

**CHEMOMETRIC CHARACTERISATION OF SOME HEAVY METALS AND
PHYSICOCHEMICAL PROPERTIES OF SELECTED WATERBODIES IN
MINNA, NIGER STATE, NIGERIA**

BY

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NIGER STATE**

NOVEMBER, 2023

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ABSTRACT

Heavy metal contamination in aquatic environment is a threat to humans due to their non-degradability and bioaccumulation in aquatic life. In this study, selected heavy metals: Pb, Mn, Zn, Cd, Cu and Cr, as well as physicochemical parameters: pH, temperature, turbidity, silica, nitrite, nitrate, nitrite-nitrogen and ammonia were analyzed in sediments and water samples from Bosso Dam, Chanchaga River and Tagwai Dam in Minna during dry and rainy seasons to determine the pollution status of the Waterbodies. A total of 120 water and sediment samples were collected during rainy and dry seasons in Chanchaga River, Tagwai Dam and Bosso Dam. The samples were digested using Wet Digestion Method. The selected heavy metals were analyzed using Atomic Absorption Spectroscopy (AAS) while other physicochemical parameters were determined using standard established methods. The data obtained were subjected to Principal Component Analysis (PCA), Hierarchical Cluster Analysis (HCA) and Correlation Analysis. The range of concentrations of the heavy metals in water and sediment samples ranged as follows: Pb (ND-0.01 mg/dm³), Mn (ND-0.09 mg/dm³), Zn (ND - 0.12 mg/dm³), Cd (ND - 0.04 mg/dm³), Cu (ND - 0.04 mg/dm³) and Cr (ND-0.03 mg/dm³) for rainy and dry seasons. The range of concentrations of the physicochemical parameters were as follows: pH (4.41 - 7.75), temperature (25.03-27.95°C), silica (ND-11.01 mg/dm³), ammonia (0.41-14.52 mg/dm³), turbidity (14.54-80.86 NTU), conductivity (74.04 - 430.07 µS/cm), nitrite (ND - 0.41 mg/dm³), nitrite-nitrogen (ND - 0.13 mg/dm³) and nitrate (ND - 21.68 mg/dm³). Principal Component Analysis of the datasets showed nitrate, nitrite-nitrogen, turbidity and pH as the most prominent variables among the water and sediment samples. Hierarchical Cluster Analysis (HCA) of the water samples grouped all 60 samples into four (4) significant clusters with similar characteristics and pollution source types. Similarly, HCA of the water and sediment samples showed four and three sample groups based on or the similarity or dissimilarity of their pollution status. Correlation analysis showed positive relationship among conductivity and temperature, nitrate and nitrite-nitrogen in the water samples. Positive correlation also occurred between temperature and silica (0.715 mg/dm³), conductivity (0.860 µS/cm) and Zn (0.601 mg/dm³). The results of the analysis showed the pollution in Bosso Dam, Chanchaga River and Tagwai Dam to be above permissible limits of World Health Organisation (Cu/0.01 mg/l; Zn/0.01 mg/l; Mn/0.10 mg/l; Cd/0.003 mg/l; Pb/0.001 mg/l; Cr/0.05 mg/l; pH/7.50; temperature/25.00; silica/10.00 mg/l; turbidity/5.00 NTU; conductivity/1000 µS/cm; nitrite/3.00 mg/l; nitrite-nitrogen/0.04; ammonia/0.40 mg/l and nitrate//10.00 mg/l).

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CHAPTER ONE

1.0

INTRODUCTION

1.1 Background to the Study

Contamination of aquatic environment by heavy metals is a critical concern due to their potential toxicity and accumulation in aquatic habitats (Tscheikner-Grantl *et al.*, 2021). Heavy metals enter water bodies through natural and anthropogenic sources (Zhou *et al.*, 2020). Heavy metals are a group of metals that have relatively high density compared to water and are toxic even at low concentrations. Examples of heavy metals include cobalt, lead, mercury, arsenic, thallium, nickel, manganese, zinc, cadmium and chromium that have a particular significance in ecotoxicology, due to their high persistence (Ghori *et al.*, 2019). Contamination of water bodies by heavy metals may result from direct atmospheric precipitation, geologic weathering or through the discharge of agricultural, municipal, domestic or industrial waste products (Franco-Uria *et al.*, 2019).

The sediments existing at the bottom of the water column play a major role in the pollution of water bodies. They reflect the pollution status of water system and are used to detect insoluble pollutants that are discharged into water bodies (Vink, 2019). Sediments act as sinks for contaminants and under favourable conditions, the contaminants in the sediments remobilizes in water systems (Nekoeinia *et al.*, 2019). It has been reported that heavy metal pollution records in sediments reveal significant impacts on the environment in aquatic environments (Selvam *et al.*, 2018). Heavy metals that enter aquatic environments are absorbed and preserved in sediment where they enrich aquatic organisms through the food chain. Ways heavy metals can recycle into the water column include sediment re-suspension, adsorption and change in chemical conditions (Bolawa and Yusuff, 2019).

Physicochemical parameters, such as pH, temperature, conductivity and turbidity define the quality of water and affect its acceptability for drinking and domestic uses. It is essential to test the water before being used for drinking, domestic, agricultural or industrial purpose. Selection of parameters for testing of water depends upon for what purpose the water will be used (Alexandra *et al.*, 2018).

It is therefore essential to prevent and control water bodies' pollution, and regularly implement monitoring programmes which help to understand the temporal and spatial variations in water bodies' quality (Osman and Faust, 2018). However, many monitoring programs result in large and complicated data sets consisting of physical properties, nutrients and inorganic constituents, and biological and microbiological situations, which are difficult to analyze and interpret because of the latent interrelationships among parameters and monitoring sites. It is therefore necessary to extract the meaning information from data sets without losing meaningful information (Chen *et al.*, 2018).

Principal component analysis (PCA) is a dimension-reduction method that is used to convert a large number of related original variables into a smaller number of uncorrelated variables called principal components, which are linear combinations of the original variables (Passos *et al.*, 2018). Among the statistical techniques, both principal component analysis (PCA) and cluster analysis (CA) are useful methods to discover common patterns in data distribution, leading to initial dimension reduction of datasets and helping its interpretation. PCA and CA assist to set up analyzed parameters in different factors/groups on the basis of contribution from their possible sources. The explanation of data processing helps to identify pollution sources and allocate natural vs. anthropogenic contribution (Han *et al.*, 2018).

Summarizing, it can be stated that chemometric techniques are useful tools for the evaluation and interpretation of pollution data. Much information is lost by using only univariate graphical or statistical methods for data evaluation and interpretation (Biancolillo and Lessandra, 2018). Previous studies have analyzed water bodies to determine the level of pollution them, However, applications of different Chemometrics methods to the analysis of water bodies are not common in Nigeria.

In this study, Chemometric methods were applied for the evaluation and interpretation of water bodies' pollution datasets. This analysis could be helpful for the appropriate authorities to optimize water monitoring plan and enhance their pollution control actions.

1.2 Statement of the Research Problem

Bosso Dam, Chanchaga River and Tagwai Dam are surrounded by places of increased anthropogenic activities. Different kinds of effluent are discharged into these water bodies including municipal effluent and run-offs. These effluent and activities are major sources of heavy metals input into the water bodies. This may result in bioaccumulation of heavy metals in consumers using the water bodies. Heavy metals in these water bodies can also come in direct contact with roots of plants planted by the river banks. When these plants are consumed by man, heavy metals become bioaccumulated and eventually result in several ailments which may subsequently cause death. In some cases, plants accumulate some of these metals which may be poisonous to animals grazing on the plants (Nabuloa *et al.*, 2019). Sediments act as carriers and possible sources of pollution because heavy metals are not permanently fixed by them and can be released back to the water column by changes in environmental conditions (Nemati *et al.*, 2018).

Environmental data are characterized by high variability. Uncertainties resulting from sampling, sample conservation and pretreatment, analytical measurement, and calibration are contained in environmental pollution data. Analytical results of river investigations, as usually obtained in routine environmental monitoring, also contain that variability (Jurgen *et al.*, 2018). Much information is lost by using conventional statistical methods for data evaluation and interpretation (Alfred *et al.*, 2018). Hence, there is need to extract as much meaningful information from pollution as possible.

1.3 Justification of the Study

Bosso Dam, Chanchaga River and Tagwai Dam are used for irrigation, fishing and domestic purposes. This analysis will provide information on the degree of contamination of the water bodies. This will make it possible to understand the present contamination level and plan management strategy accordingly. This analysis will also bridge the communication gap by providing sufficient latent data on quality of water consumed and used for domestic purposes (Jurgen *et al.*, 2018).

Monitoring of anthropogenic release of heavy metals is usually done to determine the distribution of pollutants and apportionment of sources. Chemometric method helps in the visualization of the large amount of data and extraction of latent information that is often contained in environmental data to detect differently polluted areas, pollution sources, and pathways between different environmental compartments. Thus, this analysis is justified to enable a deeper and more objective assessment and interpretation of pollution data (Idowu, 2020).

The analysis of heavy metals in sediments permits pollution detection that could escape water analysis, and also provides information about the critical sites of the water system which is under consideration (Storelli *et al.*, 2018). The distribution of heavy metals in

sediments are also very important when characterizing the pollution history of aquatic systems, and it has proved very useful for distinguishing the heavy metals in sediments that are impacted by natural or anthropogenic factors (Abliz *et al.*, 2018). Therefore, it is meaningful to study the variations of heavy metals in aquatic ecosystem and sediment throughout the entire areas.

1.4 Aim and Objectives of the Study

This research focuses on the analysis of selected heavy metals content and physico-chemical parameters in sediments and water from Bosso Dam, Chanchaga River and Tagwai Dam, and application of chemometric techniques to the data obtained.

The Objectives of the Study are to:

- i. Determine Pb, Mn, Zn, Cd, Cu and Cr in water and sediments from selected water bodies in Minna metropolis during rainy and dry seasons.
- ii. Assess the physicochemical characteristics such as pH, temperature, turbidity, silica, nitrite, nitrate, nitrite as nitrogen and ammonia in water and sediments from the selected water bodies in Minna metropolis during rainy and dry seasons.
- iii. Apply Chemometric techniques of Principal Component Analysis (PCA), Hierarchical Cluster Analysis (HCA) and Correlation analysis to classify, characterise and correlate samples and pollution parameters.

CHAPTER TWO

2.0

LITERATURE REVIEW

2.1 Heavy Metals in Aquatic Ecosystem and their Toxicity

Heavy metals refer to any metallic chemical element that has relatively high density with specific gravity that is at least five times the specific gravity of water (Ling *et al.*, 2020). Aquatic environments are receiving increasing levels of heavy metals with anthropogenic sources being the major sources of heavy metal pollutants in aquatic systems. Sediments are important sinks for various pollutants such as pesticides and herbicides while, heavy metals in surface water may exist as simple hydrated ions as well as inorganic and organic complexes (Sivakumar and Xiaoyu, 2018).

Some heavy metals such as copper (Cu), zinc (Zn), iron (Fe), chromium (Cr), manganese (Mn) and nickel (Ni) though essential to human body, are toxic at elevated levels, whereas cadmium (Cd) and lead (Pb) are non-essential metals and are toxic even in trace amounts (Selvam *et al.*, 2018). Toxicity is highly aggravated by their non-degradability and tendency to bio-accumulate to toxic levels (Masindi and Muedi, 2018). Heavy metal toxicity can result in lower energy levels and damage blood composition, lungs, liver, kidneys and other vital organs, damaged or reduced mental and central nervous function or even cause cancer (Masindi and Muedi, 2018). Heavy metal poisoning is more likely to result from inhalation, ingestion, skin contact with the metals or compounds from dust, fumes or materials from work place or in residential settings, especially homes with lead paints or old plumbing (Aminayanaba and Lawal, 2019).

2.1.1 Lead

Lead has a density of 11.3 g/cm³ atomic number 82 and is obtained from its sulphide mineral galena, carbonate cerussite, and sulphate anglesite (Isibor *et al.*, 2019). The ores

are frequently found in combination with other recoverable metals such as Cu, Zn and Cd. Lead exists in various oxidation states (0, I, II and IV), which are of environmental importance with oxidation +2, the form in which most Pb is bio-accumulated by aquatic organisms (Akan *et al.*, 2018). Lead was placed position 2 on the Agency for Toxic Substances and Disease Registry's (ATSDR), top 20 list of most dangerous heavy metals and it accounts for most of the cases of paediatric heavy metal poisoning. Lead has been used in pipe making, drains and soldering materials as well as battery manufacture, plumbing, ammunition, fuel additives, paint pigments and pesticides.

Lead pollution has been an environmental concern due to its toxicity and bioaccumulation in aquatic environments, as well as persistence in the natural environment. Some effects of Pb poisoning include deficiency in cognitive function due to destruction of the central nervous system, abdominal pain and discomfort, formation of weak bones as Pb replaces calcium and causes anaemia due to reduction of enzymes concerned with synthesis of red blood cells (Cherh and Jih-Gaw, 2018). Lead also leads to decreased fertility, causes cancer and other minor effects like vomiting, nausea, and headache (WHO, 2018). Exposure to high Pb levels can severely damage the brain and kidneys, cause miscarriage in pregnant women, damage the organs responsible for sperm production in men and it may ultimately cause death (WHO, 2018).

Mean levels of Pb in sediments from Tyume River, were reported to range between 0.040 ± 0.005 and 0.067 ± 0.003 mg/kg, and Pb in sediments from River Nile exhibited a wide range of variation ranging from 3.1 to 76.9 mg/kg that was higher than the permissible limit of 35 mg/kg, meaning that, Nile river was polluted and needed constant control and assessment (Osman and Faust, 2018).

Elevated levels of Pb could be directly detrimental to the health of the aquatic ecosystem and indirectly to man. The sediments could be a contributing source of these heavy metals in water, hence continual assessment is highly essential (Dalu *et al.*, 2018). Some of the effects of Pb poisoning include deficiency in cognitive function due to destruction of the central nervous system, abdominal pain and discomfort, formation of weak bones as Pb replaces calcium and causes anaemia due to reduction of enzymes concerned with synthesis of red blood cells.

Also, Agatha (2020) recorded Pb mean levels of 9.43 mg/kg from Forcados River in sediment samples that were lower than the WHO recommended limit of 35 mg/kg. Decreasing concentrations of Pb metal away from pollution point has been recorded which was attributed to dilution effect as a result of runoff or rain water with a big part of heavy metals in sediments being released back to water compartment in the process of remobilization (Agatha, 2020).

Studies from Ikpoba River recorded Pb mean concentration of 0.035 mg/l in water which surpassed the recommended limit of 0.01 mg/l for drinking water set by WHO (Isibor *et al.*, 2019). Isibor *et al.*, (2019) reported that the level of Pb in the water though lower than <1 mg/l value recommended for potable drinking water by the Federal Ministry of Environment and the World Health Organization requires that caution be taken in the discharge of effluents without treatment into Nigeria's in-land water bodies. This is because anthropogenic sources have been implicated as the major cause of pollution in aquatic environment (Isibor *et al.*, 2019).

2.1.2 Manganese

Mn is found naturally in rocks and soil. The major anthropogenic sources of Mn include emission from Mn ore mining, alloy production, welding, ceramic production and

leaching from electronic components (Macdonald and Okaka, 2021). Mn-related complications include psychiatric and motor disturbances, termed manganism which has occurred in people employed in the production and processing of Mn alloys. People exposed to high levels of environmental pollution by Mn suffer from cerebella dysfunctions, neurological damage as was once observed in inhabitants of Groote Eylandt off the North coast of Australia (Ernst, 2020).

Studies of Mn in sediments from Nairobi River recorded levels that ranged from 1598.33 to 4322.83 mg/kg. Mn concentration in sediments from River Nile ranged from 139.8 to 351.8 mg/kg (Osman and Faust, 2018). Various levels of Mn in river water that have fluctuated from the WHO recommended limit of 0.4 mg/l have been reported (Osman and Faust, 2018). Mn levels from River Nile that was within the recommended limits fluctuated between 0.033 and 0.14 mg/l while higher levels of 2.5 and 0.423 mg/l were recorded from Nairobi River and River Ganga respectively (Osman and Faust, 2018). The higher levels than the recommended limit of 0.4 mg/l was attributed to a sudden rainfall followed by high river discharge from upstream environment, industrial effluents and municipal wastes, geology of river bed and catchment area (Kar *et al.*, 2020). Adoption of adequate measures to remove the heavy metal load from the industrial waste water and renovation of sewage treatment plants are suggested to avoid further deterioration of the river water quality (Kar *et al.*, 2020).

MacDonald and Okaka (2021) assessed the status of Mn pollution in water samples from Warri River in Delta State of Nigeria, using Atomic Absorption Spectroscopy. Mn was observed at a value of 0.68 mg/l which is above World Health Organisation's limit of 0.10 mg/l. There result was linked with effluents from industrial, agricultural and domestic sources (Macdonald and Okaka, 2021).

Thomas (2019), described a polarographic method for determining manganese (II) in waters which covers the concentration range 10–300 µg/L. The method, which is specific to manganese (II) and its labile complexes, is used in conjunction with a colorimetric technique to compare the levels of manganese (II) and total dissolved manganese in an estuarine system. He showed that the polarographically determined manganese (II) can vary widely from 100% to less than 10% of the total dissolved manganese, determined spectrophotometrically at 450 nm by the formaldoxime method calibrated in saline medium to overcome any salt effects. It is suggested that the manganese not measured by the polarographic method is in colloidal form.

2.1.3 Zinc

The toxicity of Zn is as a result of excessive absorption which suppresses copper and iron absorption while free Zn²⁺ ion in solution is highly toxic to plants, invertebrates, and even fish. Zinc salts are intestinal irritants and can cause nausea, and abdominal pain. Prolonged exposure to high intakes of Zn results in copper deficiency and subsequent anaemia (Ernst, 2020). There is also a condition called the zinc shakes or "zinc chills" that can be induced by the inhalation of freshly formed Zn oxide formed during the welding of galvanized materials. It has been reported that zinc is able to damage nerve receptors in the nose, which can cause anaemia and recommended that consumers should stop using zinc-based intranasal cold products and ordered their removal from store shelves (Cristian, 2020).

River sediments have been found to have levels of Zn in a number of rivers with values that vary from the recommended limit of 123 mg/kg (Osman and Faust, 2018; Agatha, 2020). Zinc concentrations of 91.5 to 307 mg/kg have been recorded in sediments from Nile River during the dry season. 34.61 mg/kg from Forcados River's sediments and 126.33 - 307.00 mg/kg from Nairobi River's sediments were obtained where some did

not constitute immediate hazard to aquatic fauna and human consumers (Agatha, 2020). A concentration of 0.60 mg/kg from Nairobi River was found to be below the recommended limit of 123 mg/kg for Zn in sediment (Wachira *et al.*, 2019). Constant monitoring of levels of contamination to assess the impact of heavy metals in the aquatic system was, however, recommended (Agatha, 2020).

Levels of Zn in rivers flowing through industrial or mining areas can be as high as 20 mg/l while soils contaminated with Zn through the mining of zinc-containing ores, refining, or where zinc-containing sludge is used as fertilizer, can contain several grams of zinc per kilogram of dry soil. A higher Zn mean level of 76.25 mg/l than the 3 mg/l recommended limits was recorded from Forcados River while lower mean levels of 0.085 mg/l during dry season and 0.716 mg/l during wet season from River Ganga's water and 1.0 mg/l from Nairobi River's water were recorded (Agatha, 2020). This level was attributed to land use activities such as agriculture system and effluent from residential and industrial area.

Downstream decrease in water pollutants was observed and was attributed to the dilution effect and self-purification. Constant monitoring of the levels of contamination to assess the impact of the heavy metal in the aquatic system and use of riverine vegetation was recommended as useful in absorbing heavy metals as a means of purification (Agatha, 2020).

The effectiveness of Pd/Mg chemical modifier for the accurate direct determination of zinc in marine/lacustrine sediments was determined by graphite furnace atomic absorption spectrometry using slurry samples. A calibration curve prepared by aqueous zinc standard solution with the addition of Pd/Mg chemical modifier is used to determine the zinc concentration in the sediment. The accuracy of the method was confirmed using Certified Reference Materials, NMIJ CRM 7303-a (lacustrine sedi-

ment) from the National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, Japan, and MESS-3 (marine sediment) and PACS-2 (marine sediment) from the National Research Council, Canada (Thomas, 2019).

The analytical results obtained employing Pd/Mg modifier are in good agreement with the certified values of all the reference sediment materials. Although for NRC MESS-3 an accurate determination of zinc is achieved even without the chemical modifier, the use of Pd/Mg chemical modifier is recommended as it leads to the establishment of a reliable and accurate direct analytical method. One quantitative analysis takes less than 15 min when performed on dried sediment samples. This is several ten times faster than conventional analytical methods using acid-digested sample solutions. The detection limits are 0.13 $\mu\text{g/g}$ (213.9 nm) and 16 $\mu\text{g/g}$ (307.6 nm), respectively, in sediment samples, when 40 mg of dried powdered samples are suspended in 20 mL of 0.1 mol/L nitric acid and a 10 μL portion of the slurry sample is measured (Thomas, 2019).

2.1.4 Cadmium

Cd is carcinogenic in nature as reported by Stewart and Kliehues (2018). It is an extremely toxic chemical even in low concentrations. It leaches into the soil through water and further bio-accumulates in organisms and ecosystems. In addition, Cd has a long biological half-life in human body, ranging from 10-33 years. The long-term exposure to Cd induces renal damage. It also disturbs calcium metabolism in the body and cases of prostate cancer and lung cancer have been reported in cases of high Cd exposure.

Cadmium in sediment from River Nile exhibited narrow range of variation ranging from 0.4 to 0.7 mg/kg that were higher than the permissible limit of 0.6 mg/kg (Osman and Faust, 2018). The levels of Cd obtained in sediment samples from Tyume River varied

between trace and 0.005 ± 0.003 mg/kg and were within the South African Target Water Quality Range (TWQR) for both domestic and irrigation purposes (Awofolu *et al.*, 2017). In the Wadi Hanifah River's sediment samples, the mean concentration of Cd was 71.7 ppb (Abdel-Baki *et al.*, 2011). Heavy metal contamination in sediment can affect the water quality and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implication on human health and ecosystem (Abdel-Baki *et al.*, 2011).

Studies on Cd in various river water have recorded concentrations that are higher than the WHO recommended limit of 0.003 mg/l. Cd concentrations in water from River Nile ranged between 0.002 and 0.02 ppm while Cd mean levels of 0.02 mg/l in water from Nairobi River were all higher than the recommended limit making the water unsuitable for human consumption (Osman and Faust, 2018).

Also, the mean concentrations of Cd from Tyume River water ranged from 0.030 ± 0.002 to 0.044 ± 0.003 mg/l that was higher than the tentative TWQR guideline of 0 to 0.005 mg/l in river water for domestic use (Awofolu *et al.*, 2017).

Sources such as agricultural runoff where fertilisers are used, possible release of sediment bound-metals, industrial wastes and atmospheric inflow of dust could have resulted in these levels. It was concluded that water from Tyume River was unsuitable for domestic use and could have chronic health effects on users, hence continual assessment was highly essential (Osman and Faust, 2018).

2.1.5 Chromium

Cr is used in metal alloys such as stainless steel, protective coatings of metal (electroplating), magnetic tapes, and pigments for paints, cement, paper, rubber and its soluble form is used in wood preservatives as well as additive in water to prevent corrosion in industrial and other cooling system. Hexavalent Cr is very toxic and

mutagenic when inhaled and is a known human carcinogen. Breathing high levels of the element in this form can cause irritation to the lining of the nose and breathing problems such as asthma, cough, shortness of breath, or wheezing where long-term exposure can cause damage to liver, kidney circulatory and nerve tissues, as well as skin irritation (Al-Osman *et al.*, 2019).

Sediments act as the most important reservoir or sink of metals and other pollutants in the aquatic environment (Roseburrough and Wang, 2019). Heavy metal contamination in sediment can affect the water quality and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implication on human health and ecosystem. Increased levels of Cr in agricultural soils and thus potentially in crops, can occur through the application of sewage sludge and by atmospheric deposition of fumes produced by industry (Ernst, 2020). In the Wadi Hanifah River's sediment samples, the average concentration of Cr was 9500 µg/kg (Okafo *et al.*, 2019).

Chromium has been found to vary from the recommended level of 0.05 mg/l for domestic water. Higher Cr concentrations than the recommended limit in the Wadi Hanifah River's water samples was 6.4 ppb while Cr mean concentrations from Msimbazi River water ranged from 1.414 to 0.01 mg/l. These were from points of the rivers that receive effluents loaded with pollutants from various industries including textile, which are known to contain Cr (Okafo *et al.*, 2019).

Wachira *et al.* (2019) recorded Cr mean levels of 0.02 mg/l in water from Nairobi River which was not higher than 0.05 mg/l recommended limit for drinking water. Thus, Nairobi river water was suitable for domestic use as far as Cr is concerned (Wachira *et al.*, 2019).

Thomas (2019) reported a study on pre-concentration various chromium species (total Cr, Cr (VI), Cr (III)) in estuarine and seawater samples by co-precipitation with lead sulphate or lead phosphate prior to determination by neutron activation analysis and gamma spectrometry. Lead phosphate will collect both trivalent and hexavalent chromium while lead sulphate collects hexavalent chromium only. The procedure had a detection limit of 0.1 µg/L for chromium in seawater when 800 mL of samples was used.

