i.e. vanadium) onwards except rubidium, yttrium, caesium, barium, and francium; (ii) metals with density greater than 5; and (iii) metals which are toxic to man and other life forms when found in the environment. The eight most common pollutant heavy metals listed by the Environment Protection Agency (EPA) are: As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn (Athar and Vohora, 2001). Amounting to more than 20, heavy metals generally exist in a positively charged form and can bind on to negatively-charged organic molecules. Being metals ions, heavy metal cannot be degraded or destroyed, therefore their stability makes them as the persistent toxic substances in environment.

Heavy metals can contaminate the environment as they can be found in the air, soil and water, which pose health hazard to the general public. Presence of heavy metal in water as contaminants is an indication of global industrialization attributed to large scale of inappropriate disposal and untreated of wastewater containing heavy metal from anthropogenic sources (UNCSP, 2010). Water functions as a medium of transport for pollutants and they can be damaging to both living organisms and the environment (Harrison, 2001). Heavy metals can bio-accumulate over a period of time and the concentrations become apparent and measureable. Globally, regulatory organizations have implemented regulations through the maximum permissible limits for the discharge of heavy metal in the aquatic environment and intervention through ISO 14000 in order to control contamination. However, the heavy metals are being released at a higher concentration than the prescribed limits especially through anthropogenic point source, thus leading to the health hazard and water pollution.

Rapid acceleration of industrial growth throughout the world exerts negative impacts on the environment. Discharge of contaminated effluents without adequate treatment into the aquatic environment creates such implication. Industrial wastewater which are associated with manufacturing of automobile, purification of metals, electroplating, galvanizing, coating, paint, electronics, pharmaceutical, chemicals and battery manufacturing are the most common sources of heavy metal pollution (Table 2.1). Arsenic, cadmium, copper, chromium, lead, mercury, nickel and zinc are normally found in heavy metal contaminated wastewater (Duruibe *et al*., 2007).

Table 2.1: Sources of Heavy Metals

Metals	**Sources**	**References**
Lead (Pb)	Gasoline, automobile emissions, abrasion of tire treads, brake linings, mining and lead ore smelting, fertilizers, pesticides, and pigments.	Yu *et al*. (2007) and Kummer *et al*. (2009)
Copper (Cu)	Traffic exhaust, tires, and brake wear.	Fujiwara *et al*. (2011)
Zinc (Zn)	Traffic exhaust, tire and brake wear, fossil fuel combustion, lubricating motor oil, and tires.	Fujiwara *et al*. (2011)
Cadmium (Cd)	Abrasion of tire treads and brake linings	Kummer *et al*. (2009)
Nickel (Ni)	Abrasion of tire treads and brake linings, fossil fuel combustion, power plant, industry dumping areas, and automobile part corrosion	Kummer *et al*. (2009) and El-Hasan *et al*. (2002)
Bismuth (Bi)	Nonferrous metallurgy of copper	Cucu-Man and Steinnes (2013)
Arsenic (As)	Copper metallurgy, power plant	Cucu-Man and Steinnes (2013)
Vanadium (V)	Power plants	Cucu-Man and Steinnes (2013)
Chromium (Cr)	Power plant, industry dumping areas, and	Cucu-Man and Steinnes (2013)

	automobile part corrosion	
Cobalt (Co)	Traffic emissions, motor vehicle tire wheel	El-Hasan *et al*. (2002)
Manganese (Mn)	Industrial dumping areas and automobile part corrosion, auto workshops, electroplating industries, gasoline combustion	El-Hasan *et al*. (2002) and Shi *et al.* (2012)
Iron (Fe)	Automobile	El-Hasan *et al*. (2002)
Silver (Ag)	Photographic processing effluents, sewage sludge, biocide	Hajar *et al*. (2014)
Barium (Ba)	Internal combustion engines	Hajar *et al.* (2014)
Antimony (Sb)	Abrasion of vehicle brake linings, mining and smelting activities, electronic device	Klumpp *et al*. (2009); Bech*et al*. (2012)

Source: Mukherjee *et al*. (2016).

2.8 Heavy Metal Pollution and Its Effect on the Environment

Heavy metals pollution is a serious problem in our environment due to the fact that they are foremost in contaminating our food supply (Chauhan *et al.*, 2014).The presence of excessive amounts of heavy metals such as Pb, Cr and Fe, as well as heavy metals from industrial processes are of special concern because they produce acute or chronic poisoning in aquatic animals (Tchounwou *et al.,* 2012). Research has proven that long term use of this sewage effluent for irrigation contaminates soil and crops to such an extent that it becomes toxic to plants and causes deterioration of soil (Alnaimy *et al.,* 2021). Plants can accumulate heavy metals in their tissues in concentrations above the permitted levels which is considered to represent a threat to the life of humans, and animals feeding on such crops. This may lead to contamination of the food chain, as it was observed that soil and plants could contain toxic metals due to irrigation with water mixed with industrial effluent (Adnan and Amin, 2010).

The quality of ground water depends on various chemical constituents and their concentration, which are mostly derived from the geological data of the particular region. Industrial waste and the municipal solid waste have emerged as one of the leading causes of pollution of surface and ground water. Contamination of water resources available for household and drinking purposes with heavy metals, metal ions and harmful microorganisms is one of the serious major health problems. The recent research in Haryana (India) concluded that the high rate of exploration, its recharging, inappropriate dumping of solid and liquid wastes, lack of strict enforcement of law and loose governance are the cause of deterioration of ground water quality (Gupta, 2017). Heavy Metal has direct or indirect effect on physico-chemical parameters such as pH, temperature, oxidation reduction potential, dissolved salts, etc. of surface waters which thereby have direct or indirect influence on the incidence, transport and speciation of heavy metals on the quality of such water bodies (Patil *et al*., 2012).

2.9 Heavy Metals' Hyperaccumulators

The terms such as tolerant, indicator and hyperaccumulator are often used when categorizing plants that can grow in the presence of toxic elements (Peer *et al.,* 2005). A tolerant species is that species with the ability to grow on soil with concentrations of a particular element that are toxic or poisonous to other plants. Metal accumulators (hyperaccumulators) are plant species that concentrate metals in their above-ground tissues to levels that far exceed those present in the soil or in the non-accumulating species growing near them. These plants are capable of extracting heavy metals from their growth medium and concentrate them in their shoots thereby making them to be very suitable as well as widely used in phytoremediation. Accumulated heavy metals have been reported to play physiological and ecological functions, for example in prevention of bacterial and fungal diseases (Cutraro, 2005). Some selected species of plants can hyperaccumulate just one particular metal whereas some have the ability to hyperaccumulate more than one metal (Mganga *et al.,* 2011).

Heavy metal indicator plants on the other hand are plants that render biological and ecological functions due to their ability to indicate possible pollution and useful in absorption of pollutants in an area (Kvesitadze *et al*., 2006). The ability of plants to hyperaccumulation depends on some factors which include the type of plant species, soil physiochemical properties (pH, cation exchangeable capacity, organic matter content, electrical conductivity) and types of heavy metals Van der and Reeves, 2015). In hyperaccumulators, there is a speedy translocation of the heavy metals into the shoot through the xylem especially during the process of by transpiration (Rees *et al.,* 2015). The heavy metal uptake occurs through root cells, where they are detoxified as a result of various complex reactions with amino acids, organic acids or metal-binding peptides which are then sequestered into vacuoles (Hall, 2002). This restricts the translocation to the above-ground organs, thereby protecting the leaves, tissues as well as the active photosynthetic cells from heavy metal damage

(Chaudhary *et al.,* 2016). The high metal tolerance may also be due to highly efficient intracellular compartmentalization and chelation process (Sunitha *et al*., 2013; Sacky *et al*., 2014 and Zhao *et al*., 2015). Different chelators such as EDTA, organic acid, citric acid, or nicotianamine may be involved in translocation of metal cations through the xylem (Ghnaya *et al*., 2013 and Luo *et al*., 2015). The uptake of metal ions from the xylem apoplast into the shoot symplast is facilitated by metal transporters in the shoot cell membrane (Socha and Guerinot, 2014). Examples of hyperaccummulating plants are *Arabidopsis bisulcatus, Phytolaccaamericana, Euphorbia macroclada, Eichhornia crassipes.*

2.10 Aquatic Plants

Large Riverine aquatic plants or macrophytes, as they are known, are primary producers and can grow submerged below, floating on, or up through the water surface. They are an important constituent of aquatic ecosystems as they directly influence the hydrology and sediment dynamics of River systems through their effects on water flow and play key functions in biogeochemical cycles thereby providing shelter and refuge (Suren *et al*., 2000), act as a food source (Gross *et al*., 2001), and provide a structurally complex environment over spatial scales ranging from millimeters (Dibble *et al*., 2006) to hundreds of meters (Rennie and Jackson, 2005). Consequently, aquatic macrophytes affect the conservation ecology, the diversity and composition of other biotic assemblages.

2.11 Water Hyacinth (*Eichhornia crassipes*)

Some aquatic plants also known as hydrophytes have the ability to accumulate metals with several species suffering phytotoxicity (Fritioff and Greger, 2006; Dhir *et al*., 2008; Li *et al*., 2008) while some could easily grow in the presence of such heavy metals. One of the examples of such hyperaccumulator is *Eichhornia crassipes* (water hyacinth) (Odjegba and Fasidi, 2007).

Eichhornia crassipes is a prolific aquatic macrophyte and it is used as an indicator of pollution (that is to indicate the presence of nutrients such as nitrogen and phosphorus in eutrophic water bodies) due to its bio accumulative property (the accumulation of pollutant substances or other chemicals in the organisms (Herbert *et al.*, 2021). The presence of *E. crassipes* in aquatic environment can obstruct the flow of water in different channels, dam as well as Rivers; the damage caused by its abundance in aquatic environment can also affect the livelihood of the surrounding communities. *Eichhornia crassipes* is renewable, inexpensive, and widely available in nature, its ability to absorb recalcitrant pollutants with mutagenic and carcinogenic properties (including synthetic dyes and heavy metals), has been extensively studied by the scientific community (Herbert *et al.*, 2021).

Water hyacinth *(Eichhornia crassipes)* is a perennial and herbaceous monocotyledonous plant which belongs to the family Pontederiaceae or pickerelweed family. It is a native plant of the tropical America and it is usually found as a floating plant characterized by long feathery roots that can over 2m (6 ft) in length although they are found in shallow waters to attach their root into the surrounding sediment, and individual plants can even be found fully rooted on bank sides (Herbert *et al.*, 2021). This plant is found in a number of differing morphological growth forms, and the morphology and architecture of leaves, petioles, and clonal groups can be highly plastic. However, two forms are found to be more common; one form is typically found in open water or at the edges of plant mats and this form is characterized by short bulbous and very buoyant petioles containing air-filled aerenchyma. This short bulbous form can develop into the tall non bulbous form if crowding occurs and sufficient nutrients are available. The other common form occurs in crowded areas, such as in the middle of plant mats, with slender, tall and non bulbous petioles.

