PHYSICOCHEMICAL PARAMETERS AND TRACE METALS OF SUSPENDED SOLIDS, SIDE-SEDIMENTS AND WATER FROM ZARIA DAM, KADUNA STATE, NIGERIA

BY

ARONIMO, BAMIDELE DANIEL
M.Sc./SCIEN/02167/08-09

A THESES SUBMITTED TO THE POSTGRADUATE SCHOOL
AHMADU BELLO UNIVERSITY, ZARIA, NIGERIA

IN PARTIAL FULFILLMENT FOR THE AWARD OF
MASTER OF SCIENCE IN ANALYTICAL CHEMISTRY

DEPARTMENT OF CHEMISTRY
AHMADU BELLO UNIVERITY, ZARIA NIGERIA
AUGUST, 2011

DECLARATION

I declare that the work in this thesis titled Physicochemical Parameters and trace metals of suspended solids, side-sediments and water sample from Zaria Dam, was performed by me in the Department of Chemistry, under the supervision of Prof. V.O. Ajibola and Dr. S.O. Idris. The information derived from literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was presented for another degree in any university.

_____	_____	_____
Name of student	Signature	Date

CERTIFICATION

This Thesis titled "Physicochemical Parameters and trace metals of suspended solids, side-sediments and water sample from Zaria Dam", by Aronimo, Bamidele Daniel, meets the requirements for the award of Master of Science degree in Analytical Chemistry of the Ahmadu Bello University, Zaria and approved for its contribution to knowledge and literary presentation.

_____	_____
Prof. V.O Ajibola	Date
Chairman, Supervisory Committee	
_____	_____
Dr. S.O Idris	Date
Member, Supervisory Committee	
_____	_____
Prof. C.E Gimba	Date
Head of Department	
_____	_____
Prof. A.A Joshua	Date
Dean, Postgraduate School	

DEDICATION

This work is dedicated to the Almighty God and to all who contributed to this work in one way or the other.

ACKNOWLEDGEMENT

Now unto the King immortal the invisible and the only wise God be praise forever.

I would like to express my sincere appreciation to my supervisors; Prof. V.O Ajibola whose valuable advice, constructive criticism, encouragement, patience and assistance have helped very much in the completion of this research works. My appreciation goes to Dr. S.O Idris, a member of the supervisory committee, for his patience, thank you sir. Also my profound gratitude goes to Prof. C.E Gimba, the Head of Department for his encouragement and support. I also want to acknowledge all members of staff of Chemistry Department: Prof. E.B. Agbaji, Prof. J.O. Amupitan, Prof J.A. Kagbu and Dr. J.D. Habila.

I want to say a big thank you to Daddy and Mummy Bakare; for their support, encouragements and prayers, all the secretarial staff of JAWOM Headquarters, and all JAWOMites. I also want to acknowledge all my family members: Mr. and Mrs. D.O. Aronimo, all my brothers and sisters, and friends. Thank you all.

ABSTRACT

This work present the results of determination of some pollutants and trace metals in suspended solids, side-sediments and water from Zaria dam, which is the main water reservoir from which Zaria metropolis, is being provided with pipe-borne water. Composite samples were taken at different points in the dam, minimum of three composite samples were taken for each month of sampling. Samples were taken in May, (before the rainy season) in August, (rainy season) and in December (Dry season). Preliminary tests were carried out on all the samples and AAS was used to determine metals concentration, other parameters were determined using standard methods. The information from the data obtained was analyzed using statistical methods. To access the physicochemical composition of the suspended solids, side-sediments and water samples, descriptive statistical analyses were carried out and also a multivariate analysis method of data analysis using Hierarchical Cluster Analysis (CA), Principal Component Analysis (PCA). The samples taken in August, during the rainy season, show higher concentration of trace metals for side-sediments, suspended solids, and water samples. Trace metals in the suspended solids, side-sediments and water samples were found to be higher in the order; Zn > Pb > Ni > Cr > Cd. From the multivariate analysis results, two components were sufficient to explain the dam monitored. In the study, an attempt was made to determine factors that could cause variation in water quality at the Zaria dam by using PCA. This result showed that domestic waste, industrial waste and agricultural run-off during rainy season may be the main cause for the variation in the water.

Table of Contents

Declaration	ii
Certification	iii
Dedication	iv
Acknowledgement	v
Abstract	vi
Table of contents	vii
List of Tables	xii
List of Figures	xv
List of Appendices	xvi

Chapter One

1	Introduction	1
1.2	Justification	4
1.3	Aims	5

Chapter Two

Literature Review		6
2.1	Trace Metals	6
2.1.1	Lead	6
2.1.2	Nickel	7

2.1.3 Cadmium 8

2.1.4 Chromium 9

2.2 Parameters for Defining Water Quality 10

2..2..1 Electrical Conductivity 10

2.2.2 Dissolved and Suspended Solids 10

2.2.3 Colour and Turbidity 11

2.2.4 Sediments and Substrate 11

2.2.5 Suspended Particles 12

2.2.6 Temperature 12

2.2.7 Dissolved Oxygen 13

2.2.8 Biochemical Oxygen Demand 14

2.2.9 Chemical Oxygen Demand 15

2.2.10 pH 15

2.2.11 Alkalinity 16

2.2.12 Hardness of Water 16

2.3 Sulphate 16

2.4 Chloride 17

2.5 Nitrogen 18

Chapter Three

Materials and Methods 19

3.1 Study Area of Zaria Dam 19

3.2 Preparation of Solutions 22

3.2.1 Stock Solutions 22

3.2.2 Standard Working Solution 23

3.3 Calibration Curve 24

3.4 Samples Collection and Preparation 24

3.5 Filtration of Water Samples 24

3.6 Digestion of Samples 25

3.6.1 Digestion of Water Samples 25

3.6.2 Digestion of Side-sediments and Suspended Solids 25

3.7.1 Determination of Some Physicochemical Parameters 26

3.7.1.1 Temperature 26

3.7.1.2 Determination of pH 26

3.7.1.3 Determination of Electrical Conductivity 26

3.7.1.4 Total Dissolved Solid 27

3.7.1.5 Total Solid 28

3.7.1.6 Total Suspended Solid 28

3.7.1.7 Turbidity 29

3.7.1.8 Total Alkalinity 29

3.7.2 Determination of Sulphate 30

3.7.3 Chloride 30

3.7.4 Sulphate 30

3.7.5 Nitrogen 31

3.7.6 Biochemical Oxygen Demand 31

3.7.7 Instrumentation 32

Chapter Four

Results and Discussion 33

4.1 Physicochemical Parameters for Water Samples 33

4.1.2 Physicochemical Parameters for Side-sediment Samples 39

4.2 Trace Metals Results 41

4.3.1 Concentration of Trace Metal in Suspended Solids 45

4.3.2 Concentration of Trace Metal in Side-sediments 51

4.3.3 Concentration of Trace Metal in Water Samples 55

4.4.1 Interpretation of Water Quality Data by Multivariate Analysis 60

4.4.2 Principal Components Analysis 64

4.4.2.1 Principal Components from Correlation or Covariance Matrix 64

4.4. Scree Plot 65

4.4.4 Component Matrix 70

4.4.5 Hierarchical Cluster Analysis for Water Samples 72

4.4.6 Hierarchical Cluster Analysis for Side-sediment Samples 74

Charter Five

5.1 Conclusion 76

5.2 Recommendations 77

Reference 79

List of Tables

Table 4.1: Minimum, Maximum, Range, Skewness, and Mean of Physical and Chemical Properties of Water Samples from Zaria Dam during Research Period 34

Table 4.2: Correlation Matrix among Physicochemical Parameters in Water Samples from Zaria Dam 37

Table 4.3: Minimum, Maximum, Range, Skewness, and Mean of Physical and Chemical Properties of Side-sediment Samples from Zaria Dam during Research Period 38

Table 4.4: Correlation Matrix among Physicochemical Parameters in Side-sediment Samples from Zaria Dam 40

Table 4.5: Concentration (mg/L) of Heavy Metals in Suspended Solid from Zaria Dam 42

Table 4.6: Concentration (mg/kg) of Heavy Metals in Side-sediments from Zaria Dam 43

Table 4.7: Concentration (mg/kg) of Heavy Metals in Filtrate from Zaria Dam 44

Table 4.8: Correlation Matrix among Trace Metals in the Suspended Solids from Zaria Dam 50

Table 4.9: Correlation Matrix among Trace Metals in the Side-sediments from Zaria Dam 52

Table 4.10: Correlation Matrix among Trace Metals in the Water Samples from Zaria Dam 59

Table 4.11: Monthly Mean Concentration of Physical and Chemical Properties for Dam Water Samples 62

Table 4.12: Monthly Mean Concentration of Physical and Chemical Properties for Side-sediments 63

Table 4.13 Component Matrix for Water Samples 67

Table 4.14: Rotated Component Matrix for Water Samples 69

List of Figures

Fig. 3.1: Map of Catchment Areas of the Zaria Dam 20

Fig. 3.2: Map of Catchment Areas of the Zaria Dam 21

Fig. 4.1: Trace Metals in Filtrate, Suspended Solids and Side-sediments 46

Fig. 4.2 Trace Metals Concentration in the Suspended Solids for each Month of Sampling 47

Fig. 4.3: Mean Total Concentration of the Trace Metals in Suspended Solids for the Months of Sampling 48

Fig. 4.4: Trace Metals Concentration in the Side-sediments for each Month of Sampling 53

Fig. 4.5: Mean Total Concentration of the Trace Metals in Side-sediments for the Months of Sampling 54

Fig. 4.6: Trace Metals Concentration in the Water Samples for each Month of Sampling 56

Fig. 4.7: Mean Total Concentration of the Trace Metals in Water Samples for the Months of Sampling 57

Fig. 4.8: Scree Plot 66

Fig. 4.9: Component Plot in Rotated Space 71

Fig. 4.10: Hierarchical Cluster Analysis for Water Samples 73

Fig. 4.11: Hierarchical Cluster Analysis for Side-sediments 75

Appendices

Appendix I: Calibration Curve for the Determination of Pb 87

Appendix II: Calibration Curve for the Determination of Zn 88

Appendix III: Calibration Curve for the Determination of Ni 89

AppendixIV: Calibration Curve for the Determination of Cd 90

Appendix V: Calibration Curve for the Determination of Cr 91

Appendix VI: A Typical Sewage Analysis 92

Appendix VII: WHO Drinking Water Quality Guidelines 93

Appendix VIII: Bathing Water Quality Standards 94

Appendix IX: Effect and Drinking Water Standard for Some Water Quality Parameters 95

Appendix X: Recommended Maximum Concentrations of Trace Elements in Irrigation Water 96

CHAPTER ONE

1.1 INTRODUCTION

All living things depend either directly or indirectly on water for biological and physiological functions. However, with the continuous increase in water pollution, the water bodies are becoming very hazardous to lives. The presence of toxic metals such as lead and cadmium, in the environment has been a source of worry to environmentalists, government agencies, and health practitioners. This is mainly due to the health implication since they are non-essential metals (Tyler, 1981; Borgmann, 1983). These metals are regarded as one of the most serious pollutants to the aquatic environment because of their environmental persistence and tendency to be concentrated in aquatic organism (Harte *et.al.,* 1991; Schüürmann and Markert, 1998; Merian, 1991; O'Neil, 1993). Although these metals are natural trace components of the aquatic environment, their levels have increased due to industrial, agricultural and mining activities (Ipinmoroti and Oshodi, 1993; Asaolu *et.al.,* 1997). The higher levels of these metals have been known to cause serious impairment in the metabolic and physiological systems (Tort *et.al.,* 1987).

Digging a mine, removing ore from it, and extraction and processing of the minerals sometimes cause environmental damage. For example, mining operation can destroy habitat, farmland, and homes; cause soil erosion; and pollute waterways, via, toxic drainage. Exposure of pyrite (FeS) and other sulphide minerals to atmospheric oxygen and moisture result in oxidation of these minerals and the formation of acid-mine drainage water. The release of acid mine drainage from active and abandoned mines, particularly coal mines, have been widely

associated with serious water quality problems. It dissolves toxic elements from tailings and soils and carries them into waterways and even groundwater. Water quality problems involve relatively high levels of metals such as iron, manganese, zinc, copper, nickel, and cobalt.

Ore processing, smelting and refining operation can cause deposition of large quantities of trace metals, such as lead, zinc, copper, arsenic, and silver, into drainage basins or direct discharge into aquatic environments. Other sources of metal pollution includes: Domestic wastewater effluents which contain large amounts of trace metals from metabolic waste products, corrosion of water pipes- copper, lead, zinc, and cadmium, and household products, such as detergents - iron, manganese, chromium, nickel, cobalt, zinc, boron, and arsenic (Tyler, 1981,Csuros and Csuros, 2002). Wastewater treatment usually removes less than 50% of the metal content of the influent, leaving the influent with significant metal loading. The sludge resulting from wastewater treatment is also rich in metals. Domestic wastewater and the dumping of domestic and industrial sludge are the major artificial sources of cadmium, chromium, copper, iron, lead, and mercury pollution (Deuzuane, 1989)

Storm water run-off from urbanized area is a significant source of metal pollution in the receiving waters. Metals composition of urban run-off water is dependent on many factors, such as city planning, traffic, road construction, land use and the physical characteristics and climatology of the watershed (Csuros and Csuros, 2002). Industrial wastes and discharges contribute greatly to metal pollution. Metals and their concentrations in industrial waste and discharges are specific and depend on the profile of a specific industry. Food industry effluents are generally characterized by a high content of biodegradable pollutants. Suspended substances constitute a large part of these pollutants, in addition to the high Biochemical Oxygen Demand

(BOD) and Chemical Oxygen Demand (COD) concentrations of the effluents. Untreated effluents which may affect the ecosystems constitute hazard to both man and plants.