Recoveries of both chromium (III) and chromium (VI) were excellent for both sample types with lead phosphate. Chromium (VI) was quantitatively recovered by the lead sulphate procedure from potable water, but its recovery from seawater was incomplete (~87%) because of the considerable amount of competing species, especially sulphate, present. Under the conditions used, the detection limit based on $2(\text{background})^{1/2}$ was 0.08 µg/L chromium for 800 mL samples. Graphite furnace atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, anodic stripping voltammetry, and isotope dilution mass spectrometry have been used to determine chromium in estuary waters.

2.1.6 Copper

High level of Cu in water from River Kaduna, Niger State has also been recorded (Ighariemu *et al.*, 2019). Cu are metallic elements that can be released to the environment through mining, smelting and refining of copper. Acute exposure of Cu can lead to Cu poisoning, such as flu like condition known as metal fever, vomiting, diarrhea, stomach cramps, and nausea. Chronic exposure can result to brain damage, demyelization, renal disease and copper deposition in the cornea and even death.

Soil contamination by heavy metals has become a widespread dangerous problems in many parts of the world, including the Mediterranean. This is closely related to the increased irrigation of land by waste waters, the uncontrolled application of sewage sludge and industrial effluents, the atmospheric deposition of dust and aerosols, the vehicular emissions, and many other negative human activities. Differential pulse anodic stripping voltammetry using *in situ* plating techniques has been used to determine down to 0.1 µg/kg copper in acid extracts of marine sediments (Thomas, 2019).

Sediments contamination by heavy metals has become a widespread dangerous problem in many parts of the world, including the Mediterranean. This is closely related to the increased irrigation of land by waste waters, the uncontrolled application of sewage sludge and industrial effluents, the atmospheric deposition of dust and aerosols, the vehicular emissions, and many other negative human activities.

In this context, Thomas (2019) has predicted the spatial distribution and concentration levels of copper in the 195 km² of Naht el-Jawz watershed situated in northern Lebanon using a geographic information system and regression tree analysis. The chosen area represents a typical case study of Mediterranean coastal landscape with deteriorating environment.

2.2 Physico-Chemical Parameters

2.2.1 Temperature

Temperature is an important factor to consider when assessing water quality. In addition to its own effects, temperature influences several other parameters and can alter the physical and chemical properties of water. In an established system the water temperature controls the rate of all chemical reactions, and affects fish growth, reproduction and immunity. Drastic temperature changes can be fatal to fish. As

temperatures get too far above or below this preferred range, the number of individuals of the species decreases until finally there are none. The solubility of oxygen and other gases will decrease as temperature increases. This means that colder lakes and streams can hold more dissolved oxygen than warmer waters. If water is too warm, it will not hold enough oxygen for aquatic organism to survive (Yahaya *et al.*, 2019).

Higher temperatures can result in higher activity and ventilation rates in fish and tend to lower oxygen affinity of the blood and thus increase the rate of pollutant accumulation (Musa and Abubakar, 2019). A higher temperature could also lead to higher metabolic rates, which could induce more feeding and in turn result in increased metal concentration, if the metals are taken up via food chain.

Temperature is also important because of its influence on water chemistry. The rate of chemical reactions generally increases at higher temperature. Water, particularly groundwater, with higher temperatures can dissolve more minerals from the surrounding rock and will therefore have a higher electrical conductivity. Some compounds are also more toxic to aquatic life at higher temperatures. In addition to its effects on aquatic organisms, high water temperatures can increase the solubility and thus toxicity of certain compounds. These elements include heavy metals such as cadmium, zinc and lead as well as compounds like ammonia. Water temperature can not only increase the solubility of toxic compounds, but it can also influence an organism's tolerance limit. Mortality rates for zinc are significantly higher at temperatures above 25°C than at temperatures below 20°C. This occurs because tissue permeability, metabolic rate and oxygen consumption all increase with increased water temperature. In one study on labo bata fish by Fondriest (2019), the 24 hour 50% lethal concentration (LC50) at 15°C was 540 mg/L, while at 30°C, the LC50 dropped to 210 mg/L (Popoola *et al.* 2019).

2.2.2 pH

pH is most important in determining the corrosive nature of water. The lower the pH value, the higher is the corrosive nature of water. pH was positively correlated with electrical conductance and total alkalinity. The reduced rate of photosynthetic activity the assimilation of carbon dioxide and bicarbonates which are ultimately responsible for increase in pH, the low oxygen values coincided with high temperature during the summer month. Various factors bring about changes the pH of water. The higher pH values observed suggests that carbon dioxide, carbonate-bicarbonate equilibrium is affected more due to change in physico-chemical condition (Shawai, 2019). Nwoke *et al.* (2019) determined water quality in Nigeria, they found the pH of the water samples before storage to be 4.66 and after storage, it was 4.91, 6.87 and 4.84 for plastic, concrete and steel containers respectively and these are not within WHO limits.

2.2.3 Electrical conductivity

Conductivity shows significant correlation with ten parameters such as temperature, pH value, alkalinity, total hardness, calcium, total solids, total dissolved solids, chemical oxygen demand, chloride and iron concentration of water. Nwoke *et al.* (2019) suggested that the underground drinking water quality can be checked effectively by controlling conductivity of water and this may also be applied to water quality management of other study areas. It is measured with the help of EC meter which measures the resistance offered by the water between two platinized electrodes. The instrument is standardized with known values of conductance observed with standard KCl solution.

Nwoke *et al.* (2019) analyzed water samples in Nigeria and found that the conductivity of water in the original water sample before storage was 39 $\mu\text{S}/\text{cm}$ while that in storage

facilities (steel, plastic and concrete materials) were discovered to be 49 $\mu\text{S}/\text{cm}$, 72 $\mu\text{S}/\text{cm}$ and 92 $\mu\text{S}/\text{cm}$ for plastic, concrete and steel storage tanks respectively after storage; thus proving that there are more dissolved metal ion in steel storage tank caused by corrosion and more dissolved minerals in concrete storage tanks than plastic storage tanks.

2.2.4 Turbidity

Turbidity is the cloudiness of water caused by a variety of particles and is another key parameter in drinking water analysis. It is also related to the content of diseases causing organisms in water, which may come from soil runoff. The standard recommended maximum turbidity limit, set by WHO for drinking water is 5 nephelometric turbidity units (NTU) (WHO, 2018).

Turbidity is an important indicator of the amount of suspended sediment in water, which can have many negative effects on aquatic life. The suspended sediments that cause turbidity can block light to aquatic plants, smother aquatic organisms, and carry contaminants and pathogens, such as lead, mercury, and bacteria.

Turbidity is reported in either NTUs or JTUs. These units refer to the method used to measure turbidity. NTUs reflect a more precise measurement method, and are used by government agencies and in scientific research. Turbidity is measured by evaluating the amount of light scattered in water. This can be done with simple visual assessments, such as the original Jackson Candle turbidity meter, or more accurate, technological methods, such as the nephelometric method.

2.2.5 Silica

Silica (silicon dioxide) is a compound of silicon and oxygen (SiO_2). It is a hard, glassy mineral substance that occurs in a variety of forms such as sand, quartz, sandstone, and

granite. It is also found in the skeletal parts of various animals and plants. Silicon is the 7th most abundant element in the universe and the second most abundant element on earth after oxygen which explains why most water supplies will contain some traces of silica. In solution it can exist as silicic acid or silicate ion, depending upon the pH value. The solid crust of the earth contains 80% to 90% silicates or other compounds of silicon. Water passing through or over the earth dissolves silica from sands, rocks, and minerals as one of the impurities it collects. The silica content in natural waters is commonly in the 5 to 25 mg/l range, although concentrations over 100 mg/l occur in some areas.

Silicates are compounds that contain silicon and oxygen in combination with such metals as aluminum, calcium, magnesium, iron, potassium, sodium, and others. Silicates are classed as salts.

2.2.6 Ammonia

Ammonia is a commonly found pollutant in aquatic environments around the world. This compound can be found naturally, but there is also an additional contribution from sewage effluents, industrial waste, and agricultural run-off. The presence of ammonia in freshwater has been associated with the acidification of rivers and lakes, eutrophication, and direct toxicity to aquatic organisms. This compound damages the gills, liver, kidney, spleen and other organ tissues of fish, therefore causing breathing difficulties. This may lead to physiological alterations and, eventually, exhaustion or death. Ammonia can cause cell damage and can also affect the antioxidant defence system, thus altering the levels of oxidative stress in fish. Ammonia can also alter fish behaviour. Fish exposure to sub-lethal concentrations of ammonia can reduce swimming activity, foraging behaviour, and the ability to flee from predators (Soler *et*

al. 2021). Ammonia is a nutrient that contains nitrogen and hydrogen. Its chemical formula is NH_3 in the un-ionized state and NH_4^+ in the ionized form. Ammonia is also one of the most important pollutants because it is relatively common but can be toxic, causing lower reproduction and growth, or death. The neutral, unionized form (NH_3) is highly toxic to fish and other aquatic life (Soler *et al.* 2021).

2.2.7 Nitrates

Nitrates are a form of nitrogen, which is found in several different forms in terrestrial and aquatic ecosystems. These forms of nitrogen include ammonia (NH_3), nitrates (NO_3), and nitrites (NO_2). Nitrates are essential plant nutrients, but in excess amounts they can cause significant water quality problems. Together with phosphorus, nitrates in excess amounts can accelerate eutrophication, causing dramatic increases in aquatic plant growth and changes in the types of plants and animals that live in the stream. This, in turn, affects dissolved oxygen, temperature, and other indicators. Nitrate pollution in river water is the focus of global attention. The World Health Organization has set an upper NO_3^- -N concentration limit of 10 mg/ for water (Zhang *et al.* 2021). In recent decades, the discharge of point source pollution, such as industrial and domestic wastewater, and numerous chemical fertilizers in agricultural systems have resulted in an increase in nitrate concentration in river water.

Excess nitrates can cause hypoxia (low levels of dissolved oxygen) and can become toxic to warm-blooded animals at higher concentrations (10 mg/L) or higher) under certain conditions. The natural level of ammonia or nitrate in surface water is typically low (less than 1 mg/L); in the effluent of wastewater treatment plants, it can range up to 30 mg/l (Zhang *et al.* 2021).

2.2.8 Nitrite

Nitrites are a salt or ester anion of nitrous acid, which can be naturally or artificially occurring in groundwater. Nitrite is an intermediate product of the oxidation of ammonia to nitrate. “Nitrite, ” like ammonia, exists in two forms, the ionized nitrite (NO_2^-) and the molecular nitrous acid (HNO_2). These two forms also exist in an equilibrium primarily determined by pH with higher pH values favoring the formation of nitrite (David, 2021)

Nitrites come from fertilizers through run-off water, sewage, and mineral deposits. High levels of nitrites are toxic to humans and animals, especially infants. It can enter the body as nitrate, a nutrient which is essential to plant growth, and be converted into nitrite, which disrupts the oxygen delivering ability of hemoglobin in the bloodstream. Infants can develop a life threatening blood disorder known as blue baby syndrome (methemoglobinemia) if exposed to it in water or formula mixed with water that is contaminated with nitrate. Nitrite may accumulate in the blood of some fish species and, among other things, cause the oxidation of iron in hemoglobin producing methemoglobin, which is not capable of transporting oxygen (David, 2021).

2.3 Methods of Analysis

2.3.1 Digestion of heavy metals

Thomas (2019) reported a comparative study of methods of digesting a number of metals in marine sediments prior to their determination. The metals were those usually found in sediments, such as aluminium, iron, manganese, and titanium, and some which occur less frequently and at very low concentrations, such as zinc, copper, lead, cadmium, chromium, and arsenic. The analytical methods used were visible

spectrometry for aluminium and titanium, flame atomic absorption spectrometry for iron, manganese, and zinc, and the graphite furnace for other metals.

Digestion techniques investigated were acid digestion in hydrochloric, nitric, hydrofluoric, and perchloric acids and a dry technique involving calcining the sediments and taking up the ashes in nitric acid. The results show that the selection of a particular digestion technique is dependent on the particular metal to be analysed, but it is indicated, in general terms, that the simplest, most rapid, most free from contamination and most effective is digestion with nitric acid, in a bomb, at 150°C.

Microwave digestion techniques have also been used in the sequential extraction of calcium, iron, chromium, manganese, lead, and zinc in sediments. The extraction rates of metals in each of the five binding fractions of marine sediments (metal exchangeable, carbonate bound, iron–manganese oxide bound, organic bound, and residual) were determined for both conventional and microwave heating techniques. Microwave digested sediment samples (20 mL) were centrifuged at 10,000 rpm for 30 min. Metals were determined by flame atomic absorption spectrometry.

To prepare material for the determination of extraction rates for one particular fraction, a quantity of material was taken through the conventional sequence of steps up to the fraction for which the rate was determined. Sequential microwave extraction procedures were then established from the results of the rate experiments. Recoveries of total metals from standard sediment samples were comparable for both conventional and microwave techniques except for iron (62% by microwave and 76% by conventional method) (Thomas, 2019).

Volatilisation behaviours of Cd, Cu, Ni, and Pb in different extracting media have also been studied using graphite furnace atomic absorption spectrometry to determine metal concentrations in natural sediments. Considerable interference was found for Cd, Ni,

and Pb in the extracts of high matrix concentrations and could be largely reduced by carefully selecting the ashing and atomisation temperatures of graphite furnace atomic absorption spectrometry. Optimal heating programs are proposed to suit a variety of extracts (Cong *et al.*, 2019).

2.3.2 Inductively plasma atomic emission spectrometry

A procedure has been described which permits the simultaneous determination of six major and minor elements (aluminium, iron, calcium, magnesium, sodium, and phosphorus) and eight trace elements (beryllium, cobalt, copper, manganese, nickel, lead, vanadium, and zinc) in near-shore marine sediments by inductively coupled plasma atomic emission spectrometry. Dissolution of the samples is achieved with a mixture of nitric, perchloric, and hydrofluoric acids in sealed Teflon vessels (Thomas, 2019).

Accurate calibration for all elements can be achieved with simple aqueous standards, provided that proper correction for various spectroscopic interferences is made. The method is not suitable for the determination of arsenic, cadmium, and molybdenum in these materials because of inadequate sensitivity but not for chromium and thallium because of incomplete dissolution. Detection limits varied from 0.5 mg/kg (beryllium) to 0–5 mg/kg (arsenic) (Thomas, 2019). Inductively coupled plasma atomic emission spectrometry and graphite furnace atomic absorption spectrometry have been used to determine heavy metals in suspended matter in the Gulf of Cadiz.

2.3.3 Neutron activation analysis

This technique has been applied in the determination of cobalt, chromium, caesium, iron, rubidium, antimony, scandium, and strontium in suspended matter isolated from seawater. Detection limits achieved as reported by Thomas (2019) ranged from 0.06 mg/kg (cobalt) to 70 mg/kg (barium, iron, tin).

2.3.4 Photon activation analysis

This technique has been used to determine elements (arsenic, barium, antimony, chromium, cobalt, lead, manganese, nickel, strontium, uranium, zinc, and zirconium, sodium, manganese, potassium, calcium, titanium, and iron) in a certified marine sediment Standard Reference Material (BCSS-1). Photon activation analysis was carried out at the National Research Council of Canada electron linear accelerator using the Bremsstrahlung produced by the impact of a focussed electron beam on a tungsten converter. Eleven trace metals (As, Ba, Cr, Co, Mn, Ni, Pb, Sb, Sr, Li, and Zr) and given minor elements (Na, Mg, Cl, K, Ca, Tl, and Fe) were determined in a certified marine sediment Standard Reference Material. The precision and accuracy of the results when compared to the accepted values clearly demonstrated the reliability of this technique (Thomas, 2019).

After an irradiation period of 6 h and a cooling-off period of 15 h, the γ -ray spectrum was accumulated of 20,000 s. Peaks are labelled with γ -ray energy in KeV and assigned a parent radionuclide. An excellent agreement was obtained between results obtained by photon activation analysis on a standard marine sediment ranging from 0.63 ± 0.01 to 0.59 ± 0.06 mg/kg for antimony, 122–119 mg/kg for zinc, and 347 ± 36 mg/kg to 330 mg/kg for barium. Detection limits for these three elements were, respectively, 0.2, 7.0, and 0.4 mg/kg.

2.3.5 Atomic absorption spectroscopy

The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires a standard with known analyte content to establish the relation between the measured and the analyte concentrations and relies on Beer Lambert's law (Skoog *et al.*, 2017).

The sample is converted into atomic vapours by a process known as atomization. The precision and accuracy of this method depends on the atomization step and therefore a good choice of the atomization method is required. The two types of atomizers are continuous and discrete atomizers. In continuous atomizers the sample is fed into the atomizer continuously at a constant rate giving a spectral signal which is constant with time.

Atomization methods that are of continuous type are flame, inductively coupled argon plasma and direct current argon plasma. With the discrete atomizers, a measured quantity of a sample is introduced as a plug of liquid or solid. The spectral signal in this case rises to a maximum and then decreases to zero. An electro-thermal atomizer is one of the discrete types. The atoms then absorb radiations of characteristic wavelengths from an external source. The atoms of lead, nickel, manganese, zinc, cadmium and chromium, absorb radiations of wavelengths of 217.0 nm, 232.0 nm, 279.5 nm, 213.9 nm, 228.8 nm and 357.9 nm, respectively from an external source which is usually a hollow cathode lamp (Zamir *et al.*, 2019).

The two sources of radiation are continuous source which makes use of deuterium and mercury lamps and a hollow lamp which consists of an anode made of either tungsten wire or tungsten and a hollow cathode made of either the element of interest or its own salt. Flame atomization method consists mainly of a fuel and oxidant. Their temperatures are determined by flow rate and ratio of oxidant and fuel while the electro thermal atomizer is basically made of carbon rods. The free atoms are vaporized from the carbon atomizer into the optical light path to a monochromator which presents a monochromatic radiation to the detector. The radiations from the monochromators are received by detectors which converts them to electrical signals. Some commonly used detectors are photocells and photo multiplier tubes.

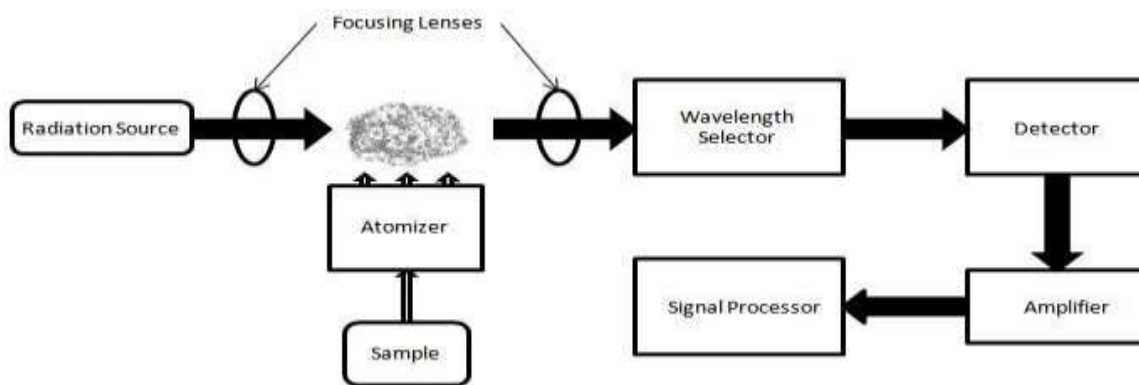


Figure 2.1: Schematic diagram of AAS equipment

a. Radiation source (Hollow cathode lamp)

This is the source of analytical light line for the element of interest and gives a constant and intense beam of that analytical line.

b. Atomiser (Flame)

The atomiser will destroy any analyte ions and break complexes to create atoms of the element of interest.

c. Wavelength selector (Monochromator)

A wavelength selector isolates analytical line photons passing through the flame and remove scattered light of the other wavelength from the flame. This only impinges a narrow line on the photomultiplier tube.

d. Detector (Photomultiplier tube (PMT))

It determines the intensity of the analytical line exiting the monochromator. The PMT is the most commonly used detector for AAS.

2.4 Chemometrics Methods of Data Analysis

Chemometrics is the application of multivariate mathematical and statistical tools to the study of chemical problems, including methods for the analysis and interpretation of analytical instrumentation data. Chemometrics provides multivariate mathematical tools to aid scientists in environmental assessment.

Chemometric analysis can be applied to multichannel spectroscopic data, multi-component chromatographic data or combinations of multivariate and univariate instrumentation that create a broad array of measures characterizing a complex environment. Variations in the chemical fingerprint pattern in chromatographic or spectral profiles of environmental samples can reveal chemical relationships which may be explainable by known natural phenomena or contributing pollution sources. For multi-constituent chemical residues, such as trace metals, polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzo furans (PCDFs), polychlorinated biphenyls (PCBs) , and polycyclic aromatic hydrocarbons (PAHs), the more advanced statistical methods are useful for addressing data quality, determining the most significant constituents among different samples, and providing classification methods for assigning samples into specifically defined groups (Hoang and Marini, 2019).

Some chemometric methods provide a way to visualize variation within large multivariate data sets as an end in itself or as a preprocessing step to discriminate information before building calibration or classification models. Principal component analysis (PCA) is the main tool for this purpose and it can be implemented through a number of algorithms, the most common being nonlinear iterative partial least squares (NIPALS) and singular value decomposition (SVD).

2.4.1 Principal component analysis

Principal Component Analysis (PCA) is a multivariate statistical technique used to reduce the dimensionality of a data matrix or to state this more accurately: PCA is used to find the “true” dimensionality within a set of data. Principal components analysis (PCA) is used to evaluate similarities in the trace element chemistry of groundwaters.

Many of the trace elements, however, occur at concentrations below the detection limits (DL), which presents problems for statistical analyses.

PCA is designed to transform the original variables into new, uncorrelated variables (axes), called the principal components, which are linear combinations of the original variables. The new axes lie along the directions of maximum variance (Bleiziffer, 2019).

With PCA, a set of correlated measured variables is transformed into a set of uncorrelated principal components. The principal components are described using two lower dimensional data matrices (scores and loadings) that capture the underlying patterns within the original data. The dominant patterns present within the samples and variables are illustrated by plotting the columns of the score matrix and the loadings matrix, respectively. The principal components are obtained through eigen analysis of the correlation or covariance matrix.

Principal components are extracted so that the maximum amount of variance is explained in the largest eigen value associated with the first principal component and progressively less variance is explained for each subsequent component.

Singh *et al.* (2019) applied both factor analysis and principal components analysis to their water quality sampling data from the Gomti River in India. Principal components analysis identified six principal components that accounted for 71% of the total variance in the water quality data. The first component was found to be related to electrical conductivity, dissolved salts, alkalinity, chloride and sodium and represented 27.9% of the total variance, while a second principal component was related to dissolved oxygen and accounted for 17.3% of the total variance.

PCA methods have been used to identify contributing sources of total suspended particulate matter in urban and rural regions of Sicily. Results on elemental

concentrations determined by particle induced X-ray emission (PIXE) analysis indicated soil (resuspended road dust) and automotive emissions, as well as specific industrial contributions, as major sources in two Sicilian cities. Vu Dang and Marini, (2019) also used factor analysis to evaluate volatile organic compounds (VOCs), particulate mass and elemental concentrations in the Kanawha Valley, surrounding Charleston, WV, USA. One short term, specific factor was attributed to a forest fire in the region. Five other factors were identified as long-term contributions from general VOCs, automotive emissions, acid particulates, combustion, and chlorinated VOCs.

2.4.2 Cluster analysis

Cluster Analysis (CA) is an unsupervised pattern detection method that partitions all cases into smaller groups or clusters of relatively similar cases that are dissimilar to other groups (Mathias, *et al.*, 2020). The goal of cluster analysis is to identify relatively similar, that is, homogeneous, groups of objects (in our case, sampling locations) in the space of measured features (Mathias *et al.*, 2020). Cluster analysis is also called unsupervised learning technique because the group membership of all objects and the number of possible groups are unknown before starting the computation. Different measures for the similarity with respect to distance between objects in the feature space and different algorithms for finding clusters are possible. CA classifies objects so that each object is similar to the others. The resulting clusters of objects should then exhibit high internal (within cluster) homogeneity and high external (between clusters) heterogeneity.

Singh *et al.* (2019) applied cluster analysis, as well as other techniques, to evaluate the water quality of the Gomti River in India, performing agglomerative hierarchical cluster analysis on a dataset consisting of 24 parameters measured at 8 locations monthly over a

5-year period, a total of 17,790 observations. The 8 regions of the river system were successfully grouped into 3 clusters representing low, moderate and high pollution.

Hierarchical cluster analysis was performed on ten temporal chlorophyll-a profiles extracted from the monthly MODIS imagery from 2006 for different areas of the South Australian coastal waters. Cluster analysis produced a dendrogram separating each location by the similarities in the chlorophyll-a temporal profiles. It was observed that the locations have different chlorophyll-a characteristics from the rest of the study area, and therefore different phytoplankton and primary productivity properties, assuming the accuracy of the satellite-based chlorophyll-A estimates (Zolfaghari, *et al.*, 2019).

2.4.3 Factor analysis

Factor analysis as a multivariate statistical method is used to find a small number of factors from a data set of many correlated variables. Factor analysis is a useful tool for extracting latent information such as underlying, not directly observable relationships between variables. Factor analysis is based on the mathematical model of the reduced factor analytical solution. The original data matrix is decomposed into the product of a matrix of factor loadings and a matrix of factor scores plus a residual matrix. The residual matrix contains that part of variance of the data set that cannot be explained by common factors, e.g., analytical uncertainties or feature-own variances. On the basis of the correlation or variance–covariance matrix orthogonal factors are extracted solving an eigen value problem.