Water hyacinth produces seeds, which contributes to the part of the water bodies seed bank although the plants generally reproduce through clonal propagation with daughter plants being produced at the ends of fragile runners or stolons which could be easily broken by wind current, animal and boat movements, thereby allowing the detached clones to disperse and colonize new areas. Apart from this method of reproduction they also have the ability to double their biomass in about six days (Herbert *et al.*, 2021).

2.12 Ecology of Water Hyacinth

The growth and reproduction of water hyacinth are greatly determined by low nutrient concentrations, salinity as well as the temperature of their surroundings (Wilson *et al*., 2005; Mangas-Ramirez and Elias-Gutierrez, 2004). This plant has been discovered to invaded freshwater systems in more than 50 countries on five continents and recent climate change models indicate that its distribution might expand into higher latitudes as temperatures continually increase (Rodrı´guez-Gallego *et al*., 2004; Hellmann *et al*., 2008; Rahel and Olden, 2008). Water hyacinth is especially pervasive throughout Southeast Asia, the southeastern United States, central and western Africa and Central America (Brendonck *et al*., 2003; Lu *et al*., 2007; Martinez Jiménez and Gomez-Balandra, 2007). It is however prevalent in tropical and sub-tropical water bodies where water nutrient concentrations are mostly increasing due to agricultural runoff, deforestation, or waste management scheme and insufficient wastewater treatment (Villamagna *et al.*, 2010). No clear record of how, why and when these plants was introduced to water bodies outside of its native range, but many populations are established and persistent though there have been several attempts to control its growth. Introductions of these plants into other water bodies have been done accidentally or intentionally; intentional introductions to ponds are done because it is an ornamental plant with aesthetic value that reduces nutrient concentrations and algae blooms. Its success as an invader is attributed to its ability to outcompete native vegetation and phytoplankton as well as the absence of consumers found within its native range (Wilson *et al*., 2005). Invasions vary in extent and duration, but they generally lead to similar problems (Villamagna *et al.*, 2010). Changes that occur in water hyacinth density or population have the potential to affect other ecological and human communities in such areas where it is established and such changes may either be positive or negative depending on the designated or beneficial uses of the water body (Villamagna *et al.,* 2010). Water hyacinth is extremely difficult to eradicate once established thus, the goal of most management efforts is to minimise economic costs and ecological damage. Recent literature on the management of water hyacinth focuses on techniques to remove the weed; however, little has been done to assess the full extent of ecological changes (i.e. abiotic and biotic) that may occur in response to the establishment and management of this non-native species (Villamagna *et al.,* 2010).

2.13 Water Hyacinth and Physicochemical Parameters

Water hyacinth has been observed to stabilize pH levels and temperature within lotic systems by increasing the rate of mixing within the water column and potentially preventing stratification (Giraldo and Garzon, 2002). Occurrence of large mass of water hyacinth also decrease dissolved oxygen concentrations beneath its mats by preventing the transfer of oxygen from the air to the water's surface (Hunt and Christiansen, 2000) or through the blockage of light used by phytoplankton and submersed vegetation during photosynthetic activities although water hyacinth does not release oxygen into the water bodies unlike phytoplankton and submersed vegetation (Meerhoff *et al.*, 2003). Water hyacinth is also known to be good in absorbing heavy metals (Tiwari *et al.*, 2007), organic contaminants (Zimmels *et al.*, 2007) and nutrients from the water body. Its leaf tissues were found in California (U.S.A.) to have the same mercury concentration as the sediment beneath it, thereby suggesting that plant harvesting could help mediate mercury contamination if disposed of properly (Greenfield *et al*., 2007). Its capacity to absorb nutrients also makes it a potential biological alternative to both secondary and tertiary treatment of wastewater (Cossu*et al*., 2001).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

The study was carried out in two different locations within Kwara State i.e. Asa and Malete Rivers. These two Rivers are the major sources of water for the two communities. Asa River (Figure 3.1) is located in Ilorin and it serves as the major River of economic, agricultural, and environmental significance in the city as it supplies the bulk of water used by majority of the people of this city and its environments for different activities depending on its point of contact (Adekola *et al.,* 2007). This is due to the fact that it is about the longest and the most stretched River in Ilorin. The River is approximately 56 km long with a total surface area of about 302 hectares with a maximum depth of 14m located approximately 4km south of Ilorin town (Adekeye, 2004). This River has its source from Oyo State i.e South-Western part of Nigeria and flows through Ilorin, capital of Kwara State in a South-Northern direction, thereby forming a dividing boundary between the eastern and western parts of Ilorin metropolis (Balogun *et al.*, 2017). River Asa has various tributaries which stretch to join another body of water. Its tributaries carry various pollutants along its course and this has contributed to the pollution rate of the River (Ajibade, 2004). Various surveys carried out also revealed that some of these pollution sources include washouts from agricultural lands in form of pesticides, herbicides, industrial waste effluents, domestic wastes etc and these have impacts on the pollution rate of the River.

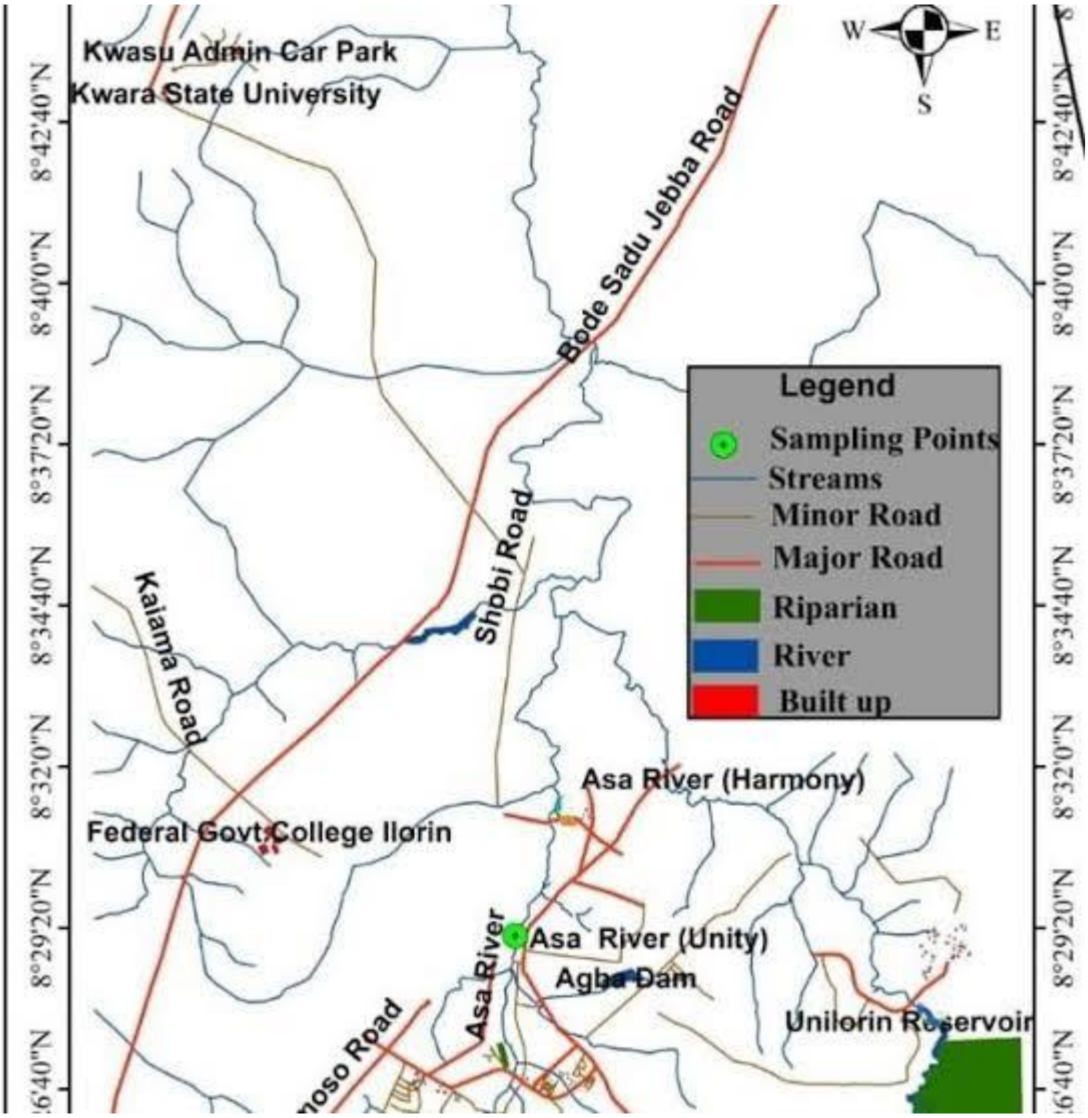

Figure 3.1: Map of Asa River
Source: Kolawole *et al*. (2011)

Malete River is found in Moro Local Government area of Kwara State. Malete, a rural settlement is involved in farming and hunting. It is found between latitude 8°42’31.83’’N and longitude 4°28’09.25’’E (Figure 3.2). This community is majorly involved in farming and hunting. Ganiyu *et* al., (2019) in his report noted the available sources of water in Malete are flowing River, bore hole and well water.

3.2 Sample Collection

Samples collection was done between the month of September and October, 2020. Water samples were randomly collected at three different locations along the course of the two Rivers. Points from Malete River were labeled as point A, B and point C; where point A represents the entry point into the Malete River, Point B is the central part of Malete River and C represents the extreme end of Malete River. Water obtained from Asa River were labeled as D, E and F; where point D is the main Asa dam, point E is Asa River extension along Amilengbe while F is the Asa River extension along Gada bridge.

The surface water was collected from each of the point (A to F) at a distance of 10 m apart using sample bottle prewashed and properly labeled accordingly (Nnamonu *et al.*, 2015). Ten replicate water samples were collected from each point A to F making a total of sixty samples for both Rivers. All these samples were packed in a cooler filled with ice block in order to maintain their properties prior to analysis. Also, plant and soil samples were collected from the same point where the water samples were collected and were kept in a polyethylene bag (APHA, 1999). A total number of sixty *Eichhornia crassipes* was collected from both Rivers and the same thing was done for soil. All samples were labeled appropriately and carried to the laboratory for analysis. This was done according to the method described by Oyedeji *et al*. (2013).