The metal contents of agricultural run-off originates in sediments and soils saturated by animals and plants residues, specific herbicides and fungicides, and use of sewage and sludge nutrient. The increased use of metal-based fertilizer in agricultural revolution by the government could result in continued rise in concentration of metal pollutions in fresh water reservoir due to the water run-off. Also feacal pollution of drinking water cause water-borne disease which has led to the death of millions of people both in cities and villages (Asaolu, 1998). The discharge of these wastes may adversely affect the aquatic nature of such river thereby altering the river chemical composition (Adewoye, 1998). Water quality characteristic of aquatic environment arise from a multitude of physical, chemical and biological interactions (Deuzuane, 1989; Dee, 1989). The water bodies, river, lakes, dams, and estuaries are continuously subjected to dynamic state of change with respect to the geological age and geochemical characteristics (Dee, 1989). This is demonstrated by continuous circulation, transformation and accumulation of energy and matter through the medium of living things and their activities. The dynamic balance in the aquatic ecosystem is upset by human activities, resulting in pollution which is manifested dramatically as fish are killed. Also offensive taste, odour, colour and unchecked aquatic weeds are produced. Industrial units located in and at the outskirts of the city, intensive agricultural practice along the river side and indiscriminate disposal of domestic and municipal waste are the major source of Galma River water pollution. These are known to contain toxic components such as heavy metals ions, which are of great concern as they pose not only a health risk to human, but also potentially unacceptable ecological risk to plants, animals and microorganisms (Miro *et al.,* 2004)

The accurate determination of trace elements in a variety of environmental samples has received considerate attention in the battle against environment pollution (Lee and Choi, 2001). For the determination of trace elements various methods have been used including Inductive couple plasma mass spectrometry (Kagaya *et al.,* 2003), Instrumental Neutron Activation Analysis (Ewa *et al.,* 2002), Total Reflection X-Ray Fluorescence Spectrometry and Hydride Generation Atomic Fluorescence Spectrometry (Townsend *et al.,* 2001)**.**

1.2 Justification

The Zaria Dam is the main water reservoir from which Zaria metropolis, with over 695,069 population, is being provided with pipe borne water. The people depend directly on this water source for domestic, irrigation, and livestock activities.

The location where the outlet river runs through is noted for rural agricultural practices both for subsistence and medium-scale commercial farming with irrigation farming for major part of the year. The larger proportion of vegetable cropping in Zaria is carried out along the Galma River and these are supplied to major markets in Zaria and neighbouring villages.

Obviously, the chemical status of the water would have its influence on the receiving land, which might possibly reflect on the farm produce cultivated on such land and the health status of the people living in the land. These, therefore, necessitate this research, since availability of good quality water is an indispensable feature for preventing diseases and improving quality of life (Oluduro and Adewoye, 2007).

1.3 Aims

1.The principal objective of the study is to investigate the input and distribution of trace elements and examine the pollution levels in Galma River water, side-sediments and suspended solids with respect to some trace elements, namely Cr, Zn, Ni, Cd and Pb

2.To study the distribution of these trace metals between the water samples, suspended solids and the side-sediments.

3.To confirm the suitability of water from Galma River for irrigation and domestic use by comparing the concentration of heavy metals of interest in water with the recommended maximum concentration of trace elements in irrigation and drinking water.

Objectives

1. To collect composite samples of the water and the side-sediments by taking series of small samples of equal volume and mixed properly to give a composite samples.
2. To measure physicochemical parameters of the sample such as; the pH, temperature, conductivity, turbidity, residual chloride, dissolved oxygen, total hardness, COD, BOD, alkalinity, sulphate and percentage nitrogen.
3. To filter the water samples immediately after collection using 0.45μm filter membrane, the filtrate is to be used for determination of dissolved metal while the filter membrane and suspended solids will be used for the determination of the suspended solids.
4. To determine the concentration of Ni, Pb, Cr, Cd and Zn in the samples
5. To compare the concentration determined with WHO standard for drinking water and irrigation water
6. To use descriptive and multivariate analysis to explain the data obtained.

CHAPTER TWO

LITERATURE REVIEW

2.1 Trace Metals

Trace metals are metals which exist at extremely low concentration, 10^{-9} to 10^{-14} mol/dm^3 in natural waters (Donat, 1992), however, several of them are toxic to the aquatic phytoplankton at the base of the food chain. These metals exist in different forms in natural waters which include ionic forms, inorganic and organic complexes and those associated with colloidal materials, particulate matters and biota (Donat, 1992). Some important processes control the distribution and species of trace metals in different fractions. These includes oxidation and reduction, association and dissociation in solution, desorption and adsorptions, precipitation, dissolution, aggregation, disaggregation and complex formation (APHA, 1992). Species of trace metals are more important compared to total concentration when information is needed to assess trace metal bioactivity and toxicity (Florence, 1981). Trace metals have high affinity for humic soils, organic clays and oxides coated with organic matter (APHA, 1992).

2.1.1 Lead

The United States Environmental Protection Agency has classified Pb as being potentially hazardous and toxic to most forms of life (USEPA, 1986). It has been found to be responsible for quite a number of ailments in human such as chronic neurological disorder especially in fetuses and children. Lead is toxic to the nervous system, and children are especially susceptible to its effects. It is readily absorbed through the intestinal tract and deposited in the central nervous system and when released into the environment has a long residence time compared with most other pollutants. As a result, lead and its compounds tend to accumulate in soils and

sediments. This is partly due to their relatively low solubility and not being prone to microbial degradation. Many investigations have been carried out on environmental lead, including soil and water, over the last 30 years and a detailed understanding of its soil chemistry, ecological and health significance is well understood.

Automobile exhaust fumes have been reported to account for about 50% of the total inorganic Pb absorbed by human beings (Mohan and Hosetti, 1998). Other inputs of Pb into the environment are from used dry-cell batteries, from sewage effluent, run-off of wastes, atmospheric deposition and lead- containing paint,

The presence of lead in the body is indicated by lead blood levels expressed as microgram of lead per deciliter. Although Zn has been found to have low toxicity to man, prolonged consumption of large doses can result in some health complication such as fatigue, dizziness and neutropenia (Hess and Schmid, 2002). Lead is very toxic and maximum permissible limit in drinking water and water for domestic uses is 0.1 mg/L. When taken in higher concentration it may result in abdominal cramp, constipation, loss of appetite and anaemia. In children, it is known to result in kidney disease and mental retardation which may be attributed to inhibition of growth of the central nervous system. Acute toxicity is quite unusual, as lead is a relatively insoluble, cumulative poison. Some lead-poisoning victims develop weakness in the extensor muscles, known as wrist drop or foot drop. Some literature sources have also revealed that zinc could be toxic to some aquatic organism such as fish (Alabaster and Lloyd, 1980).

2.1.2 Nickel

Nickel also is a naturally occurring element found in a number of mineral ores including Ni sulphides, oxides and silicates. It is present in the enzyme urease and as such is considered to be essential to plants and some domestic animals. Its properties such as strength, corrosion

resistance, high ductility, good thermal and electric conductivity and catalytic properties enhance its commercial importance and applications. However, Ni-related health effects such as renal, cardiovascular, reproductive, and immunological effects have been reported in animals. Toxicity of Ni to rainbow trout has been reported (Pane *et al.,* 2003). Nickel itch usually begins with a sensation of burning and itching, followed by erythema and a nodular eruption, which may progress to postules or ulcers.

Nickel in drinking water also correlates with mortality from oral and intestinal cancer, but not respiratory cancer (Csuros *and Csuros,* 2002).

2.1.3 Cadmium

Cadmium is a relatively rare soft metal that occurs in the natural environment typically in association with zinc ores and, to a lesser extent, with lead and copper ores. Some inorganic cadmium compounds are soluble in water, while cadmium oxide and cadmium sulphide are almost insoluble. Fresh water typically contains levels of cadmium below 1μg/L, but concentrations up to 10μg/L may occur on rare occasions due to environmental disturbances such as acid rain. Concentration in non-polluted agricultural soils varies between 0.01 and 0.7 μg/g (WHO, 1975).

Cadmium is emitted into the atmosphere from natural sources, mainly volcanic activities, and from anthropogenic sources. Metal production (drying of zinc concentrates and roasting, smelting, and refining of ores) is the largest source of anthropogenic atmospheric cadmium emissions, followed by waste incineration and by other sources, including the production of nickel-cadmium batteries, fossil fuel combustion, and generation of dust by industrial processes such as cement manufacturing (Kazantzis, 1987). The largest contributors to the contamination of water are mines (mine water, concentrate processing water, and leakages from mine tailings);

process water from smelters; phosphate mining and related fertilizer production; and electroplating wastes. The largest sources of cadmium in landfills are smelters, iron and steel plants, electroplating wastes, and battery production. Mine tailings generated as the result of zinc mining also have potential to transfer cadmium to its environment. Cadmium is mainly used as an anticorrosion coating in electroplating, as an alloying metal in solders, as a stabilizer in plastics (organic cadmium), as a pigment, and as a component of nickel-cadmium batteries. Cadmium production may use by-products and wastes from the primary production of zinc.

2.1.4 Chromium

Chromium is a naturally occurring element found in rocks, animals, plants, soils, and in volcanic dust and gases. Chromium is present in the environment in several different forms. The most common forms are Cr, Cr (III), and Cr (VI) and no taste or odor is associated with its compounds. The metal chromium, which is the Cr form, is used for making steel. Cr (VI) and Cr (III) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving. Cr (III) is an essential nutrient that helps the body use sugar, protein, and fat. The exact level where chromium becomes toxic is not clear. The recommended therapeutic value is between 50 - 200 ppm. However, this is applicable only to organic chromium that the body absorbs and retains and therefore not usually excreted and found in urine. The toxic form of chromium is inorganic chromium that the body does not absorb and therefore eliminated in urine. It is this inorganic chromium that requires testing and its presence should be 0.

2.2 Parameters for Defining Water Quality

The level of parameters obtained for a sewage analysis cannot be the same used for a drinking water source, bathing or a freshwater stream. The WHO standard for drinking water, irrigation water and their ecological or health effect are shown in appendix VI, VII, VIII, IX and X. The properties of water can be based on its physical, chemical and biological properties. With information of the physical, chemical and biological properties, much can be said about the quality of the water. Some of these parameters are described below.

2.2.1 Electrical Conductivity

Electrical Conductivity (EC) is the ability of water to conduct an electric current due to dissolved salts present in it. The dissolved salts produce ions that migrate in solution and then generate electric currents. The conductivity of water is a more or-less linear function of the concentration of dissolved ions. Conductivity itself is not a human or aquatic health concern, but because it is easily measured, it can serve as an indicator of other water quality problems, if it suddenly increases; it indicates that there is a source of dissolved ions in the vicinity. Therefore, its measurements can be used as a quicker way to locate potential water quality problems. It is measured in term of conductivity per unit length, and meters typically use the unit micrograms/cm.

2.2.2 Dissolved and Suspended Solids

Solids may be present in solution or suspension. Suspended solids are discrete particles that can be measured by filtering a water sample through appropriate filters. Dissolved solids are due to soluble materials obtained by evaporating a known volume of water the sample in an oven at 105^{o}C and weighing the residue.

All natural water contains some dissolved solids due to the dissolution and weathering of rock and soil. Some but not the entire dissolved solids act as conductors and contribute to conductance. Water with high total dissolved solids (TDS) is unpalatable and potentially unhealthy. Water treatment plants use flocculants to aggregate suspended and dissolved solids into particles large enough to settle out of the water column in settling tanks. A flocculants is a chemical that uses double-layer kinetics to attract charged particles.

2.2.3 Colour and Turbidity

Good water should be transparent and clear. The colour of water is expressed in Hazen units which correspond to the colouration of a series of platinum/cobalt salt dilutions. Turbidity measure the loss of transparency of a solution. The presence of colloidal solids gives water a cloudy appearance which reduces the transparency. It measures the amount of solid that is scattered or absorbed. Suspended silt and clay, organic matter, and plankton can contribute to turbidity. Photoelectric turbimeters measure turbidity in nephelometric turbidity units (NTU). Turbidity units are supposed to correspond to total suspended solid (TSS) concentration, but this correlation is only an approximate.

Turbidity in a stream will fluctuate before, during and after storm flow. Turbidity of 10 NTU or less represents very clear waters, 50NTU is cloudy; and 100-500 or greater is very cloudy to muddy. Some fish species may become stressed at prolonged exposures of 25NTUs or greater. Turbidity and TSS can reduce light penetration, decreasing algae growth and low algal production can reduce productivity of algactic invertebrate, a food source of many fish.

2.2.4 Sediments and Substrate

Sediments enter stream via up load soil erosion, bank erosion and land sliding. They are natural component of streams, but excessive sediments can be carried into streams and rivers

from erosion of instable streams banks, construction sites, agricultural activities, and urban run-off. It moves downstream in a river in two forms: suspended load and bed load. Load includes the particles in suspension in the water column. The redish brown colour of Zaria dam water is due to clay and colloid particles in suspension. Bed load refers to the sediment pushed along the button of the channel. Coarser substrate such as sand and gravel tend to move as bed load, not suspended load.

Suspended particles are usually measured as concentrations of total suspended solids (TSS), which are the dry weight after filtering a water sample, expressed in mg per litre. To determined suspended sediment load (mass/time), the TSS concentration must be multiplied by the flow rate (volume/time). Average concentrations of 25 - 80mg/l represent moderate water quality. An average concentration of 25mg/l has been suggested as an indicator of unimpaired stream water quality (Holmbeck-pelham and Rasmussen, 1997)

2.2.5 Suspended Particles

Suspended particles play an important role in rivers and are the amount of soil moving along in streams or rivers. It is highly dependent on the speed of the water flow as fast-flowing water can pick up and suspend more soil than calm water.

The materials transported by rivers consist of dissolved ions, sediments suspended in flow, sediments transported along the bed of the river. It constitutes the majority of sediment transported by most rivers, usually more than 80% (Campbell, 1995).

2.2.6 Temperature

The temperature of water is not the main issue when considering it as a physical parameter but its effect on other properties e.g. metabolic rate and the reproductive activities of aquatic life

are controlled by water temperature. Metabolic activities increase with a rise in temperature, thus increasing a fish's demand for oxygen; however, an increase in stream temperature also causes a decrease in DO, limiting the amount of oxygen available to these aquatic organisms. A rise in temperature can also provide conditions for the growth of disease-causing organisms. Water temperature varies with season, elevation, geographic location and climatic conditions and is influenced by stream flow, streamside vegetation, ground water inputs and water effluent from industrial activities. Water temperature rise when streamside vegetation is removed.