In general, the number of extracted factors is less than the number of measured features. So the dimensionality of the original data space can be decreased by means of factor analysis. After rotation of the factor loading matrix the factors can often be interpreted as origins or common sources. The last step of factor analysis is the computation of new

coordinates of the objects (in this case, sediments/water at different sampling locations) in the factor space, the so-called factor scores.

Factor analysis was applied to reduce the contribution of less significant variables from PCA. Factor analysis revealed six factors, comprised of 14 of the original 24 parameters, which explained 71% of the variance. The six factors from most significant to least significant were found to be related to the mineral composition of the river water, anthropogenic pollution sources, dissolution of soil constituents, mineral related hydrochemistry, fluoride, and suspended sediments (Singh *et al.*, 2019).

2.4.4 Partial least squares modeling

The partial least squares (PLS) method is a multivariate regression with latent variables to characterize relationships between matrices. This regression model considers both the interactions between predictor variables and the interactions between predicted variables simultaneously. Both matrices are decomposed into a matrix of latent vectors and a loading matrix plus a residual matrix under the condition of maximum correlation between both matrices of the latent vectors. The number of vector pairs can be determined using cross-validation for error minimization (Xuan, 2018).

Santos *et al.* (2019) estimated the levels of lead (Pb), nickel (Ni), manganese (Mn), vanadium (V) and chromium (Cr) in the city of Dunkerque (northern France) by means of statistical models based on partial least squares regression (PLSR), artificial neural networks (ANNs) and principal component analysis (PCA) coupled with ANN. According to the European Air Quality Directives, because the levels of these pollutants are sufficiently below the European Union (EU) limit/target values and other air quality guidelines, they may be used for air quality assessment purposes as an alternative to experimental measurements. An external validation of the models has been conducted, and the results indicate that PLSR and ANNs, with comparable performance, provide

adequate mean concentration estimations for Pb, Ni, Mn and V, fulfilling the EU uncertainty requirements for objective estimation techniques.

2.4.5 Direct analysis

Direct Analysis is a method of analyzing dependence that is a special case of canonical correlation used to analyze dependence; one of its objectives is to discriminate between two or more groups in terms of the means of the discriminating variables. DA is performed on original data without affecting the results and comparability with other chemometrics methods, and constructs a discriminant function for each group (Franco-Uria *et al.*, 2019).

Singh *et al.* (2019) also applied DA to determine the variables responsible for variations between the regions of the river determined through cluster analysis. As for the temporal DA the standard and forward stepwise methods obtained 92% accuracy using 23 and 17 parameters respectively, while the backwards stepwise method obtained 91% accuracy using just 9 parameters. The backward stepwise method showed that pH, temperature, alkalinity, Ca-hardness, DO, BOD, chloride, sulphate, and TKN are responsible for the majority of variation between the study regions. Therefore, DA was able to contribute to a significant reduction in the multivariate dataset, while providing insight into the variables contributing to variations in water quality between periods and regions.

DA has also been used with remote sensing data. Andrefouet *et al.* (2018), for example, applied discriminant analysis to hyperspectral airborne remote sensing imagery to determine the best wavelengths for discriminating between different species and communities in coral reefs in French Polynesia. DA highlighted the key non-redundant wavelengths capable of achieving good separation between the ecological groups. By

measuring only, the necessary wavelengths, rather than the full spectrum, the study was able to achieve greater spatial resolution and better signal-to-noise ratios.

2.5 Review of Previous Works on Heavy Metals Analysis on Water and Sediments

2.5.1 Determination of heavy metal concentrations in sediments and water

Heavy metal concentrations of some environmentally toxic metals in inter-tidal sediments of the Okrika river system in River State has been examined by Micheal *et al.* (2018). The determination of the heavy metal loadings and other chemical parameters has revealed some significant correlation in inter-tidal sediments taken from the Okrika river system as it passes through Okrika. The metal concentrations (mean \pm RSD in μg^{-1} dry weight) were: Pb, 18.74 ± 0.08 ; Ni, 46.51 ± 0.70 ; Cd, 1.05 ± 0.78 ; Co, 11.41 ± 0.87 ; Zn, 245.49 ± 0.51 ; Cu, 66.70 ± 0.49 . Chemical variables related to the retention of heavy metals by sediments were also measured and their average levels are % H₂O (52.34), % organic matter (3.93), % CaCO₃ (14.67), and % organic nitrogen (0.98). The results revealed a higher environmental risk for cadmium and lead, and a lesser degree for zinc due to their higher percentage in the more easily remobilized fractions (Micheal *et al.*, 2018).

Ogbunike and Ezeibeonu (2019) analyzed heavy metals in drinking water from different sources in Lagos state, Nigeria with a view of comparing the effects of level of Industrialization, population density and urbanization on the water quality in the centre of Lagos and off town of Lagos (Ikorodu LGA, a relatively less Industrialized and less Urbanized town of Lagos state) as a case study. The different sources of drinking water considered were wells, boreholes, surface water and tap water. In each of Lagos and Ikorodu, the heavy metals were analysed; Pb, Cd, Cu, Fe, Cr, Zn, Na, Ni, Mg and Ca using Atomic Absorption Spectrophotometer (Perkin-Elmer 305B model with air-

acetylene flame). The results show that Pb, Ni, and Mg values exceeded the permissible limits set by WHO, EU and NIS for all the samples from all the sources in all study area while Fe has values above the standards set by all the regulatory bodies in Ikorodu boreholes (i.e. 1.804 mg/L) but all other sources as well as all Lagos samples have values of Fe within the permissible limits (0.2-0.3 mg/L) and this could be traced to the geology of the area. Cu, Zn, Na, Cr, and Ca all have higher values in Lagos centre samples than in Ikorodu samples but are all within the permissible limits. Cd was not detected in any of the samples at all.

Paul *et al.* (2017) evaluated contamination of coastal sediments along Fongafale Islet, Central Pacific, a field survey was conducted in densely populated, sparsely populated, open dumping and undisturbed natural areas. The total concentrations of Cr, Mn, Ni, Cu, Zn, Cd and Pb were relatively high in all of the areas except the undisturbed natural area. The indices of contamination factor, pollution load index and geo-accumulation index were indicative of heavy metal pollution in the three areas. The densely populated area has the most significant contamination; domestic wastewater led to significant contamination of coastal sediments with Cr, Zn, Cu, Pb and Cd (Paul *et al.*, 2017).

Yahaya *et al.* (2019) assessed the seasonal variation in physiochemical properties and concentration of the heavy metals in road side soil in Yauri, Nigeria, during the two major seasons of Nigeria. Soil samples collected during rainy and dry seasons were treated and digested using microwave acid digestion methods. The heavy metal concentrations were determined with atomic absorption spectrophotometer. The mean levels range of As, Cd, Cr, Cu, Fe, Ni, Pb and Zn were $\mu\text{g/g}$ for wet season respectively. When metals concentrations in the soil of dry and wet seasons were correlated ($p < 0.05$) it was revealed that there were strong correlations between all the metals with the exception of Ni. Generally, higher mean heavy metal concentrations were recorded in

the soil during the dry season than in wet season. The analytical results indicated that in both wet and dry seasons most of the heavy metals were above the natural heavy metals concentrations of surface soil which is a cause for concern as these metals can accumulate to pollute the environment.

Davies *et al.* (2020) studied the accumulation of three heavy metals; chromium, cadmium and lead in water and sediment collected from four stations along Elechi Creek. Elechi Creek receives effluents discharges from heavily industrialized and highly populated settlements. The results showed that the sediment concentrated more heavy metals than the water. The results of the levels of concentration of heavy metals in the water and sediments, showed the concentration for Cr in water was highest in uppermost station (<0.002 mg/kg) while the concentration (< 0.001 mg/ kg) was the same for other stations. The same concentrations (< 0.001 mg/ kg) were observed for Cd and Pb in all the stations. However, in the sediments, the concentration of Cr was highest in the uppermost station and lowest in other stations. The order of heavy metals concentration in sediments in all stations was Cr > Pb > Cd. The sequence of metals in the stations was 1 > 3 > 4 > 2. The sediments accumulated more heavy metals than the water (Davies *et al.*, 2020).

Chukwuemeka *et al.* (2020) investigated the level of Pb, Cu, Mn, and Fe in both surface water and sediment of Tagwai Lake, Minna, Nigeria. Atomic Absorption Spectrometry investigation was carried out on the collected and digested water and sediment samples to determine the extent of these heavy metals' contamination in the water. The values obtained were Pb (0.00 mg/l), Cu (0.19-0.27 mg/l), Fe (2.15 - 2.42), Mn (0.01 – 0.05 mg/l).

Ezemonye *et al.* (2018) evaluated the health risk consequences of consumption of heavy metal-contaminated water, shrimp (*Macrobrachium macrobrachion*) and fish (*Brycinus*

longipinnis) from Benin River in Nigeria. Three stations around Koko Community (Abialebe, Ebenco/Optima and Total Facility) with known anthropogenic activities (industrial and petrochemical installations and loading) were studied. Samples of surface water, shrimp and fish were collected and analyzed using Buck scientific atomic absorption spectrophotometer, model 210VGP. Health risk indices were reported as Estimated Daily Intake (EDI), Target Hazard Quotient (THQ) and Total Target Hazard Quotient (TTHQ). Eight heavy metals were analyzed in water, shrimp and fish. Nickel (Ni) was observed to be the most dominant heavy metal in water, while Iron (Fe) was the most dominant in shrimp and fish. Heavy metal levels in water were below recommended limits set by World Health Organization (WHO) and Standard Organization of Nigeria (SON) except for cadmium (Cd), nickel (Ni) and lead (Pb).

Mohammad *et al.* (2019) reported the measurement of concentration and chemical fractionation of globally alarming six heavy metals (Cr, Ni, Cu, As, Cd and Pb) in surface water and sediment of an urban river in Bangladesh. The decreasing trend of metals were observed in water as $Cr > Cu > As > Ni > Pb > Cd$ and in sediment as $Cr > Ni > Cu > Pb > As > Cd$. The level of studied metals exceeded the safe limits of drinking water, indicated that water from this river is not safe for drinking and/or cooking purposes.

However, the investigated metals showed low mobility except for Cd and Pb which could pose a severe threat to the aquatic environment. The result demonstrated that most of the sediment samples were moderately to heavily contaminated by Cr, As, Cd and Pb. The pollution load index (PLI) values were above one (>1) indicates progressive deterioration of the sediment quality. The extent of pollution by heavy metals in the river Korotoa implies that the condition is much frightening to the biota and inhabitants in the vicinity of the river as well (Mohammad *et al.*, 2019).

Prasanna *et al.* (2017) carried out an integrated approach of pollution evaluation indices and statistical techniques to assess the intensity and sources of pollution in Curtin Lake water, Miri City, East Malaysia. Fe, Pb and Se concentrations in most of the water samples exceed the maximum admissible concentration. Samples from 25 locations in the lake were classified as high in Cd. Cluster analysis, principal component analysis and pollution indices revealed that the quality of water is mainly controlled by natural/geogenic processes with minor anthropogenic input. The current distribution level of heavy metal in the lake water is of environmental and health concerns and needs attention (Prasanna *et al.*, 2017).

Mwangi (2018) determined levels of Pb, Ni, Mn, Zn, Cd and Cr in sediments and water from Ruiru and Mbagathi tributaries of Athi River (Kenya) during wet and dry seasons in 2014. Statistical sampling was done for sediments (N=40) and water (N=40) samples. Atomic absorption spectroscopy was used for measurement of the levels of elements. The mean concentrations (mg/kg DW) of the heavy metals in sediments ranged from: Pb (23.19-51.08), Ni (0.15-2.21), Mn (280.88-1294.01), Zn (10.98-50.79), Cd (0.05-1.81) and Cr (0.69-7.33). In water, the range of mean concentration (mg/l) of heavy metals were as follows: Pb (0.004-0.047), Ni (0.007-0.062), Mn (0.187-1.048), Zn (0.002-0.695), Cd (ND - 0.01) and Cr (ND-0.068). The levels of the heavy metals increased from water and sediments. In the wet season, Zn was found to be significantly high in the fish gills, while Pb and Mn were significantly high in the sediments ($P < 0.0001$). In the dry season, Zn and Cr were found to be significantly high in the sediment ($P < 0.0001$). As far as the WHO's set limits are concerned, Pb was found to be high in all samples with Mn being high in fish and water while Ni and Cd were high in fish and sediments, the results show evidence of alarming levels that are higher than WHO limits, therefore posing potential risk for inhabitants that depend on the river.

Oshishanya *et al.* (2021) studied the seasonal variation of heavy metals in sediment and water of Lagos lagoon. The concentration of chromium (Cr), lead (Pb), zinc (Zn), cadmium (Cd) and physicochemical parameters were determined in surface water and sediment at different stations in Lagos lagoon during the wet season. The result showed that the concentration of Cr (0.039 mg/l), (Pb 0.043 mg/l), Zn (0.107mg/l), (Cd 0.04 mg/l) in surface water were generally low when compared to the standard of WHO (2014). The concentration of Zn in the water is within the limits permitted by the Lagos State Environmental Protection Agency (LASEPA) of 1.0 mg/L Zn set for water. The mean levels of heavy metals in the sediment of Lagos lagoon were generally low and fell within the acceptable limits described by WHO, 2004 and FEPA. The average concentration for the heavy metals were Cr 0.046 mg/g, Pb 0.054 mg/g, Zn 0.730 mg/g, Cd 0.523mg/g respectively. Comparism of these values with that of the surface water indicates that most metals were adsorbed to the sediment.

Thomas (2019) reported the examination of the heavy metal fraction in 17 sediment samples from the Tinto river and its main tributaries. For each of these samples, the association of metals (Cu, Zn, Cd, Pb, Fe, Ni, Cr, and Co) was determined in four fractions: acid soluble, reducible, oxidizable, and residual. The total metal content was also determined. Results showed high mean concentrations of Fe (109,000 mg/kg), Pb (2330 mg/kg), Zn (901 mg/kg), Cu (805 mg/kg), and Cd (2.7 mg/kg) in the sediments studied. However, the mean values found for Co (21 mg/kg), Cr (56 mg/kg), and Ni (17 mg/kg) are comparable to those in unpolluted areas. Heavy metal fractionation of the Tinto River sediments showed that the metals with the greatest mobility are Cd and Zn. These are the metals that showed the highest percentages in the first two fractions (the most labile) and the lowest percentages in the residual fraction. However, the

percentage of metal present in the fourth fraction (residual) was high for Cr (78%) and Co (66%), which implies that these metals are strongly linked to the sediments.

In an exposure assessment of heavy metals (Pb, Cr, Cu, Ni, and Pb) in water and sediments from a Western Mediterranean basin (Rio Guadalhorce Region of Analusie, Southern Spain), concentrations of heavy metals in sediment and water from the Guadalhorce River was measured. In the later twentieth century, cities such as Málaga (capital of Costa del Sol) have suffered the impact of mass summer tourism.

The ancient industrial activities, abandoned mine sites and the actual urbanisation and coastal development, recreation and tourism, and wastewater treatment facilities have been sources of pollution. This river has been heavily modified, with three dams for volume regulation purposes due to the climate cycles, with some years very dry and others with torrential rains. In this study, different indices for the assessment of sediment contaminations, statistical tools (Kruskal–Wallis test, conglomerate analysis), sequential extraction methods, and environmental quality guidelines were employed to assess the possible contamination of this basin. Other physical–chemical parameters such as chloride concentrations, pH, and conductivity were also measured.

The results indicated that Ni and Cu were the most troublesome metals because they were more easily mobilisable than Cr and Pb; Ni exceeds the SQGs guidelines and Cu presents considerable contamination. These metals were derived from lithogenic and anthropogenic sources, respectively, according to the values of enrichment factors.

Ni was the most dangerous because in 96.6% of the samples analysed, Ni concentrations exceeded the threshold effect concentration below which harmful effects are likely to be observed, and even the probable effect concentration (PEC) above which harmful effects are likely to be observed in 56.6%. The cause of this pollution was

postulated to be by abandoned Ni mines, which indicates that the pollution from mining persists after several decades (Thomas, 2019).

2.5.2 Some physicochemical analysis study of polluted water and sediment samples

Physicochemical parameter study is very important to get exact idea about the quality of water and we can compare results of different physicochemical parameter values with standard values.

Tukura *et al.* (2017) studied the effects of pH and total organic carbon on the distribution of trace metals in Kubanni Dam sediments, Zaria, Nigeria. They determined Cd, Cr, Cu, Pb and Zn in the exchangeable, carbonate, Fe-Mn-oxides, organic matter and residual sediment chemical fractions of Kubanni Dam during dry and raining seasons using the spectrophotometric method. The pH and Total Organic Carbon (TOC) of the sediment samples were also determined to study their effects on the distribution of metals. The results indicate that pH influenced the release or adsorption of each metal in the different sediment fractions. At low average pH of 4.9 recorded during dry season, desorption of metals from the reducible sediment fraction into the water column occurred, which may have effect on aquatic organisms. Due to increased metal complexation at high pH, total extractable fractions of metals generally increased. Higher TOC levels during the rainy season indicated larger adsorption surfaces for Cr (19.92%) Pb (19.97%) and Zn (21.14%) on the organic matter fraction, which, under oxidizing condition, these metals may be remobilized into the aquatic environment. Cu correlated positively with the organic carbon content of the sediment samples.

Begum *et al.* (2018) studied various physico-chemical parameters and analysis of untreated fertilizer effluent. His result revealed that the parameters like EC, TDS, TSS, BOD, COD and ammonia were high, and fungal analysis showed the presence of 15

species isolated on Malt Extract Agar (MEA) medium thereby indicating the pollutional load of the effluent.

Saravanakumar *et al.* (2018) determined the physicochemical characteristics of water and sediment and the textural aspects of sediments in western mangroves of Kachchh-Gujarat, west coast of India. Surface water and sediment temperatures varied from 17°C to 37°C and from 18.4°C to 37°C respectively. The pH in water and sediment ranged between 7.0 and 8.9 and 6.29 and 8.45 respectively. Variation in dissolved oxygen content was from 3.42 to 5.85 ml. Concentrations of nutrients such as nitrate (0.23 to 7.26 µM), nitrite (0.04 to 0.87 µM), phosphate (0.13 to 3.12 µM) and reactive silicate (4.23 to 19.02 µM) also varied independently

Shawai (2019) reviewed various water analysis carried out by some researchers from different locations in the Kano State, Nigeria. The water status of rivers, dams, ground water and sachet water used in Kano were presented in their paper. Based on the data considered in the review paper, revealed that parameters in sachets and ground water consumed in Kano are within the WHO recommended standards for potable water and ensures the suitability of the water for human consumption. Industrial effluents activities contributed immensely in making the river water sources unfit for human and irrigation purposes.

Ogueri *et al.* (2018) investigated some physico-chemical parameters, and also examined Nickel, Lead, Manganese, and Copper from Gill, liver, and fillet of three selected fin fish species; *Oreochromis niloticus*, *Synodontis clarias*, and *Hepsetus odoe* of the lake to provide information on the human consumption safeties of these fish samples from the lake. Surface water, and fish samples from three stations and fisherman landing site respectively were collected bi-monthly for three months. Surface water temperature, pH,

and Dissolved Oxygen were measured *in situ*, while other parameters were determined according to APHA (2012) standard methods. Data were analyzed using descriptive statistics, ANOVA, and Duncan Multiple Range Test (DMRT) at $\alpha 0.05$. All the measured physico-chemical parameters were within the recommended permissible limit for aquaculture. Copper recorded the highest metal concentration (1.55 $\mu\text{g/g}$) in the gill of *Oreochromis niloticus*. Nickel was not detected in all the observed fish species. The mean concentrations of all the metals in the present study were lower than the permissible limits, thus the sampled fish from the lake are generally safe for human consumption (Ogueri *et al.*, 2018).

Bojarczuk *et al.* (2018) determined the anthropogenic and natural factors affecting spatial and temporal changes in the physicochemical parameters and bacterial indicators of water quality in the river Białka. Water samples were collected over a period of 2.5 years, once per each month in four sites along the river. Temperature, electrolytic conductivity, pH, and water level were measured onsite; flow rate data were acquired from the Institute of Meteorology and Water Management; chemical analyses allowed to determine the amount of fourteen ions, while microbiological indicators included total and thermo-tolerant coliforms, total and thermo-tolerant *Escherichia coli*, and mesophilic and psychrophilic bacteria. The combination of hydrological, hydrochemical, and microbiological methods generated large amount of data, which were processed by multivariate statistical analysis. A downstream cumulative effect was observed in the contamination of the river water. Fecal coliforms and *E. coli* were detected in all sites, suggesting the source of fecal contamination even in the protected areas.

Sakhiya *et al.* (2018) assessed the drinking water quality of some selected drinking water sources in Abuja area using water quality index (WQI). Samples of drinking

waters were collected from four different sources- river, sachet (packaged), borehole and well in Jabi, Abuja, Nigeria for physicochemical and bacteriological analyses using standard methods. With the exception of pH, river water had the highest content of all the physicochemical parameters examined. Excluding dissolved oxygen in river sample, the physicochemical parameters of the water sources were generally within the World Health Organization (WHO) standards. The bacteriological analyses revealed that the highest total coliform counts of $1.03 (0.08) \times 10^2$ cfu/ml were in the river sample while the least counts of $0.03 (0.00) \times 10^2$ cfu/ml were in the sachet water. All the bacteriological values did not meet international standard as they were higher than WHO standard of zero per 100 ml. Three bacterial isolates *Escherichia coli*, *Pseudomonas* spp and *Aeromonas* spp, were isolated from well water while *Pseudomonas* spp and *Proteus* spp were isolated from borehole water.

2.5.3 Some previous applications of chemometrics techniques to river pollution data

Metal chemical fractions obtained by multivariate analysis techniques were exploited for assessing 7 heavy metals (Cr, Pb, Cd, Co, Cu, Zn and Ni) in sediments from Gansu province, Ningxia and Inner Mongolia Autonomous Regions of the Yellow River in Northern China. The results indicated that higher susceptibility and bioavailability of Cr and Cd with a strong anthropogenic source were due to their higher availability in the exchangeable fraction (Xiaoling *et al.*, 2017).

A portion of Pb, Cd, Co, Zn, and Ni in reducible fraction may be due to the fact that they can form stable complexes with Fe and Mn oxides. Substantial amount of Pb, Co, Ni and Cu was observed as oxidizable fraction because of their strong affinity to the organic matters so that they can complex with humic substances in sediments. The high geo-accumulation indexes (I_{geo}) for Cr and Cd showed their higher environmental risk to

the aquatic biota. Principal component analysis (PCA) revealed that high toxic Cr and Cd in polluted sites may be contributed to anthropogenic sources, it was consistent with the results of dual hierarchical clustering analysis (DHCA), which could give more details about contributing sources (Xiaoling *et al.*, 2017).

Iqbal *et al.* (2018) carried out a Geochemical variation and distribution patterns of selected metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn) in the sediments from five sites from Mangla Lake, Pakistan. Among the metals, Cd, Co, Ni, Pb and Sr exhibited relatively higher mobility and bioavailability, while Cu, Fe, Mn and Zn were found mainly in the residual fractions. Principal component analysis (PCA) revealed four groups of the metals in the sediments; I (Cd–Cr–Ni–Sr), II (Co–Pb), III (Fe–Zn), and IV (Mn–Cu); first two groups were mostly contributed by anthropogenic sources.

The pollution indicators (individual contamination factor, enrichment factor and geoaccumulation index) revealed significant anthropogenic contamination of Cd, Co, Ni, Pb, Sr and Zn in the sediments. Risk assessment code (RAC) indicated medium risk for Co and Ni; high risk for Cd and Pb; and very high risk for Sr in the sediments.

Cluster analysis (CA) and global contamination factor (GCF) were used to identify the pollution hotspots, which indicated more severe metal contamination at sites near to Mirpur city and other urban/semi-urban areas especially for Cd, Co, Ni, Pb and Sr. Overall, Cd, Pb, Sr, Ni and Co emerged as major pollutants in the sediments. CA and GCF identified certain sites as pollution hotspots, which were in close proximity to thickly populated urban/semi-urban areas where various anthropogenic activities contributed most of the pollutants in the study area.

According to Thomas (2019), two groups of researchers have studied the speciation of copper, lead, and cadmium in coastal and estuary waters. These elements were fractionated and speciated in coastal waters from the Inner Oslofjord, Norway. It was

found that cadmium was present entirely in a low-molecular-weight labile species; lead was mainly in non-labile low-molecular-weight species, with half of the total lead probably occurring in low-molecular-weight organometallic compounds; copper distribution was irregular with extensive organic and colloidal association.

Another study showed the speciation of the same three elements in estuarine and coastal waters. They evaluated the potential of a heavy metal speciation scheme to reflect differences in metal distribution within water mass obtained in a study of soluble copper, lead, and cadmium speciation in water samples from five stations in the Port Hacking Estuary (Australia) and one coastal Pacific Ocean station. The observed metal distribution was found to be consistent with the other measured physical and chemical properties of the sample waters (Thomas, 2019).

In all samples, the percentages of metals associated with colloidal matter were high, amounting to 40%–60% of total copper, 45%–70% of total lead, and 15%–35% of total cadmium. The scheme was used to follow changes in metal speciation under different sample storage conditions. Storage at 4°C in polythene containers was shown to prevent losses or changes in the speciation of the metals studied (Thomas, 2019).