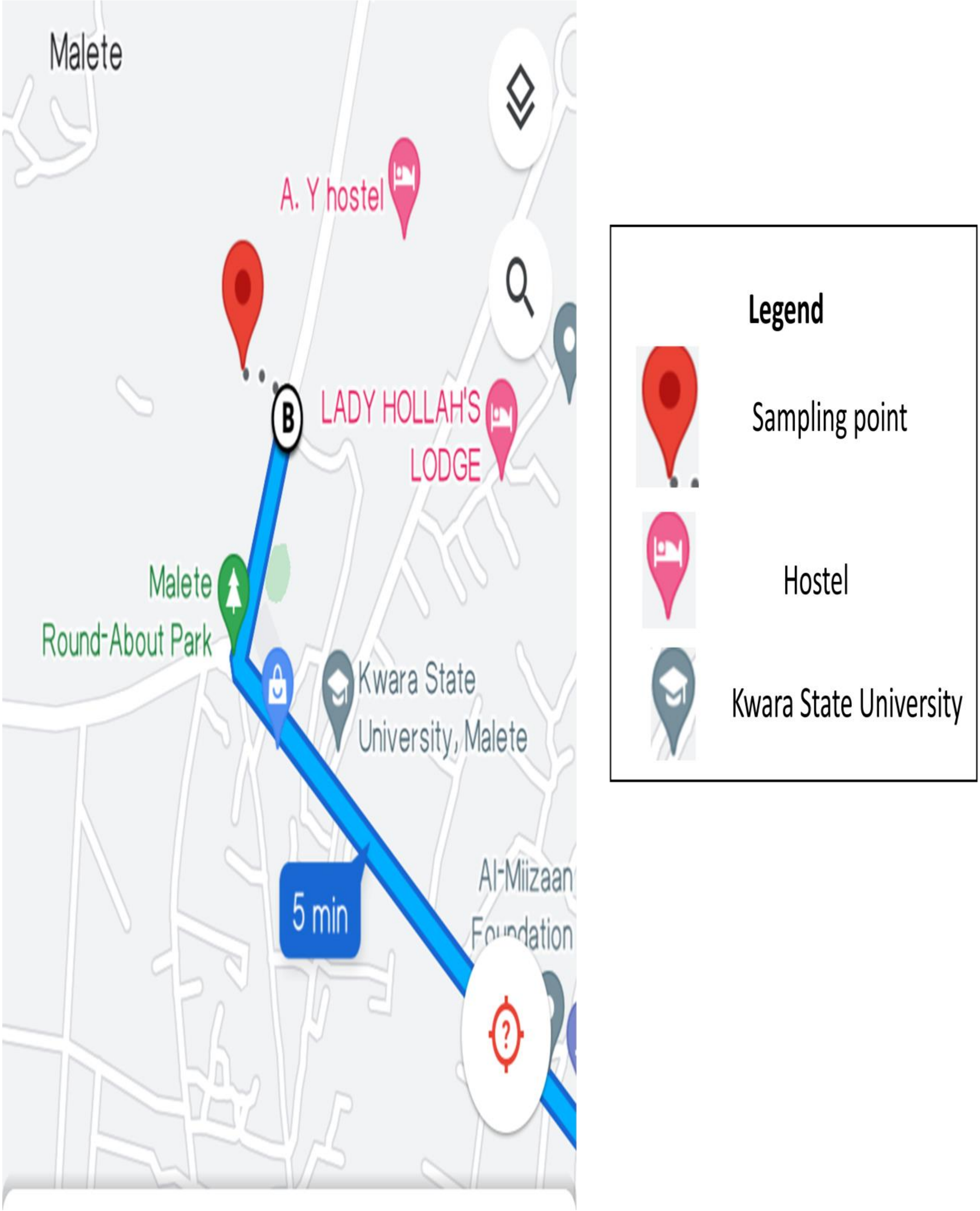

Figure 3.2: Map of Malete River (Source: https://www.google.com/maps/search/Malete+River+kwara+state/@8.5661094,4.5952058,8z)

3.3 Laboratory Analysis

3.3.1 pH Determination

The pH of the water samples was determined in- situ following the procedure of Onwughara *et al.* (2013) using Hanna Hi 98130 (pH meter combo). The pH meter was standardized with a buffer of 7and then inserted into the water bodies. The reading was then carefully observed and recorded.

3.3.2 Determination of Dissolved Oxygen (DO):

In determining dissolved oxygen, a redox titration is involved. This was done in accordance with the method used by Onwughara *et al.* (2013) where he adopted Winklers method. This method involves the use of an excess of Manganese (II) salt, iodide (I^-) and hydroxide (OH^-) ions which were added to the samples to form a white precipitate of $Mn(OH)_2$. The precipitate formed was then oxidized by the dissolved oxygen in the water sample into a brown Manganese precipitate. Concentrated hydrochloric acid was then added to acidify the solution. This made the brown precipitate to convert the iodide ion (I^-) to iodine. The amount of dissolved oxygen in the sample is thus directly proportional to the titration of iodine with a thiosulphate solution. The bottle was tightly covered and inverted several times to dissolve the precipitate. One hundred milliliters of the resulting solution was measured into a two hundred and fifty millilitres conical flask and titrated with standard sodium thiosulphate solution until a pale straw-coloured solution is formed. After obtaining this colour, eight drops of starch indicator solution were re-added to the solution to form a blue-ish solution and titration continued until the new colour formed disappeared (solution turned colourless).

Therefore, D O (mg/L) = $[16000 \times M \times V] / [V2 / V\,1\,(V1\text{-}2)]$

Where M = Molarity of thiosulpahte used.

V = volume of thiosulphate used for titration

V1 =Volume of bottle with stopper

V2 = Volume of aliquot taken for titration (Onwughara *et al.*, 2013).

3.3.3 Determination of Total Hardness of Water.

Hardness of water is due to the presence of calcium and magnesium minerals naturally in water. The method adopted by Adekunle *et al.* (2007) was used: two millilitres of buffer was added to 50cm^3 of the water sample in a conical flask. The mixture was stirred continually until a uniform solution was formed. Three drops of eriochrome black T indicator was added to obtain a pink colour. The solution was titrated against 0.1 M EDTA until a blue solution was formed. The titre value obtained was multiplied with 44.892 (the approved conversion factor) and the total hardness of water was converted to mg/L.

3.3.4 Determination Total Acidity of water:

To determine the acid level of water sample, the procedure used was in line with that of Onwughara *et al*. (2013). The procedure involves titrating fifty millilitres of the sample against 0.01M NaOH. The water sample was pipetted into a clean 250mL conical flask and two drops of phenolphthalein indicator was added then the solution was titrated against a standard 0.01M NaOH solution to a pink end-point. The following calculation was then done to get the acidity in mg/L.

Acidity (mg/l) = $[V \times M \times 100{,}000] / 50$ml of sample used

Where V = volume of NaOH used

M = molarity of NaOH used.

3.3.5 Determination of Total Alkalinity of water:

Fifty millilitres of the water sample was pipetted into a clean 250ml conical flask then two drops of methyl red indicator were added. The solution was then titrated against a standard

0.01M HCl solution until a pink end-point was reached (Onwughara *et al*., 2013). The following calculation was done to get the alkalinity of the water sample:

Total alkalinity (mg/L) = [V × M × 100,000] / ml of water sample used

Where V = volume of acid used

M = Molarity of acid used.

3.3.6 Determination of Total Solids (TS):

This was determined using Gravimetric Method as described by Onwughara *et al.* (2013). Here, 10ml of the water samples were measured into a pre-weighed evaporating dish. This was dried at a temperature of 103 to 105^{o}C for two and half hours in an oven. After this, dish was transferred into a desiccator and allowed to cool down to a room temperature; the weight was then taken again. Thus, total solid presented is represented by the increase in the weight of the evaporating dish. Therefore,

Total solids (mg/L) = (W2-W1) mg × 1000 / ml of sample used

Where W1 = initial weight of evaporating dish

W2 = Final weight of the dish (i. e evaporating dish + residue)

3.3.7 Determination of Total dissolved solids (TDS):

The determination of TDS involves filtering out certain quantity of the sampled water and then measured about 20ml of the filtrate into a pre-weighed evaporating dish. The process for the determining total solids was then repeated. Therefore,

The amount of total dissolved solids (mg/l) = [(W2-W1) mg × 1000] / ml of filtrate used.

Where W1 = initial weight of evaporating dish

W2 = Final weight of the dish (evaporating dish + residue).

3.3.8 Determination of Total suspended solids (TSS):

Total suspended solids in the water sample were calculated as the difference between TDS and TS, i.e.

Total suspended solids = Total solid (T S) — Total Dissolved Solids (TDS). (Onwughara *et al.*, 2013).

3.3.9 Biochemical Oxygen Demand (BOD)

In determining BOD, as described by Onwughara *et al.* (2013) where 50ml of the sample was filled into an airtight bottle and then incubated at a specific temperature for 5days. The difference between initial and final Dissolved oxygen (DO) before and after incubation gives BOD. One Millimeter (1ml) of each of $MgSO_4$, $CaCl_2$, phosphate buffer, $FeCl_3$ was diluted into 1L of water. It was shaken thoroughly until a uniform saturated solution was formed. One hundred millilitres of the samples were measured into different one Liter flasks and then add the previously prepared solution until a 1L mark is reached. These diluted sample solutions were then poured into BOD bottles and incubated at 20°C in the dark for 5 days. Note that initial dissolved oxygen was measured before incubation while the final dissolved oxygen was measured after the 5day incubation period.

Therefore, BOD (mg/L) = $[D_I - D_F] / B$

Where D_I = initial dissolved oxygen (before incubation or immediately after preparation)

D_F= final dissolved oxygen (after incubation) B = Fraction of used sample.

3.3.10Salinity Test (Chloride Ion Test):

About 50ml of the sample was poured into a conical flask and 3-5 drops of a phenolphthalein indicator was added. The solution was neutralized with 0.1N sulphuric acid, the solution turned colourless. About One milliliter of potassium chromate ($K_2Cr_8O_4$) indicator solution was added and then titrated with standard silver nitrate (Ag_2NO_3) solution until a pinkish-yellow endpoint was reached. A blank titration was done using distilled water of 25 ml, 1 ml of Potassium Chromate ($K_2Cr_8O_4$) indicator was added, then titrated against standard Silver Nitrate (Ag_2NO_3) until the colour changes. Thus, the amount of Chloride quality was deduced as follows:

Chloride, mg/l = $[(A_1 - A_2)\ (N)\ (35.45) / V] \times 100$

A = Ag_2NO_3 solution, in ml for sample titration

B = Ag_2NO_3 solution, used for blank titration with distilled water (in ml)

N = Normality Ag_2NO_3 solution

V = Sample volume (in ml).(Onwughara *et al.*, 2013).

3.3.11 Determination of Chemical Oxygen Demand (COD):

Two hundred and fifty millilitres of the sample was poured into a clean conical flask and then warmed to 27ºC. Another Ten millilitres of potassium permanganate ($KMnO_4$) of 0.0125M concentration was added together with H_2SO_4. It was gently shaken and the mixture was incubated at 27ºC for 4 hours. The solution was examined at intervals of 4 hours and ($KMnO_4$) was added till pink colour of permanganate disappeared. After 4 hours, another 1mL of potassium iodide (KI)solution with starch indicator was added then titrated with 0.0125M $Na_2S_2O_3$, until a colourless solution was formed (Onwughara *et al.*, 2013).

COD (mg/l) = $[K_1 - K_2 \text{ x } 1000] / A \times$ Volume of sample used.

Where A = Total Volume of $KMnO_4$ 0.0125M added to samples.