2.2.7 Dissolved Oxygen

Dissolved oxygen (DO) is the measure of the concentration of free (not chemically combined) molecular oxygen (a gas) dissolved in water usually expressed in milligram per liter, part per million, or percent saturation. Adequate concentrations of dissolved oxygen are necessary for the life of fish and the prevention of offensive odour. Dissolved oxygen level is considered the most important and commonly employed measurement of water quality and indicator of a water body ability to support desirable aquatic life.

Levels above 5 milligrams per litre are considered optimal and most fish cannot survive for long period at level below 3 milligram per litre. Levels below 1 miligram per litre are often referred to as hypoxic and when oxygen is totally absent anoxic (often called anaerobic which technically means without air). Secondary and advanced waste water treatment systems are generally designed to degrade organic matters to ensure adequate dissolved oxygen in waste receiving water.

Different life form in water needs oxygen for survival. Like terrestrial animals, fish and other aquatic organisms need oxygen to survive. As water moves past their gills (or other breathing apparatus), microscopic bubbles of oxygen gas in the water, called dissolved oxygen,

are transferred from the water to their blood. Like any other gas diffusion process, the transfer is efficient only above certain concentrations. In other words, oxygen can be present in the water, but at too low a concentration to sustain aquatic life. Oxygen also is needed by virtually all algae and all macrophytes, and for many chemical reactions that are important to lake functioning.

The amount of dissolved oxygen in streams is dependent on the water temperature, the quantity of sediments in the stream, the amount of oxygen taken out of the system by respiration and decaying organisms, and the amount of oxygen put back into the system by photosynthetic plants, stream flow and aeration. It is measured in milligrams per litre or amount of dissolved oxygen present less oxygen dissolves in warm water than cold water. Water low in dissolved oxygen has an unpleasant taste while water high on dissolved oxygen is good for drinking purposes.

2.2.8 Biochemical Oxygen Demand

Biochemical Oxygen Demand (BOD) is a measure of the oxygen used by microorganisms to decompose waste; oxygen used by microorganism per unit volume of water at a given temperature for a given time. Microorganisms such as bacteria are responsible for decomposing organic waste. Natural organic detritus and organic water from waste water treatment plants, failing septic systems, and agriculture and urban run-off, act as a food source for water-borne bacteria, the measure of the amount of oxygen that bacteria will consume while decomposing organic matter under aerobic condition is referred to as biochemical oxygen demand.

When BOD levels are high DO levels decrease, because the oxygen that is available in the water is being consumed by bacteria. Since less dissolved oxygen is available in the water, fish

and other aquatic organisms may not survive. Generally, when BOD levels are high, there is a decline in DO levels. This is because the demand for oxygen by the bacteria is high and they are taking that oxygen from the oxygen dissolved in the water. If there is no organic waste present in the water, there won't be as many bacteria present to decompose it and thus the BOD will tend to be lower and the DO level will tend to be higher.

2.2.9 Chemical Oxygen Demand

This is the amount of oxygen required to decompose the organic compound waste water. The quantity does not differentiate between biological available and inert organic matter, and it is a measure of the total quality of oxygen required to oxidize all organic materials into carbondioxide and water. COD measurements can be made in a few hours while BOD measurement takes five days.

2.2.10 pH

pH is a measure of the amount of free hydrogen ions in water, the level of acidity or alkalinity. Specifically, it is the negative logarithm of the molar concentration of hydrogen ions. The reactions tends to keep pH of most waters around 7 – 7.5, unless large amount of acid or base are added to the water.

The pH of water affects the solubility of many toxic and nutritive chemical; therefore, the availability of these substances to aquatic organisms is affected. As acidity increases, most metals become more water soluble and more toxic. Toxicity of cyanides and sulphide also increases with the decrease in pH (increase in acidity). Ammonia however becomes more toxic with only a slight increase in pH.

2.2.11 Alkalinity

Alkalinity is the capacity to neutralize acids, for water, it is derived principally from the salts of weak acids. Hydroxides, carbonates, and bicarbonates are the dominant sources of natural alkalinity. Reactions of carbondioxides with calcium or magnesium carbonate in the soil creates considerable amount of bicarbonates in the soil. Alkalinity itself has little public significant, although waters with high alkaline are unpalatable and can cause gastrointestinal discomfort.

2.2.12 Hardness of water

Hardness of water is a phenomenon which occurs when soap does not lather easily and metal scales are produced in pipes and boilers or kettles. It is caused by metallic ions of Ca and Mg and sometimes Fe.

2.3 Sulphate

A variety of organic and inorganic sulphur compounds occur in soil plant-water system. In soil of the most humid and semi-humid regions the organic sulphur compounds account for >95% of sulphate. The proportion of organic and inorganic sulphur, however, varies widely according to soil type. Similarly, sulphur occurs in plants in such compound as sulphate, coenzymes A, methionine, alkaloid and thiocyanates. Although, the sulphate ion is predominant in most natural waters, other inorganic sulphur species and organic compounds could become predominant under certain conditions. These range from accumulation of thiosulphuate in mine tailing effluents to accumulation of sulphides and organic sulphur compounds in surface water originating from peat and other organic deposit. Also rain, caused by large SO_2 emissions and over-used chemical fertilizer, are the main causes of exceeding safe limit of inorganic sulphur compound concentration in the natural environment of waters and side-sediments of lakes,

rivers, and freshwater reservoirs. Atmospheric fallout of particulate matter from natural source as well as from anthropogenic inputs, which includes the combustion of fossil fuels and mineral processing, can introduce relatively large quantities of sulphur compound into the natural water systems.

Sulphur is present in water generally as the result of industrial waste contamination or reduction of SO_4^{2-} ions by anaerobic action. The occurrence of SO_3^{2-} ions in natural water is rare because SO_3^{2-} ions is so readily oxidized by air to SO_4^{2} ions but drainage water from agricultural hand does not contain reduced inorganic sulphur compound, $S_2O_3^{2-}$ and $S_4O_6^{2-}$ are produced in soil when treated with sulphur. In addition to these inorganic sulphur forms, some natural waters may contain small amount of organic sulphur. The suspended solids in natural water may contain organic sulphur. (Tabatabai, 1952)

2.4 Chloride

Chlorides are mineral salts and therefore, are not affected by biological action of sewage. Their presences in natural water result from the leaching of chloride-containing rocks and soils with which the water comes in contact. Chlorine found in domestic sewage is derived from kitchen wastes, human faeces and urinary discharge. Human faeces, for example, contain about 6g of chloride per person per day.

Water softeners also add large quantities of chlorides. Large amount of chlorides may also enter in wastewater from industries like ice cream plant, meat salting. Infiltration of ground water into sewers adjacent to saltwater is also a potential source of high chloride. The chloride of wastewater can be measured by titrating the sample of wastewater with standard silver nitrate solution, using potassium chromate as indicator.

2.5 Nitrogen

The presence of nitrogen in wastewater indicates the presence of organic matter in it. Nitrogen is important to the growth of protista and plants and as such is known as nutrient or biostimulant. Since nitrogen is an essential building element in the synthesis of protein nitrogen data is required to evaluate the treatability of wastewater by biological processes. Organic nitrogen present in wastewater is determined by Kjeldahl method. The sample is digested, during which the organic nitrogen is converted to ammonia, and from it the quantity of nitrogen is calculated.

Total Kjeldahl nitrogen which is the sum of organic and ammonia nitrogen, is determined in the same manner as the organic nitrogen, except that the ammonia is not driven off before the digestion. The level of parameters obtained for a sewage analysis cannot be the same used for a drinking water source, bathing or a fresh water stream.

Although water is commonly employed as a pollution indicator by trace metals, sediment can also provide a deeper insight into the long-term pollution state of the water body. Sediment has been described as a ready sink or reservoir of pollutants including trace metals where they concentrate according to the level of pollution (Becker *et al;* 2001; Onyari *et.al;* 2003). The need to access the state and quality of the Galma River and sediment in terms of the metallic load become imperative since water from the river is being used for domestic, irrigation and livestock activities by people living in the neighbouring villages, in view of the health implications of polluted water.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area of Zaria Dam

The Zaria dam, which was constructed across Galma River in 1975 to solve the rapidly increasing water demand in Zaria, is aimed to supply Zaria with pipe-borne water. It had a gross storage capacity of 16.0 x 106m^3 (16 million cubic meters), with maximum depth of 14.9m and a catchment area of 3200km^2 with a supply capacity of 50 million liters per day (11 million gallons) to cater for about 695,069 people.

The continuous reduction of the maximum depth of the dam from 4.9m over the span of 30 years due to sediment in the dam, if not checked will lead to a chain of event that can harm aquatic life, impair water quality for drinking and reservoir storage capacity (Abu, 2006).

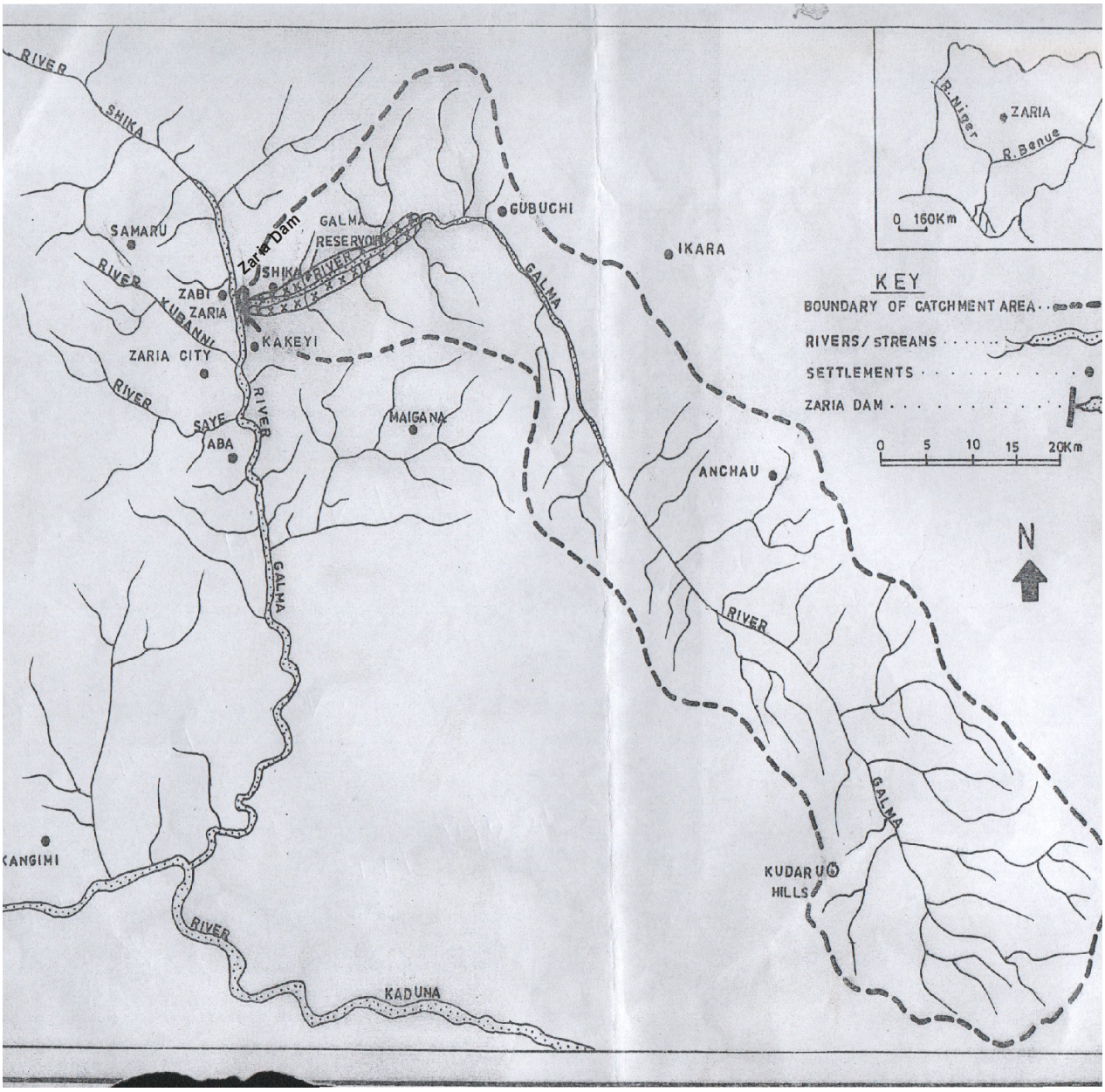


Fig. 3. 1: Map of Catchment Areas of the Zaria Dam (Galma River)