Ahmed *et al.* (2019) evaluated metal pollution and their sources in sediments by pollution indices and multivariate statistical techniques in association with a geographical information system (GIS). They collected surface samples in dry season from different locations of Dhaka Aricha highway and analyzed by energy dispersive X-ray fluorescence (EDXRF). Thirteen different metals were found in the tested samples. Pollution indices were determined by enrichment factor in an order of $Zr > Sn > P > Mn > Zn > Rb > Fe > Ba > Sr > Ti > K > Ca > Al$.

The resulting geoaccumulation index (I_{geo}) value showed the following order: $Sn > Zr > P > Mn > Zn > Rb > Fe > Ba > Ti > Sr > K > Ca > Al$. Contamination factors (CFs) of

the metals range from 1.422 to 3.979 (Fe); 0.213 to 1.089 (Al); 0.489 to 3.484 (Ca); 1.496 to 2.372 (K); 1.287 to 3.870 (Ti); 2.200 to 14.588 (Mn); 5.938 to 56.750 (Zr); 0.980 to 3.500 (Sr); 2.321 to 4.857 (Rb); 2.737 to 6.526 (Zn); 16.667 to 27.333 (Sn); 3.157 to 16.286 (P); and 0.741 to 3.328 (Ba). Pollution load index calculated from the CFs indicates that sediments are strongly contaminated by Zr and Sn. Principal Component Analysis (PCA) of parameters exhibited three major components. R-mode cluster analysis revealed three distinct groups in both site and metal basis clustering that showed a similar pattern with the PCA (Ahmed *et al.*, 2019).

Jiawei *et al.*, (2018), studied the Spatial variation, environmental assessment and source identification of heavy metals in sediments of the Yangtze River Estuary. In order to analyze the spatial distribution patterns, pollution sources and ecological risks of heavy metals (As, Cd, Cr, Cu, Mn, Ni, Pb and Zn), 30 sediment samples were taken from in the Yangtze River Estuary. The results indicated that the contamination ranking of heavy metals was As > Cr > Cd > Ni > Mn > Pb > Zn > Cu.

In the various areas, the pollution magnitude decreased as follows: adjacent sea > river mouth > inner-region. Compared to data published for other regions, the YRE data indicated that the sediment was not severely contaminated by heavy metals. In the YRE, natural and anthropogenic inputs dominated the distribution patterns of the heavy metals. Beyond that, the hydrodynamic conditions, such as the Taiwan warm current, coastal current and Yangtze diluted water, also caused distribution variations in the study areas.

The values indicated that a considerable degree of contamination existed in the river, and in the adjacent sea, the contamination was more prominent. They reported that the sediment in the river was not significantly impacted by heavy metal pollution. However, more attention should be focused on Cr and As. From their report, three PCs were

extracted from the analysis. PC1 was mainly related to Cr, Cu, Mn, Ni, Pb and Zn, which were naturally sourced. PC2 was mainly related to Cd, which was anthropogenically sourced. PC3 was mainly related to As and represented the combination of anthropogenic and natural sources.

Deming *et al.* (2019) determined the spatial distribution, potential risks and sources of seven heavy metals in sediments of the Yangtze River Estuary. Analyses of 55 sediment samples revealed that the distributions of metals within the river were determined by the combined effects of their sources, hydrodynamic conditions, pH and Eh. According to the geoaccumulation index (I_{geo}) and sediment quality guidelines, Pb, Cd and Cr were present at low levels of pollution, with Cd posing the largest ecological risk.

Positive Factor Matrix (PMF) results indicated that Hg, Zn, As, Pb and Cr mainly originated from natural geological background sources, while Cu originated from anthropogenic activities and atmospheric deposition was the source of Cd. These three sources contributed to 53.0%, 32.8% and 14.2%, respectively of total heavy metal concentrations. These results suggest that reducing the emission of Cd would promote a reduction of potential risks in sediments of the river.

Ayari *et al.* (2017) conducted an extensive spatial survey on heavy metal content in stream sediments from Oued ElMaadene basin, northern Tunisia. Their objectives were to evaluate the level of trace metal pollution and associated ecological risk and identify the major sources of metal pollution. For this purpose, enrichment and contamination levels of these heavy metals and their potential risk to ecosystems were assessed using various geochemical methods (geochemical background threshold, enrichment factor, geoaccumulation index, and potential ecological risk index). Statistical analyses, including descriptive parameters and principal component analysis, were applied to study the spatial patterns of investigated trace metals and identify their possible sources.

A total of 116 stream sediment samples were collected and analysed for total As, Cd, Cr, Cu, Ni, Pb, V, Zn, and Zr concentrations. The results showed that concentrations of Cr, Ni, V, and Zr were close to natural levels.

In contrast, As, Cd, Cu, Pb, and Zn had elevated concentrations and enrichment factors compared to other contaminated regions in northern Tunisia. Ecological risk to aquatic ecosystems was highlighted in most areas. Principal component analysis showed that Cr, Ni, V, and Zr mainly derived from local soil and bedrock weathering, whilst As, Cd, Pb, and Zn originated from mining wastes (Ayari *et al.*, 2017).

Yunqian *et al.* (2019) analyzed surface sediment samples collected from 18 sites in Dongping Lake for selected heavy metals including As, Cd, Cr, Cu, Hg, Pb, and Zn to determine their spatial distribution, source, and potential ecological risks. The enrichment degree of the studied metals decreased in the order of Cd > Hg > As > Pb > Cu > Cr > Zn, and the average concentrations of Cd, Hg and As were 3.70, 3.69 and 3.37 times their background values.

With the exception of Cd, the concentrations of heavy metals decreased progressively from the southeast to the north and west within the lake. Based on the enrichment factor (EF) and the potential ecological risk index (PERI), As, Cd and Hg were the heavy metal contaminants of most concern in surface sediments. Moreover, referencing to the results of multivariate statistical analyses, it was deduced that anthropogenic As and Hg were mainly from industrial and mining sources within the Dawen River watershed, whereas, Cd originated from agricultural sources.

2.6 Critical Challenges and Major Vacuum in River and Sediment Analysis

In recent years, various published reports have focused attentions on the levels of nutrients in water bodies and the evaluation of water quality in some Nigerian rivers, which indicated that the rivers has been polluted by anthropogenic activities and has

affected the safety of drinking water, agricultural irrigation and aquaculture. Nevertheless, information concerning the pollution of heavy metals in the sediment, pollution source identification and the potential ecological risk in Nigeria has been limited (Ayari *et al.*, 2017).

Previous studies have proven that various natural and anthropogenic sources contribute to the concentrations of heavy metals found in river and sediments. Multivariate principal component analysis (PCA) will be performed to explore the sources of heavy metals in surface sediments found in the selected rivers. PCA is used to simplify the data and make it easier to identify the factors that explain most of the variance in the data. PCA has been proven to be an effective tool that can be used to identify potential sources of heavy metals and has been widely used in combination with correlation analysis (Daniel *et al.*, 2018).

Although heavy metal pollution in these water bodies has been investigated, only sparse systemic research on the spatial distribution of heavy metals in the selected rivers has been performed. Hence, assessing the contamination and ecological risks of heavy metals in sediment and river water using multiple approaches that are based on the various metal assessment indices and spatial analysis tools is meaningful. The assessment would help characterize the contamination sources in river and surface sediments and provide a tool for effectively protecting the river environment.

In this study, based on the heavy metal sample data in the Tagwai Dam, Bosso Dam and Chanchaga river, and sediments, the principal components (PCs) will be applied to determine the degree of contamination. The contributing sources of heavy metals will be identified using multivariate statistics.

The major challenge and vacuum from the review of previous studies is that there is little no information on pollution data of the Nigerian aquatic environment that used

Multivariate analysis considering the fact that there is a possibility of loss of so much data by use of the conventional statistical analysis. There is also the vacuum of no river water pollution source identification in Nigerian rivers considering the fact that agriculture (particularly fishing) is highly practiced in Nigeria and is also considered a major source of Nigeria's revenue generation.

Previous studies support that multivariate statistical methods including CA and PCA/FA can be applied to interpret complex datasets of heavy metals in river water and sediments, understand spatial variation in heavy metals along riverside areas, and identify latent pollution sources/factors. PCA, FA, and CA will be excellently used in the current study to find inter-parameter associations existing between different pollutants. This data-mining technique will further help in reducing the number of pollution parameters to be tested and subsequent cost of analysis.

Therefore, this evaluation study can help managers identify the main sources of pollution in different regions so as to determine their priorities for pollution minimization and source reduction. Since multivariate statistical methods are easily applied to heavy metal data, using them can be a practical approach to environmental impact assessment. The selected rivers are pollution hotspots, dispersing the toxic metals in the environment. For source identification, important heavy metals, and their hotspot location, we can easily use multivariate tools for pollution source zonation and to reveal the main harbor of contamination of heavy metals in those areas.

The common methods for distinguishing the pollution sources include element speciation, profile distribution, and spatial distribution. In the last decade, studies on the sources of pollution using GIS were primarily limited to the mapping of pollutants/pollution indices; however, this method is not sufficiently reliable to

distinguish the sources of pollutants. Additional methods should be incorporated, such as multivariable statistics and chemometrics, to identify the sources of pollutants, apportion natural versus anthropogenic contributions, and provide information on transport processes and environmental conditions. Multivariate statistical approaches to identify heavy metal sources in river water and sediments have not been widely used in river water and sediment pollution studies in Nigeria.

In this study, we can easily identify the major metals in the study areas and their sources. We can reduce their point and non-point sources of pollution and reduce their concentration in the selected rivers. Thus, we can easily manage or handle the pollution reduction strategy and also give priority to those sites where close monitoring is needed.

2.7 Source Identification and Apportionment

PCA and cluster analysis methods have been used to identify contributing sources of total suspended particulate matter in urban and rural regions of Sicily. Results on elemental concentrations determined by particle induced X-ray emission (PIXE) analysis indicated soil (resuspended road dust) and automotive emissions, as well as specific industrial contributions, as major sources in two Sicilian cities.

Ogunlaja, *et al.* (2019) determined the concentrations of metals (Cd, Cr, Cu, Mn, Ni, Pb, V and Zn) in groundwater, surface-water and soil from a total of 216 samples acquired bi-monthly for two years by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) to evaluate the impact of oil spills. Multivariate analyses using principal component analysis (PCA) and cluster analysis (CA) were also used to study the interactions between metals and identify the possible sources of contamination.

The concentrations of heavy metals in soil and water samples (surface and groundwater) were in decreasing order of $Mn > Ni > Zn > Cu > V > Cr > Pb > Cd$ and $Ni > Zn > V > Cu > Mn > Pb > Cr > Cd$ respectively. Ni concentration ranged from 0.42–

8.05 mg kg⁻¹ and 0.10–2.85 mg L⁻¹ for soil and groundwater respectively. Ni and V were more enhanced ($P < 0.05$) in soil samples. The study showed that there was significant relationship between elevated levels of Cr, Cu, Ni and Zn and oil spillage, due to petroleum spills and that residents were vulnerable to and at greater risk of non-carcinogenic hazards if they consumed groundwater. Multivariate analyses showed significant anthropogenic intrusions of two diagnostic heavy metals (Ni and V) for petroleum contamination in the soils and water sources (Ogunlaja, *et al.*, 2019).

Srishti *et al.* (2017) carried out source apportionment of particulate matter (PM₁₀) in Delhi, India using principal component analysis with absolute principal component scores (PCA/APCS). All models used the PM₁₀ chemical composition (organic carbon (OC), elemental carbon (EC), water soluble inorganic ions (WSIC), and trace elements) for source apportionment. The average PM₁₀ concentration during the study period was $249.7 \pm 103.9 \mu\text{g}/\text{m}^3$ (range: 61.4–584.8 $\mu\text{g}/\text{m}^3$). The UNMIX model resolved five sources (soil dust (SD), vehicular emissions (VE), secondary aerosols (SA), a mixed source of biomass burning (BB) and sea salt (SS), and industrial emissions (IE)).

The PCA/APCS model also resolved five sources, two of which also included mixed sources (SD, VE, SD+SS, (SA+BB+SS) and IE). The PMF analysis differentiated seven individual sources (SD, VE, SA, BB, SS, IE, and fossil fuel combustion (FFC)). All models identified the main sources contributing to PM₁₀ emissions and reconfirmed that VE, SA, BB, and SD were the dominant contributors in Delhi (Srishti, *et al.*, 2017).

Rehman *et al.* (2018) conducted a study in six subcatchments of the Indus River Basin. A total of 84 surface water samples were collected from main stream and tributaries. The pH, electric conductivity (EC), and total dissolved solids (TDS) were measured in situ, whereas major ions (Ca²⁺, Mg²⁺, K⁺, Na⁺, Cl⁻, SO₄²⁻, and NO₃⁻) and Si were analyzed in the laboratory. The results exhibited alkaline pH (8.55 ± 0.20) with diverse

TDS ($114.69 \pm 77.65 \text{ mg L}^{-1}$) and ion concentrations that were characterized primarily by the Ca-Mg-HCO₃ type in the whole basin.

The average TDS in the Upper Induce Basin (UIB) and Lower Induce Basin (LIB) were 93.99 ± 39.73 and $181.67 \pm 167.82 \text{ mg L}^{-1}$, respectively, under the influence of the arid to semi-arid climatic conditions and relatively higher anthropogenic interference in Lower Induce Basin compared to the UIB. Principal component/factor analysis indicated that the major sources of dissolved loads in the basin are carbonates followed by silicates. Significant influences of silicate minerals were observed in the LIB, and there was a large contribution of evaporites in the UIB-II, UIB-III, and LIB (Rehman *et al.*, 2018).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials/Reagents

The chemicals used were of analytical grade with percentage purity and supplier shown in Table 3.1, while Table 3.2 shows the list of equipment in this study.

Table 3.1: List of Reagents/Chemicals

S/N	Item	%Purity	Manufacturer
1	Nitric acid	68	Sukha Chemical Industries India
2	Hydrogen peroxide	30-32	BDH Chemicals England
3	Potassium chromate	99	Muby Chemicals
4	N-stannous chloride	99.5	Sukha Chemical Industries India
6	N-(1-naphthyl)- ethylenediamine dihydro chloride	96	Sukha Chemical Industries India
7	Potassium sulphate	99	BDH Chemicals England
9	Ammonium molybdate- antimony potassium tartrate	5	Sukha Chemical Industries India
10	Sulphanilamide	5	Sukha Chemical Industries India

11	Sulphuric acid	35	Sukha Chemical Industries India
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Table 3.2: List of Equipment

S/N	Instrument	Model	Manufacturer
1	pH Meter	CER 232	Interface
2	Colorimeter	DR/890	HACH
3	Turbidity Meter		
4	Conductivity meter	470 Conductivity meter	Jenway
5	Electronic weighing balance	AAA	Adam Co limited
6	UV-visible spectrometer	Shimadzu 1800	

3.2 Location of Study Sites

The study was carried out in River Chanchaga, Tagwai Dam and Bosso Dam, which are located in Minna, Niger State.

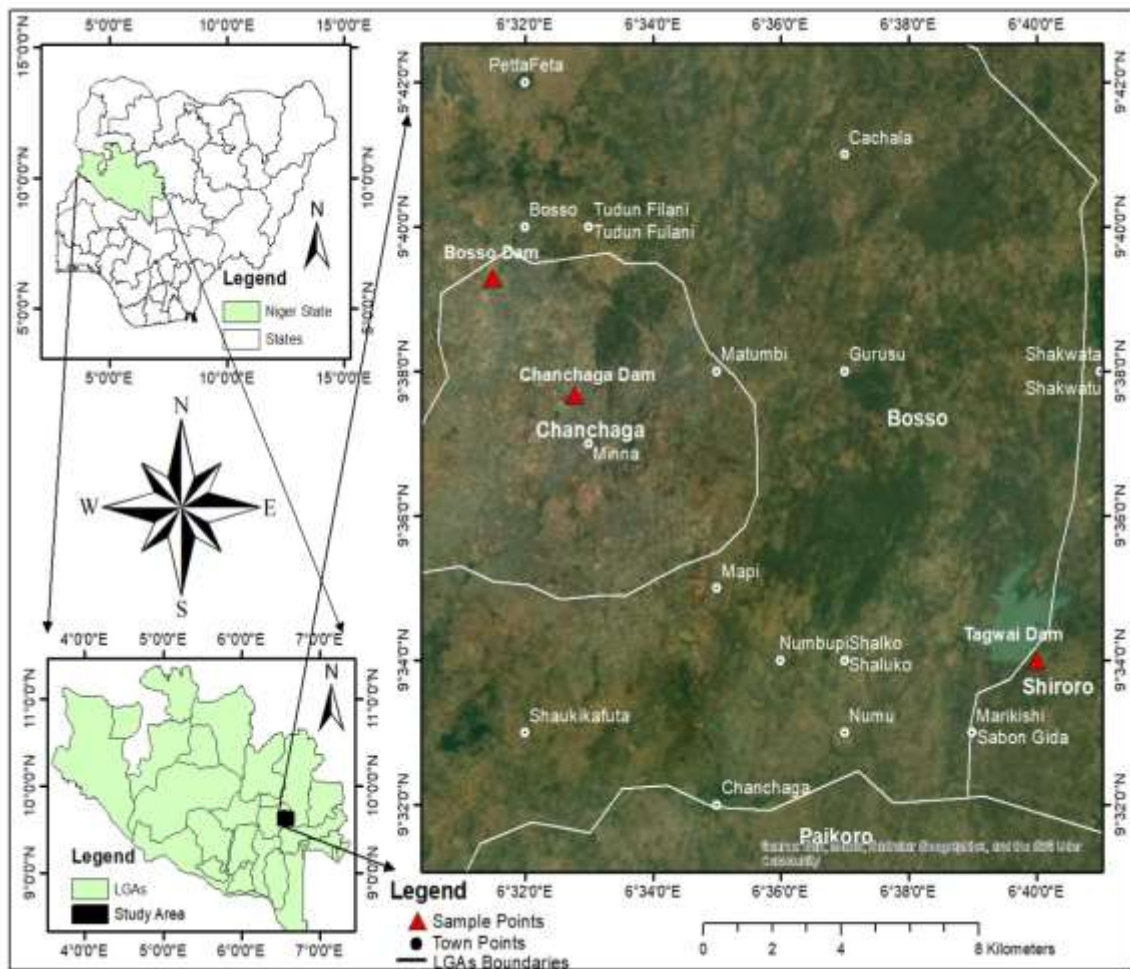


Figure 3.1: Map of Minna Showing the Study Areas

3.2.1 Chanchaga River

Chanchaga River transverses Muya, Shiroro, Paikoro, Bosso, and Katcha Local Government Areas and can be located on Longitude $6^{\circ}33'E$ –longitude $6^{\circ}38'E$ and latitude $9^{\circ}32'N$ -latitude $9^{\circ}35'N$.The total land area covered by the basin is 159,259 km. River Chanchaga plays very important role to many people because it serves many purposes ranging from irrigation farming, fishing and domestic water supply sources to Minna city, and some towns along the river (e.g. Gidan Kwano, Katregi).

River Chanchaga is predominantly underlain by the pre-Cambrian Basement Complex rocks. The local lithological units in the river are granite, gneiss and schist. The granite is the most wide spread rock unit and are porphyritic, medium-coarse-

grained in texture. The granites mostly occur as intrusive, low-lying outcrops into the gneisses. They are severely jointed and fairly incised by quartz veins. The major structural features in the study area are fractures and lineaments. North of the river, the lineaments trend NE-SW direction while in the south, close to River Chanchaga, lineaments trend NW-SE. This implies that the NW-SE flow of River Chanchaga is structurally controlled. Evidence from satellite imagery of the area revealed that the southeastern part of the study area with low fracture density correspond with areas covered by soil and highly weathered thick overburden. The major fractures observed in the area are the signatures of the Pan African Orogeny (600ma), which is the major tectonic event that produced structural deformation of the area (Nda *et al.*, 2019).

3.2.2 Tagwai Dam

Tagwai Dam is located in Chanchaga area of Niger state of Nigeria. It lies between Latitudes 09° 37' N to 09° 33' N of the equator and longitudes 06° 39' E to 06° 42' E of the Greenwich meridian of Nigerian sheet 142 North Western (Minna) Nigeria. It covers an area of 9 km². Most parts of the area are covered by vegetation. Some of the outcrops are not accessible due to thick vegetation. The river was constructed for the purpose of domestic water supply to Minna metropolis. Fishing in the area is dominated by artisanal fishermen that use manually operated wooden canoes, using mostly cast net, gill nets, drift net and traps for fishing.

3.2.3 Bosso Dam

Bosso Dam is located at latitude 9° 39N and longitude 6° 33E in Minna, Niger state. It is a small water body with a mean depth of 6.1 m (20.2ft). The dam is shaded by shrubs, trees and bushes especially in the rainy season. The main use of the dam is for water supply (i.e. potable water) supply for domestic use and irrigation. The resources in the

Dam are conserved and protected from poachers by making it a restricted area. Most changes in the dam were brought about by flooding of terrestrial organic and inorganic materials, defecation of animals and siltation. The dominant fish species in the Dam is *Tilapia zilli*. Crocodiles also occasionally inhabit the dam.

3.3 Sample Collection and Preservation

3.3.1 Water

Each study site was divided into ten sections. Water samples were collected randomly at 10 points in each section and homogenized to get a composite sample. A total of thirty (30) composite samples were collected from the three sample locations. Water samples were acidified to a pH of < 2 with analytical grade nitric acid while in the field and then transported to the laboratory for storage awaiting digestion. Water samples were collected in rainy and dry seasons.

3.3.2 Sediments

Each study site was divided into ten sections. Sediment samples were collected from ten points in each section and homogenized to get a composite sample. A total of thirty (30) composite samples were collected from the three sample locations. Samples of sediment were collected with a PVC pipe which was pushed with pressure through the water to obtain sediment layer at a depth of approximately 15 cm. Sediment samples were packed in polythene bags and transported to the laboratory where they were dried at 105 °C until there was no further change in weight. Dried sediments for each sampling station was mixed and crushed with a pestle and mortar to homogenize. The homogenized samples were sieved and packed in clean polythene bags and kept for digestion and measurement of the heavy metals. Sediment samples were collected in rainy season and dry season.

3.4 Methods of Analysis

3.4.1 Physicochemical parameters

Selected physicochemical measurements such as temperature, silica, pH, turbidity, conductivity, nitrite, nitrite nitrogen, ammonia, copper, nitrate, zinc, manganese, cadmium, lead and chromium were analyzed. Some parameters, such as pH, temperature, salinity, conductivity, and turbidity were measured directly at the place of sampling in the water.

3.4.1.1 On-site analysis

On-site analyses of pH, conductivity, and turbidity were carried out at the site of sample collection following the standard protocols and methods of American Society for Testing and Materials (ASTM D3557-12) using different calibrated standard instruments. The pH of the water samples was measured by using a pH meter. The pH meter was calibrated, with three standard solutions (pH 4.0, 7.0, and 10.0), before taking the measurements. The value of each sample was taken after submerging the pH probe in the water sample and held for a couple of minutes to achieve a stabilized reading. After the measurement of each sample, the probe was rinsed with deionized water to avoid cross contamination among different samples.

The conductivity of the samples was measured using a conductivity meter. The probe was calibrated using a standard solution with a known conductivity. The probe was submerged in the water sample and the reading was recorded after the disappearance of stability indicator. After the measurement of each sample, the probe was rinsed with deionized water to avoid cross contamination among different samples.

The turbidity of the water samples was measured using a turbidity meter. Each sample was poured in the sample holder and kept inside for a few minutes. After achieving the reading stability, the value was recorded.

3.4.1.2 Laboratory analysis

Silica was determined using the Standard Test Method for Silica in Water as described by ASTM D859-16. A test of the molybdenum-blue method was used for silica measurement. In each of a series of 100 cm³ flasks, 5 cm³ of 5% ammonium molybdate and 3 ml in hydrochloric acid was placed and 25 cm³ of distilled or seawater containing known additions of silicon was added. After 10 minutes, 5 cm³ of 35% v/v sulphuric acid was added, the solution was allowed to stand for 5 mins and 1 ml 0.1 N-stannouschloride was added. After a further 10 min, the extinctions of the solutions were measured in a 1 cm cuvette using red filters.

For nitrite-nitrogen determination, the nitrate/nitrite-N in water and biosolids by Manual Colorimetry method as described by U.S. Environmental Protection Agency (2011) was used. 2 cm³ of color reagent (prepared by adding 100 cm³ 85% phosphoric acid (H₃PO₄) and 10 g sulfanilamide was added to about 800 cm³ reagent water and mixed to completely dissolve the sulfanilamide. 1 g N-(1-naphthyl)-ethylenediamine dihydrochloride was added and mixed to dissolve. It was diluted to 1 L with reagent water and added to 50.0 cm³ of sample. It was allowed ten minutes for the color to develop, the absorbance of the sample was measure at 540 nm.

Ammonia was measured by Berthelot or indophenol method using a UV-VIS spectrophotometer Perkin Elmer Lambda 25 with double beam. The method is based on ammonium ion reaction with phenol and hypochlorite in alkaline medium to form indophenol blue. The blue color formed is intensified with sodium nitroprusside and the absorbance is measured at 655 nm.

Nitrates were analyzed by a standardized method of molecular absorption spectrometry based on the formation of a yellow compound through the reaction of nitrates with sulphosalicylic acid (2-hydroxy-5sulfobenzoic acid) under acidic conditions followed

by treatment with an alkaline solution containing also the disodium salt of the ethylenediaminetetraacetic acid (EDTANa_2) to prevent the precipitation of calcium and magnesium salts (SR ISO 7890-3-1998). The absorbance of the resulted compound was measured at 415 nm with a UV-VIS spectrophotometer Perkin Elmer Lambda 25.