K_1=ml of Blank

K_2=ml sample required.

3.3.12 Determination of Electrical Conductivity (EC) of Water:

The electrical conductivities for each water sample were measured using a digital conductivity bridge as described by Oyedeji *et al*. (2013). Ten milliliters of the samples was weighed into 50ml beaker each. The solution was allowed to stand for thirty minutes after adding ten milliliters of distilled water and stirred occasionally within a glass rod. The glass electrode of digital conductivity bridge was inserted into the partly suspended solution and the readings were taken.

3.4 Soil Samples Preparation

The soil samples were collected with sterile equipment into a polyethylene bag and it was taken to the laboratory for further analysis (Ghare *et al*., 2021). These samples were air-dried by placing in shallow trays in a well-ventilated area; soil lumps were crushed so that gravel, plant roots and large organic residues became separated. The air-dried soil samples were then sieved, repacked into another polythene bags and labelled accordingly. These were then analyses for soil colour, particle size, soil pH, available phosphorus, cation exchange capacity CEC, total nitrogen, total acidity, organic carbon and soil organic matter content.

3.4.1 Determination of Soil Colour

Soil colour was determined using Munsell soil colour chart by placing 2mg of sieved soil sample under the chart in order to isolate the colour of soil that correspond with the colour on the Munsell soil colour chart.

3.4.2 Soil Particle Size Determination

Soil particle size of the sample was determined according to the method described by APHA (1999). Fifty grams of air-dried sieved soil were weighed into sample containers each and 4ml of 40% NaOH was added to the containers. Fifty millilitres of water was added and stirred continually with magnetic stirrer in order to isolate the type of soil. The mixtures were quantitatively transferred into 1L measuring cylinder, soil hydrometer was then inserted into the mixture and were made up to 1000ml. The soil hydrometer was removed and agitated for 20secs into palm inversely and 40secs hydrometer reading was recorded. The contents were left for two hours for the second hydrometer reading to be taken.

Calculation involved:

$$\% \text{ Silt} + \text{Clay} = \frac{\text{40secs corrected hydrometer reading}}{\text{Weight of Sample}} \times 100$$

$$\% \text{ Clay} = \frac{\text{2hrs corrected hydrometer reading}}{\text{Weight of Samples}} \times 100$$

$$\% \text{ Sand} = 100 - (\% \text{ silt} + \% \text{ clay})$$

3.4.3 Soil pH Determination

The soil pH was determined using the method described by (Ghare *et al.*, 2021) where glass electrode pH meter was used. Ten grams of air-dried soil samples were weighed into 50ml beakers each and 10ml of distilled water was added to each of the beakers. The soil solution was allowed to stand for about 30minutes and was continually stirred with a glass rod. The glass electrode pH meter was inserted into the partly settled suspensions and the readings were taken.

3.4.4 Determination of Available Phosphorus

Bray's method of phosphorus detection as described by (Ghare *et al.*, 2021) was adopted where 5g of air-dried soil samples was weighed into a sample bottle. Thirty five millilitres of extract solution that contains 1N of Ammonium Fluoride and 0.5ml of hydrogen Chloride was added to each of the samples. This mixture was then shaken for 5minutes and then filtered using Whatman No42 filter paper. Five millilitres of the extract was pipetted and 5ml of the solution prepared were added. These contents were then made up with distilled water until a 50 ml mark was reached and then allowed to stand for 30minutes. The absorbance's were read at 660 nm wavelength using spectrophotometer. This same method of titration was carried out without the soil samples that is., blank titration (APHA, 1999).

$$\% \text{ Available Phosphorus} = \frac{\text{Reading in ppm} \times 35\text{ml of extract}}{5\text{g of sample}}$$

3.4.5 Determination of Total Acidity

This was done using method described by APHA (1999). Five grams of air-dried sieved samples of soil were weighed into sample containers each. Fifty millilitres of 1N KCl was added to each of these samples and then allowed to stand for 30minutes after which it was filtered with Whatman No 42filter paper. Twenty five mililitres of the aliquot extracts was prepared into a 100ml conical flasks each, 2 drops of 1% phenolphthalein indicator was added to the samples and the mixtures were titrated against 0.01N of NaOH. There was a colour change from a colourless substance to a reddish colour at the end point.

$$\text{Total Acidity} = \frac{\text{Titre value} \times 0.01 \times \text{volume of extracts} \times 10}{\text{Weight of Samples}}$$

3.4.6 Cation Exchangeable Capacity (Ca, Mg, Na, K)

The cation exchangeable capacity of the sample was done using method described by APHA (1999). Five grams of air-dried soil samples was sieved into a sample container and 50ml of 1N NH_4OH was added. The contents were shaken and left for an hour and then filtered.

3.4.7 Calcium (Ca) and (Mg) Determination

This was done using method described by APHA (1999). A portion of 5ml of the extracts each were prepared into 100ml conical flask. Five millilitres of each of the concentrated Ammonium solution, 5 drops of 10% Hydroxylamine, Hydrochloride and 2 drops of 5% potassium cyanate were added to the samples and finally titrated against 0.01N EDTA

(Ethylene disodium Tetra Acetate) using Erichrome black T indicator which indicated the colour changes from red to blue.

Calculation

Ca + Mg = titre value × 0.02 $\times\frac{50}{5}\times\frac{50}{5}$

Normality of EDTA = 0.02

Volume of extracts = 5ml

Weight of samples = 5g

3.4.7.1 Calcium Alone

Calcium alone was determined using method described by APHA (1999). Five millilitres of extracts were prepared into 100ml conical flask and 5ml of 40% NaOH with colour change from red to colourless solution.

Ca = titre value × 0.02 $\times\frac{50}{5}\times\frac{50}{5}$

3.4.7.2 Sodium and Potassium determination

The ammonium acetate NH_4OA extracts were analysed using flame photometer as described by APHA (1999). The standards of sodium and potassium were prepared with concentration in ppm with Na in 10ppm and K in 20 ppm.

Na = $\frac{Standardppm\ (10ppm)}{StandardReading(100)}\times$ sample Reading (R)

K = $\frac{20ppm}{100}\times$ R

3.4.8 Determination of Total Nitrogen

This was determined using Ghare *et al.* (2021) where Kjeldahl method was employed. One gram of air-dried soil samples were weighed into Kjeldahl flasks. Ten grams of K_2SO_4, 0.5ml of $CuSO_4$ and 25ml conc. H_2SO_4 were added and then heated until the cleared mixtures changed to green colour which indicated digestion and was then allowed to cool. The digests were then made up to 250ml volumentric flasks with distilled water (APHA, 1999).

Distillation process

This was done by preparing 5ml of the digests each from the 250ml into a micro kjeldahl distillation apparatus and 5ml of 40% NaOH was then added. The ammonium liberated was distilled into a 5ml boric acid indicator (Bromo cresol green methyl red) in a titration flask i.e., burette where about 50ml distillate were collected. The NH_4 in the distillate was determined each by titrating against 0.01N HCl until colour changed from green to blue.

$$\text{Total Nitrogen} = \text{Titre value} \times 0.01 \times 0.014 \times \frac{250}{5} \times 100$$

Normality of HCl = 0.01

Equivalent of Nitrogen = 0.014

Vol =5

Weight =1.

3.4.9 Determination of Total Organic Carbon

This was determined using Walkley-Black Wet Oxidation method. A portion of 1g of air dried finely ground soil samples was weighed into 250ml conical flasks each. Five millilitres of 1N $K_2Cr_2O_7$ solution was pipetted accurately into each conical flask and were gently shaken. 10ml of conc. H_2SO_4 was rapidly added to the contents and were gently swirled immediately until the contents were properly mixed after which it was allowed to stand for 30 minutes. Fifty millilitres of distilled water was added to each suspension and 2-3 drops of ferroin indicator was also added and were then titrated against 0.5N of ferrous sulphate solution in the burette. There was a colour change from green to maroon when end point was reached. Blank titration was also done in the same manner but in the absence of soil samples. Organic matter was also determined by multiplying the organic carbon content obtained by a conversion factor of 1.729 (APHA, 1999).

$$\% \text{ Organic Carbon} = \frac{(\text{blank} - \text{Sample}) \times 0.003 \times 1.33}{Weightofsamples} \times 100$$

$$\% \text{ Organic matter} = \% \text{ Organic Carbon} \times 1.729$$

3.5 Digestion of Samples for Determination of Presence of Heavy Metals

Samples of water, soil and plant were digested using the wet digestion method described by Plank (1992) as reported by Oyedeji *et al.* (2013). The soil samples were air-dried at room temperature, ground in a ceramic mortar and then sieved at 500 microns. About 1g of this soil was digested with fifteen millilitres HNO_3 and five millitres HCl. These mixtures were then heated at a temperature range of 50 – 60^0C until a brownish fume color was released, indicating that digestion has taken place. The same thing was repeated for both water and plant samples. The digested samples were then subjected to heavy metal analyses with the use of Atomic Absorption Spectrophotometer (AAS) UNICAM model 929.

3.6 Statistical Analysis

The data collected were subjected to one-way Analysis of Variance (ANOVA) using SPSS version 25.0. In cases of significant difference in means, data were further subjected to Duncan Multiple Range Test (DMRT) which is presented by alphabets in superscripts in the tables presented. Also, the results of the physicochemical parameters of water and soil samples were further subjected to correlation analysis in order to detect the relationship or association that exists between the parameters. These parameters were also subjected to

Principal Components Analysis (PCA) in order to detect the relationship of the parameters in different sites.

CHAPTER FOUR

RESULTS

4.1 Physicochemical Properties of Asa and Malete Water Samples

The physicochemical properties of Asa and Malete Rivers are presented in Table 4.1. The pH level of water samples of the two River was significantly different ($p<0.05$) and ranged from 6.73±0.05 (Malete River) to 7.25±0.05 (Asa River). The pH level of each sampling site was also significantly different ($p<0.05$) except for site B and C of the Malete River.

The level of Dissolved Oxygen of the two Rivers ranged from 3.60±0.80 (Malete River) to 5.95±0.20mg/L (Asa River). There is significant difference ($p<0.05$) between the level of Dissolved Oxygen of the two Rivers.

The Electrical Conductivity of the water samples varied significantly across the two locations and sampling sites. Site E (Asa River) had the highest ($p<0.05$) conductivity level among the sampling sites with a value of 86.21±0.10 Us/cm and site C had the lowest conductivity level of 60.41±0.23 Us/cm.

The BOD and COD content of the samples varied significantly ($p<0.05$) among the different sampling sites of the two Rivers. The BOD level ranged from 2.10 mg/L (site B) to 3.75mg/L (Site D) and COD ranged from 1.40 mg/L(site B) to 3.30mg/L (site E).