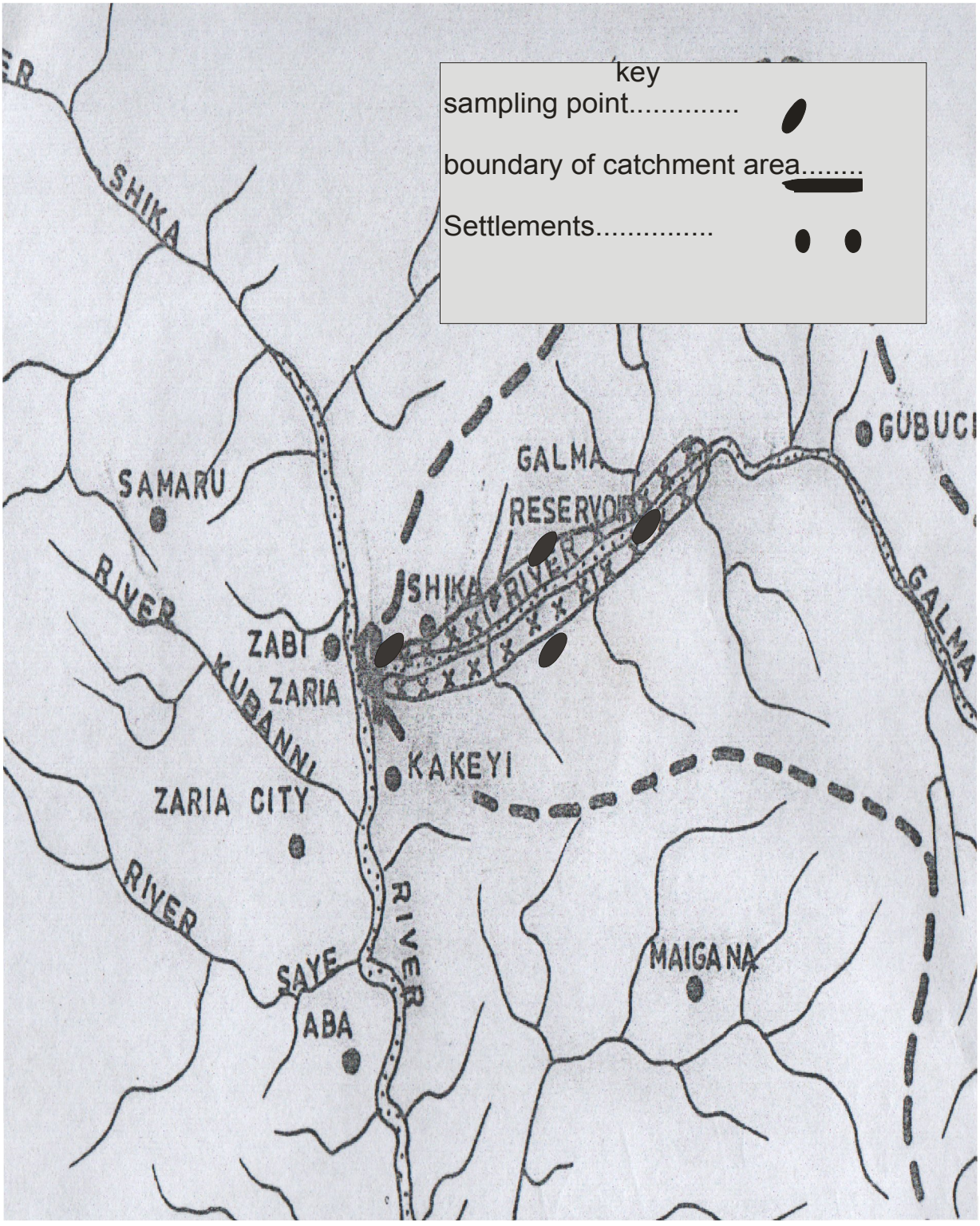


Fig. 3.2: Map of Site Location of the Zaria Dam (Galma River)

3.2 Preparation of solutions

All reagents used were of AnalaR grade and prepared using distilled deionized water.

3.2.1 Stock solutions

1. Lead stock solution was prepared by dissolving 1.5985g $Pb(NO_3)_2$ in 50ml of distilled deionized water and making up to 1litre giving 1000mgL^{-1} lead solution.

2. Cadmium stock solution was prepared by dissolving 2.7442g $Cd(NO_3)_2.4H_2O$ in 50ml of distilled deionized water and making up to 1litre giving 1000mgL^{-1} cadmium solution.

3. Nickel stock solution was prepared by dissolving 4.9434g $Ni(NO_3)_2.6H_2O$ in 50ml of distilled deionized water and making up to 1 litre giving 1000mgL^{-1} nickel solution.

4. Zinc stock solution was prepared by dissolving 0.1g zinc powder in 20ml 1:1 HCl and making up to 1 litre with distilled deionized water giving 1000mgL^{-1} zinc solution.

5. Chromium stock solution was prepared by dissolving 2.8289g $K_2Cr_2O_7$ in 50ml of distilled deionized water and making up to 1 litre giving 1000mgL^{-1} chromium solution.

6. Preparation of 5% potassium chromate solution K_2CrO_4 (indicator): 1.0 g of K_2CrO_4 was dissolved in 20 ml of distilled water.

7. Preparation of standard $AgNO_3$ solution: 9.0 g of $AgNO_3$ was weighed out, transferred to a 500 ml volumetric flask and made up to volume with distilled water. The resulting solution was approximately 0.1 M. This solution was standardized against NaCl.

Reagent-grade NaCl was dried overnight and cooled to room temperature. 0.25 g portion of NaCl was weighed into Erlenmeyer flasks and dissolved in about 100 ml of distilled water. In order to adjust the pH of the solutions, small quantities of $NaHCO_3$ were added until effervescence ceased. About 2 ml of K_2CrO_4 was added and the solution was titrated to the first permanent appearance of red $Ag_2Cr_2O_4$.

8. Barium perchlorate, 0.00521M. Obtained from Hach Chemical Co. catalogue No. 250.

9. Barium chloride, 0.005M. 122.16g of $BaCl_2$ was dissolved in distilled water in a litre volumetric flask and standardized by adding standard 0.005M $MgCl_2$ and titrated with EDTA. 5ml of 0.005M $MgCl_2$ was used for 10mls of 0.005M $BaCl_2$

10. Sulfaver indicator: Obtained from Hach chemical Co., catalogue No, 251.

11. Phenoldisulphonic acid: 113.5g phenol was dissolved by placing a beaker containing the phenol in warm water. The dissolved phenol was poured slowly, with constant stirring, into 66ml. concentrated H_2SO_4. 255ml. fuming H_2SO_4 was slowly added and stirred well. The mixture was heated on a steam bath.

12. Standard nitrate solution, 0.722g of dry KNO_3 was weighed out and place in a 100ml. volumetric flask. This was dissolved and diluted to exactly a litre. This contains 0.1mg nitrogen per ml. 100ml. of this solution was diluted with distilled water to 100ml in a volumetric flask. The second solution contains 0.01mg nitrogen per ml. Also 0.01mg nitrogen – 0.0443mg NO_3.

13. Silver sulphate. 4.397g of reagent grade silver sulphate, Ag_2SO_4, was dissolved in distilled water in a 100ml. volumetric flask; this was then diluted to the mark and mixed thoroughly, then transferred to an amber coloured bottle and stored in a dark place. One ml is equivalent to 1mg or chloride.

3.2.2 Standard Working Solution

A working standard concentrations 0.5, 1.0, 2.0, and 4.0mgL^{-1} of Ni and Zn; 1.0, 2.0, 3.0 and 4.0 mgL^{-1} of Cr; 2.0, 4.0, 6.0, and 8.0 mgL^{-1} of Pb and 0.5, 1.0, 2.0, and 4.0 of Cd were

prepared. Standard working solutions were prepared from 1000 mgL^{-1} of each metal stock solution by serial dilution. All solutions were prepared in distilled deionized water.

3.3. Calibration Curves

Calibration curves of absorbance against concentration for each, of Cd, Cr, Ni, Pb, Zn, were prepared as shown in Appendices I-VII respectively. The calibration curves were used for the determination of metal concentrations in samples. The actual concentrations of the metal in suspended solid, side-sediment and water samples were then determined

3.4 Samples Collection and Preparation

The quality of any analytical system depends primarily on the sample from which it is taken so that chemical analysis result in turn, represents the system.

To have a representative sample from the Zaria dam composite samples were taken by taking series of four small samples (subsample) of equal volume in a single pre-washed and mixed to give a composite sample, four composite samples were taken in May 2010. The composite samples will reflect the average characteristic during the sampling period. This was done at different times of the year to account for the seasonal variation: in August 2010 and also in December 2010 (rainy season and dry season).

Composites of the side-sediment and the water samples were taken on the same day using a plastic container which was thoroughly washed with detergent and rinsed with water and then with distilled water before soaking in 5% HNO_3. Containers were finally rinsed with double distilled water before being used for sampling**.**

3.5 Filtration of Water Samples

The water samples were filtered immediately after collection through 0.45µm pore-diameter membrane filter (polycarbonate) supported on Buckner funnel, pre-conditioned by

rinsing the assembled unit with 50ml deionized water and then with 100ml sample. A known volume of sample was filtered under pressure. The filtrate was acidified with concentrated HNO_3 and analyzed for dissolved metals and the filter was also retained and digested for direct determination of suspended metals.

3.6 Digestion of Samples

3.6.1 Digestion of Water Samples

100ml aliquot of well mixed sample was measured with a beaker, 2ml of concentrated HNO_3 acid and 5ml of concentrated HCl were added and covered with a ribbed watch glass then was heated in a steam bath at a regulated temperature of about 95^oC until the volume was reduced to 15ml without boiling . Then it was removed and cooled and the beakers wall glass was washed down with deionized water. It was filtered using pre-washed filter paper and the volume adjusted to 100ml with deionized water.

100ml of analyte samples free water and duplicate for all samples were also digested.

3.6.2 Digestion of Side-sediments and Suspended Solids

A representative weight of well mixed sample was digested in 10ml (1+1) HNO_3. 2g of the soil sample was mixed with 10ml concentrated HNO_3 and covered with a watch glass, heated at a regulated temperature of about 95^oC until the sample was almost dried and then cooled and refluxed for 10minutes with another 10ml of concentrated HNO_3 without boiling followed by addition of 10ml of 2M HCl. The digested sample was warmed with 20ml of 2M HCl, and then filtered into volumetric flask and made up to the mark with deionized water.

3.7.1 Determination of Some Physicochemical Parameters

Tests were carried out to determine the following water quality parameter on the different water samples, side-sediments and suspended solids.

3.7.1.1 Temperature

The temperature of the samples were taken by suspending the Mercury bulb thermometer with a thread into the container, and the readings were taken after allowing the thermometer to assume the temperature of the system and the temperature readings were recorded.

3.7.1.2 Determination of pH

The pH of each of the water samples was taken immediately after collecting the samples using a Crison micropH2000 meter by inserting pre-calibrated electrodes of pH meter in the beaker containing about 100ml of the water samples (Herdershot *et al.,* 1993). This was repeated for all water samples

For soil samples:

10g of the air, dried soil samples were weighed into 50ml beaker and 20ml distilled deionized water added. The mixture was allowed to stand for 30minutes with occasional stirring with glass rod. The electrodes were inserted into the partly settled suspension and the pH of the soil taken (Herdershot *et al.,* 1992).

3.7.1.3 Determination of Electrical Conductivity

Water Samples

A conductivity meter, conductivity measuring bridge Umhos - Electronic Instrument Ltd, London, was used for this measurement; samples were measured according to Hendershot *et al.,*

(1992). The electrode of the meter was inserted in the beaker containing the water sample and the readings were observed and recorded.

Side-sediment Samples

The electrical conductivities of soil samples were measured according to Hendershot *et al.,* (1992) as follows: Soil water ratio was 1:2 10g of 2mm air-dried soil samples were weighed into plastic containers and 20cm^3 of distilled deionized water added. The mixture was stirred several times for 30 minutes. Then the soil suspensions were allowed to stand for another 30minutes undisturbed. The electrodes of the conductivity meter were inserted into the settled suspension and the electrical conductivity of the soil samples were observed and recorded.

3.7.1.4 Total Dissolved Solid

The total dissolved solid was determined using the procedure describe by Csuros and Csuros (2002). A known volume of sample was filtered through a standard 0.45µm filter membrane, and the filtrate was evaporated to dryness in a weighed dish and dried to constant weight at 180^{0}C. The increase in dish weight represents the total dissolved solids.

Procedure:

A vacuum pump was attached to a Buckner flask, and about 1litre of the water sample was filtered, 20ml of the filtrate was taken in a pre-washed dish with a known weight, it was then evaporated to dryness in a drying oven, a successive portion of the sample water was added to the same dish and evaporated. The evaporated sample was dried for one hour in an oven at 180±2^{o}C. It was cooled in desiccators to balance temperature and weighed. Drying and weighing were repeated until a constant weight was obtained.

Calculations:

$$\text{mg total dissolved solids/L} = \frac{(A - B) \times 1000}{\text{Sample Volume, ml}}$$

where: A = weight of dried residue + dish, grams and B = weight of dried dish, grams

3.7.1.5 Total Solid

The total solid was determined using the procedure described by Csuros and Csuros (2002). A known volume of well-mixed sample was evaporated in a weighed dish and dried to constant weight in an oven at 105^0C**.** The increase in weight over that of the empty dish represents the total solids.

Procedure

A weighing dish was heated at 105^oC for 1 hour and stored in the dessicator until needed, it was weighed immediately before use, and 20ml of water sample was pipetted from the approximate midpoint of the container into the dish. The sample was evaporated in an oven at 105^oC, successive sample portion was added to obtain reasonable amount of solids. The evaporated sample was dried for 1hour at 105^oC**,** it was cooled in dessicator to balance temperature and weighed. These were repeated until a constant weight was obtained.

Calculations :

$$\text{mg total solids/L} = \frac{(A - B) \times 1000}{\text{Sample Volume, ml}}$$

where: A = weight of dried residue + dish, grams and B = weight of dried dish, grams

3.7.1.6 Total Suspended Solid

The Total suspended solid was determined using the procedure described by Csuros and Csuros (2002). A known volume of well-mixed sample was filtered through a pre-weighed 0.45µm filter membrane and the residual retained on the filter was dried to constant weigh at 105^oC. The increase in the weight of the filter represents the total suspended solids

Procedure

A vacuum pump was attached to Buckner flask, and about 2 litres of the water sample was filter to obtain a reasonable amount of suspended solid, the suctioning was continued until all traces of water was removed, the filter and the residue was then transferred to an aluminum weighing dish, it was dried in an oven at 105^0C for 1hour. The drying and weighing were repeated until a constant weight was obtained. It was stored in the desiccators until needed.

Calculation: mg total suspended solids/L = $= \frac{(A - B) \times 1000}{\text{Sample Volume, ml}}$

where: A = weight of filter + dried residue, grams and B = weight of filter, grams

3.7.1.7 Turbidity

A portable HACH 2100N turbidity meter was used for this measurement. The readings for water sample were taken.

3.7.1.8 Total Alkalinity

The process used was the volumetric determination of alkalinity. $100cm^3$ of the water was transferred into a 250ml conical flask. 3 drops of 1% phenolphthalein indicator were added. No colour was observed when titrated with an alkalimetric reagent therefore the phenolphthalein alkalinity was zero.