The analyses of six heavy metals such as Cu, Zn, Mg, Cd, Pb, Cr, was carried out based on ASTM standards (ASTM, 2012), which are approved by APHA, 2012 (American Public Health Association) using Atomic Absorption. For analysis of Cd, Cr, and Pb, direct extraction/air-acetylene flame method was used. The standard solution for each tested element was prepared according to its concentration and used to calibrate the system before analyzing each water sample. The results were recorded automatically on a computer connected with the AAS system. The mean of the triplicate measurement was taken.

3.4.2 Digestion of sample

3.4.2.1 Water sample

This was done according to the method described by Türkmen and Ciminli (2017). The preserved water samples were measured and put in a clean conical flask and 5 cm³ of nitric acid was added. The mixture was heated with the addition of few drops of hydrogen peroxide until there are no brown fumes. The mixture was filtered in a volumetric flask and topped to the labeled mark. The samples of water were transferred into separate plastic bottles, labeled and stored for analysis.

3.4.2.2 Sediments

Sediments were wet digested as described by Türkmen and Ciminli (2017), where dried sediments samples were weighed using electronic weighing balance Model AAA Adam Co limited. Concentrated HNO_3 was first added in a Kjeldahl flask and then gently

heated on hot mantle until the dense brown fumes begin to appear. Hydrogen peroxide was added drop wise to clear the brown fumes and improve the dissolving power of nitric acid. Digestion of sediments was allowed to evaporate to about 5 cm³. This was cooled and filtered (using Whatman No 42 filter paper) into 25 cm³ different clean and dry volumetric flask and then diluted to the mark with distilled water. The digested samples were then transferred into separate plastic bottles, labeled and stored for analysis. Samples were analyzed for Pb, Mn, Zn, Cd, Cu and Cr by atomic absorption spectrophotometer. Triplicate measurement was done and the mean recorded.

3.4.3 Preparation of solutions and calibration

Stock solutions of 1000 ppm for each metal was either prepared from analar grade granulated metal or salts of high purity (99.9%). Each metal was first dried at 105 °C, cooled in desiccators prior to weighing and transferred into 1 litre volumetric flasks.

To prepare 1000 mg/dm³ of Pb, Mn, Zn, Cd, Cu and Cr solutions; 1.598 g of lead nitrate was dissolved in 2% (v/v) HNO₃ and diluted to volume in a 1-L flask to make a standard solution of lead. 1.000 g of pure Mn, Zn, Cu and Cd granules were each separately dissolved in a minimum volume of pure HNO₃ and diluted to volume in a 1-L volumetric flask with 2% (v/v) HNO₃ and 3.735 g of potassium chromate (K₂CrO₄) was dissolved in 2% (v/v) HNO₃ and diluted to volume in a 1-L flask with distilled water to make standard solutions. The stock solutions were stored in plastic bottles and labeled appropriately. Working standards were freshly prepared from stock solutions by serial dilution. During serial dilution of stock solutions, the final acid concentration was maintained at about 1% to keep the metal in free ionic state. Calibration curves of the elements under study were prepared by determining the absorbance of different concentrations.

3.4.4 Analysis of the metal solutions using Atomic Absorption Spectrometer

For the elemental analysis using atomic absorption spectrometer, a solution containing each metal analyte was introduced into acetylene flame to convert the samples into free ground state atoms that can be excited. A lamp emitting light at a wavelength specific to the atoms was passed through the flame, and as the light energy was absorbed, the electrons in the atoms are elevated to an excited state.

For Pb, Cd, Cu, Cr, Zn and Mn analysis, a thin beam of light was passed through the flame containing each analyte. The beam contained light at 283.3, 228.8, 324.8, 357.9, 213.9 and 279.5 nm respectively. The light was absorbed by the atoms as excitation of electrons from the ground state to the first energy level occurred. The amount of absorption allowed a calculation of the concentration of the analytes in the samples to be determined. To calibrate an AAS, first a blank solution containing none of the elements was measured to determine the baseline absorption measurement. The absorption of solutions containing different known amounts of the elements were measured. From the obtained data, a calibration curve was created. The calibration curve determines the relationship between the absorbance of the light and the concentration of the element in the solution.

3.4.5 Chemometrics and statistical analysis of data

Analyzed data was subjected to multivariate analysis of PCA and HCA using Eigenvector Research Inc Solo software, stand-alone chemometrics software powered by PLS_Toolbox for pattern recognition. Microsoft Excel 2014 (Multivariate Analysis Add-in) was used to carry out the descriptive statistics and correlation analysis.

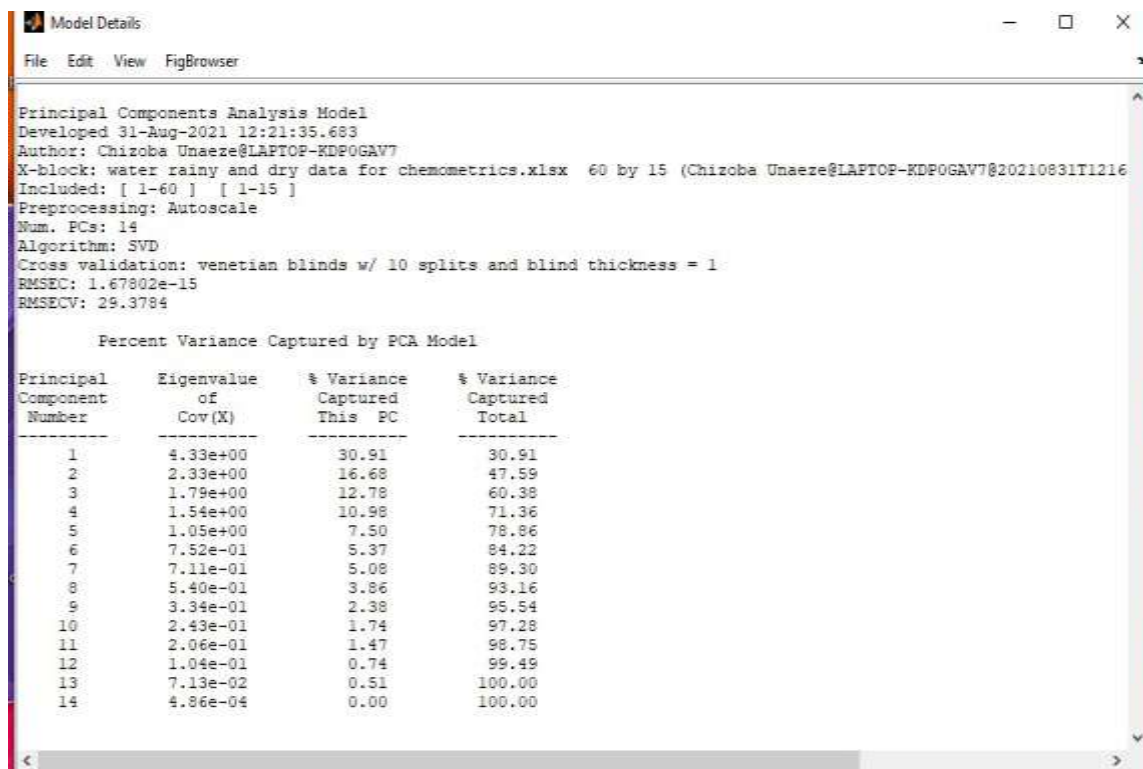


Figure 3.2: PCA Analysis Model details

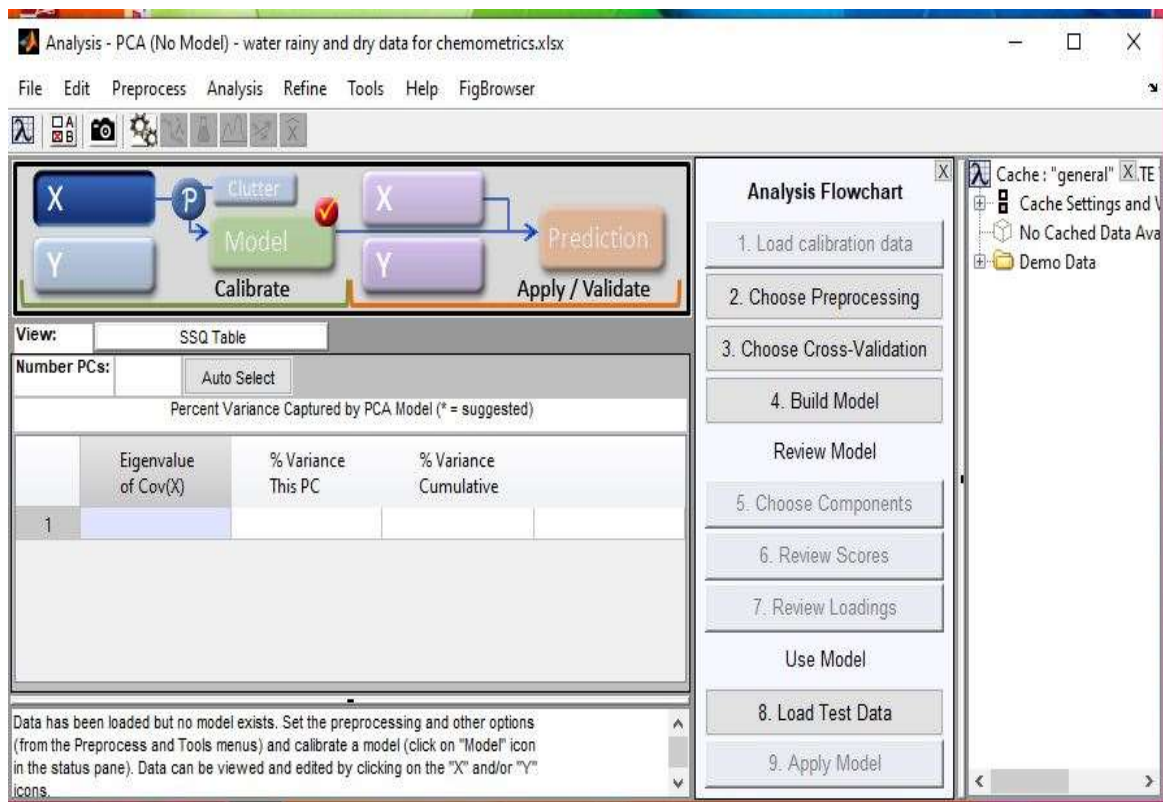


Figure 3.3: PCA Analysis Model page

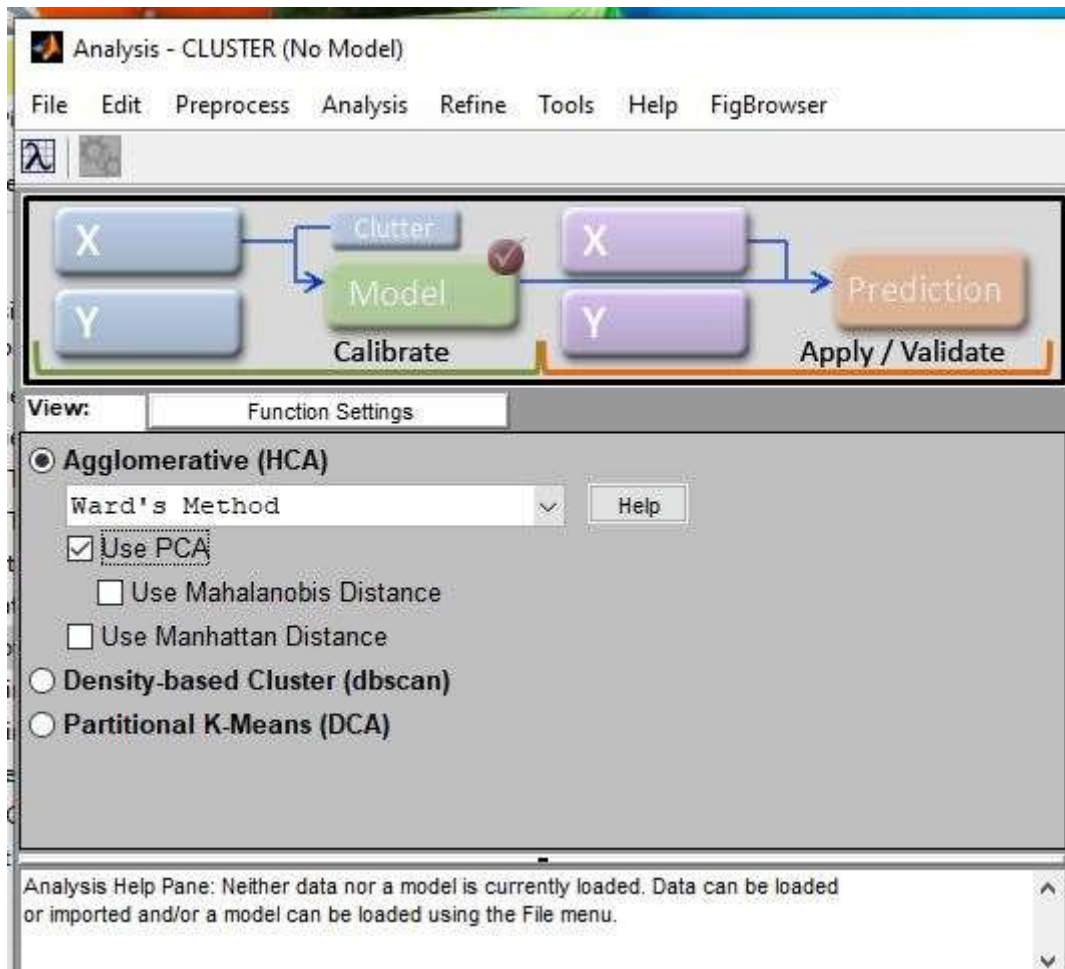


Figure 3.4: Cluster Analysis Model Page

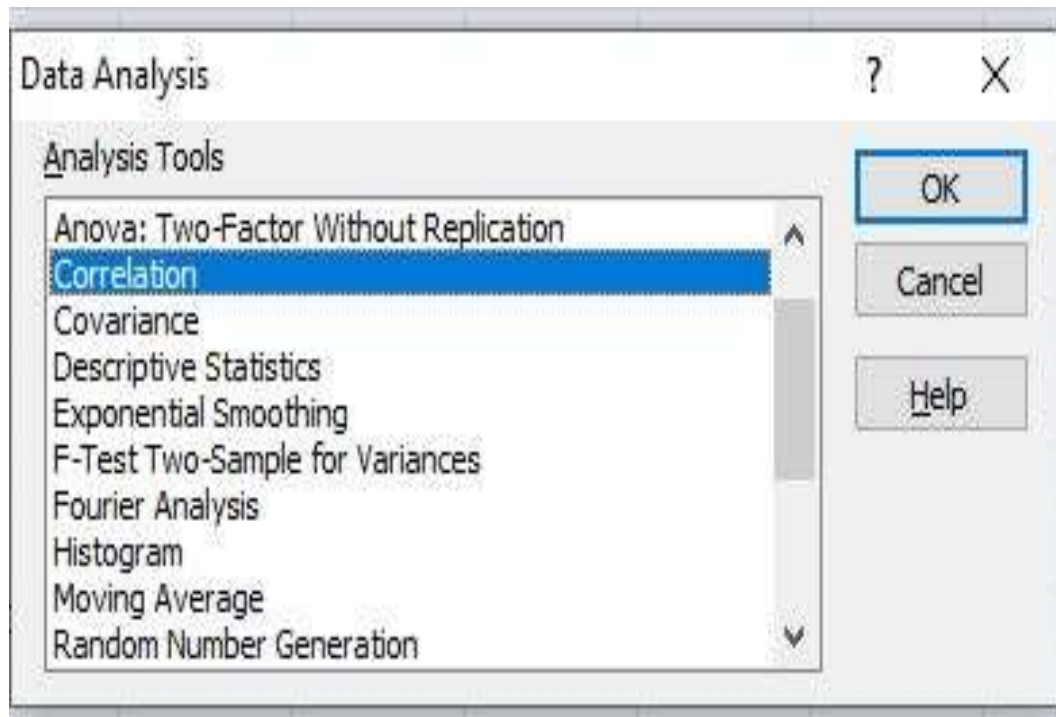


Figure 3.5: Correlation Analysis Tools page

Table 3.3: Water Sample Labels and their Numbers

S/ N	Sample s	S/ N	Sample s	S/ N	Sample s	S/ N	Sample s	S/ N	Sample s	S/ N	Sample s
1	BWR1	11	CWR1	21	TWR1	31	BWD1	41	CWD1	51	TWD1
2	BWR2	12	CWR2	22	TWR2	32	BWD2	42	CWD2	52	TWD2
3	BWR3	13	CWR3	23	TWR3	33	BWD3	43	CWD3	53	TWD3
4	BWR4	14	CWR4	24	TWR4	34	BWD4	44	CWD4	54	TWD4
5	BWR5	15	CWR5	25	TWR5	35	BWD5	45	CWD5	55	TWD5
6	BWR6	16	CWR6	26	TWR6	36	BWD6	46	CWD6	56	TWD6
7	BWR7	17	CWR7	27	TWR7	37	BWD7	47	CWD7	57	TWD7
8	BWR8	18	CWR8	28	TWR8	38	BWD8	48	CWD8	58	TWD8
9	BWR9	19	CWR9	29	TWR9	39	BWD9	49	CWD9	59	TWD9
10	BWR10	20	CWR10	30	TWR10	40	BWD10	50	CWD10	60	TWD10
1	BSR1	11	CSR1	21	TSR1	31	BSD1	41	CSD1	51	TSD1
2	BSR2	12	CSR2	22	TSR2	32	BSD2	42	CSD	52	TSD2
3	BSR3	13	CSR3	23	TSR3	33	BSD3	43	CSD3	53	TSD3
4	BSR4	14	CSR4	24	TSR4	34	BSD4	44	CSD4	54	TSD4
5	BSR5	15	CSR5	25	TSR5	35	BSD5	45	CSD5	55	TSD5
6	BSR6	16	CSR6	26	TSR6	36	BSD6	46	CSD6	56	TSD6
7	BSR7	17	CSR7	27	TSR7	37	BSD7	47	CSD7	57	TSD7
8	BSR8	18	CSR8	28	TSR8	38	BSD8	48	CSD8	58	TSD8
9	BSR9	19	CSR9	29	TSR9	39	BSD9	49	CSD9	59	TSD9
10	BSR10	20	CSR10	30	TSR10	40	BSD10	50	CSD10	60	TSD10

BWR-Bosso water rainy season

CWR-Chanchaga water rainy season

TWR- Tagwai water rainy season
BSR-Bosso sediment rainy season
CSD-Chanchaga sediment rainy season
TSD-Tagwai sediment rainy season
BWD-Bosso water dry season
CWD-Chanchaga water dry season
TWD-Tagwai water dry season
CSR-Chanchaga sediment rainy season
TSR-Tagwai sediment rainy season
BSD-Bosso sediment dry season

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Results

4.1.1 Heavy metals in water and sediment

Table 4.1 presents heavy metal accumulation in water samples during rainy and dry seasons in the study locations. Cu was observed at the range of ND - 0.01 mg/l for all three locations which is within the WHO recommended limit. Zn was detected within the range of 0.002 mg/l – 0.02 mg/l in both seasons for all three locations. Zn concentration values exceeded the WHO limit for water in Chanchaga River during dry season. Mn concentration was in the range of ND- 0.01 mg/l for both seasons which is below the permissible limit. Highest Cd level was detected at 0.01mg/l in Bosso dam during rainy season while Pb was not detected in all water samples. Cr values ranged from ND – 0.03 mg/l for all locations in both seasons. This value is below the threshold.

Table 4.2 presents heavy metal accumulation in sediment samples during rainy and dry seasons in the study locations. Cu was observed at ND-0.03 mg/l for all three locations which is above the WHO recommended limit. Mn concentration was in the range of ND- 0.09 mg/l for both seasons which is within the permissible range. Highest Cd level was detected at 0.04 mg/l above the recommended limit while that of Pb was at 0.001

mg/l. Cr values ranged from ND – 0.02 mg/l for all locations in both seasons which is within the recommended limit.

Table 4.1: Heavy Metal Accumulation in Water Samples during Rainy and Dry Seasons

Parameters	Bosso Rainy Season	Bosso Dry Season	Chanchaga Rainy Season	Chanchaga Dry Season	Tagwai Rainy Season	Tagwai Dry Season	WHO (2014)
Copper (mg/l)	0.01±*0.01 ^a _b	*0.03±*0.01 ^d	0.01±0.00 ^b	*0.02±0.00 ^c	*0.04±0.00 ^e	ND ^a	0.01 ^b
Zinc (mg/l)	0.01±0.01 ^a	*0.02±0.00 ^b	0.01±0.00 ^a	0.02±0.00 ^b	*0.03±*0.01 ^c	*0.02±0.00 ^b	0.01 ^a
Manganese (mg/l)	0.01±*0.01 ^a _b	ND ^a	0.01±0.00 ^b	ND ^a	ND ^a	ND ^a	0.10 ^c
Cadmium (mg/l)	0.01±*0.01 ^b	ND ^a	ND ^{a d}	ND ^a	ND ^a	ND ^a	0.03* ^c
Lead (mg/l)	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a	0.01 ^b
Chromium (mg/l)	0.03±*0.02 ^b _c	ND ^a	0.02±0.01 ^{bc}	ND ^a	0.01±0.00 ^b	*0.04±*0.01 ^c	0.05 ^d

Values are reported as average mean ± standard error of triplicate determinations. Values along the rows with the differential alphabetic superscripts are significantly different at $p \leq 0.05$ while values with the same alphabet are not significantly different ($p \leq 0.05$).

* = 10^{-1} ND = Not Detected

Table 4.2: Heavy Metal Accumulation in Sediment Samples during Rainy and Dry Seasons

Parameters	Bosso Rainy Season	Bosso Dry Season	Chanchaga Rainy Season	Chanchaga Dry Season	Tagwai Rainy Season	Tagwai Dry Season	WHO (2014)
Copper (mg/l)	0.02±0.00 ^c	0.02±0.01 ^{bc}	0.03±0.01 ^c	ND ^a	0.03±0.02 ^c	0.01±0.01 ^{ab}	0.01 ^b
Zinc (mg/l)	ND ^a	ND ^a	0.12±0.01 ^c	ND ^a	ND ^a	ND ^a	0.01 ^b
Manganese (mg/l)	0.01±0.00 ^b	0.01±0.01 ^{ab}	ND ^a	*0.01±0.01 ^{ab}	0.09±0.01 ^c	0.02±0.01 ^b	0.10 ^c
Cadmium (mg/l)	0.04±0.01 ^c	0.01±0.01 ^d	0.02±0.01 ^{bc}	ND ^a	0.03±0.01 ^c	*0.03±0.01 ^b	0.03 ^{*c}
Lead (mg/l)	ND ^a	*0.01±0.01 ^b	ND ^a	ND ^a	ND ^a	ND ^a	0.01 ^b
Chromium (mg/l)	0.01±0.01 ^{ab}	0.02±0.01 ^b	0.02±0.01 ^b	*0.02±0.01 ^b	0.02±0.01 ^b	ND ^a	0.05 ^c

Values are reported as average mean ± standard error of triplicate determinations. Values along the rows with the different alphabetic superscripts are significantly different at $p \leq 0.05$ while values with the same alphabet are not significantly different ($p \leq 0.05$).

* = 10^{-1} ND = Not Detected

4.1.2 Physicochemical parameters in water and sediment

Table 4.3 displays physico-chemical parameters in water samples during rainy and dry seasons in the study locations. The pH of the water sediment samples collected from the three study locations ranged from 6.75 – 7.44 in rainy season and 6.35 – 7.46 in dry season. The temperature values were in the range 27.57 – 30.70°C during rainy and dry seasons. Silica values ranged from ND – 6.09 mg/l in both seasons. Lowest turbidity value was obtained at 14.54(NTU) in Bosso dam during dry season while the highest turbidity value was at 80.86 (NTU) in Tagwai dam during rainy season. Conductivity values were in the range 74.03 – 115.70 μ S/cm in all three locations during rainy and dry seasons. Nitrite values ranged from 0.02 – 0.12 mg/l during rainy season to ND – 0.07 mg/l during dry season. Highest concentration value for nitrite as nitrogen was observed at 0.03 mg/l in Tagwai dam during rainy season while the lowest value was observed at 0.001 mg/l in Bosso dam during dry season. Ammonia concentration ranged from 0.41/l – 7.54 mg/l in both seasons. Nitrate levels were in the range of ND - 8.13 mg/l.

Table 4.4 presents physicochemical parameters and heavy metal accumulation in sediment samples during rainy and dry seasons in the study locations. The pH of the water sediment samples collected from the three study locations ranged from 4.41 – 5.58 in rainy season and 6.22 – 7.75 in dry season. The temperature values were in the range 25.35 – 27.91°C during rainy and dry seasons. Silica values ranged from 0.86 mg/l – 11.01 mg/l in both seasons. Lowest turbidity value was obtained at 15.31 NTU in Bosso dam during dry season while the highest turbidity value was at 66.30 NTU in Tagwai dam during rainy season. Conductivity values were in the range 209.00 – 430.07 μ S/cm in all three locations during rainy and dry seasons. Nitrite values ranged

from 0.04 – 0.05 mg/l during rainy season to 0.09 mg/l – 0.09 mg/l during dry season. Highest concentration value for nitrite as nitrogen in sediment sample was observed at 0.12 mg/l in Chanchaga river during rainy season while the lowest value was observed at 0.01 mg/l in Bosso dam during rainy season. Ammonia concentration ranged from 4.50 – 10.69 mg/l in both seasons. Nitrate levels in sediment samples were in the range of 2.80 mg/l – 21.62 mg/l.