The level of nitrate and nitrite ion of the water samples also varied significantly across each sampling site of the two Rivers but there was no significant different ($p<0.05$) in the nitrate concentration in site A and C as well as D and F. Total Solids TS, Total Suspended Solids TSS and Total Dissolve Solids TDS ranged from 5.17 (site C) to 9.39mg/L (site D); 2.55 (site C) to 4. 56mg/L (site D) and 3.56 (site B) to5.52mg/L (site F) respectively. There was significant difference ($p<0.05$) in the TS level in all the sites except sites B and C as well as

D and E. Significantly different ($p<0.05$) values of TSS and TDS were observed in all the sites except for B and C as well as E and F which had significantly similar TDS values.

Magnesium hardness varied significantly ($p<0.05$) among the sites and ranged from 0.78(site D) to 1.24mg/L (site E) respectively. No significant ($p<0.05$) difference among the Calcium hardness of water samples obtained in the two sites `.

Total alkalinity and total Acidity ranged from 2.40 to 4.00mg/L 1.26 to 1.58mg/L respectively. There was significant different ($p<0.05$) in these parameters in all of the sample sites. Total hardness ranged from 1.14mg/L to 1.64mg/L and there was a significant difference ($p<0.05$) in this parameter in all the sample sites. Sulphate ion ranged from 21.49mg/L to 33.23mg/L. There was no significant difference among sites A, B and C while site E and F was observed to be statistically the same. Chloride ion varied from 12.76mg/L to 21.98mg/L with significant differences in all sample sites. Turbidity ranged from 1.63mg/L to 3.51mg/L and a significant difference was observed in all sites except D and E. Phosphate ion concentration ranged from 0.4mg/L to 1.35mg/L with no significant difference in site A and C as well as E and F.

Table 4.1: The Physicochemical Properties of Asa and Malete Water Samples

Parameters/site	Site A	Site B	Site C	Site D	Site E	Site F
pH	6.83±0.03^{cd}	6.73±0.03^{de}	6.73±0.05^{de}	6.70±0.00^{e}	7.13±0.03^{b}	7.25±0.05^{a}
Dissolve oxygen(mg/L)	5.11±0.10^{c}	3.60±0.80^{e}	4.96±0.04^{d}	5.91±0.15^{a}	5.44±0.05^{b}	5.95±0.20^{a}
Total hardness(mg/L)	1.34±0.02^{b}	1.22±0.02^{d}	1.26±0.02^{cd}	1.14±0.02^{e}	1.64±0.04^{a}	1.32±0.00^{bc}
Sulphate ion(mg/L)	21.59±0.01^{c}	21.49±0.01^{c}	21.51±0.01^{c}	33.23±0.02^{a}	32.60±0.02^{b}	32.62±0.02^{b}
Chloride ion(mg/L)	14.10±0.08^{e}	15.70±0.00^{d}	12.76±0.00^{f}	17.10±0.08^{c}	21.98±0.71^{a}	18.64±0.21^{b}
Total alkalinity(mg/L)	3.10±0.10^{c}	2.40±0.00^{d}	3.10±0.10^{c}	3.40±0.20^{bc}	3.50±0.1^{b}	4.00±0.00^{a}
Electrical conductivity(uS/cm)	63.61±0.39^{e}	67.16±0.06^{d}	60.41±0.23^{f}	70.54±0.08^{c}	86.210±0.10^{a}	85.30±0.10^{b}
Nitrate ion (mg/L)	2.70±0.10^{c}	2.35±0.05^{d}	2.63±0.08^{c}	3.55±0.05^{a}	3.35±0.05^{b}	3.57±0.02^{a}
Nitrite ion (mg/L)	0.20±0.00^{b}	0.20±0.00^{b}	0.10±0.00^{c}	0.20±0.00^{b}	0.20±0.00^{b}	0.30±0.00^{a}
BOD(mg/L)	2.92±0.02^{c}	2.10±0.00^{e}	2.60±0.10^{d}	3.73±0.07^{a}	3.55±0.05^{b}	3.75±0.05^{a}
COD(mg/L)	1.70±0.10^{d}	1.40±0.00^{e}	2.30±0.10^{c}	3.10±0.10^{ab}	3.30±0.10^{a}	2.90±0.10^{b}
Turbidity (NTU)	2.79±0.03^{c}	1.79±0.03^{d}	1.63±0.03^{e}	3.51±0.07^{a}	3.39±0.01^{a}	3.14±0.04^{b}
TS(mg/L)	7.65±0.15^{c}	5.75±0.15^{d}	5.17±0.16^{d}	9.39±0.19^{a}	9.06±0.51^{a}	8.54±0.11^{b}
TSS(mg/L)	3.34±0.04^{bc}	2.70±0.29^{cd}	2.55±0.25^{d}	4.56±0.5^{a}	3.61±0.31^{b}	2.92±0.04^{cd}
TDS(mg/L)	4.60±0.10^{b}	3.56±0.06^{c}	3.63±0.09^{c}	5.03±0.07^{ab}	5.46±0.26^{a}	5.52±0.8^{a}
Calcium hardness(mg/L)	0.42±0.02^{a}	0.26±0.02^{c}	0.30±0.02^{ab}	0.36±0.04^{ab}	0.40±0.00^{a}	0.36±0.00^{ab}
Magnesium hardness(mg/L)	9.20±0.00^{b}	9.60±0.00^{b}	9.70±0.07^{b}	7.80±0.06^{c}	12.40± 0.04^{a}	9.70±0.01^{b}
Phosphate ion (mg/L)	0.70±0.01^{b}	0.40±0.00^{c}	0.60±010^{c}	1.35±0.05^{a}	1.20±0.00^{b}	1.31±0.12^{a}
Total Acidity(mg/L)	1.32±0.04^{b}	1.50±0.02^{a}	1.51±0.01^{a}	1.58±0.02^{a}	1.34±0.06^{b}	1.26±0.02^{c}

Means followed by the same letter in a row are not significantly different from each other according to DMRT at $P \leq 0.05$.TDS: total dissolved solids, TSS: total suspended solids, TS: total solids, COD: chemical oxygen demand, BOD: biochemical oxygen demand, NTU: Nephelometric Turbidity Unit and uS/cm: microSiemens/centimeter

4.2 Heavy Metal Contents of Asa and Malete Water Samples

The heavy metal content of water samples from both Asa and Malete Rivers are presented in Table 4.2. Lead was not detected in all the water samples except site D (0.20mg/L) and E (0.21mg/L). Cadmium was not detected in site C; equal concentrations of Cd were observed at sites A, B and D with a value of 0.01mg/L and sites E and F with a value of 0.02 mg/L. Chromium was detected in all the sites with the highest concentration of 0.05mg/L at site D.

4.3 Physicochemical Properties and Heavy Metal Content of Asa and Malete Soil Samples

The physicochemical properties and heavy metal content of soil obtained from Asa and Malete Rivers are presented in Table 4.3. The pH of the soil sample varied significantly ($p<0.05$) across all the sites and ranged from 6.26 (site D) to 6.75 (site C). Nitrogen, Phosphorus, Organic Carbon, organic matter, magnesium, Potassium, total Acidity, sulphate ion and CEC of the soil were observed to vary significantly across all the sites.

The calcium and sodium content of the soil ranged from 2.01 to 2.80 mg/L and 0.13 to 0.17mg/L respectively; the calcium content of site D and F have no statistical difference and the sodium content of site C, D and F are statistically the same. The silts, clay and sand content of the soil were observed to have significant differences in all the sample sites.

Lead was not observed in all the soil samples except site F with a value of 0.20mg/L, cadmium was also not detected in all the sites while chromium was found in sites A (0.01mg/L), B (0.04mg/L) and D (0.03mg/L) but it was not detected in sites C, E and F.

Table 4.2: Heavy Metal Contents of Asa and Malete Water Samples

Parameters/site	Site A	Site B	Site C	Site D	Site E	Site F
Lead (Pb)(mg/L)	ND	ND	ND	0.02	0.21	ND
Cadmium(Cd)(mg/L)	0.01	0.01	ND	0.01	0.02	0.02
Chromium(Cr)(mg/L)	0.02	0.01	0.02	0.05	0.04	0.04

ND: Not Detected

Table 4.3: The Physicochemical Properties and Heavy Metal content of Asa and Malete Soil Samples.

Parameters/site	Site A	Site B	Site C	Site D	Site E	Site F
PH	6.55 ± 0.01^{c}	6.68 ± 0.02^{ab}	6.75 ± 0.05^{a}	6.26 ± 0.01^{d}	6.54 ± 0.01^{c}	6.64 ± 0.01^{b}
Organic carbon(g/Kg)	1.93 ± 0.01^{a}	1.78 ± 0.01^{e}	1.91 ± 0.01^{b}	1.72 ± 0.01^{f}	1.89 ± 0.01^{c}	1.86 ± 0.08^{d}
Nitrogen (g/Kg)	0.34 ± 0.00^{a}	0.29 ± 0.01^{c}	0.31 ± 0.00^{b}	0.28 ± 0.00^{d}	0.28 ± 0.00^{d}	0.28 ± 0.01^{d}
Sulphate ion(g/Kg)	18.25 ± 0.25^{c}	21.70 ± 0.30^{a}	19.23 ± 0.03^{b}	21.80 ± 0.03^{a}	19.40 ± 0.10^{b}	21.90 ± 0.30^{a}
Organic matter(%)	3.32 ± 0.01^{a}	3.08 ± 0.01^{d}	3.29 ± 0.01^{b}	3.00 ± 0.01^{c}	3.22 ± 0.01^{c}	3.22 ± 0.01^{c}
Sodium(g/Kg)	0.17 ± 0.01^{a}	0.13 ± 0.00^{c}	0.15 ± 0.01^{bc}	0.14 ± 0.01^{bc}	0.15 ± 0.00^{b}	0.14 ± 0.00^{bc}
Potassium (g/Kg)	0.09 ± 0.00^{a}	0.07 ± 0.01^{c}	0.07 ± 0.00^{c}	0.05 ± 0.01^{d}	0.05 ± 0.01^{d}	0.08 ± 0.00^{b}
Nitrate ion(g/Kg)	0.34 ± 0.00^{a}	0.29 ± 0.01^{c}	0.31 ± 0.00^{b}	0.28 ± 0.00^{d}	0.28 ± 0.00^{cd}	0.28 ± 0.01^{cd}
CEC(Cmol/Kg)	8.35 ± 0.01^{a}	6.06 ± 0.01^{e}	8.04 ± 0.00^{b}	5.87 ± 0.01^{f}	7.46 ± 0.00^{c}	7.07 ± 0.01^{d}
Silt content (g/Kg))	8.34 ± 0.04^{a}	4.49 ± 0.05^{f}	5.82 ± 0.02^{c}	6.80 ± 0.05^{b}	4.99 ± 0.01^{d}	4.76 ± 0.01^{e}
Sand content(g/Kg))	52.38 ± 0.03^{f}	83.12 ± 0.02^{a}	65.50 ± 0.01^{b}	56.94 ± 0.07^{e}	61.39 ± 0.01^{d}	63.13 ± 0.03^{c}
Clay content(g/Kg))	29.23 ± 0.03^{a}	12.17 ± 0.17^{f}	28.69 ± 0.01^{e}	36.27 ± 0.02^{b}	33.66 ± 0.02^{c}	32.13 ± 0.02^{d}
Calcium content(g/Kg)	2.80 ± 0.20^{a}	2.01 ± 0.01^{d}	2.22 ± 0.02^{ab}	2.41 ± 0.01^{bc}	2.62 ± 0.02^{ab}	2.41 ± 0.01^{bc}
Magnesium content(g/Kg)	4.61 ± 0.01^{a}	3.10 ± 0.10^{c}	4.70 ± 0.10^{a}	2.42 ± 0.02^{d}	3.81 ± 0.01^{b}	3.61 ± 0.01^{b}
Phosphate ion(g/Kg)	22.80 ± 0.03^{a}	21.83 ± 0.06^{e}	23.87 ± 0.01^{b}	24.64 ± 0.01^{f}	23.72 ± 0.01^{c}	22.93 ± 0.04^{d}
Total acidity	0.89 ± 0.01^{b}	0.86 ± 0.01^{c}	0.82 ± 0.01^{d}	0.91 ± 0.01^{a}	0.87 ± 0.01^{bc}	0.85 ± 0.01^{c}
Heavy metal						
Lead (Pb) (g/Kg)	0.15	ND	ND	ND	ND	0.20
Cadmium (Cd) (g/Kg)	ND	ND	ND	ND	ND	ND
Chromium (Cr) (g/Kg)	0.01	0.04	ND	0.025	ND	ND