Also, the burette was filled to zero mark with the alkalimetric reagent. 100ml of the water was transferred into a 250ml conical flask. 3drops of methyl orange indicator was added. The solution was titrated with alkalimetric reagent till an orange colour was observed. The readings were recorded.

3.7.2 Determination of Sulphate (IITA, 1979)

2.14g of KH_2PO_4 was dissolved in 1 litre of distilled water (500mg/L phosphorus solution) given the extracting solution. 5g of air dried sample was weighed into a 250ml conical flask and 25ml of extracting solution added. It was shaken on mechanical shaker for 30minutes, centrifuged and supernatant decanted.

0.5434g of anhydrous K_2SO_4 was dissolved in 1 litre of distilled water in volumetric flask giving 100mg/L SO_4^{2-} stock solution. 250ml of the stock solution was diluted to 1 lire giving intermediate solution. This was used to prepare working standards of 5, 10, 15, 20 and 25mg/L). Absorbances were measured with Corning Colorimeter 253 and calibration curve of absorbance against concentration was plotted. 5g of sieved soil sample was weighted into Erlenmeyer flask 25ml distilled added. The mixture was shaken for 30minutes and filtered with Whatman no. 42 filter paper. 10ml of the filtered sample was pipette into a 25ml volumetric flask distilled water added to bring the volume to about 20ml. 1ml of gelatin $BaCl_2$ reagent was added and volume made up to 25ml with distilled water. The contents were mixed thoroughly and allowed to stand for 30 minutes. Absorbance of this solution was measured with the Corning Colorimeter 253 along with that of the blank solution.

3.7.3 Chloride

To 20ml of water sample was an added drop of potassium chromate while stirring and titrated under a bright light with the silver nitrate reagent to the first permanent reddish brown colour.

3.7.4 Sulphate

The column was filled with the water sample or saturation extract to be analyzed after placing a beaker of flask under it was allowed to drain (about 30 seconds) and the water that has passed through the column was discarded. This was repeated twice with smaller amounts of

water. This flushed the column but this time the filtrate was collected. 20ml of the filtrate was pipetted and 25ml of isopropyl alcohol added followed by two drops of sulfaver indicator. It was then titrated with standard barium solution, 0.005M barium chloride until the colour changed from yellow to pink or orange. The ion exchange column was rinsed frequently with 1:9 HCl

3.7.5 Nitrogen

The sample was filtered to obtain a clear sample. 10ml was diluted first and the filter paper washed three times with distilled water. 20ml of clear water sample was pipetted; 10ml. of a 1 to 2 soil-water extract was taken into a small porcelain evaporation dish then evaporated to dryness on a hot plate on moderate heat equivalent to a steam bath and removed as soon as dryness was achieved.

This was cooled and 2ml. of phenoldisuphonic acid added and dish rotated until the acid covered the entire evaporated residue. This was stirred and sample diluted to about 15ml. 50ml of the sample was transferred to a volumetric flask with three small rinses and was alkalized with 8ml concentrated NH_2OH in a fume hood; this was then diluted to the mark on the volumetric flask and mixed. The light transmission was measured at 410nm in a Corning Colorimeter 253. A standard curve was prepared by pipetting 1, 2, 5, and 10ml of the 0.01mol/dm^3. Readings were taken from the standard curve.

3.7.6 Biochemical Oxygen Demand

Samples were diluted prior to incubation, then were incubated for five days, the measurement of the loss oxygen from the beginning to the end of the test were taken. The BOD level were then determined by comparing the initial and the final DO level of the sample.

3.7.7 Instrumentation

A SHIMADZU AA 6800 Atomic Absorption Spectrophotometer was used in the analysis of the trace metal concentrations of the samples.

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1. Physicochemical Parameters for Water Samples

The physicochemical parameters of water from Zaria dam are presented in Table 4.1. The temperature range of the sample was from 20° - 31°C for water sample with the mean temperature of 25.4 ± 5.1°C. The temperature obtained in August was higher than those obtained in May and December. This could lead to increase in rate of chemical reaction and nature of biological activities in August, since temperature is one of the factors that govern the assimilation capacity of the aquatic system (EPA, 1976).

In all the water samples, the pH values ranged from 6.60 - 7.38, with the average value of 7.21 ± 0.34. Water acidity is known to influence the solubility, availability, and toxicity of metals in the aquatic ecosystem. This result is similar to the one obtained by Adefemi *et al.,* (2007) in water sample from Urege, Igbe, Ero, and Itapaji dams all in Ekiti State and also in water sample from Ilaogbolu area of Ondo State by the same author (Adefemi and Awokunmi, 2010). Asaolu *et al.,* (1997) also obtained similar result in water sample from Ondo State coastal water. Several studies have shown that availability of heavy metals is pH dependent (Iwegbue *et al.,* 2006; Fernandez *et al.,* 2008). The pH of the dam water fell within the WHO standards for pH in water intended for domestic uses (WHO, 1990). Electrical conductivity (EC) values ranged from 0.01 – 0.09 μscm^{-1} for the water samples. The range between the EC values obtained is 0.07 ± 0.01μscm^{-1}. Variation observed in electrical conductivity between months of sampling could be due to content of available soluble ions during month of sampling.

Table 4.1: Minimum, Maximum, Range Skewness, and Mean of Physical and Chemical Properties of Water Samples from Zaria Dam during the Research period (May, August and December 2010)

Parameters	May					August					December				
	min	Max	range	mean	skew-ness	min	Max	range	Mean	skew-ness	min	max	range	mean	skew-ness
Temperature	20.00	29.00	9.00	24.50 (4.50)	0.00	20.00	31.00	11.00	25.50 (5.50)	0.00	20.00	27.00	7.00	23.50 (3.50)	0.00
pH	7.38	7.40	0.02	7.39 (0.01)	0.00	6.60	7.30	0.70	6.95 (0.35)	0.00	6.60	7.38	0.78	6.99 (0.39)	0.00
Alkalinity (mg/L)	7.00	9.80	2.80	8.40 (1.40)	0.00	10.00	12.00	2.00	11.00 (1.00)	0.00	10.00	11.00	1.00	10.50 (0.50)	0.00
Hardness (mg/L)	50.50	61.00	10.50	55.75 (5.25)	0.00	17.70	65.00	47.30	41.35 (23.65)	0.00	65.00	90.90	25.90	77.95 (12.95)	0.00
DO(mg/L)	2.20	6.90	4.70	4.55 (2.35)	0.00	2.00	2.30	0.30	2.15 (0.15)	0.00	2.30	7.40	5.10	4.85	0.00
B.O.D (mg/L)	0.14	0.30	0.16	0.22 (0.08)	0.00	0.10	0.90	0.80	0.50 (0.40)	0.00	0.10	0.13	0.03	0.12 (0.02)	0.00
C.O.D (mg/L)	10.00	150.00	140.00	80.00 (70.0)	0.00	30.00	153.00	123.00	91.50 (61.5)	0.00	153.00	160.00	7.00	156.50 (3.50)	0.00
Chlorine(mg/L)	0.02	0.35	0.33	0.19 (0.17)	0.00	0.02	0.02	0.00	0.02 (0.00)	-	0.02	0.35	0.33	0.19 (0.17)	0.00
TS (mg/L)	2.37	2.44	0.07	2.40 (0.03)	0.00	2.00	2.62	0.62	2.31 (0.31)	0.00	2.00	2.91	0.91	2.45 (0.46)	0.00
TDS (mg/L)	1.97	2.15	0.18	2.06 (0.09)	0.00	1.72	2.15	0.43	1.94 (0.22)	0.00	1.72	2.32	0.60	2.02 (0.30)	0.00
TSS (mg/L)	0.29	0.40	0.11	0.34 (0.06)	0.00	0.28	0.47	0.19	0.37 (0.10)	0.00	0.28	0.59	0.31	0.43 (0.16)	0.00
Sulphate(mg/L)	0.85	3.26	2.41	2.06 (1.20)	0.00	0.73	1.93	1.21	1.33 (0.60)	0.00	0.73	2.14	1.42	1.43 (0.17)	0.00
Turbidity (NTU)	52.00	232.00	180.00	142.00 (90.0)	0.00	43.00	191.00	148.00	117.00 (74.0)	0.00	43.00	210.00	167.0	126.50 (83.5)	0.00
EC (μscm^{-1})	0.01	0.09	0.07	0.05 (0.04)	0.00	0.01	0.04	0.03	0.028 (0.02)	0.00	0.04	0.06	0.02	0.053 (0.01)	0.00
%Nitrogen	0.00	0.00	0.00	0.004 (0.00)	0.00	0.00	0.00	0.00	0.002 (0.00)	0.00	0.00	0.04	0.03	0.019 (0.02)	0.00

ND= Not detected, (xxx) =Standard deviation for triplicate sample

Dissolved oxygen content varies from 2.0 – 7.4mg/L with average value of 3.48 ± 2.62mg/L. DO plays a vital role in supporting the aquatic life and is susceptible to slight environmental changes. Oxygen depletion often results during time used as a parameter delineating water quality and to evaluate the degree of freshness of a river (Fakayode, 2005). It is also an important limnological parameter indicating level of water quality and organic pollution in the water body (Wetzel and Likens, 2006). The samples obtained in May and also in August were found to have DO values below the WHO limit. Seasonal variation in DO content is related to temperature and biological activities (Chapman and Kimstach, 1992).

The COD and BOD values ranged from 10.00 – 153.00mg/L and 0.02 – 0.10mg/L respectively. Turbidity values ranged from 43.00 – 232mg/L with higher turbidity values in May and August, which is expected due to the run-off entering the dam. Total dissolved solids and suspended solids have range values of 2.00 – 2.91mg/L, 1.72 – 2.32mg/L and 0.28 – 0.59mg/L respectively.

Sulphate content was in the range of 0.73 – 3.26mg/L, hardness ranged from 17.70 - 90.9mg/L, percentage nitrogen 0.002 – 0.004mg/L while EC and alkalinity were in the range of 0.01 – 0.85mg/L and 7.00 – 12.00 respectively. Water hardness values ranged from 17.70 – 90.9mg/L with the average ,value of 58.35 ± 26.5mg/L, this degree of hardness of the water was low and it might encourage the dissolution of heavy metals (Adeyeye and Ayejumo, 2002).

Residual chlorine was in the range of 0.02 – 0.35mg/L; the dam water samples were having low chlorine content. Chlorides are relatively harmless to organisms except when converted to

some forms which are known to be toxic. High chloride content imparts taste and could cause corrosion (WHO, 2009).

Table 4.2 showed the correlation between the physicochemical parameters of the water samples. Turbidity and sulphate show a positive correlation (r = +1.00) at 95% confidence level, a common factor will be responsible for the increase of both in the dam water. A significant negative correlation was found between the BOD and hardness of water (r = -1.00) at 95% confidence level. The increase of hardness will lead to lowering the BOD of the dam water, since hardness of water have a direct effect on the dissolution of substances (Adeyeye and Ayejumo, 2002).

Table 4.2: Correlation Matrix among Physicochemical Parameters in Water Samples from Zaria Dam

	pH	Alkalinity	Hardness	DO	BOD	COD	Residual Chlorine	TS	TDS	TSS	Sulphur	Turbidity	EC	Percentage nitrogen
pH	1.00													
Alkalinity	-0.72	1.00												
Hardness	-0.21	0.00	1.00											
DO	0.46	-0.30	0.70	1.00										
BOD	0.21	0.00	-1.00(**)	-0.70	1.00									
COD	-0.36	0.40	0.90(*)	0.60	-0.90(*)	1.00								
Residual Chlorine	0.74	-0.29	0.29	0.87	-0.29	0.29	1.00							
TS	-0.67	0.60	0.10	-0.50	-0.10	0.30	-0.57	1.00						
TDS	-0.53	0.46	0.21	-0.36	-0.21	0.36	-0.44	0.98(**)	1.00					
TSS	-0.82	0.50	0.00	-0.70	0.00	0.10	-0.87	0.90(*)	0.82	1.00				
Sulphate	-0.41	-0.20	-0.20	-0.70	0.20	-0.40	-0.87	0.40	0.36	0.70	1.00			
Turbidity	-0.41	-0.20	-0.20	-0.70	0.20	-0.40	-0.87	0.40	0.36	0.70	1.00(**)	1.00		
EC	-0.10	-0.60	0.40	0.10	-0.40	0.00	-0.29	-0.20	-0.15	0.10	0.60	0.60	1.00	
Percentage nitrogen	0.72	-0.60	0.40	0.90(*)	-0.40	0.20	0.87	-0.80	-0.67	-0.90(*)	-0.60	-0.60	0.20	1.00

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

Table 4.3: Minimum, Maximum, Range Skewness, and Mean of Physical and Chemical Properties of Side-sediment Samples from Zaria Dam during the Research period (May, August and December 2010)

	May					August					December				
Parameters	min	max	range	mean	skewness	min	max	range	mean	skewness	min	max	range	mean	skewness
Zn (mg/L)	0.06	0.32	0.26	0.19	0.00	0.02	0.29	0.27	0.16	0.00	0.02	0.18	0.16	0.10	0.00
Ni (mg/L)	ND	0.03	0.03	0.02	0.00	ND	0.03	0.03	0.02	0.00	ND	0.02	0.02	0.01	0.00
Cd (mg/L)	ND	ND	0.00	0.00		ND	0.01	0.01	0.01	0.00	ND	0.01	0.01	0.01	0.00
Pb (mg/L)	0.01	0.07	0.06	0.04	0.00	ND	0.07	0.07	0.04	0.00	ND	0.07	0.07	0.04	0.00
Cr (mg/L)	ND	0.03	0.03	0.02	0.00	ND	0.04	0.04	0.02	0.00	ND	0.04	0.04	0.02	0.00
pH	6.95	7.11	0.16	7.03	0.00	5.88	5.88	0.00	5.88		6.99	7.05	0.06	7.02	0.00
Residual Cl (mg/L)	-	-	0.00	-	-	0.00	0.08	0.08	0.04	0.00	0.07	0.08	0.01	0.08	0.00
Sulphate (mg/L)	13.89	18.11	4.22	16.00	0.00	0.00	18.10	18.10	9.05	0.00	1.81	10.87	9.06	6.34	0.00
EC	0.05	0.07	0.02	0.06	0.00	0.00	0.07	0.07	0.04	0.00	0.06	0.07	0.01	0.07	0.00
% Nitrogen	0.02	0.07	0.05	0.05	0.00	0.00	0.02	0.02	0.01	0.00	0.04	0.05	0.01	0.05	0.00

As can also be seen from the Table 4.2 at 95% significant (< 0.05) level, positive correlation were found between COD and hardness, percentage nitrogen and DO, TDS and TS for the water significant ($p < 0.05$) correlation were obtained between DO and residual chlorine, percentage nitrogen and TSS. Other physicochemical parameters did not show significant relationships. However, positive and negative correlation indicates influence of one parameter on the other.