Table 4.3: Physicochemical Parameters in Water Samples During Rainy and Dry Seasons

Parameter	Bosso Rainy Season	Bosso Dry Season	Chanchaga Rainy Season	Chanchaga Dry Season	Tagwai Rainy Season	Tagwai Dry Season	WHO (2014)
pH	6.75±0.01 ^b	6.93±0.01 ^c	6.93±0.01 ^c	7.46±0.05 ^d	7.44±0.01 ^d	6.35±0.07 ^a	6.5-8.5(7.50 ^d)
Temperature (°C)	27.57±0.01 ^b	30.70±0.10 ^d	27.57±0.10 ^b	30.57±0.01 ^{cd}	27.64±0.01 ^b	30.48±0.01 ^c	12-25(16.50 ^a)
Silica (mg/l)	5.63±0.01 ^c	ND ^a	6.09±0.01 ^d	ND ^a	4.38±0.01 ^b	ND ^a	10.00 ^e
Turbidity (NTU)	24.03±0.01 ^d	14.54±0.01 ^c	80.86±0.01 ^f	58.37±0.0 ^b	76.25±0.01 ^g	30.87±0.01 ^e	5.00 ^a
Conductivity (µS/cm)	74.03±0.01 ^a	103.09±0.01 ^d	96.49±0.29 ^c	115.70±0.05 ^f	87.43±0.01 ^b	115.06±0.19 ^e	1000 ^g
Nitrite (mg/l)	0.02±*0.01 ^{bc}	0.01±0.01 ^{ab}	0.07±0.01 ^d	ND ^a	0.12±*0.01 ^e	0.03±*0.01 ^c	3.00 ^f
Nitrite as N ₂ (mg/l)	0.01±*0.01 ^a	*0.01±0.01 ^a	0.02±0.01 ^{ab}	0.01±0.00 ^a	0.04±*0.01 ^c	0.01±0.00 ^a	0.04 ^c
Ammonia (mg/l)	6.24±0.04 ^d	5.06±0.05 ^c	7.54±0.01 ^f	0.41±0.01 ^a	6.49±0.05 ^e	2.63±0.01 ^b	0.40 ^a
Nitrate (mg/l)	0.63±0.01 ^b	2.19±0.01 ^d	7.16±0.04 ^e	ND ^a	8.13±0.06 ^f	0.92±0.05 ^c	10.00 ^g

Values are reported as average mean ± standard error of triplicate determinations. Values along the rows with the different alphabetic superscripts are significantly different at p≤0.05 while values with the same alphabet are not significantly different (p≤0.05).

* = 10⁻¹

ND = Not Detected

Table 4.4: Physicochemical Parameters in Sediment Samples during Rainy and Dry Seasons

Parameters	Bosso Rainy Season	Bosso Dry Season	Chanchaga Rainy Season	Chanchaga Dry Season	Tagwai Rainy Season	Tagwai Dry Season	WHO (2014)
pH	4.64±0.01 ^b	7.33±0.02 ^e	4.41±0.01 ^a	6.22±0.01 ^d	5.58±0.03 ^c	7.75±0.01 ^g	6.5-8.5 ^f
Temperature (°C)	27.88±0.01 ^e	27.55±0.01 ^d	25.35±0.01 ^b	27.50±0.01 ^c	27.91±0.01 ^f	27.57±0.01 ^d	12-25 ^a
Silica (mg/l)	11.01±0.06 ^g	0.86±0.01 ^a	8.57±0.01 ^d	1.42±0.01 ^b	10.11±0.01 ^f	1.97±0.01 ^c	10.00 ^e
Turbidity (NTU)	20.30±0.05 ^d	16.77±0.01 ^c	27.90±0.01 ^b	20.57±0.02 ^d	66.30±0.01 ^e	15.33±0.01 ^b	5.00 ^a
Conductivity (µS/cm)	411.90±0.03 ^c	430.07±0.01 ^b	412.80±0.01 ^d	421.93±0.01 ^e	209.00±0.01 ^f	260.23±0.01 ^a	1000 ^g
Nitrite (mg/l)	0.04±0.00 ^a	0.10±0.01 ^{cd}	0.05±0.01 ^{ab}	0.05±0.02 ^{ab}	0.41±0.04 ^d	0.09±0.01 ^c	3.00 ^e
Nitrite as N ₂ (mg/l)	0.01±0.00 ^a	0.03±0.01 ^b	0.12±0.01 ^c	0.04±0.01 ^b	0.13±0.01 ^c	0.03±0.01 ^b	0.04 ^b
Ammonia (mg/l)	10.69±0.06 ^e	14.52±0.01 ^g	14.33±0.02 ^f	4.50±0.01 ^b	8.29±0.01 ^d	7.97±0.01 ^c	0.40 ^a

Nitrate (mg/l)	3.61±0.02 ^c	4.12±0.01 ^e	4.05±0.01 ^d	2.80±0.01 ^a	21.62±0.01 ^g	3.49±0.01 ^b	10.00 ^f
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Values are reported as average mean ± standard error of triplicate determinations. Values along the rows with the different alphabetic superscripts are significantly different at $p \leq 0.05$ while values with the same alphabet are not significantly different ($p \leq 0.05$).

* = 10^{-1}

ND = Not Detected

4.1.3 Principal component analysis in water dataset

Figure 4.1 is a curve showing the Principal Component Analysis Eigen value plot for water samples during rainy and dry seasons. The curve shows that Principal Component 2 (PC2), which was selected for this analysis, captured 47.59% of cumulative variance responsible for the variations among the samples.

Figure 4.2 represents the Hotelling T^2 /Residual plot for water samples during rainy and dry seasons. The Q Residuals Reduced at a p-value of 0.950 plotted on the X-axis while Hotelling T^2 at p-value of 0.950 with 47.59% captured variance on the y-axis. It reveals samples 1, 28 and 31 as the outliers having unusual pollution

Figure 4.3 shows the PCA Score plot for water samples during rainy and dry seasons. Scores on Principal Component 2 at 16.68% plotted on the x-axis while scores on Principal Component 1 at 30.91% on the y-axis. Six sample groups were observed from the plot. Sample 28 stands as the only member of its group.

Figure 4.4 represents the Principal Component Analysis Loadings plot for water samples during rainy and dry seasons. Principal component 1 at 30.98% cumulative variance plotted on the x-axis while principal component 2 at cumulative variance 16.68% on the y-axis. The plot shows pH, nitrate, nitrite-nitrogen and turbidity as the most prominent variables.

Figure 4.5 is a Principal Component Analysis (PCA) Biplot for water samples during rainy and dry seasons with Principal Component 2 (PC2) at cumulative variance of 16.68% plotted on the x-axis and Principal Component 1 (PC1) on the y-axis. It shows three groups of samples with common variables or similar pollution status.

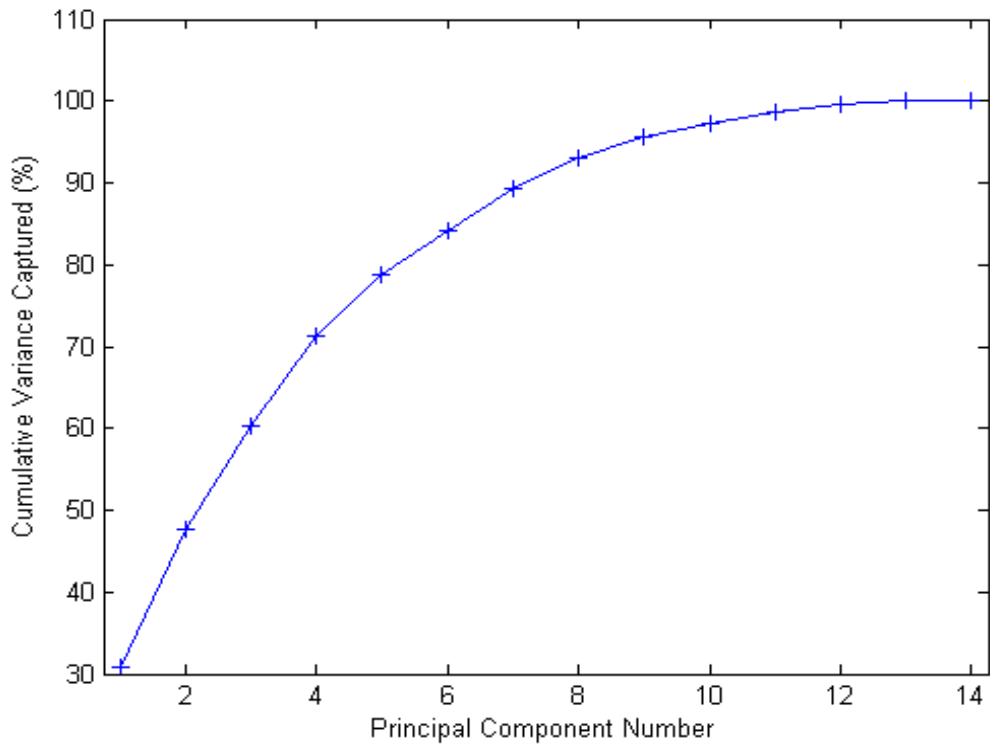


Figure 4.1: PCA Eigen value plot for water samples during rainy and dry seasons

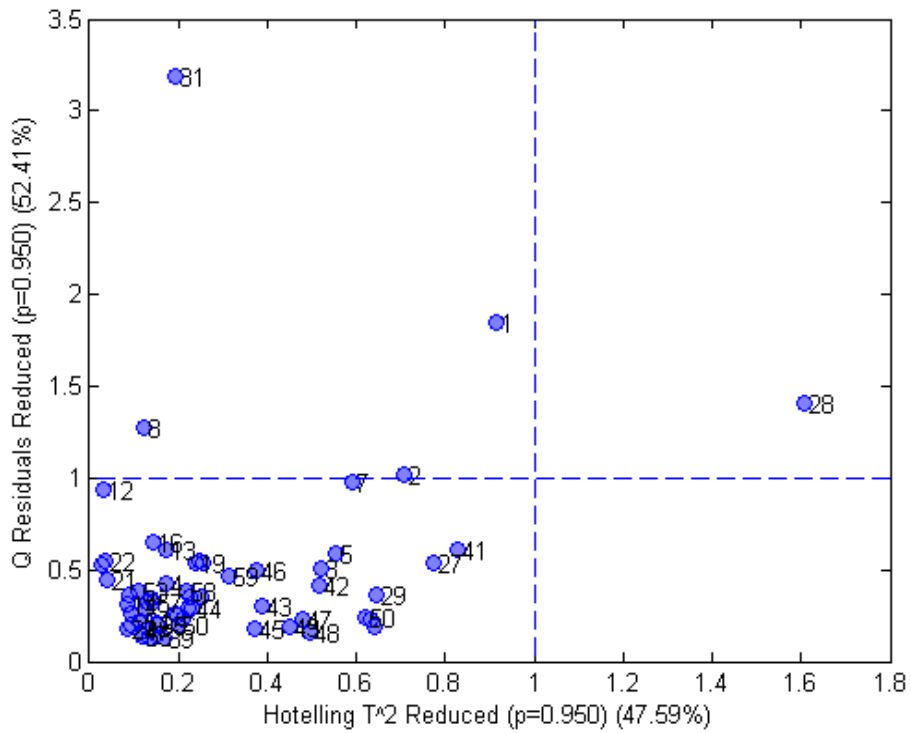


Figure 4.2: Hotelling T²/Residual plot for water samples during rainy and dry seasons

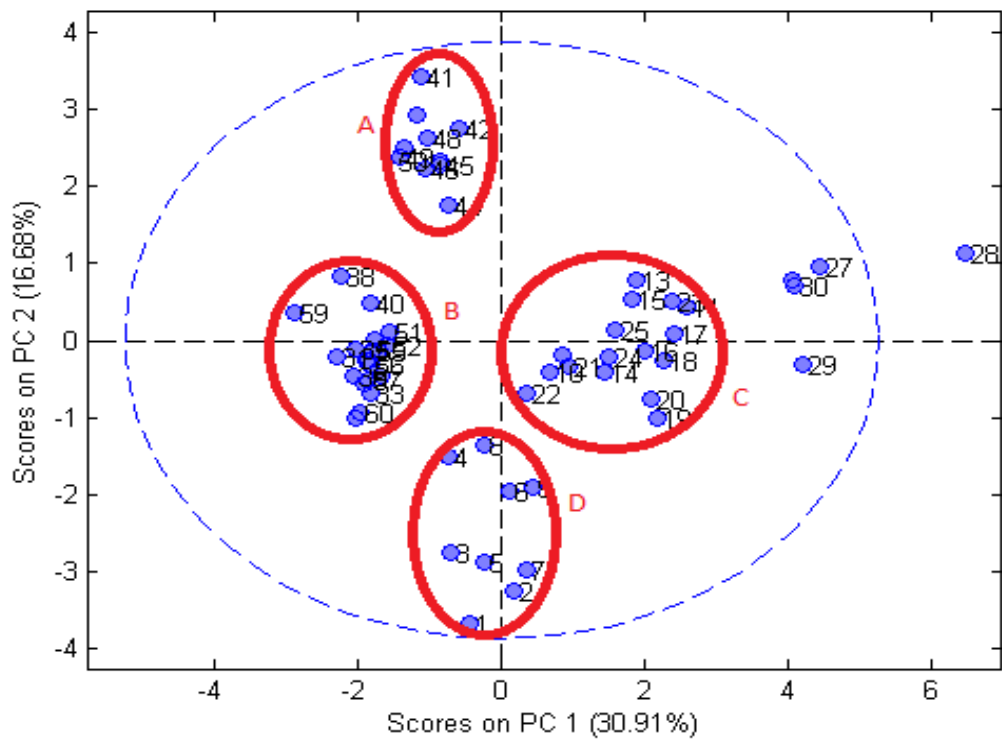


Figure 4.3: PCA Score plot for water samples during rainy and dry seasons

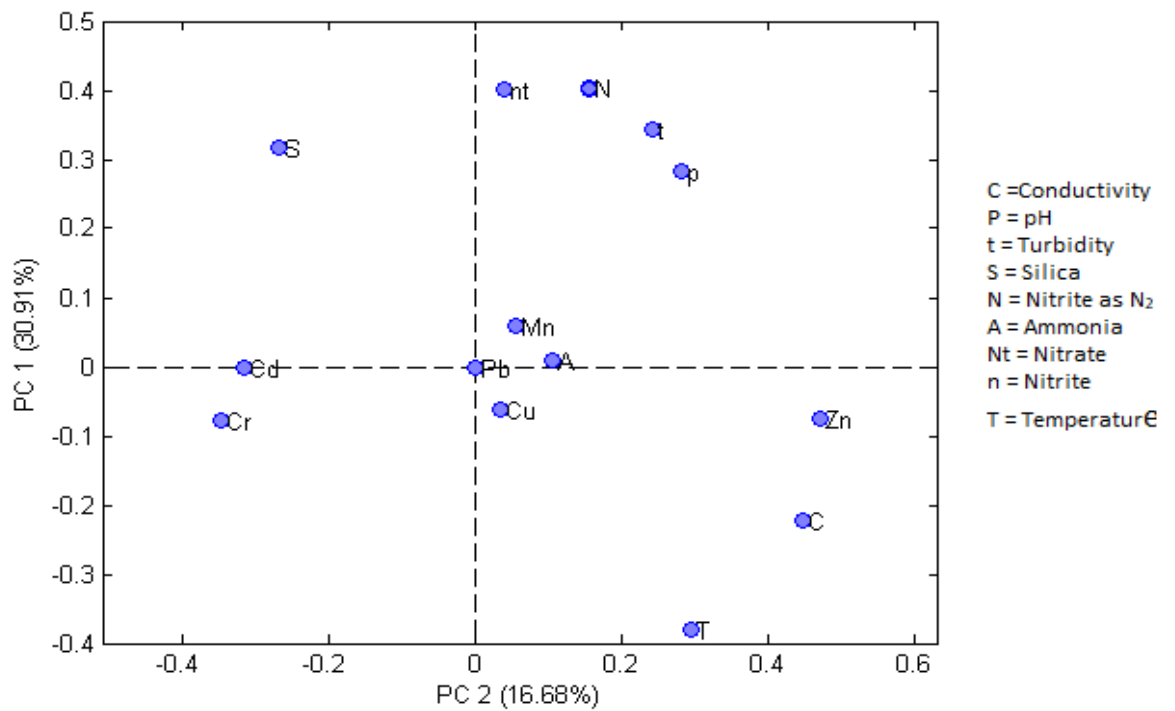


Figure 4.4: PCA Loadings plot for water samples during rainy and dry seasons

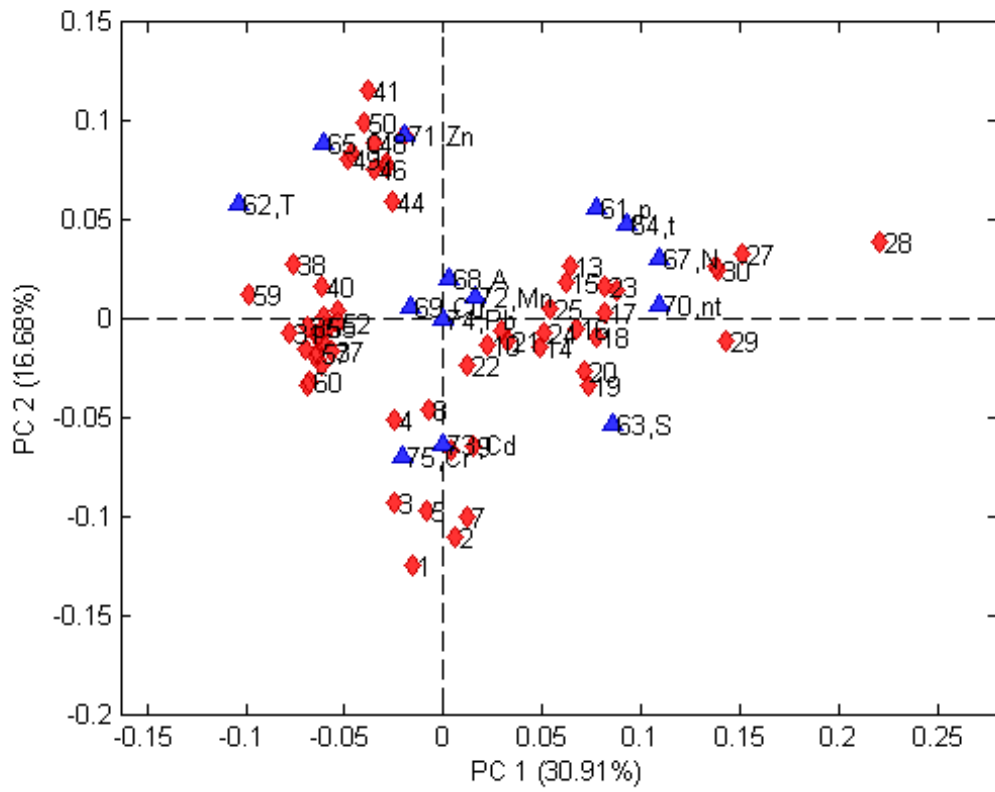


Figure 4.5: PCA Biplot for water samples during rainy and dry seasons

4.1.4 Principal component analysis in sediment dataset

Figure 4.6 is a curve showing the Principal Component Analysis Eigen value plot for sediment samples during rainy and dry seasons. The curve shows that Principal Component 2 (PC2) captured 55.95% of cumulative variance responsible for the variations among the samples while other Principal Components captured fewer percentage of cumulative variance.

Figure 4.7 represents the Hotelling T^2 /Residual plot for sediment samples during rainy and dry seasons. The Q Residuals Reduced at a p-value of 0.950 and 44.05% plotted on the X-axis while Hotelling T^2 at p-value of 0.950 with 55.95% captured variance on the y-axis. It revealed samples 23, 31, 22 and 39 as the outliers having unusual pollution.

Figure 4.8 is a Principal Component Analysis (PCA) Biplot for sediment samples during rainy and dry seasons with Principal Component 2 (PC2) at cumulative variance of 21.10% plotted on the x-axis and Principal Component 1 (PC1) at 34.85% cumulative variance on the y-axis. It shows six groups of samples with common variables or similar pollution status.

Figure 4.9 shows the PCA Score plot for sediment samples during rainy and dry seasons. Scores on Principal Component 2 at 16.68% plotted on the x-axis while scores on Principal Component 1 at 30.91% on the y-axis. Five sample groups were observed from the plot. Samples 21, 22, 25, 26, 27, 28, 29, 30 and 23 were most prominent.

Figure 4.10 represents the Principal Component Analysis Loadings plot for sediment samples during rainy and dry seasons. Principal component 1 at 34.85% cumulative variance plotted on the y-axis while principal component 2 at cumulative variance 21.10% on the x-axis. The plot shows nitrate, nitrite-nitrogen and turbidity as the most prominent variables. It also shows cadmium, silica, ammonium, conductivity, zinc,

copper, chromium and temperature above zero on PC1 axis and then lead, manganese and pH above zero on the PC2 axis.

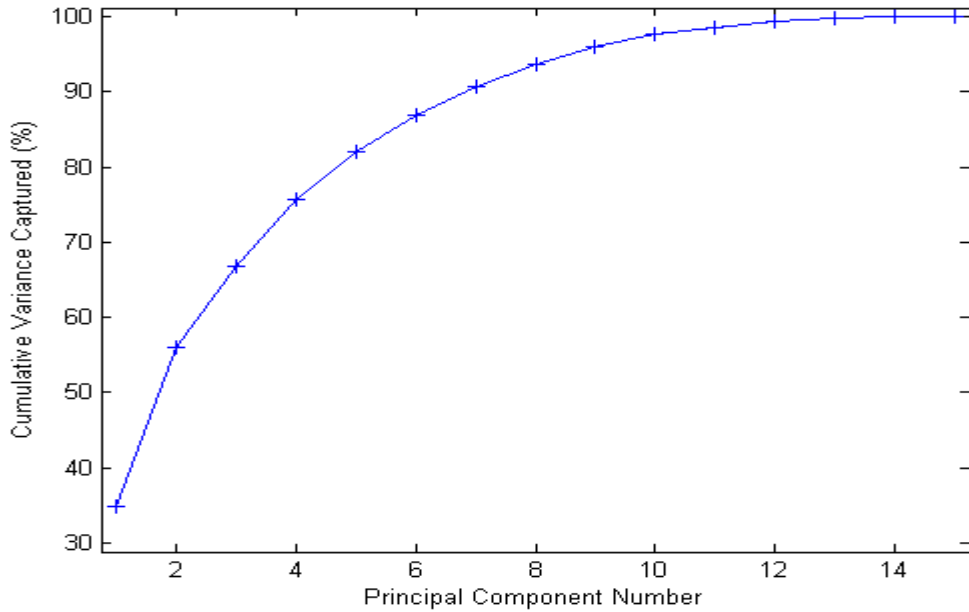


Figure 4.6: PCA Eigen value plot for sediment samples during rainy and dry seasons

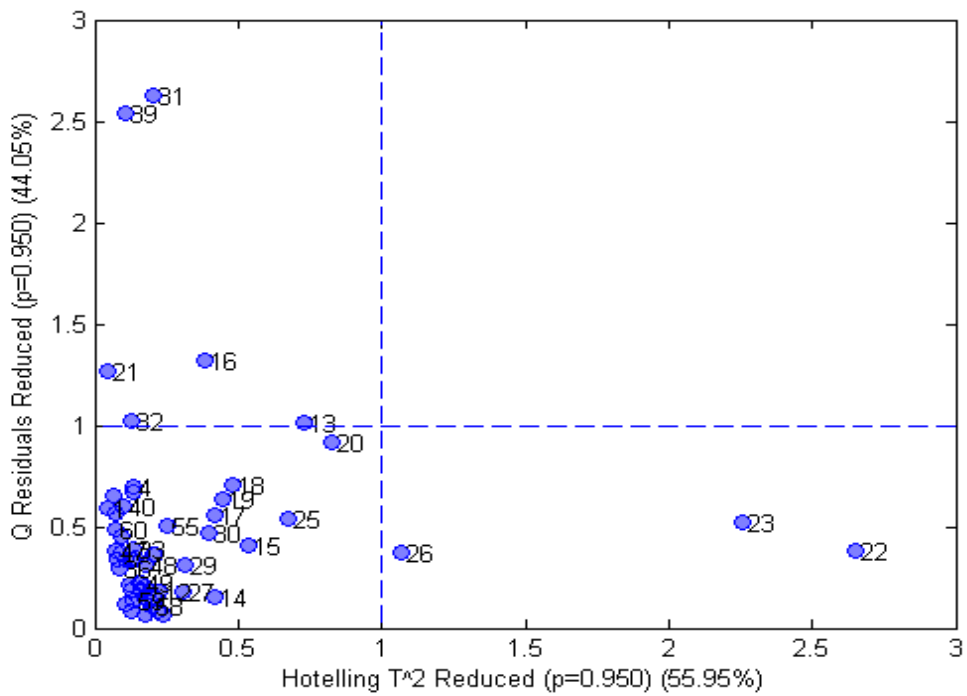


Figure 4.7: Hotelling T^2 /Residual plot for sediment samples during rainy and dry seasons