Means followed by the same letter in a row are not significantly different from each other according to DMRT at $P \leq 0.05$.
ND: Not Detected

4.4 Heavy Metal Contents of Samples of Water Hyacinth Plant (*Eichhornia crassipes*) collected from Asa and Malete River

The heavy metal contents of plant samples collected from Malete and Asa River are presented in Table 4.4. It was observed that lead was not detected in plant samples from all the sites except D and F with the value of 0.10 and 0.30mg/L respectively. Cadmium was found to be present in plant samples of sites A (0.01mg/L), C (0.02mg/L) and F (0.02mg/L) but was not found at sites B, D and E. Chromium was found to be present in all the sites except at sample site C; chromium content in plant samples A and B was observed to be the same (0.01mg/L) while plant samples from site D, E and F had chromium content of 0.03, 0.04 and 0.02mg/L respectively. Plant samples from site F were observed to contain all the three metals i.e., lead, Cadmium and chromium at 0.30, 0.02 and 0.02 mg/L respectively.

4.4 Heavy Metals Content of *Eichhornia Crassipes* from Malete and Asa River

Heavy Metals/Site **(mgL^{-1})**	Site A	Site B	Site C	Site D	Site E	Site F	WHO Standard	Status
Lead (Pb)	ND	ND	ND	0.10	ND	0.30	0.30	Normal
Cadmium (Cd)	0.01	ND	0.02	ND	ND	0.02	0.2	Normal
Chromium (Cr)	0.01	0.01	ND	0.03	0.04	0.02	0.02	Normal

ND: Not Detected

4.5 Relationship between the Physicochemical Parameters of Water Samples from Asa and Malete River

The correlation matrix of the physicochemical parameters of water samples are presented in Table 4.5. pH of water shows a strong negative correlation with electrical conductivity and total suspended solids respectively, that is, increase in pH value leads to a decrease in electrical conductivity and total suspended solids. Total nitrogen content of water also shows a negative correlation with sulphate ion, total alkalinity, electrical conductivity and phosphate ion. As such, increase or decrease in total nitrogen brings about decrease or increase in the negatively correlated parameters. Also, from the matrix, it was observed that all other physicochemical parameters of water were strongly positively correlated; phosphate ion was positively correlated with Cl^-, TA and EC. Dissolved Oxygen was positively correlated with NO_3, BOD, COD, TUR, TDS and PO_4^2 although DO shows negative correlation with TS. Total Hardness and Magnesium Hardness are also positively related. SO_4^{2-} also correlated positively with Cl^-, TA, EC, NO^{3-}, BOD, COD and TDS. Chloride ion was also positively correlated with EC, NO^{3-}, BOD, and PO_4^-, Total Alkalinity was positively correlated with TDS and PO_4^-. Electrical Conductivity was also positively correlated with TUR and TDS. NO^{3-} was also positively related with BOD, COD, TUR, and PO_4^-. Turbidity also showed a positive correlation with TSS, TDS and calcium hardness. Finally, TDS and calcium hardness were also seen to be positively correlated.

4.6 The Relationship between the Physicochemical Parameters of Soil Samples from Asa and Malete River

The correlation matrix of the physicochemical properties of soil sample is presented in Table 4.6. Sulphate ion of soil was observed to be negatively correlated with total nitrogen, available phosphorus, organic matter, magnesium ion, sodium and cation exchange capacity while soil pH showed a negative correlation with total acidity. There was a positive correlation between total nitrogen, available phosphorus, magnesium, sodium, and CEC. Available phosphorus was observed to be positively correlated with Magnesium, sodium and CEC. Organic matter content of soil was also positively correlated with Magnesium, sodium and CEC. A positive correlation was also observed between Magnesium ion content of soil, sodium and CEC. Finally, sodium ion and CEC of soil was observed to be positively correlated.

Table 4.5: Correlation Matrix Showing the Relation in the 22 Physicochemical Parameters of Water Samples from Asa and Malete River.

Variables	pH	TN	AP	Ph	DSO	TH	SO_4	CL	TA	EC	NO_3	BOD	COD	NO_2	TUR	TSS	TDS	CH	MH	TS	PO_4
Ph																					
TN	0.26																				
AP	0.53	0.79																			
Ph	0.16	-0.47	0.09																		
DO	-0.50	-0.21	-0.09	0.54																	
TH	0.15	0.06	0.57	0.59	0.17																
SO_4	-0.61	**-0.65**	-0.42	0.66	0.83	0.27															
CL^-	-0.34	-0.62	-0.17	**0.77**	0.49	0.67	**0.82**														
TA	**-0.26**	**-0.24**	0.04	**0.75**	0.95	0.31	**0.81**	0.56													
EC	**-0.15**	**-0.59**	-0.09	**0.93**	0.56	0.61	**0.81**	**0.94**	0.70												
NO_3	-0.61	-0.48	-0.31	0.62	**0.94**	0.21	**0.97**	**0.70**	0.90	0.72											
BOD	-0.61	-0.32	-0.16	0.59	**0.97**	0.26	**0.92**	**0.66**	0.92	0.69	**0.98**										
COD	-0.47	-0.49	-0.22	0.62	**0.87**	0.38	**0.91**	0.72	0.83	0.69	**0.91**	0.88									
NO_2	-0.25	-0.38	-0.19	0.61	0.42	0.11	0.57	0.56	0.53	0.71	0.56	0.55	0.24								
TUR	-0.79	-0.28	-0.19	0.42	**0.79**	0.33	0.87	0.73	0.70	**0.65**	**0.88**	**0.91**	0.74	0.59							
TSS	**-0.98**	-0.26	-0.47	-0.12	0.54	-0.03	0.64	0.40	0.30	0.19	0.63	0.64	0.56	0.16	**0.80**						
TDS	-0.56	-0.27	-0.02	0.66	**0.85**	0.49	**0.88**	0.79	**0.84**	**0.80**	**0.91**	**0.94**	0.79	0.66	**0.95**	0.59					
CH	-0.49	0.36	0.43	0.22	0.61	0.53	0.42	0.40	0.54	0.35	0.53	0.67	0.44	0.31	**0.77**	0.53	**0.77**				
MH	0.39	-0.08	0.50	0.60	-0.04	**0.94**	0.14	0.60	0.15	0.57	0.03	0.04	0.26	0.00	0.06	-0.27	0.25	0.20			
TS	0.24	-0.35	-0.39	-0.23	**-0.80**	-0.27	-0.39	-0.10	-0.73	-0.15	-0.57	-0.67	-0.62	0.06	-0.49	-0.33	-0.56	-0.70	-0.04		
PO_4	-0.65	**-0.46**	-0.30	0.59	**0.94**	0.22	**0.97**	**0.71**	**0.88**	0.71	**1.00**	**0.99**	0.91	0.54	**0.91**	0.68	0.92	0.57	0.03	-0.58	
Total acidity	-0.24	-0.26	-0.64	-0.65	-0.31	-0.63	-0.19	-0.40	-0.50	-0.57	-0.25	-0.35	-0.12	-0.62	-0.33	0.25	-0.55	-0.59	-0.50	0.30	-0.24

TDS: total dissolved solids , TSS: total suspended solids, TS: total solids, COD: chemical oxygen demand and BOD: biochemical oxygen demand

Table 4.6: Correlation matrix of the physicochemical parameters of Asa and Malete soil samples

Variables	**pH**	**Total Nitrogen**	**Available Phosphorus**	**TOC**	**Organic Matter**	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**K^{+}**	**Total Acidity**	**Sulphate ion**
pH											
Total Nitrogen	0.26										
Available Phosphorus	0.53	**0.79**									
TOC	0.58	0.70	0.99								
Organic Matter	0.58	0.70	0.99	1.00							
Calcium	-0.47	0.32	0.44	0.43	0.42						
Magnesium	0.63	**0.81**	**0.94**	**0.94**	**0.94**	0.24					
Sodium	0.19	**0.96**	**0.85**	**0.76**	**0.76**	0.50	**0.78**				
Potasium	0.48	0.69	0.57	0.53	0.53	0.00	0.59	0.64			
Total Acidity	**-0.89**	-0.14	-0.35	-0.44	-0.44	0.48	-0.55	0.01	-0.46		
Sulphate Ion		**-0.86**	**-0.91**	**-0.86**	**-0.86**	-0.46	**-0.87**	**-0.90**	-0.37	0.10	
CEC	0.45	**0.84**	**0.97**	**0.96**	**0.96**	0.47	**0.97**	**0.85**	0.55	-0.36	**-0.91**

Total Organic carbon TOC, Cation Exchangeable capacity CEC

4.7 Principal Component Analysis of the Physicochemical Parameters of Water Samples from Asa and Malete River

Biplot of a standardized PCA-analysis performed on the physicochemical parameters of water samples obtained from both Malete and Asa Rivers is represented in Figure 4.1. The arrows indicate each variable while the dotted points represent the sampling sites of Malete and Asa River. All Parameters such as pH, total nitrogen TN, available phosphorus AP, phosphorus P, dissolved oxygen DO, total hardness TH, Sulphate ion SO_4^{2-}, chloride ion Cl^-, total alkalinity TA, electrical conductivity EC, NO_3, Biological oxygen demand BOD, chemical oxygen demand COD, turbidity TUR, total suspended solids TSS, total dissolve solids TDS, calcium hardness CH, magnesium hardness MH, total solids TS, PO_4 and total acidity were all shown in the biplot. PCA axes 1 and 2 accounted for a variation of 78.27% in the physicochemical parameters of all the sampling sites and the data shows that the sampling sites are consistently different in their characteristics. Axis 1 or PC2 with Eigenvalue of 61.56% mainly represents pH, TN, AP, P, DO, SO_4^{2-}, Cl^-, TA, EC, NO_3, BOD, COD, TUR, TSS, TDS, CH, MH and PO_4. This gradient was negatively associated with axes 2 represented by PC2 of eigen value 16.71% which represents total acidity and total solids.