4.1.2. Physicochemical Parameters for the Side-sediments

Table 4.3 showed the result of the physicochemical parameters of side-sediments within the vicinity of Zaria dam. The side-sediments' pH varied from 5.88-7.11 for the months of sampling which indicated moderately acidic to slightly alkaline conditions. Moderately acidic condition was observed in August (5.88) hence, this could imply high mobility of metals between the dam water and the side-sediments in the environment. This is consistent with the result by Becker *et al.,* (2001) and Onyari *et al.,(*2003) that sediments serves as a ready sink or reservoir of pollutant including trace metals where they concentrate according to the level of pollution. Table 4.4 shows a correlation between the physicochemical parameters, positive correlation was observed between residual chlorine and electrical conductivity at 95% confident level, chloride ions could be responsible for electrical conductivity of the sediment. A negative correlation was observed between EC and percentage nitrogen.

Table 4.4: Correlation Matrix among Physicochemical Parameters in Side-sediment Samples from Zaria Dam

	pH	resdual chlorine	sulphate	EC	percentage nitrogen
pH	1.00				
residual chlorine	-0.31	1.00			
sulphate	-0.41	0.64	1.00		
EC	-0.27	0.92(*)	0.34	1.00	
percentage nitrogen	0.43	-0.86	-0.51	-0.92(*)	1.00

* Correlation is significant at the 0.05 level (2-tailed).

4.2 Trace Metals

The results of concentration of trace metals in the suspended solids, side-sediments and the filtrate were shown in Tables 4.5, 4.6 and 4.7 respectively. The means concentration of trace elements in the filtrate, suspended solids and side-sediments are shown in Figure 4.1. The chart gives some indications of average values over the stretch of the dam surveyed, rather than for each sample.

The concentrations of nickel, zinc, lead, cadmium and cadmium were generally high in the filtrate, than both the suspended solids and side-sediments, whereas chromium and zinc concentrations were found to be higher in the side-sediments compared with their concentration in the suspended solids but Pb was generally found to be high in the suspended solid. The concentration of metals: zinc, nickel, cadmium, lead and chromium in side-sediments and suspended solids, lead and cadmium in the filtrate shows higher values in August (rainy season), this could be attributed to the domestic and industrial waste introduced into the dam by the floods in the rainy season. Poikane *et al.,* (2005) had analyzed the fate of trace metals in suspended particulate matter and suspended sediments of Dangara River and the Gulf of Riga and reported that the fluvial particulate matter and particulate Al, Fe, Cr and Ni were brought into the golf during spring flood.

Also the result of investigation by Gaur *et al.,* (2005) showed high concentration of all the metals in both water and sediment in raining season and this was attributed to run-off from open contaminated sites, agricultural fields and industries. This suggests the influence of season on the fate of trace metals in water bodies. The works of Gaur *et al., (*2005) supports the assertion that the impact of domestic and industrial wastes contribute to high concentration of metals in water and sediments in rainy season due to run-off.

Table 4.5: Concentration (mg/kg) of Trace Metals in Suspended Solids from Zaria Dam

	May					August					December				
metals	min	max	range	Mean	skewness	min	max	range	mean	Skewness	min	max	range	mean	skewness
Zn	0.15	0.32	0.17	0.21 (0.09)	0.84	0.18	0.30	0.12	0.23 (0.06)	1.26	0.02	0.06	0.04	0.03 (0.02)	0.94
Ni	0.02	0.03	0.01	0.02 (0.01)	0.94	0.02	0.03	0.01	0.03 (0.00)	-0.94	ND	ND	ND	ND	-
Cd	ND	ND	-	ND	0.00	ND	ND	-	ND	0.00	ND	ND	-	ND	-
Pb	0.02	0.04	0.02	0.03 (0.01)	0.00	0.07	0.07	0.00	0.07 (0.00)	-	ND	0.01	0.01	ND	0.94
Cr	ND	ND	ND	ND	-	0.03	0.05	0.02	0.04 (0.01)	ND	ND	ND	ND	ND	-

ND= Not detected, (xxx) =Standard deviation for triplicate sample

Table 4.6: Concentration (mg/kg) of Trace Metals in Side-sediment Samples from Zaria Dam

	May					August					December				
metals	min	max	range	Mean	skewness	min	max	range	mean	skewness	min	max	range	mean	skewness
Zn	0.10	0.14	0.04	0.12 (0.02)	-1.06	0.16	0.25	0.09	0.21 (0.05)	-0.27	0.04	0.07	0.03	0.05 (0.02)	0.33
Ni	0.02	0.02	0.00	0.02 (0.00)	-	0.02	0.03	0.01	0.02 (0.00)	0.94	0.00	0.10	0.10	0.00 (0.00)	0.94
Cd	ND	ND	-	-	-	ND	ND	-	-	-	ND	ND	-	-	-
Pb	0.03	0.05	0.02	0.04 (0.01)	0.00	0.03	0.05	0.02	0.04 (0.01)	0.94	0.10	0.02	-0.08	0.07 (0.02)	-0.94
Cr	0.00	0.02	0.02	0.01 (0.01)	-1.41	ND	ND	-	-	-	0.02	0.04	0.02	0.03 (0.01)	0.00

ND = Not detected, (xxx) = Standard deviation for triplicate sample

Table 4.7: Concentration (mg/L) of Trace Metals in Filtrate from Zaria Dam

	May					August					December				
parameters	min	max	range	mean	skewness	min	max	range	mean	skewness	min	max	range	mean	Skewness
Zn (mg/L)	0.18	0.48	0.30	0.38 (0.15)	-0.94	0.41	0.76	0.35	0.56 (0.18)	0.37	0.62	0.80	0.18	0.69 (0.09)	0.54
Ni (mg/L)	0.06	0.09	0.03	0.07 (0.02)	0.33	0.06	0.09	0.03	0.07 (0.02)	0.33	0.04	0.07	0.03	0.06 (0.02)	-0.33
Cd (mg/L)	0.01	0.02	0.01	0.01 (0.01)	0.94	0.01	0.02	0.01	0.01 (0.01)	0.94	0.01	0.02	0.01	0.01 (0.01)	0.94
Pb (mg/L)	0.06	0.12	0.06	0.10 (0.03)	-0.94	0.12	0.15	0.03	0.14 (0.02)	-0.94	0.10	0.15	0.05	0.12 (0.03)	0.20
Cr (mg/L)	ND	0.05	0.05	0.02 (0.03)	0.94	0.00	0.10	0.10	0.04 (0.05)	0.40	ND	0.03	0.03	0.01 (0.02)	0.94

ND= Not detected, (xxx) =Standard deviation for triplicate sample

4.3.1 Concentration of Trace Metals in Suspended Solids

The results in Table 4.5 shows the concentration of trace metals in suspended solid, the concentration of Zn, Cd, Ni, Cr and Pb range between 0.15-0.32, ND - 0.01, ND - 0.03, ND - 0.05 and ND - 0.07 respectively. Lead concentrations were found to be high in the suspended materials. This shows that suspended materials could be good indicators for lead pollution, suggesting the dominant role played in the transport of lead in the reservoir by the suspended materials. The knowledge of the origin and transport of the suspended solid is found to be essential for an interpretation of seasonal variation in the trace metal contents (Wufem *et. al.,* 2007). The suspended materials can act as scavengers for the trace metals in the water and may be introduced into the nature bodies of water by nature forces such as weathering, hydrothermal activities, and biosynthesis or human activities through sewage discharge, dredging and agriculture excavation (Allen, 1973; Aston, and Thornton, 1973; 1977). With treatment of the dam water, some of the trace metals in the water sample can easily be removed by removing the suspended particles in the water. The mean concentrations of trace metals in suspended solids are shown in Figs. 4.2 and 4.3.

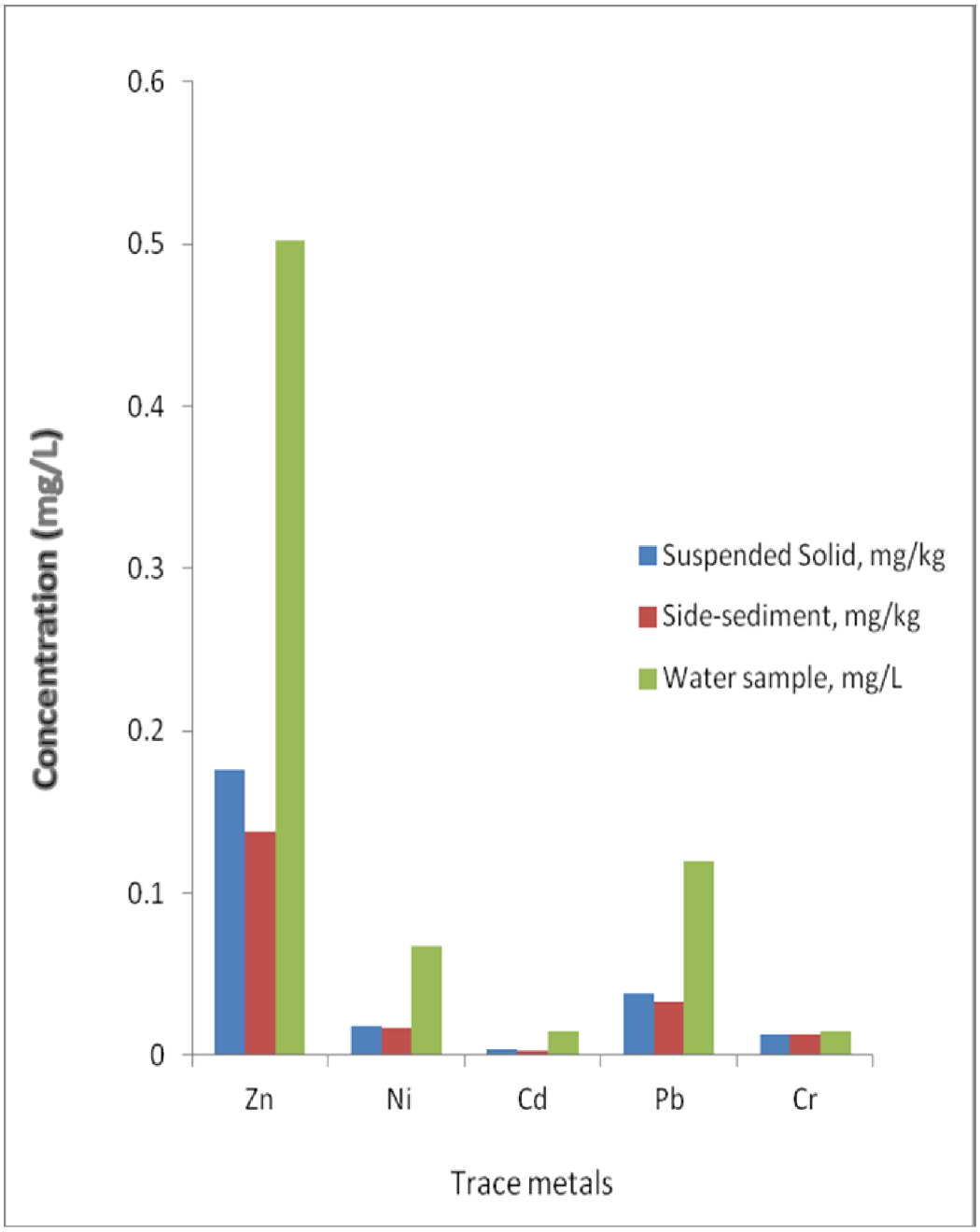


Fig. 4.1: Trace Metals in Filtrate, Suspended Solids and Side-sediments

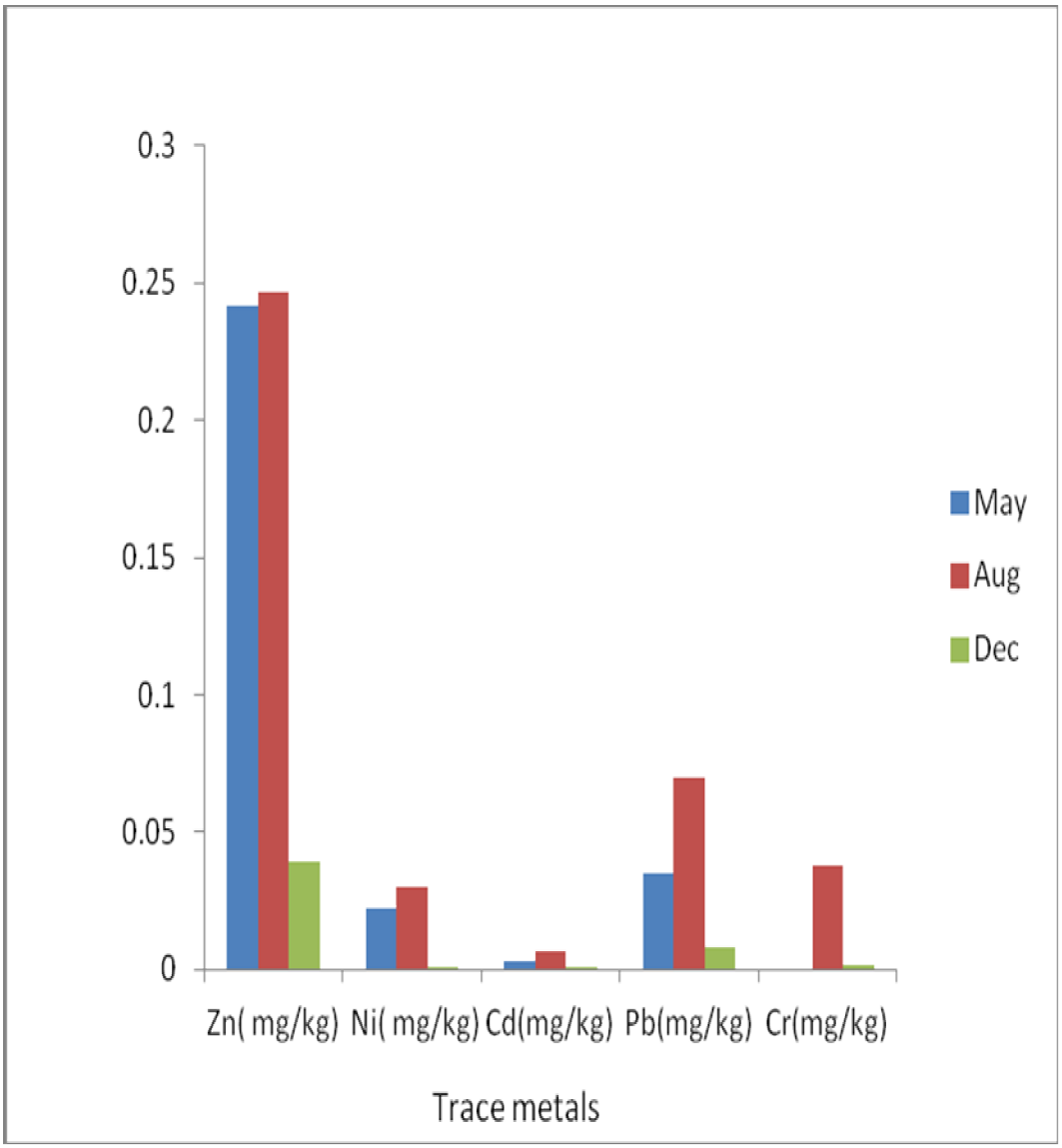


Fig. 4.2 Trace Metals Concentrations in the Suspended Solids for each Month of Sampling