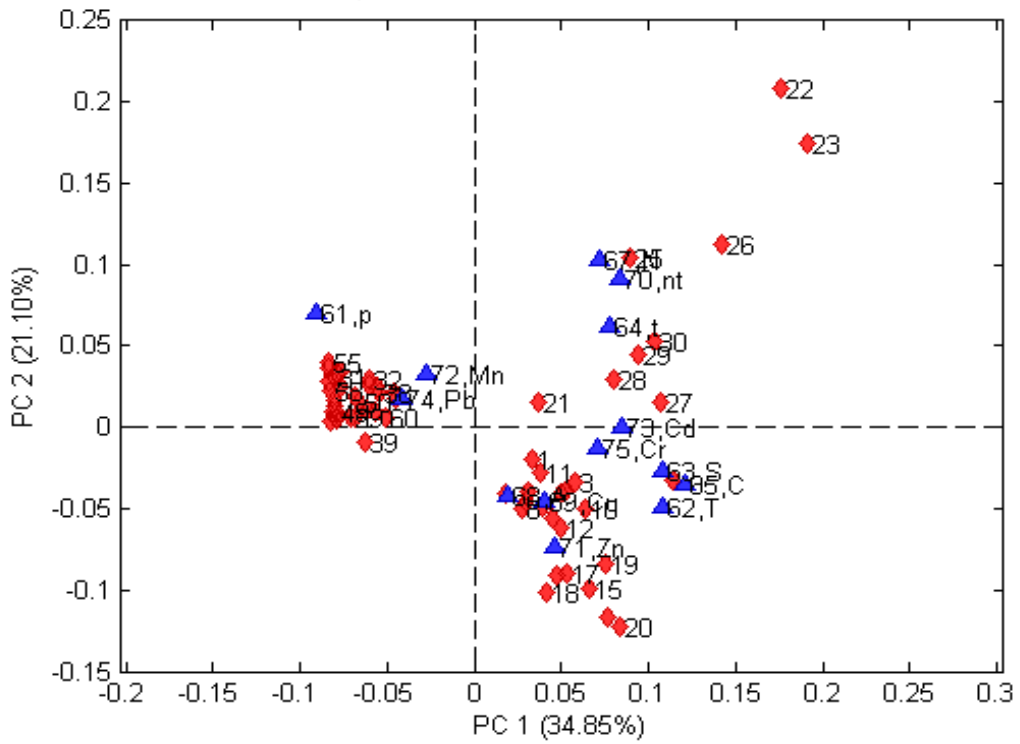


Figure 4.8: PCA Biplot for sediment samples during rainy and dry seasons

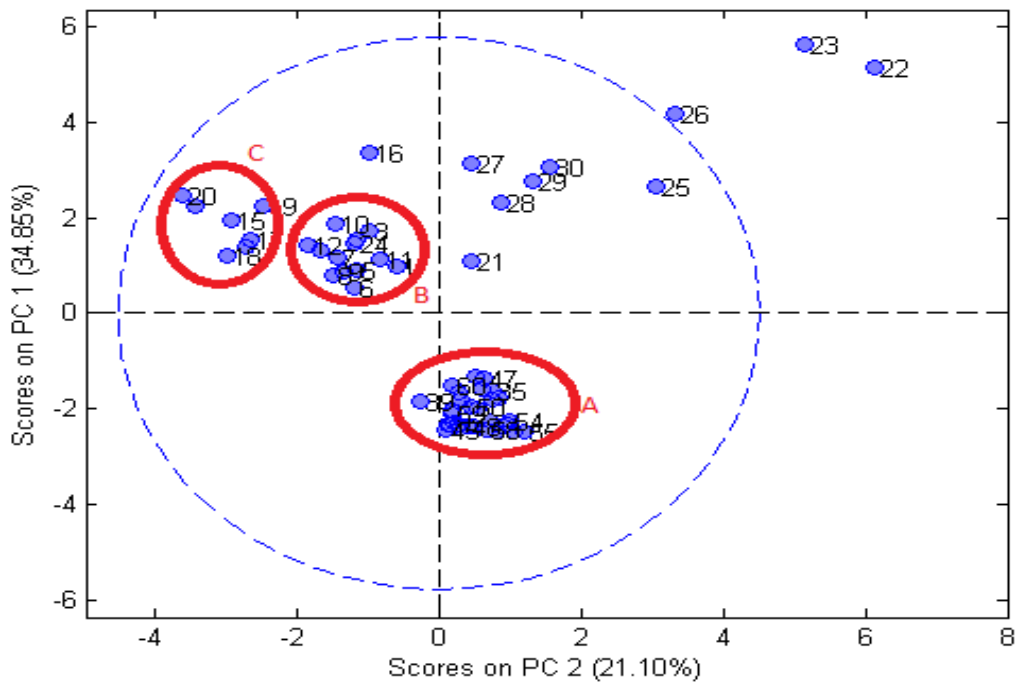


Figure 4.9: PCA Score plot for sediment samples during rainy and dry seasons

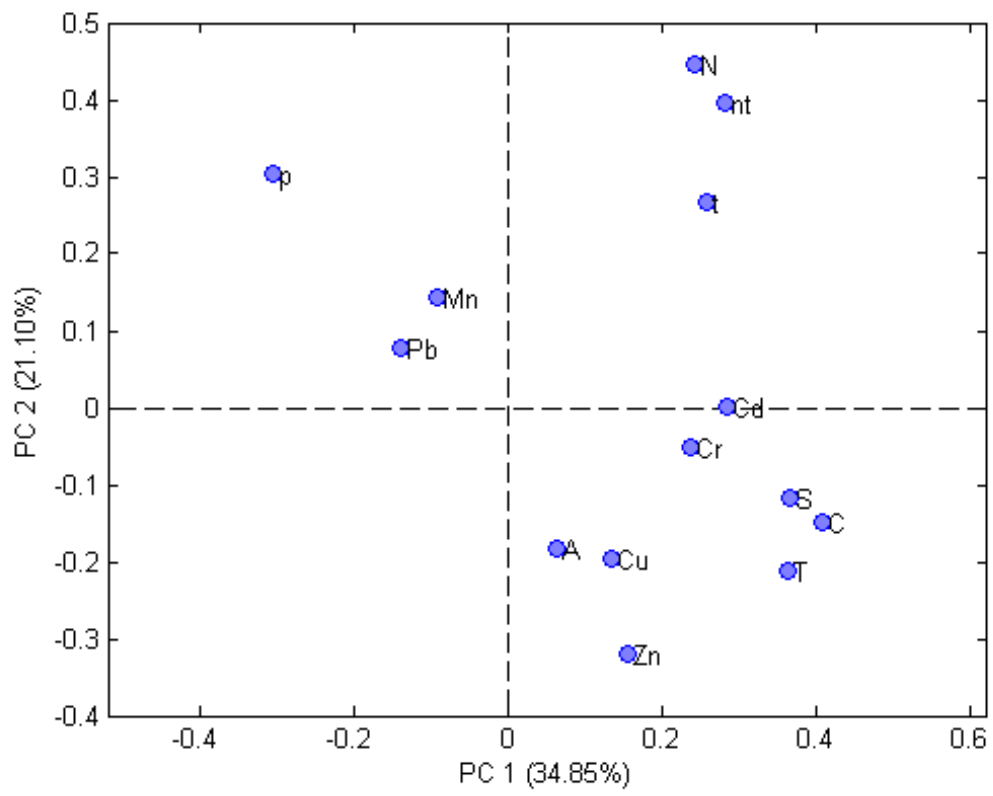


Figure 4.10: PCA Loadings plot for sediment samples during rainy and dry seasons

4.1.5 Hierarchical cluster analysis (HCA) of water samples dataset

Figure 4.11 presents HCA Dendrogram for water during rainy and dry seasons showing the sixty samples plotted on the x-axis and variance weighted distance between cluster centers on the y-axis. It shows different pairs or groups of samples with common variables or characteristics.

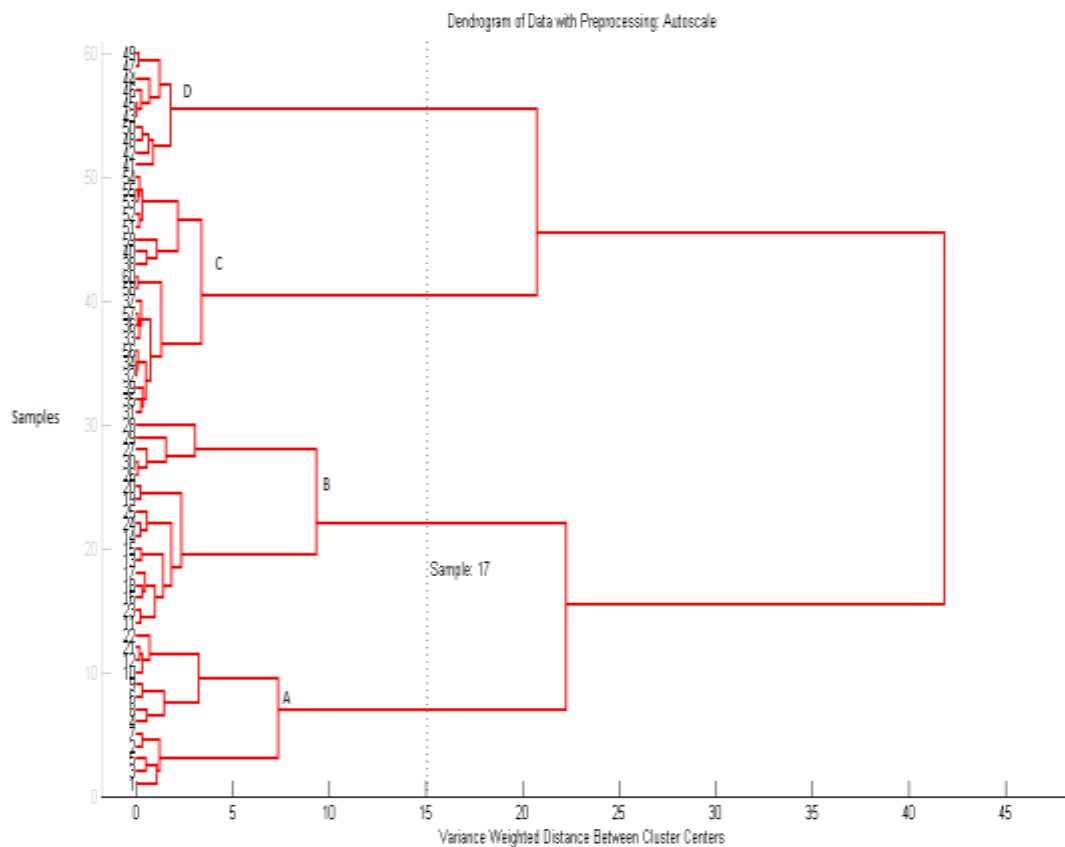


Figure 4.11: HCA Dendrogram for water during rainy and dry seasons

4.1.6 Hierarchical cluster analysis (HCA) of sediment samples dataset

Figure 4.12 presents HCA Dendrogram for sediment during rainy and dry seasons showing the sixty samples plotted on the x-axis and variance weighted distance between cluster centers on the y-axis. It shows different pairs or groups of samples with common variables or characteristics.

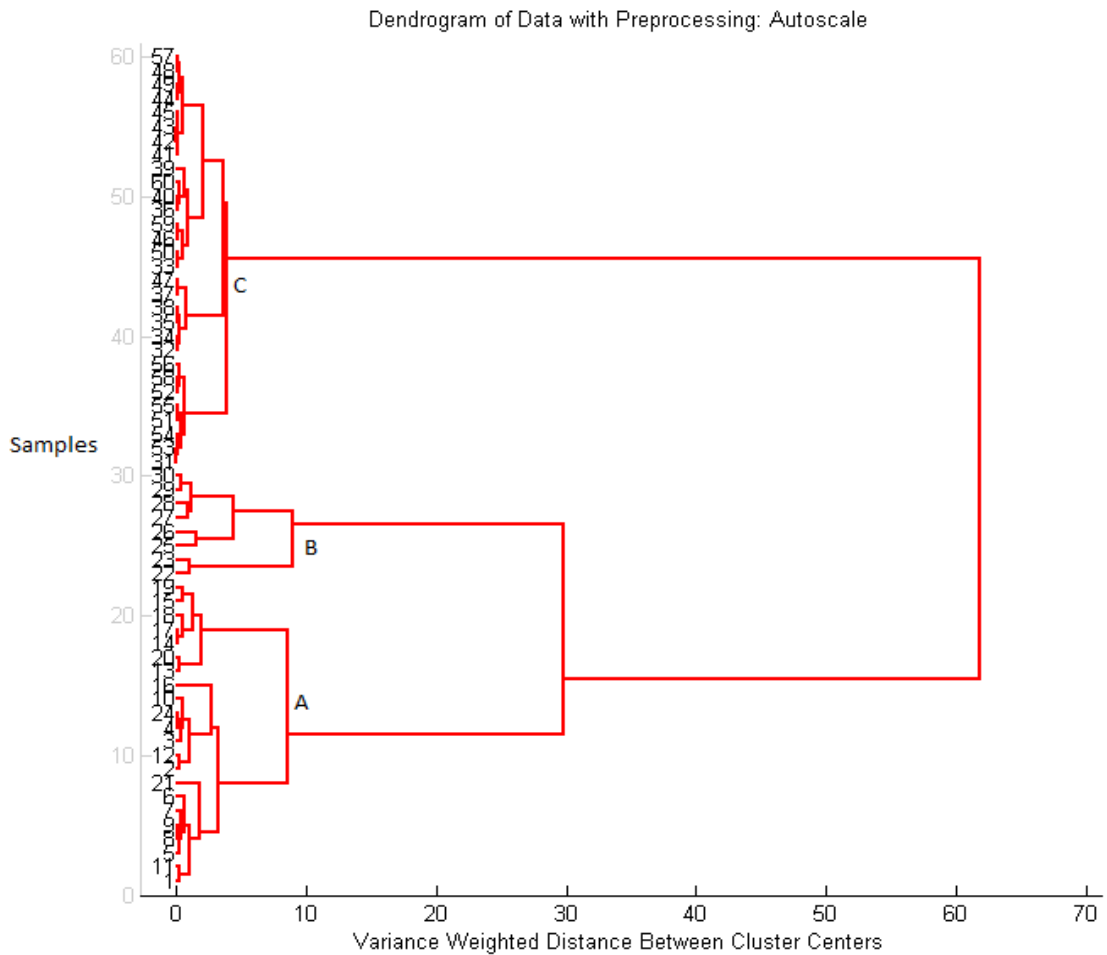


Figure 4.12: HCA Dendrogram for sediment during rainy and dry seasons

4.1.7 Correlation analysis of water dataset

Table 4.5 presents the correlation output of the parameters determined in the water samples during rainy and dry seasons. Strong positive relationship is found among conductivity-temperature, nitrate - nitrite as nitrogen, nitrite – nitrite as nitrogen which was also observed in PC2. pH showed weak negative correlation with temperature (-0.401), conductivity (-0.118), Cu (-0.059) and Cr (-0.294).

Table 4.5: Correlation Analysis of water samples during rainy and dry seasons

	pH	T	S	t	C	n	N	A	Cu	nt	Zn	Mn	Cd	Pb	Cr
Ph	1.000														
T	-0.401	1.000													
S	0.268	-0.802	1.000												
T	0.581	-0.470	0.375	1.000											
C	-0.118	0.726	-0.556	0.006	1.000										
N	0.456	-0.403	0.289	0.528	-0.163	1.000									
N	0.464	-0.411	0.290	0.534	-0.166	0.999	1.000								
A	0.237	0.101	-0.199	-0.181	-0.199	0.179	0.181	1.000							
Cu	-0.059	0.118	-0.113	-0.208	0.013	-0.043	-0.043	0.091	1.000						
Nt	0.261	-0.527	0.396	0.561	-0.241	0.807	0.807	-0.139	-0.018	1.000					
Zn	0.440	0.277	-0.198	0.189	0.437	-0.122	-0.121	0.120	-0.020	-0.285	1.000				
Mn	0.167	-0.268	0.211	0.282	0.039	-0.122	-0.118	-0.144	-0.100	0.023	0.264	1.000			
Cd	0.047	-0.216	0.073	-0.202	-0.350	-0.086	-0.080	0.151	-0.003	-0.138	-0.146	-0.095	1.000		
Pb	0.273	0.279	-0.136	-0.089	-0.042	-0.059	-0.037	-0.063	0.071	-0.084	-0.262	0.003	-0.137	1.000	
Cr	-0.294	-0.072	0.044	-0.190	-0.073	-0.157	-0.160	-0.191	-0.170	-0.186	-0.298	0.068	0.171	-0.184	1.000

C =Conductivity
 P = pH
 t = Turbidity
 S = Silica
 N = Nitrite as N₂
 A = Ammonia
 nt = Nitrate
 n = Nitrite
 T = Temperature

4.1.8 Correlation analysis of sediment dataset

Table 4.6 presents correlation analysis of sediment samples during rainy and dry seasons. Temperature showed strong positive correlation for silica (0.715), conductivity (0.860) and Zn (0.601). Silica showed a strong positive correlation with conductivity (0.877) and Cd (0.708). Turbidity strongly correlated positively with nitrate, nitrite and nitrite as nitrogen. Conductivity exhibited strong positive correlation with Cd. Nitrite strongly correlated positively with nitrate (0.919) and nitrite as nitrogen (0.999).

Table 4.6: Correlation Analysis of sediment samples during rainy and dry seasons

	pH	T	S	t	C	N	Nn	A	Cu	nt	Zn	Mn	Cd	Pb	Cr
pH	1.000														
T	-0.725	1.000													
S	-0.723	0.715	1.000												
t	-0.134	0.312	0.340	1.000											
C	-0.832	0.860	0.877	0.391	1.000										
n	0.056	0.194	0.219	0.674	0.291	1.000									
N	0.062	0.191	0.216	0.672	0.287	0.999	1.000								
A	-0.079	0.218	0.082	-0.013	0.172	-0.123	-0.122	1.000							
Cu	-0.208	0.333	0.260	0.008	0.320	-0.045	-0.041	0.356	1.000						
nt	-0.059	0.286	0.367	0.624	0.401	0.919	0.918	-0.121	-0.047	1.000					
Zn	-0.470	0.601	0.159	0.073	0.422	-0.143	-0.145	0.254	0.296	-0.125	1.000				
Mn	0.416	-0.354	-0.146	-0.161	-0.208	0.045	0.045	0.299	0.077	0.043	-0.364	1.000			
Cd	-0.517	0.370	0.708	0.224	0.665	0.284	0.282	0.102	0.261	0.383	-0.069	0.180	1.000		
Pb	0.266	-0.279	-0.310	-0.098	-0.323	-0.062	-0.048	-0.086	0.018	-0.098	-0.125	0.002	-0.145	1.000	
Cr	-0.289	0.492	0.360	0.222	0.469	0.217	0.222	0.256	0.236	0.321	0.267	-0.055	0.211	-0.057	1.000

C =Conductivity; P = pH; t = Turbidity; S = Silica; N = Nitrite as N₂; A = Ammonia; nt = Nitrate; n = Nitrite; T = Temperature

4.2 Discussion

4.2.1 Concentration of heavy metals

4.2.1.1 Concentration of heavy metals in water

The results of heavy metal analysis on water samples collected during rainy and dry seasons are presented in Table 4.1. The table presents the average mean concentration values for the determined elements during both seasons.

Table 4.1 shows increased average mean value of ND - 0.01 mg/l for Cd in water samples collected from Bosso Dam but was not detected in samples from Chanchaga and Tagwai. Probable sources of Cd in water bodies include wastewater effluent, run-offs from agricultural lands and landfills (Awofolu *et al.*, 2017). The observed concentration in Bosso dam may be due to effluents from wastewater treatment plant located in the area. Previous studies by Awofolu *et al.* (2017) have reported increased levels of Cd in water from other rivers. In their study, Cd concentrations ranged between 0.00 mg/l and 0.02 mg/l. These values are lower than those reported in this study and were higher than the recommended limit of 0.003 mg/l for Cd in water.

The average mean concentration of Zn in the water samples was observed at values ranging from 0.003 to 0.01 mg/l which is above the recommended limit of 0.01mg/l (WHO, 2014). Zn pollution in rivers has been reported to be introduced by discharge of waste materials, fertilizers that may leach into groundwater, refuse incineration and effluent from residential and industrial area (Mohammad, *et al.*, 2019). Increased refuse incineration along Chanchaga River during dry season could explain the observed Zn contamination in them. The increased value during rainy season could also be attributed to the increased leaching during the season. In a similar study, a higher Zn mean level of 76.25 mg/l than the 3.00 mg/l recommended limit was recorded from Forcados River while lower mean levels of 0.085 mg/l during dry season and 0.716 mg/l during rainy

season from River Ganga's water and 1.0 mg/l from Nairobi River's water were recorded (Agatha, 2020). The observed Zn pollution in this study could be attributed to land use activities such as agricultural system.

The average mean levels of Cr for all sampling locations under study are shown in Table 4.1. The concentration of Cr was found to range from 0.004 – 0.03 mg/l in water samples. These values are lower than the recommended limit of 0.05 mg/l for Cr in water. While the levels of Cr in water do not exceed the recommended limit, the element is very toxic and mutagenic when inhaled and is a known human carcinogen. Breathing high levels of Cr can cause irritation to the lining of the nose, runny nose and breathing problems (Mwangi, 2018). Chromium concentrations that ranged between 0.01 and 1.414 mg/l from Msimbazi river water were reported which were higher than the values reported in this study. Elevated Cr levels could be attributed to the effluent into the streams that are loaded with pollutants from various industries including textile, which are known to contain Cr (Mwangi, 2018). The fact that Cr was detected gives indication that activities such as release of textile effluent or domestic laundry could have contributed.

4.2.1.2 Concentration of heavy metals in sediments

Table 4.2 presents the average mean concentration values for heavy metals in sediment samples from Bosso Dam, Chanchaga River and Tagwai Dam during rainy and dry seasons. Elevated levels of Cd were detected at the range of 0.01 – 0.04 mg/l in all sediments except in Chanchaga during dry season. High concentrations of Cd in sediment was observed during the rainy season (0.04 mg/kg) and could be attributed to high precipitation which subsequently led to higher run-off of Cd containing materials from agricultural and semi industrial lands into the rivers. The higher concentrations of

Cd in Bosso and Chanchaga observed during rainy season may be because these areas are densely populated, developed and industrialized, so, the possibility of disposing of E-wastes is high within these regions. It has been found that Cd ions are leached from disposed E-waste materials such as cathode ray tube and other electronic chips. A significant amount of Cd from electronic wastes discharged into the water bodies can mix with water and turn it acidic which is a common occurrence in landfills (Zhou *et al.*, 2020). This may have contributed to the acidic pH observed in the samples and discussed in later section. Cadmium naturally exists in soil and rocks to some extent or rarely (Ojelabi *et al.*, 2018). The notable surrounding rocks in the vicinity of Bosso Dam may have also contributed to Cd detection.

Pb was not detected in sediment samples from other locations except in sediment sample collected from Bosso Dam during dry season at an average mean concentration of 0.001mg/l. While this Pb concentration was below the recommended limit of 0.01mg/l by WHO, the metal is toxic even at low levels as it is non-degradable and has a tendency to bioaccumulate to toxic level (WHO, 2017). Pb has been reported to emanate from mining, agricultural, residential effluent and waste from car wash (Kithiia, 2020). Some or all the listed activities around Bosso may have contributed to the presence of Pb in the water. Also, effluent from the waste water treatment plant located close to the dam could be a cause of Pb pollution in the location. The significantly low concentration (0.001 mg/l) in Bosso sediment sample could be attributed to dilution effect as a result of runoff or rain water with a big part of heavy metals in sediments being released back to water compartment in the process of remobilization. Agatha (2020) recorded similar result for Pb levels from Forcados River in sediment samples that were lower than the WHO recommended limit.

Zn was not detected in the sediment sample except in samples collected from Chanchaga during rainy season at an average value of 0.12 mg/l which is higher than the WHO recommended limit of 0.01 mg/l, indicating pollution of this metal in the sediment sample. The most important sources of anthropogenic zinc in sediments come from discharge of wastes, mine tailings, urban runoff, industrial effluents, and the use of commercial products such as fertilizers and wood preservatives that contain zinc. Among the study locations, Chanchaga river is surrounded by more industries and also records increased inflow of waste discharge into the river which may contribute to Zn pollution.

The average mean concentration of Cu was found in the range of 0.01mg/l - 0.03mg/l which is above the World Health Organisation's permissible limit of 0.01mg/l. Cu can enter water bodies from natural processes like soil weathering and human activities such as agriculture and manufacturing. Generally, average concentration values increased during rainy season but decreased during dry season. This could be influenced by the waste liquid which flowed into the rivers via rainfall, and leaching during rainy season. High concentrations of Cu in water may cause chronic anaemia, make the water bitter and could intensify the corrosion of galvanized iron and steel fittings (Agatha, 2020). Mean values of 0.84 mg/L in sediment were obtained by Edward *et al.*, (2018) from Odo-Ayo River in Ado-Ekiti, Ekiti-State, Nigeria was slightly higher than the obtained values in the study.

The average mean concentration of Mn in all the collected sediment samples was 0.01 mg/l in all three locations except in sediment samples from Tagwai Dam where the average mean value of 0.09 mg/l was observed during rainy season (Table 4.2). These values are below the WHO recommended limit of 0.10 mg/l. Tagwai Dam (0.09 mg/l) recorded significantly high Mn concentrations. Mn is introduced into aquatic

environments mainly through anthropogenic sources, such as sewage sludge, emissions from alloy, iron, and steel industries, municipal wastewater discharges, and mining and mineral processing (Chukwuemeka *et al.*, 2020). The mean Mn concentrations observed in this study are below previous values of 2.54 – 3.45mg/l in sediment samples reported by Chukwuemeka *et al.*, (2020).