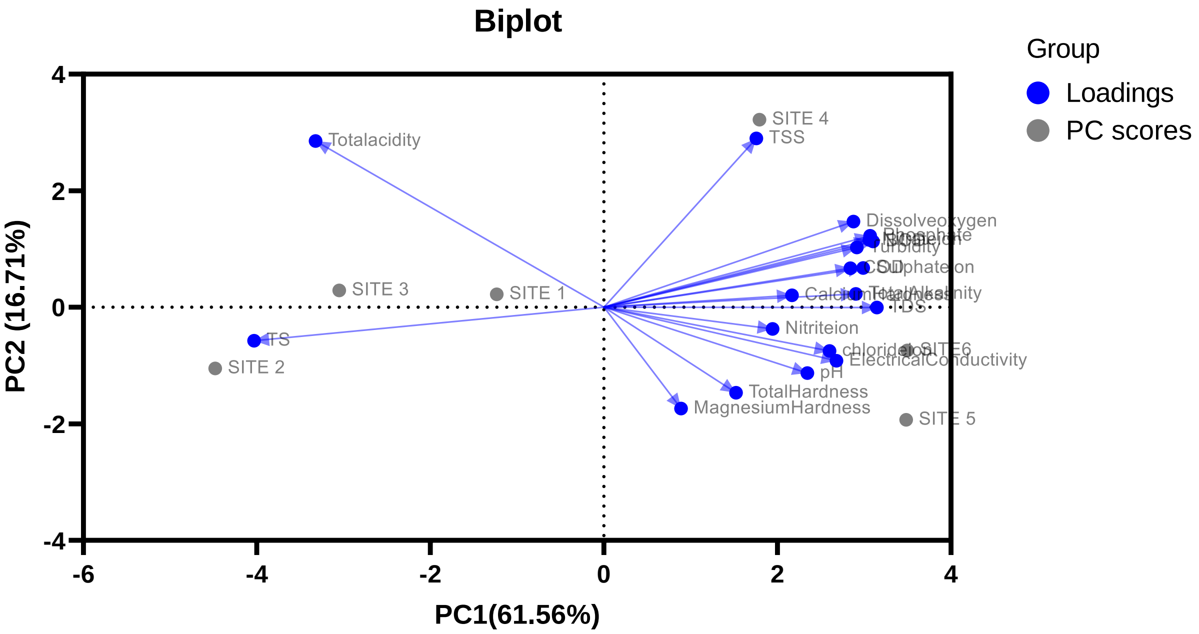

Figure 4.1: Biplot For Water Sample showing the relation among all physicochemical parameters of water in different sites

4.8 Principal Component Analysis of the Physicochemical Parameters of Soil Samples from Asa and Malete River

The biplot of a standardized PCA-analysis performed on the physicochemical parameters of soil samples obtained from both Malete and Asa Rivers is represented in Figure 4.2. The arrows indicate each variable while the dotted points represent the sampling sites of Malete and Asa River. All Parameters such as pH, sulphate ions, potassium, magnesium, Cation exchange capacity CEC, Total nitrogen, available phosphorus, organic carbon, calcium and total acidity were all shown in the biplot. PCA axes 1 and 2 accounted for a variation of 87.64% in the physicochemical parameters of all the sampling sites and the data shows that the sampling sites are consistently different in their characteristics. Axis 1 or PC2 with Eigen value of 67.53% mainly represents Calcium, Sodium, Total nitrogen, Cation exchange capacity CEC, available phosphorus, organic matter, organic carbon, Magnesium and potassium and pH. This gradient was negatively associated with axes 2 represented by PC2 of eigen value of 20.11% which represents total acidity and sulphate ion.

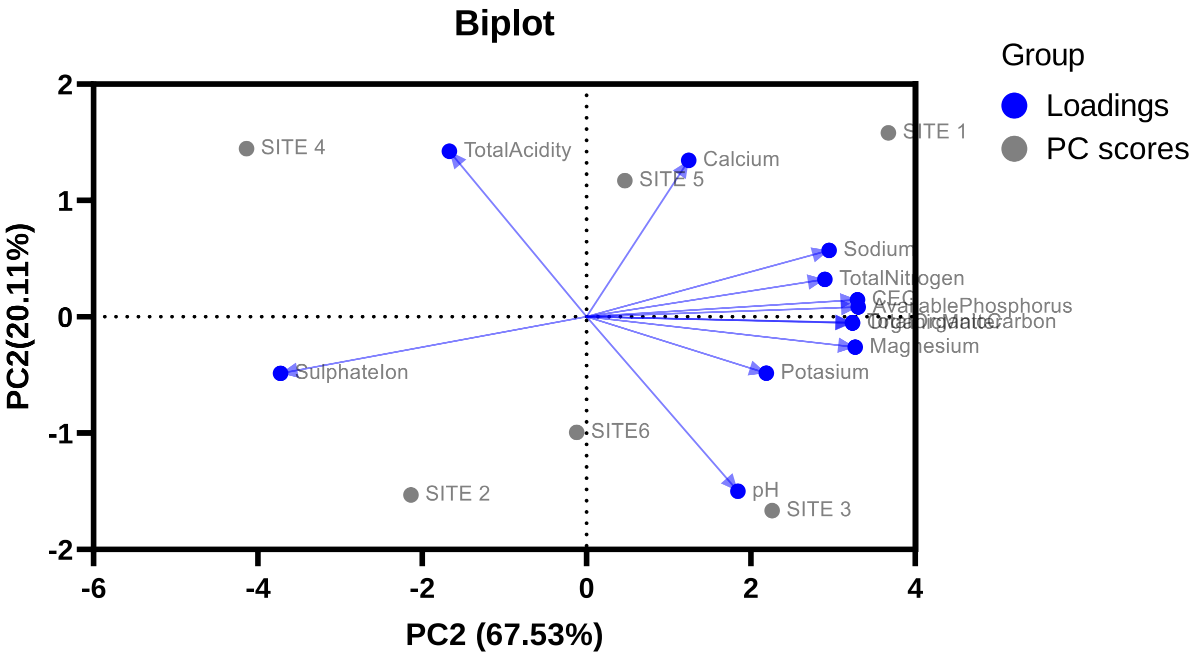

Figure 4.2: Biplot for Soil Sample Showing the Relation Among All Physicochemical Parameters Of Soil In Different Sites

CHAPTER FIVE

DISCUSSION, CONCLUSION AND RECOMMENDATIONS

5.1 Discussion

The physicochemical properties of Malete and Asa Rivers revealed information about the condition of the two water bodies. The pH of water obtained from Malete was observed to be less acidic or close to neutrality. Edokpayi *et al*. (2016) in their study on Mvudi River reported that the slight acidic nature of the water could be as a result of farming, cattle rearing and other agricultural activities that are usually being carried out around this area. It could also be an indication of River being impacted by anthropogenic activities such as discharge of organic refuse, organic matter, municipal drains, sewage discharge or industrial effluents (Arimieari *et al*., 2014). Water samples from Asa were observed to be slightly alkaline in nature especially those obtained from Amilengbe and Gada bridge; this could be as a result of the presence of carbonates and bicarbonate of Ca and Mg from runoff from agricultural fields (Patil *et al.*, 2016). It could also be as a result of pollution caused by continual dumping of refuse that contain some element of Ca or Mg into the water bodies in the location. In the report of Naka *et al*. (2016), variation in pH values maybe as a result of retention of metals which possibly translated to the corresponding increase in conductivity value. However, the pH range of the water samples from the two site falls within the standard pH range of 6.50-8.50 for drinking water and irrigation purposes according to WHO and FAO (WHO, 2008); thus, water samples from the two sites (i.e. Asa and Malete River) are safe for consumption and irrigation although some form of purification is required in order to further ensure its safety before usage.

The correlation matrix also shows that pH value correlate negatively with electrical conductivity and total suspended solids. This implies that high pH value brings about reduction in the level of electrical conductivity and total suspended solids available in the water while a decrease in the pH value leads to an increase in these parameters (Narendra *et al.,* 2008). This negative correlation could be as a result of different pollution loads from each of the sampling sites which might have different contents.

The WHO standard for Dissolved Oxygen of drinkable water is 5.0 mg/L for drinking water and while that for agricultural purposes should be more than 5 mg/L (Adekunle *et al.,* 2007). The low level of Dissolved Oxygen observed at site B could be the reason why there is little or no form of any biological activities in this site and very low DO may result in anaerobic conditions that cause bad odors (Adekunle *et al., 2007*). Amah-Jerry *et al*. (2017) and Okey-Wokeh *et al*. (2021) in their reports on Aba River attributed the reduced level of dissolved oxygen to abattoir and sewage discharges into the water that thereby indicates the water pollution level which can affect the aquatic life. The high level of DO at site F (Gada bridge) indicates that there is high level of biological activities going on in this site and as such increase the level of oxygen available for the aquatic life in that area.

Dissolved oxygen was observed to be positively correlated with Biological oxygen demand, Chemical oxygen demand, nitrate ion, turbidity, total dissolve solids and phosphate ion though a negative correlation was observed with total solid. Thus, the high level of Dissolved Oxygen observed at Gada bridge could be responsible for the increase in other parameters that correlates positively with it. In other words, dissolved oxygen was observed to be generally low at Malete River compared to that of Asa and as such there is more biological activities going on in Asa compared to Malete

Amilengbe water samples were observed to have high value for total hardness due to the presence of high magnesium content. The high sulphate ion contents observed at Gada bw12ridge was observed to increase the level of chloride ion, total alkalinity, electrical conductivity, nitrate ion Biological oxygen demand, chemical oxygen demand, total dissolve solids and phosphate ion.

The total hardness of water varied between 1.14 mg/L to 1.64mg/L which is lower than those reported by Oyedeji *et al.* (2013). Water samples from Amilengbe (site E) had the highest level of hardness and this implies that there is presence of some bicarbonates of either magnesium or calcium in this site while site D (i.e. main body of Asa water) with a low value for total hardness has little or no bicarbonates of such ions in them. Total Hardness occur mainly due to weathering of Ca and Mg-rich rocks that surrounds such area (Zeitoun and Mehana, 2014) and the heavy concentrations of these ions could lead to massive salt build-up on the roots of plants found in this area as well as the aquatic environment thereby leading to nutrient lockout of varying degrees. In plants, hardness could lead to inability of plants to take up a proper balance of all the required nutrients and when hardness becomes very high, the plant could be hindered from getting the essential nutrients required for normal plant growth and survival which could eventually lead to the death of the plant (Patil *et al*., 2012).