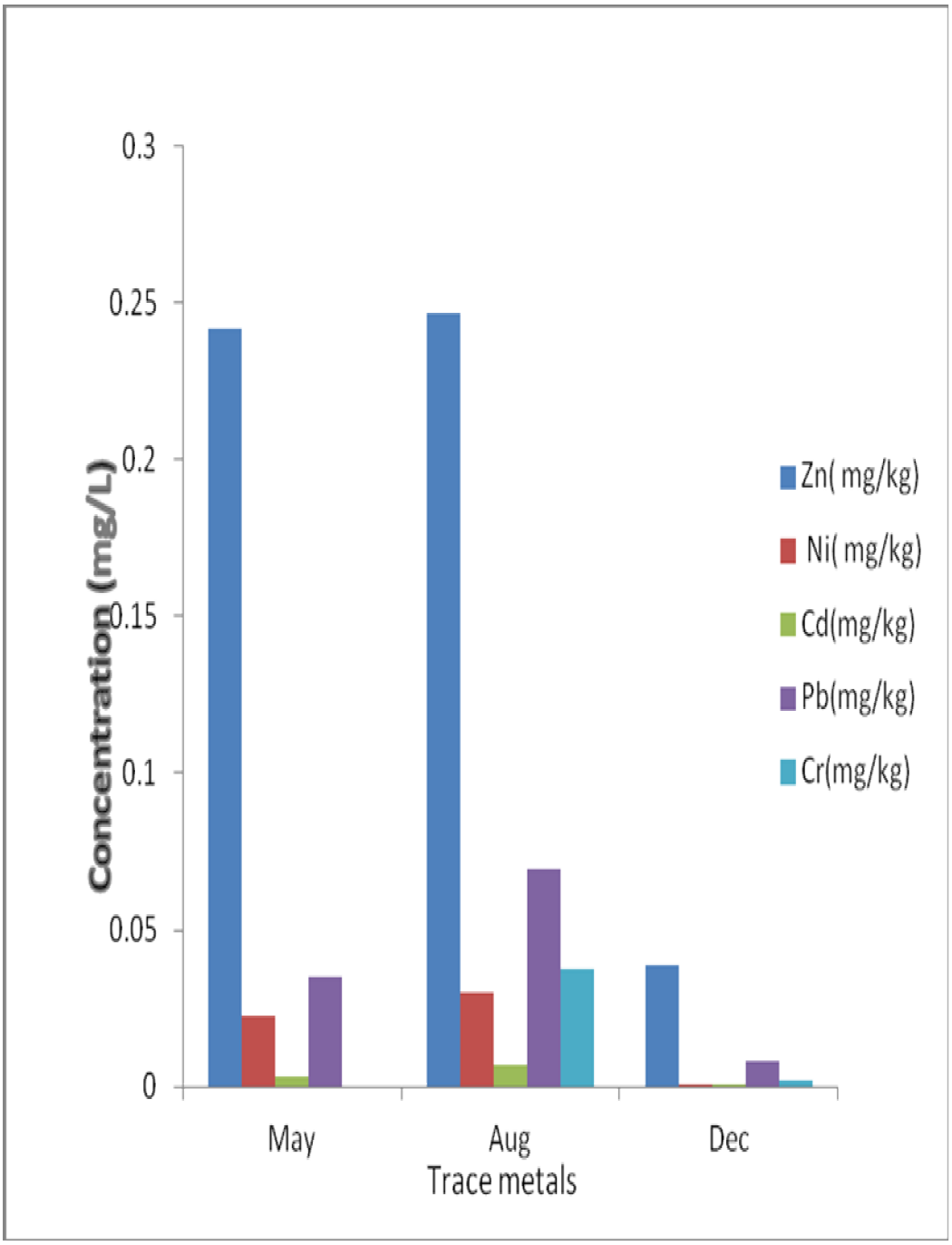


Fig. 4.3: Mean Total Concentration of the Trace Metals in Suspended Solids for the Months of sampling

In Fig.4.2, higher concentrations were indicated in August compared to the ones in May and December; the run-off during rainy season could be said to have contributed to the increase. Zinc showed the highest concentration throughout the sampling period and chromium was not detected in December.

From Table 4.8, the suspended solids show a significant positive correlation for Ni, Zn, Cd and Pb (r =1.00) at 95% degree of confidence. These trace metals in the dam could probably have been introduced into the water body through the same or similar sources. No significant relationship between Cr and all other trace metals determined.

Table 4.8: Correlation Matrix among Trace Metals in the Suspended Solids from Zaria Dam

	Zn	Ni	Cd	Pd	Cr
Zn	1.000				
Ni	1.000(**)	1.000			
Cd	1.000(**)	1.000(**)	1.000		
Pd	1.000(**)	1.000(**)	1.000(**)	1.000	
Cr	0.500	0.500	0.500	0.500	1.000

** Correlation is significant at the 0.05 level (2-tailed).

4.3.2 Concentration of Trace Metals in Side-sediments

The results in Table 4.6, shows the concentration of trace metals in side-sediments, the concentration of Zn in the side-sediments were found to range between 0.04 -0.25mg/g with highest concentration value recorded in August, during rainy season. This could be associated with human activities such as the use of chemicals and zinc-based fertilizers by farmers which are being carried down to the dam by the run-off. (Egila and Nimyel, 2002). Generally, for all trace metals, higher concentrations were recorded in August during rainy season which could be attributed to run-off from farm, domestic and industrial wastes. The levels of Cd obtained in sediment samples were within the recommended values and also similar to the value reported in the Tyume River in South African.

The mean concentrations of trace elements in the side-sediments are shown in Fig. 4.4 and Fig. 4.5. Similar trends were also recorded in side-sediments as in the suspended solids. In Table 4.9, Correlation for the concentration values obtained for the side-sediments showed significant negative correlation between Ni and Cr (r = -1.00) at 95% level of confidence. The increase of these metals in the sediments will lead to a decrease of the other. Ni and Zn show a positive correlation of (r = 1.00) at 95% level of confidence but a negative correlation was indicated between Ni, Cr and Zn. The increase of Cr in the side-sediments will lead to decrease of Zn and Ni.

Table 4.9: Correlation Matrix among Trace Metals in the Side-sediments from Zaria Dam

	Zn	Ni	Cd	Pd	Cr
Zn	1.000				
Ni	1.000(**)	1.000			
Cd	0.500	0.500	1.000		
Pd	0.866	0.866	0.866	1.000	
Cr	-1.000(**)	-1.000(**)	-0.500	-0.866	1.000

** Correlation is significant at the 0.01 level (2-tailed).

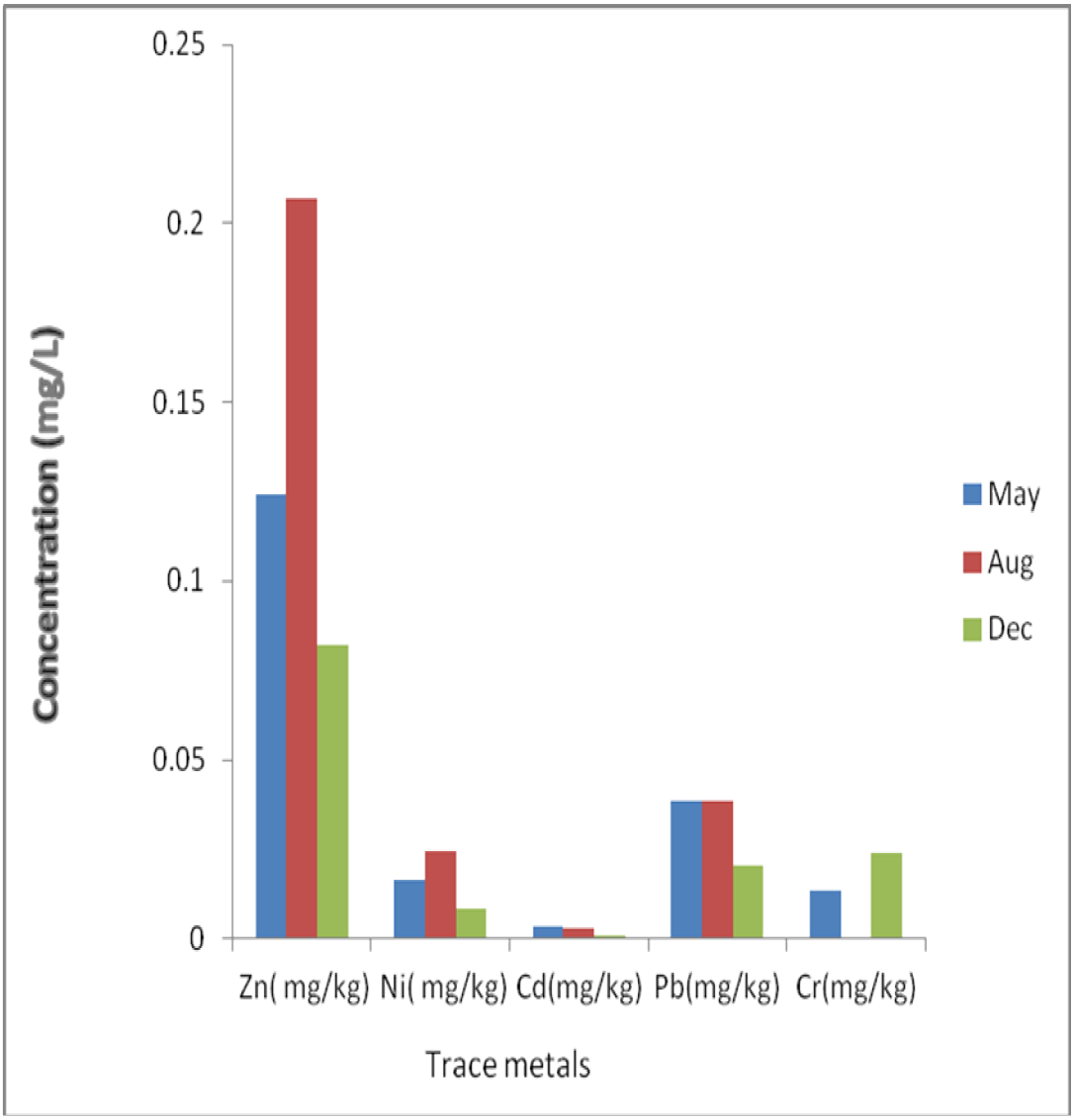


Fig. 4.4: Trace Metals Concentrations in the Side-sediments for each Month of Sampling