4.2.2 Assessment of the physicochemical parameters of water and sediments

4.2.2.1 Physicochemical parameters in water

The average mean concentrations of the physicochemical parameters (Temperature, pH, Silica, nitrite, nitrite as nitrogen, nitrate, turbidity, conductivity and ammonia) in water samples for all sampling locations in dry and rainy seasons are shown in Table 4.3.

The average mean values of water temperature had significant variation among the locations except for samples collected from Bosso Dam and Tagwai Dam during rainy season. The lowest water temperature was 27.57°C in samples collected from Bosso dam and Chanchaga river during rainy season while the highest water temperature was 30.70°C in samples collected from Bosso dam during dry season. The observed increased values could be attributed to turbidity and thermal inertia of the water bodies. Seasonal variation in temperature may be due to absorption of solar energy and subsequent release to the atmosphere. During rainy season, low values of temperature observed could be due to freshwater flow as stated by Saravanakumar *et al.* (2018). One of the implications of increased temperature for water bodies is that metabolic rate and the reproductive activities of aquatic life are controlled by temperature. Metabolic activity increases with a rise in temperature, thus increasing the demand for oxygen by fish. However, an increase in river temperature also leads to decrease in dissolved oxygen, limiting the amount of oxygen available to these aquatic organisms. With a limited amount of dissolved oxygen, fishes in these water bodies may become stressed

(Kurnaz *et al.*, 2017). This result showed the obtained values were above the WHO threshold of 25°C and the temperature of the water bodies were at the level that can affect the aquatic life negatively.

The average pH values of water samples in the study locations during rainy and dry seasons shown in Table 4.1 were found to be in the range of 6.35-7.75 mg/l which complies with that of the World Health Organization (WHO) guideline value of 6.50 - 8.50 mg/l for water. An average pH value of 4.30mg/l, 6.21mg/l and 7.50mg/l for water and sediment samples were obtained for Bosso dam, Chanchaga river and Tagwai dam respectively in rainy season. The values were lower than 5.10mg/l, 6.90mg/l and 7.80mg/l for Bosso dam, Chanchaga river and Tagwai dam respectively in the dry season. These levels differ significantly ($p \leq 0.05$) for both the rainy and the dry seasons in each location. This implies that seasonal variations lead to considerable changes in pH.

Fluctuations in pH values during different seasons of the year is attributed to factors like removal of CO₂ by photosynthesis through bicarbonate degradation, dilution of waterbodies by freshwater influx, reduction of salinity and temperature and decomposition of organic matter. It was observed that the pH of the water samples reduced during rainy season but increased during the dry season. The average mean concentration of the heavy metals also increased with increase in pH values. A reduction in pH may allow the release of toxic metals that would otherwise be adsorbed to sediment.

The average mean values for turbidity recorded in all study locations were above recommended limit. The average mean turbidity values obtained increased during rainy season but decreased in dry season in each location. The highest turbidity value was observed in water sample collected from Chanchaga river (80.86NTU) in rainy season

while lowest was observed in Bosso dam (14.54NTU) during dry season. High turbidity is caused by waste discharge, algae growth and urban runoff. The observed elevated values during rainy season may be due to runoff.

The average conductivity values were in the range of 74.03 – 115.70 mS/cm for water samples, with the values for the rainy and dry seasons differing significantly ($p \leq 0.05$), indicating that seasonal variations have the potential to cause change in the conductivity. The Highest conductivity value at 430.07 mS/cm was observed in sediment sample from Bosso dam while the lowest value was observed in Tagwai dam during dry season. Also, highest conductivity at 115.70mS/cm was observed in water sample from Chanchaga river during dry season while the lowest value was observed from Bosso during season. Increased conductivity values were observed during dry season and reduced during rainy season in both water and sediment samples. The low values obtained during the rainy season may be due to dilution of the water by rainfall. Also, the lower values of conductivity observed in the rainy season could be caused by dilution of dissolved salts due to rainfall (WHO, 2017). As rainfall decreases, the level of conductivity (C) increases due to the concentration of the ions due to evaporation in the river. Similar findings were reported in the literature (Agbaire and Obi, 2019). However, Benjamin, (2019), and Shabalala *et al.* (2018) recorded higher values of EC in the rainy season. High conductivity could be attributed to runoff of ionic materials from soils into the rivers during rainfall. The values obtained in this study for both seasons were within the recommended guidelines of WHO (1000 mS/m) for water bodies.

All samples for all sampling locations contained ammonia, significantly ($P \leq 0.05$) on the high side above the WHO recommended value. Generally, there were increased concentration values in the rainy season than in the dry season. This could be due to the

increased agricultural activities in the study locations during rainy season. Elevated levels of ammonia in water bodies usually result from human activities such as overuse of chemical fertilizers and improper disposal of human and animal wastes as sources of nitrogen-containing compounds, which are converted in the soil. Also, elevated ammonia pollution levels are sustained in the rainy season because sludge deposits with high ammonia content become suspended in water and are washed into water bodies. This may explain the high levels of ammonia seen in rainy season when compared to dry season. Exposure to ammonia pollution can lead to health issues such as fever, difficulty breathing, chest pain and cough.

4.2.2.2 Physicochemical parameters in sediments

Table 4.4 shows the average mean temperature of the sediment samples to have significant variation among the locations except for samples collected from Bosso Dam and Tagwai Dam during dry season. The lowest average mean temperature of the sediments was 25.55 °C while the highest temperature was 27.91 °C. The water temperature during dry season (Table 4.3) was higher than the values recorded during rainy season. Saravanakumar *et al.* (2018) also observed rise in water temperature during dry season. The observed elevated values could be due to absorption of heat from sunlight by the sediment particles.

In Table 4.4, the pH values indicated acidic nature of the sediments in the study locations during rainy season. Although the average mean values are within the acidic range, the sediment pH was high in dry season and low during rainy season possibly due to redox changes in the sediments and water column apart from the influence of freshwater. The pH of sediment and the interstitial water affects metal retention by developing a pH-dependent charge at a weak acidic surface and determines the extent of

ion-exchange reactions. Similarly, protons and hydroxide ions compete with absorbing cations and anions respectively. pH variation in sediments influences the release or adsorption of each metal into sediment fraction. High pH lowers desorption of metals and possesses high buffering capacity against acidic conditions that may be created as a result of wastes accumulation. Association of metals with the carbonate and organic fraction are affected by pH variations. Low pH is known to influence the sorption of heavy metals by organic fraction in sediments (Oshisanya *et al.*, 2021). In this study, the total extractable fraction of the metals in the sediment samples generally increased during rainy season with a relatively lower average pH. This may be due to increase in metals complexation. Acidic pH was obtained by Tukura *et al.* (2017) in water and sediment samples from Kubanni Dam, Zaria. Although their mean value (4.9) was higher than the mean values obtained in this study, it still falls within acidic range.

In sediment samples, the highest turbidity value was obtained from Chanchaga River during rainy season while the lowest value (1.93NTU) was obtained in Tagwai Dam during dry season. This may be due to higher rainfall in rainy season than in the dry season. The mean values obtained during the sampling period for both seasons were higher than the WHO standards of ≤ 5.00 NTU. Seasonal variations in turbidity levels in various rivers in Nigeria have been reported by Ojelabi *et al.*, (2018). High turbidity increases water temperature due to the particles absorbing sunlight. This may be part of the reason for the increased temperature values recorded in this study. The suspended particles scatter the light, this decreases the photosynthetic activity of plants and algae, which further lowers the oxygen concentration.

The average mean ranges of silica concentration were 0.86 – 11.01mg/l in all the three locations (Table 4.1). The silicate content was within the permissible range for other

locations except in Bosso during rainy season. Silica is derived from water-rock interaction. The circulating water dissolves the silica derived from the chemical weathering of silicate minerals. Bosso dam is surrounded by rocks which may contribute to the presence of silicate. The recorded high values in rainy season may be due to heavy influx of freshwater derived from land drainage carrying silicate leached out from rocks. The results also showed that the values increased during rainy season but decreased during dry season. The low concentration during dry season may be attributed to uptake of silicate by phytoplankton for their biological activity (Saravanakumar *et al.*, 2018). Research has shown that acidic water enhanced dissolution of silica which may explain the result obtained in this study.

Nitrate values varied from 0.63 to 21.62 mg/l respectively. The average mean value for sediment samples in other locations were within acceptable limit except in Tagwai dam (21.62mg/l) during rainy season. The main source of nitrate contaminant in water is through run-off from farmlands. These water bodies are surrounded by farmlands and have increased agricultural activities surrounding them. Nitrate is a major ingredient of farm fertilizer and is necessary for crop production. Nitrate can also get into water bodies from leaking of wastewater (where latrines and septic tanks are poorly sited) or other organic wastes (from livestock, fish and birds) into groundwater. Nitrate in rivers also result from sewage disposal systems and livestock facilities. Considering the fact that the sites with high nitrate contents are agrarian, the high nitrate in our study is related to runoff from farmlands due to the wide scale use of nitrogenous fertilizer [nitrogen-phosphorus-potassium (N-P-K)].

In general, the nitrate values were increased during rainy season and decreased during dry season. The highest nitrate value recorded during rainy season may be attributed to

heavy rainfall and land runoff. Another possible way of nitrate entry is through oxidation of ammonia form of nitrogen to nitrite and then consequently to nitrate. The low values recorded during dry period may be due to utilization by phytoplankton. The higher value of nitrite recorded during rainy season may be due to various reasons including variation in phytoplankton excretion, oxidation of ammonia and reduction of nitrate and by recycling of nitrogen and bacterial decomposition of planktonic detritus present in the environment. The nitrite sources in waters are the organic matters, fertilizers, and some of minerals. Nda *et al.* (2019) also observed elevated nitrate pollution values in Chanchaga river during rainy season. Nitrates are higher during rainy season but reduce towards dry season because rain flushes out deposited nitrate from the near surface (Nda *et al.*, 2019).

Ammonia was observed in the sediment samples at elevated levels above the permissible limit in all locations and in both seasons ranging from 4.50 – 14.50 mg/l. The concentration increased during rainy season and decreased during dry season. Natural sources of ammonia include the decomposition or breakdown of organic waste matter, gas exchange with the atmosphere, forest fires, animal and human waste, and nitrogen fixation processes. Ammonia can enter the aquatic environment via direct means such as municipal effluent discharges and the excretion of nitrogenous wastes from animals, and indirect means such as nitrogen fixation, air deposition, and runoff from agricultural lands. The study areas are surrounded by farmlands. The agricultural activities within the areas may contribute to ammonia pollution in the water bodies as both chemical fertilizers and human manure may leach from farmlands. The observed elevated values in rainy season may be due to increased runoffs during this season.

4.2.3 Application of chemometric techniques

4.2.3.1 Principal component analysis (PCA) in water dataset

Figure 4.1 shows the eigenvalue plot for data obtained from water analysis. Two principal components (PCs) were extracted which accounted for 47.59% of the cumulative variance in the data set.

Figure 4.2 presents the Hotelling T^2 /Residual plot for water samples during rainy and dry seasons. Hotelling T^2 enables us to visualize unique samples. It revealed samples 1, 28 and 31 as the outliers, that is, unique samples. They are considered as outliers because while other samples were precipitating towards zero, samples 1, 28 and 31 stood out. Samples 1 and 28 were collected from Bosso dam during rainy and dry seasons respectively. Sample 31 was collected from Tagwai dam during rainy season. These samples have extreme levels of ammonia and Cu concentration in them and that makes them unique from other samples.

Figure 4.3 represents the loadings plot for water samples during rainy and dry seasons. The plot shows pH, nitrate, nitrite nitrogen and turbidity as the most prominent variables. The prominent variables are significant in differentiating the samples. PC1 accounts for 30.91% of the total variance and It showed a positive loading on silica, nitrate, nitrite as nitrogen, Mn, pH and turbidity. Nitrate and nitrite as nitrogen were the most significant variable to PC1 because they had the highest component loading. Positive loading on nitrate, nitrite as nitrogen as shown indicates their presence in the samples and may be due to run-off from farmlands containing fertilizers used in agriculture. PC2 showed positive loadings for Zn, conductivity and temperature, and accounts for 16.68% of the total variability in the data set. Negative loading of Cd in PC

2 reflects their reduction due to dilution process during rainy season (Singh *et al.*, 2019).

On the basis of sample grouping, Figure 4.4 shows the scores plot for water samples, four clusters were identified for water samples during rainy and dry seasons. Cluster A comprises water samples collected from Chanchaga river during dry season. The samples in this cluster are characterized by extreme ammonia and Zn pollution. Nitrate was not detected in these samples. Cluster B comprises water samples collected from Bosso and Tagwai Dams during dry season and they are characterized by high conductivity values. Cluster C comprises samples collected from Chanchaga river and Tagwai dam during rainy season. Samples in cluster C are characterized by elevated nitrate pollution. Group D comprises samples collected from Bosso dam during rainy season. These samples have extreme Cd pollution. Also, Cr pollution was detected in Group D samples.

Figure 4.5 is a Biplot for water samples during rainy and dry seasons with Principal Component 2 (PC2) at cumulative variance of 16.68% plotted on the x-axis and Principal Component 1 (PC1) on the y-axis. It shows four groups of samples with common variables. Group A is characterised by elevated Zn pollution. Group B is characterised by high temperature values while group C is characterized by increased nitrate and nitrite concentration values. Samples clustered in group D showed extreme Cd and Cr levels. Similar observation was made from the scoresplot and dendogram.

4.2.3.2 Principal component analysis (PCA) in sediment dataset

Figure 4.6 is a curve showing the eigenvalue plot for sediment samples during rainy and dry seasons. Two principal components (PCs) were extracted which captured 55.95% of the total variation in data set.

Figure 4.7 presents the Hotelling T^2 /Residual plot for sediment samples during rainy and dry seasons. It revealed samples 23, 31, 22 and 39 as the outliers having unique pollution. Samples 23 and 22 were collected from Tagwai dam during rainy season while samples 31 and 39 were collected from Bosso dam during dry season. Sample 22 had extreme nitrate pollution level (42.16 mg/l) with the highest conductivity mean average, while sample 23 recorded very high turbidity mean average (175 NTU). These samples were collected within the river bank with on-going irrigation farming. The observed increased nitrate level could be attributed to fertilizers applied on the crops being washed directly into the water body. Sample 31 is the only sample with Pb pollution while sample 39 had extreme ammonia contamination (44.07mg/l).

Figure 4.8 is a Biplot for sediment samples during rainy and dry seasons with Principal Component 2 (PC2) at cumulative variance of 21.10% plotted on the x-axis and Principal Component 1 (PC1) at 34.85% cumulative variance on the y-axis. It shows three groups of samples with common variables or similar pollution status. The biplot shows group A to have Cu and Zn in common. Group B is characterised by Pb and Mn pollution while group C showed Cd, Cr, conductivity, temperature and silica as their common variable.

Figure 4.9 shows the score plot for sediment samples collected in rainy and dry seasons. Three clusters were identified for sediment samples during rainy and dry seasons. Cluster A comprises water samples collected from Chanchaga River and Tagwai Dam during dry season. The samples in this cluster are characterized by acidic pH and low Mn concentration values. Nitrate was not detected in these samples. Samples in cluster B were collected from Bosso dam during rainy season. Cluster B comprises sediment samples characterized by extreme Cd concentration values ranging from 0.02-0.07 mg/l which is much higher than the WHO threshold of 0.003 mg/l. This may be due to

sedimentation as suggested by Cotman *et al.* (2019). Muhammed *et al.* (2018) got similar result in Sokoto river. The discharge of heavy metals into rivers by domestic and industrial activities causes their rapid association with particulates and incorporation into sediments. Cluster C comprises samples collected from Chanchaga river and Tagwai dam during rainy season. Samples in cluster C are characterized by elevated nitrate pollution and little or no Zn concentration.

Figure 4.10 presents the loadings plot for sediment samples during rainy and dry seasons. The plot shows nitrate, nitrite as nitrogen and turbidity as the most prominent variables. PC1 accounts for 34.85% of the total variance and It showed a positive loading on Cd, Cr, Cu, Zn, conductivity, ammonia, silica and temperature. Positive loading on nitrate, nitrite as nitrogen as shown indicates their presence in the samples and may be due to run-off from farmlands containing fertilizers used in agriculture. PC2 showed positive loadings for Pb, Mn and pH, and accounts for 21.10% of the total variability in the data set. There was no negative loading for any of the variables.

4.2.3.3 Hierarchical cluster analysis (HCA)

To further analyze variations of the water quality and the similarity of the samples, data were subjected to HCA. The dendrogram obtained by Ward's method is shown in Figure 11. The resulted dendrogram grouped all 60 samples into four (4) significant clusters. The clustering procedure highlighted groups in which the sites have similar characteristics and natural source types. The sample pairs in each of the groups had similar pollution status. Cluster A comprises pairs of samples from Bosso dam and are considered as samples with extreme levels of Cd and Cr pollution level. Common source of pollution in these sites include waste water effluents and run off from agricultural lands and landfills. Cluster B comprises sample pairs from Chanchaga river and Tagwai dam during rainy season. These sample pairs have similar elevated levels of

nitrate pollution in them. The nitrate sources in waters are the wastewaters, organic nitrogen and the fertilizers used in agriculture. Cluster C contains sample pairs with high conductivity values. These samples were collected from Bosso dam and Tagwai dam during rainy season. Cluster D contained pairs of samples from Chanchaga during dry season. These samples have very low nitrate pollution. They were also characterized by elevated Zn and ammonia pollution.

For the sediment samples, the dendrogram obtained by Ward's method is shown in Figure 12. The resulted dendrogram grouped all 60 sediment samples into three (3) significant clusters. Group A contains samples with low pH values ranging from 3.80 – 5.70. Extreme Cd pollution was also detected in group A samples. Group B comprises samples with elevated nitrate concentration. These samples were collected from Tagwai dam during rainy season. The increased nitrate content of sediment during the rainy season can be considered an indication of increased pollution of from organic sources and increased agricultural activities during this period. Group C contains samples with no Cr detected.

4.2.3.4 Correlation analysis

Correlation matrix brings out some interconnection between the parameters. Table 4.5 presents the correlation output of parameters determined in the water samples during rainy and dry seasons. Strong positive relationship is found among conductivity-temperature, nitrate - nitrite as nitrogen, nitrite – nitrite as nitrogen which was also observed in PC2. pH showed weak negative correlation with temperature (-0.401), conductivity (- 0.118), Cu (-0.059) and Cr (-0.294). This means that changes in pH of water are associated with those in temperature, conductivity, Cu and Cr concentrations. A negative correlation implies that a decrease in pH is related to an increase in temperature, conductivity, Cu and Cr levels in the water bodies and vice versa. It

implies that as water becomes more acidic, more Cu and Cr are dissolved into it. A weak negative correlation between pH-temperature (- 0.365), pH-conductivity (-0.359) and pH-Cu (-0.249) were found by Daraigan *et al.* (2017). This is similar to the findings of this study which indicates a weak correlation instead. Turbidity correlated positively with pH, nitrate, nitrite and nitrite-nitrogen. This implies that the presence of nitrate, nitrite and nitrite-nitrogen at an appropriate pH will be associated with turbidity of groundwater. Temperature has a strong positive correlation with conductivity (0.726). This means that increase in temperature is associated with increased conductivity. Conductivity exhibited positive correlation with manganese and weak negative correlation with temperature. It is not surprising because conductivity deals with ionic species in water, and manganese exist in an ionic form but not temperature. Strong positive correlations were found between nitrite and nitrite as nitrogen (0.999) and nitrate and nitrite as nitrogen (0.807).

Table 4.6 presents correlation analysis of sediment samples during rainy and dry seasons. Temperature showed strong positive correlation for silica (0.715), conductivity (0.860) and Zn (0.601). This means that changes in temperature of water are associated with those in silica, conductivity, and Zn concentrations. A positive correlation implies that an increase in temperature is related to an increase in silica, conductivity, and Zn levels in the sediments and vice versa. Silica showed a strong positive correlation with conductivity (0.877) and Cd (0.708). Turbidity strongly correlated positively with nitrate, nitrite and nitrite as nitrogen. This implies that increase in the concentration of nitrate, nitrite and nitrite-nitrogen increases the turbidity of the water bodies. Conductivity exhibited strong positive correlation with Cd. This also implies that the presence of Cd associated with the conductivity of the sediment samples. Nitrite

strongly correlated positively with nitrate (0.919) and nitrite as nitrogen (0.999). This means that increased nitrite level leads to increase in nitrate and nitrite as nitrogen.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

5.1.1 Concentration of heavy metals in water and sediments

With the exception of Cd (0.0 mg/l - 0.04 mg/l), Zn (0.00 - 0.12 mg/l) and Cu (0.00 – 0.04 mg/l), the concentrations of the other heavy metals in water were found below their maximum allowable limits. Cd, which was the highest (0.04 mg/l) heavy metal recorded above WHO permissible limit (0.003 mg/l) was detected in Bosso Dam during rainy season. The sediment samples accumulated more heavy metals than the water samples in this study as has also been observed by Chukwuemeka *et al.* (2020) for both dry and wet seasons. The mean levels of Cd (0.00 - 0.04 mg/l) were higher than those of the other elements in both water and sediment samples with Bosso Dam recording the highest concentrations. The observed low concentrations of Cr (0.00 - 0.03 mg/l) and Pb (0.00 - 0.01 mg/l) in this present work are consistent with the findings of Oshishanya *et al.* (2021). Generally, seasonal variations were observed as higher levels of the heavy metals were recorded during rainy season than in dry season in study locations. Identifiable sources of the heavy metal pollution include agricultural activities, discharge of waste materials and industrial effluents.

5.1.2 Physicochemical parameters in water and sediments

This study reveals that the selected water bodies were polluted with ammonia, nitrate, nitrite and are highly turbid. Based on the research findings, the temperature of the

water samples was in the range of 25.57 – 30.70 °C while that of the sediment samples were in the range of 25.35 °C – 27.88 °C which were above WHO permissible limit of 25°C. The pH of both water and sediment samples increased during dry season and decreased during rainy season. The pH of the sediment samples indicated that they were acidic in rainy season, with the average mean pH value at 4.88. Bosso Dam showed elevated silica concentration in the sediment samples at the value of 11.01 mg/l which is above the recommended limit of 10 mg/l. The observed values for the physicochemical parameters were higher in the sediment samples than the water samples. The values also increased during rainy season and decreased during dry season. Probable sources were identified as human activities such as improper disposal of human and animal wastes, agricultural activities and the surrounding rocks in the case of Bosso Dam.

5.1.3 Application of chemometric techniques

Principal Component Analysis (PCA) showed nitrate, nitrite nitrogen, turbidity and pH to be the most prominent variables among the water samples. In the sediment samples, it revealed nitrate, nitrite nitrogen, Cd and turbidity as prominent variables that differentiated the samples. The hierarchical cluster analysis (HCA) for the water samples revealed four major quality categories of the samples while that of the sediment samples revealed three groups of the samples. The HCA (Hierarchical Cluster Analysis) grouped the water samples into four clusters with clusters A and D having extreme levels of Cd and Cr, and nitrate respectively. For the sediment samples, the clusters revealed pairs of samples with similar Cd, Cr and nitrate pollution status. This means that similar pollution control measures can be applied on those sites represented in pairs. This study has shown that the use of chemometric methods is very useful for a better understanding of water quality issues.

5.2 Recommendation

There is need for constant monitoring of the pollutants in Bosso Dam, Chanchaga River and Tagwai dam since they serve as source of drinking water, irrigation and fish for the local inhabitants in the study area.

Agricultural activities and waste disposal were the common pollution sources identified in the study locations, therefore, there is need to promote wise application of fertilizer to stem further runoff and any health impact. Bosso Dam is the major source of water for Minna water Board which distributes drinking water to households in Minna metropolis and beyond, however, it recorded the highest level of heavy metal pollution. Based on the above findings, it is recommended that control measures should be taken to protect the population using this water against Cd poisoning.

5.3 Suggestion for Further Studies

This study did not consider the microbiological aspect of water quality assessment. Although the results of the study have provided evidences of chemical pollution in the selected water bodies, an in-depth microbiological examination of these drinking water sources is necessary to help establish a more comprehensive understanding of the suitability of the water bodies for agricultural and domestic purposes.

5.4 Contribution to Knowledge

The pollution status in Bosso Dam, Chanchaga River and Tagwai Dam has been monitored and the data obtained showed that the selected waterbodies are highly acidic during rainy season. The study revealed that ammonia (0.41-14.52 mg/l), turbidity (14.54-80.86 NTU), silica (11.01 mg/l), Cu (0.04 mg/l), and Cd (0.04 mg/l), were above the World Health Organization's permissible limits (0.40 mg/l, 5.00 mg/l, 10.00 mg/l,

0.01 mg/l, and 0.00 mg/l respectively) in the selected waterbodies and are therefore, not recommended for domestic use.

Chemometric evaluation approach was applied which revealed deeper and intrinsic details much more than conventional statistics that is widely used. Information such as signature contaminants were revealed which include nitrate, nitrite and turbidity in both water and sediments. Hydro-geological classification and characterisation of water and sediment samples were revealed. Application of chemometrics also contributed information about existence of unusual samples with variant heavy metals and physicochemical parameters. Co-equivalent samples pairs which are pairs of samples with similar physicochemical properties were also identified across Chanchaga River, Bosso and Tagwai Dams in both rainy and dry seasons among water and sediments samples.

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