Sulphate ion content for both water and soil was low at Malete while it was high at Asa Rivers. Sulphate ion is one of the major anions in natural waters and is contributed by industrial and household discharges, as contaminant from tanneries, textiles, etc. This often leads to decrease in pH of River water and increases bacterial load, i.e. sulphate reducing bacteria (Ftsum *et al.,* 2015). As such, it could be deduced that the amount of debris entering Malete River is low compare to those in Asa River. Generally, the sulfate ion concentration in natural water bodies ranges from a few to a several hundreds of mg/l with no major negative impact of sulfate on human health (Abdolmajid *et al.*, 2014). The WHO standard of sulphate for drinking water should not exceed 500 mg/L thus all the water samples used for this experiment conform to the WHO standard.

The chloride ion content of the water sample as shown in the table varied between the range of 12.76mg/L for extreme end of Malete River and 21.98mg/L for water samples obtained from Amilengbe. According to WHO, the standard concentration of chloride should not exceed 250mg/L (Abdolmajid *et al.*, 2014) therefore all the water samples from the two sites falls within the WHO standard.

In this study, Electrical Conductivity was observed to be highest at the main body of Asa while it was found to be low at the extreme end of Malete River. Conductivity which could be as a result of groundwater seepage or a sewage leakage sometimes, usually gives an estimate of the presence of electrically charged ions in water especially in oil producing states. Such electrically charged ion includes carbonate, bicarbonates, chloride, sulphate, nitrate, sodium, potassium, calcium and magnesium ions (Tadesse *et al.*, 2018). The recommended value for conductivity is ≈ 750 μS/cm (WHO, 2008), therefore, the conductivity for the two sample sites was very low compared to the WHO standard indicating that the electrically charged ion in the two Rivers are very minute thereby making the water safe for aquatic life, agricultural process/ irrigation as well as human consumption.

High electrical conductivity is an indication of the presence of electrically charged ion. High concentration value of electrical conductivity recorded in Asa River could probably be associated with the effluent discharge from dissolved substance from soap factory, municipal effluent discharged from residential community and chemicals that are applied to farm land which are being washed into the water body as reported by Tadesse *et al.*(2018) in his work on Rebu River.

According to WHO, the normal standard BOD for drinking water should not exceed 6 mg L^{-1} (De, 2003), therefore, the BOD of water from all the selected sites which ranged from 2.10 – 3.75mg/L conform with that of WHO standard. In cases where the level of BOD is high, it is an indication of a higher rate of decomposition of organic matter at a very high temperature aided by less water current (Sanap *et al.*, 2006) thereby indicating pollution, which could be attributed to high level of organic content of abattoir effluent released into the water body (Okey-Wokeh *et al.*, 2021).

In most water bodies, turbidity imparts a brown or other colour depending on the light absorbing properties of such water and it may interfere with light penetration, aesthetic view as well as photosynthetic reactions or activities. Turbidity also increases the total available surface area of solids in suspension that can aid the growth of bacteria. High turbidity value reduces light penetration; thereby affecting photosynthesis of submerged vegetation and algae which in turn suppresses fish productivity (Tadesse *et al.*, 2018). According to WHO (2008), the turbidity level is 5NTU, thus, the range of turbidity for this study is lower than that of the WHO standard. The high turbidity value observed at site E (Amilengbe bridge) may be due to human activities going on in this area especially dumping of refuse which affect the light penetration in the site there by bringing about the reduced photosynthetic activities in this area. Site C had the lowest turbidity value which indicates that the water here is crystal clear and also gives an insight into the light penetrating properties of this site thereby enhancing the photosynthetic activities that was observed in this area as could be seen by the high number of plants found in this area.

Total Suspended Solids in both sites fall within the standard limit of >500 mg/ L reported by the World Health Organisation (Jain *et al.*, 2006). Furthermore, the TSS range for Asa River in this report is 2.92 – 4.56 mg/L; this is quite lower compared to the range of 182.0 - 218.4 mg/L reported by Oyedeji *et al.* (2013).

According to WHO, the normal values of total dissolve solids (TDS) for water ranges from 500-1000mg/L (Wali *et al.*, 2015), thus site D, E and F (all water samples from Asa River) fall within the WHO standard range while samples obtained from sites A, B and C (all water samples from Malete River) fall below the range. The low level of TDS observed at Malete water body shows that the rate of human activities as well as dumping of refuse into this water body is reduced or very low compared to that of Asa. High content of dissolved solid elements as found in site F, affect the density of water, influences osmoregulation of freshwater in organisms, reduces solubility of gases (like oxygen) and utility of water for drinking, irrigation and industrial purposes (Tadesse *et al*., 2018). It could also cause harmful effects to public health such as damage of central nervous system, dizziness and provoking paralysis of tongue (Gupta *et al*., 2003).

Calcium is one of the required elements for plant growth and as such most farmers apply it to the soil (i.e. the plant root) in form of lime or gypsum. Thus, excessive application of this could be washed away into the surrounding body of water which could change the aquatic environment and affect the life that exists there. Thus, the high content of calcium observed at samples site A could be due to the farming activities going on there as well as human day to day activities seen to be carried out in this region. Calcium is known to be one of the causes of hardness of water though it is essential to human nutrition and a key element in the formation of teeth and bones (Pooja, 2017). The high content of this particular element as observed in main body of Asa water and its surrounding soil could make the water to become hard, unsafe for consumption, dangerous for plant growth as well as threat to aquatic life at large. Magnesium is one of the most common elements in the earth's crust and its sulfates at a very high concentration may have a laxative effect on health (Pooja, 2017). Magnesium is also one of the constituents of hardness in water thus it gives an unpleasant taste at high concentration.

Phosphoric content of water ranged from 0.31 – 1.36 mg/ L. This range is quite well above the 5mg/ L that was likely to reduce the survival of algal bloom and growth of aquatic plants

(Adekola and Eletta, 2005). Site D was observed to have the highest level of phosphorus while site B had the lowest. The phosphoric content of soil ranged from 24.64 to 21.83mg/L with soil sample of site D having the highest and B having the lowest content of phosphorus. By virtue of implication, we can say that the runoff from the soil which likely contains phosphorus is probably due to the use of phosphorus-based fertilizer which is most responsible for the level of phosphorus in the surrounding water bodies. This therefore leads to the high growth of algal bloom observed in site D and the low growth found in site B, which goes in line with the report of Kroiss *et al.* (2011) that Phosphorus has been known to be the limiting nutrient factor for algae (autotrophic) growth in most fresh water bodies (lakes, Rivers and reservoirs) and some coastal waters influenced by River discharges. Thus, the continual discharge of phosphorus to the water bodies led to increase in the potential growth of algae which is the starting point of eutrophication. Furthermore, the increasing build-up of phosphorus in lawns, gardens, pastures and croplands can lead to deterioration of plant growth or in some cases; it could lead to death (Raymond *et al*. 2011). Also, Water hyacinth (*Eichhornia crassipes*) from Gada bridge was detected to have high value of lead content compared to the amount found in other sample sites. This indicates that the refuse being dumped in this River possibly contain lead which thereby leads to accumulation of this metal in the plant body especially during nutrient uptake. Cadmium was detected from samples of this plant obtained from Asa River but was absent from those of Malete. Also, there was a trace of chromium in the entire sample site except at site C, thus, the pollution level of site C is very low compared to that found in other sites.

The PCA results from this study showed that physicochemical parameters of water and soil of the Rivers such as PH, salinity, EC and TDS showed strong variation amongst different sampling sites across the two Rivers. The different types of activities at different points of the Rivers negatively affected the water and soil quality and made relationships between most of the parameters complex. It was observed that DO, PH, Nitrated ion, electrical conductivity total hardness, sulphate ion, turbidity, magnesium, chloride and calcium significantly contributed to the quality of water in Asa River and most of the parameters did not have significant impact on the quality of water in Malete River.

5.2 Conclusion

Water from Asa Dam was observed to be high in total alkalinity, Dissolved Oxygen, Total Hardness, sulphate ion, chloride ion, electrical conductivity, Biological Oxygen Demand, Chemical Oxygen Demand, Turbidity, Total suspended Solids, Total dissolve solids, Magnesium hardness, Total solid and phosphate ion while that of Malete was high only in calcium hardness. This indicates that water from Asa River had higher values of physicochemical parameters compared to that of Malete River though both Rivers still fall within the permissible limit of drinkable water as recommended by World Health Organisation. Although the parameters studied were within WHO standards, it is advisable to still take some purification techniques before using for domestic purposes. The level of the presence of these physicochemical parameters had effects on the surrounding soil as well as on the growth of *Eichhornia crassipes* in each of the sites. In other words, the abundance of plants especially *Eichhornia crassipes* found in all sample sites of Asa could be as a result of the high presence of some of these parameters as shown in the PCA which hereby makes the environment favourable for their survival. Therefore, it could be concluded that water from Malete is safer with low level of physicochemical parameters compared to that of Asa.

5.3 Recommendations

Water, for both domestic and commercial use, is very crucial for survival. Thus, there is every need to ensure that water remain safe and clean at all time. The presence of high level of physicochemical parameters that was observed at Asa River is quite expected because people from this location are fond of dumping refuse carelessly due to the fact that there is little or no proper form of refuse disposal. Governments are hereby encouraged to look into the waste management scheme and ensure that there is adequate provision for disposal of waste. The citizenry should also be enlightened on the dangers attached to indiscriminate dumping of refuse and should desist from it.

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Appendix 1: Comparison between the Observed Range Value of Some Physicochemical Parameters of Water and other Articles

Physico chemical parameters	Observed Ranges	Standard Range
pH	6.70-7.25	6.50-7.25(WHO, 2008)
Dissolved Oxygen (mg/L)	3.60-5.94	5.00-7.00(WHO, 2008)
Total Hardness(mg/L)	1.14-1.64	300(WHO, 2008)
Sulphate ion(mg/L)	21.49-33.23	250(WHO, 2008)
Chloride ion(mg/L)	12.76-21.98	250(WHO, 2008)
Total Alkalinity(mg/L)	2.40-4.00	120(WHO, 2008)
Electrical conductivity(µS/cm)	60.41-86.21	750(WHO, 2008)
Nitrate ion(mg/L)	2.63-3.57	50(WHO, 2008)
BOD(mg/L)	2.10-3.75	7.78-13.90(Oyedeji *et al., 2013*)
COD(mg/L)	1.40-3.30	129.00-150.30(Oyedeji *et al., 2013*)
Nitrite ion(mg/L)	0.01-0.03	3(WHO, 2008)
Turbidity (NTU)	1.63-3.51	5(WHO, 2008)
TSS(mg/L)	2.70-4.56	182-218.40(Oyedeji *et al., 2013*)
TDS(mg/L)	3.56-5.52	<100(WHO, 2008)
TS(mg/L)	5.17-9.39	-
Calcium Hardness (mg/L)	0.26-0.42	100(WHO, 2008)
Magnesium Hardness(mg/L)	0.78-1.24	50(WHO, 2008)
Phosphate(mg/L)	0.40-1.35	0.44-3.43 (Oyedeji *et al., 2013*)

Pictorial representation of Malete River

Pictorial representation of Asa River

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