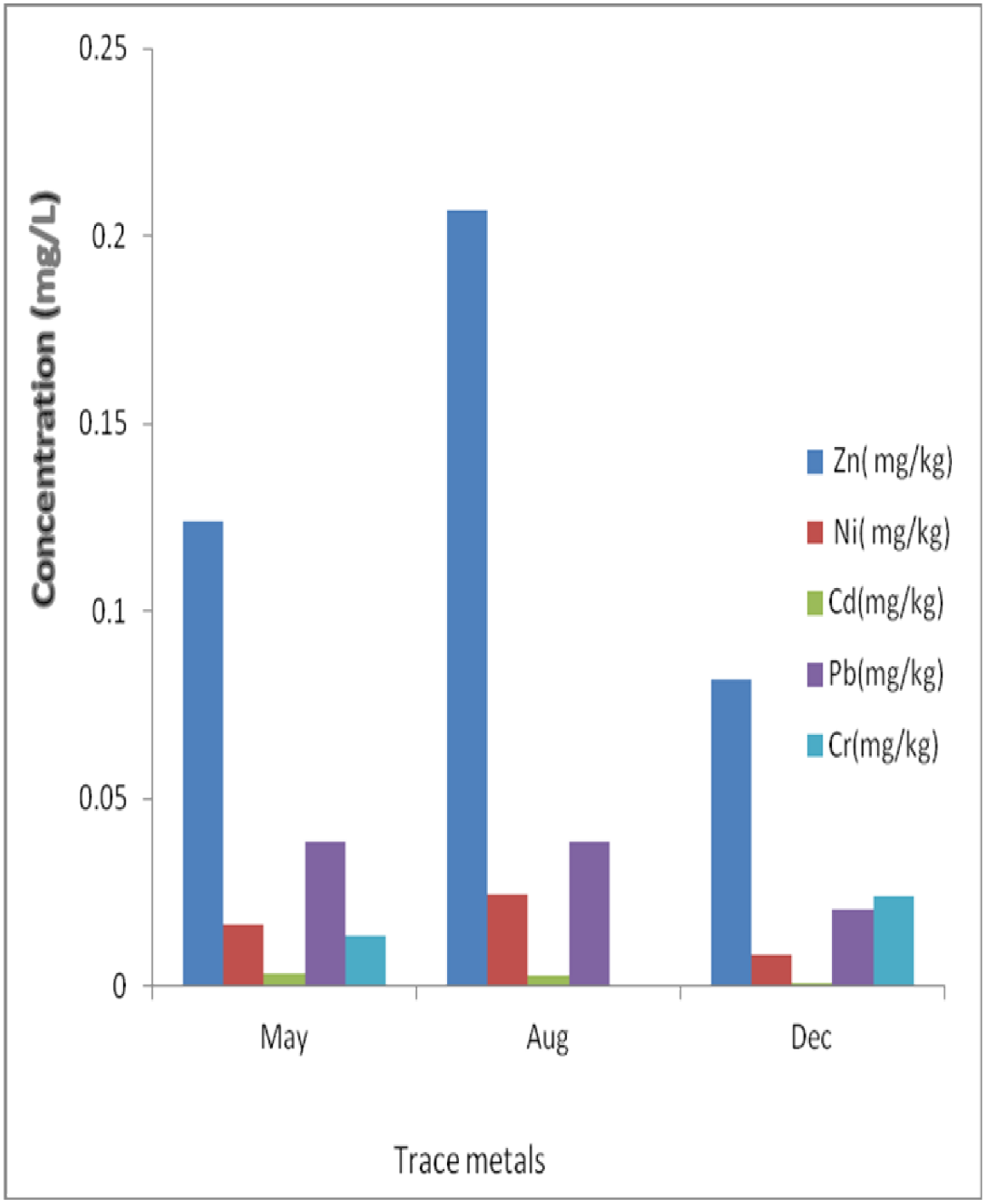


Fig 4.5: Mean Total Concentration of the Trace Metals in Side-sediments for the Months of sampling

4.3.3 Concentration of Trace Metals in Water Samples

The concentrations of the trace metals in the filtrate were recorded in Table 4.7. The concentration of Pb was found to be between 0.05 - 0.15mg/L with the average value of 0.10± 0.03mg/L. The lead content may be due to run-off of waste water containing tyres, batteries, garbage containing lead and soldered tins and fittings. The result obtained in this work was higher than the maximum allowable limit for Pb in drinking water (0.01mg/L) (WHO, 1984)

The concentration for Cd ranged from 0.01 - 0.02mg/L with the average value of 0.01 mg/L in the water samples. The range obtained for water was higher than the WHO guideline of 0 to 0.03 mg/L in river for domestic use (WHO, 1993) and higher than the 0.005mg/L as the maximum contaminant level (USEPA, 1986) and also higher than the maximum concentration for irrigation and livestock watering (DWAF, 1996). The construction works going on at the dam, which involved the use of metal pipes could also have contributed to the Cd concentration since cadmium is mainly used as an anticorrosion coating in electroplating, as an alloying metal in soldering, as a stabilizer in plastics (organic cadmium), as a compound of nickel-cadmium batteries (PPA Handbook, 1998)

The concentration for the Cr and Ni in the water samples ranged from 0.00 - 0.05mg/L and 0.04 - 0.09 mg/L respectively. These values were below the WHO limit for drinking water and also below the EPA standard for irrigation water.

The average concentration of trace metals in the filtrate samples were shown in Fig.4.6 and Fig. 4.7. August shows a higher concentration for most of the metals except Zn and Cr which were found in samples obtained in December. The partitioning of metals between particles and water is influenced by the residence time, hence the residual concentration of these elements in the water.

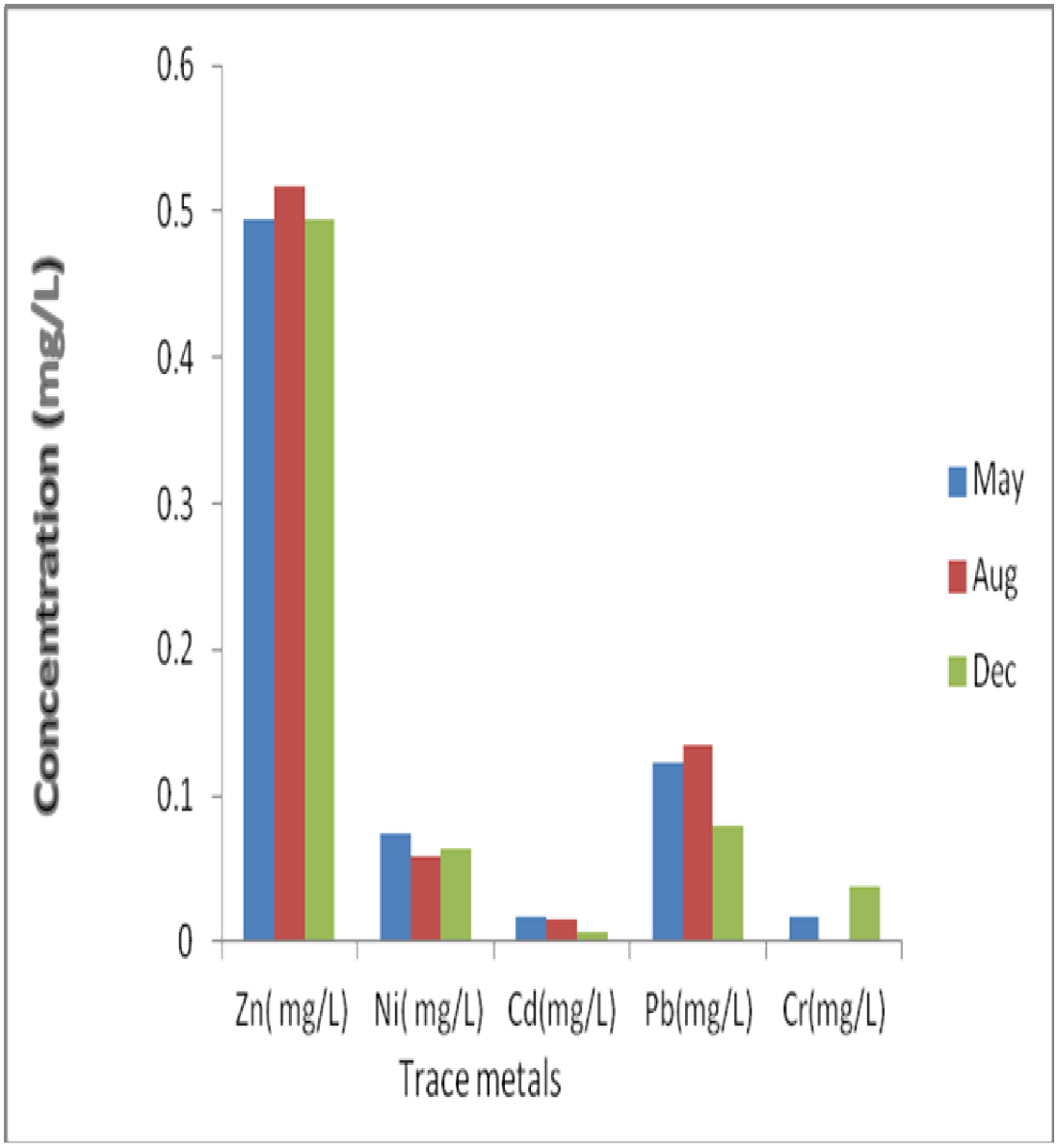


Fig. 4.6: Trace Metals Concentrations in the Water Samples for each Month of Sampling

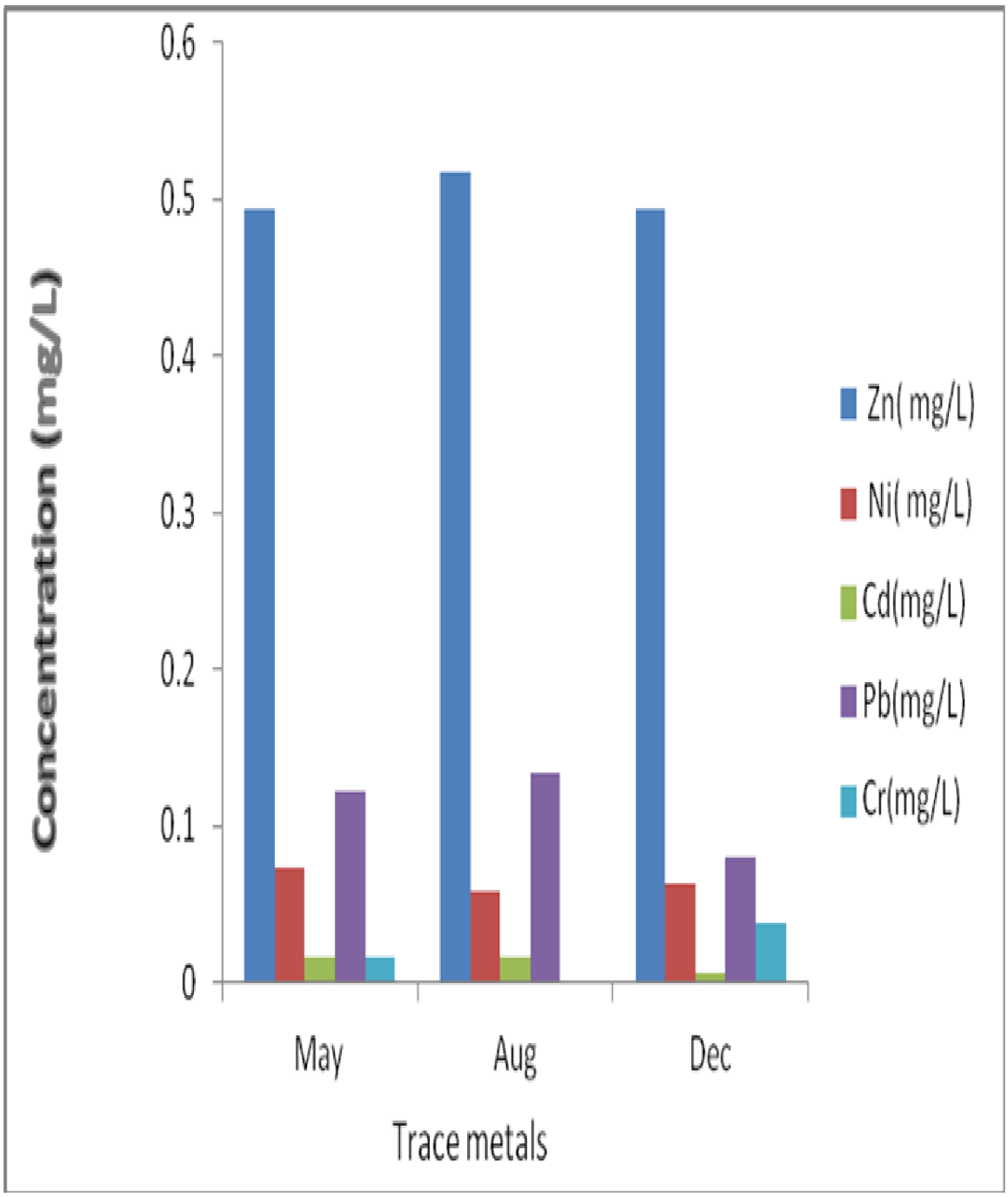


Fig. 4.7: Mean Total Concentration of the Trace Metals in Water Samples for the Months of sampling

In Table 4.10, the filtrate shows a significant negative correlation between Zn and Cd ($r = -1$) at 95% level of confidence. A decrease in one of the metals will mean an increase in the other and there was a significant correlation between Cr and Pb ($r = -1$) at 95% level of confidence.

Table 4.10: Correlation Matrix among Trace Metals in the Water Samples from Zaria Dam

	Zn	Ni	Cd	Pd	Cr
Zn	1.000				
Ni	-0.500	1.000			
Cd	-1.000(**)	0.500	1.000		
Pd	-0.500	-0.500	0.500	1.000	
Cr	0.500	0.500	-0.500	-1.000(**)	1.000

** Correlation is significant at the 0.01 level (2-tailed).

4.4.1 Interpretation of Water Quality Data by Multivariate Analysis

Multivariate analysis techniques are very useful in the analysis of data corresponding to a large number of variables. A wide variety of multivariate analysis techniques is available. The choice of the most appropriate technique depends on the nature of the data, problem, and objectives. The underlying theme of many multivariate analysis techniques is simplification. In other words, it is desired to summarize a large body of data by means of relatively few parameters. One fundamental distinction between the techniques is that some analyses are primarily concerned with relationships between variables, while others are primarily concerned with relationships between samples. Techniques of the former type are called variable-directed, while the latter are called individual-directed (sample-directed) multivariate analysis. In the analysis of dependence between variables, if the variables do not arise on an equal footing, multivariate regression analysis is recommended.

When there are only two variables, correlation analysis provides the desired information to some extent. With more than two variables, principal components analysis may be appropriate. This technique aims to transform the observed variables to a new set of variables which are uncorrelated and arranged in decreasing order of importance. The principal aim is to simplify the problem and to find new variables (principal components) which make the data easier to understand.

In this multivariate analysis study, principal component analysis was employed to investigate the factors which caused variations in the observed quality data at the Zaria dam. This study also demonstrates the usefulness of the technique in the analysis of water quality data. A literature review on principal components analysis, a technique that was formerly used in the field of hydrology, has shown its appropriateness for water quality data, as confirmed by some

recent case studies in the literature (Mahloch, 1974; Schetagne, 1985; Karpuzcu and Senes, 1987). For this multivariate analysis, the mean values of the monthly data obtained were used, as seen in Tables 14.11 and 14.12 for both analyses for water samples and side-sediments.

Table 4.11: Monthly Mean Concentration of Physical and Chemical Properties for Dam Water Samples

Sampling Month	Zn	Ni	Cd	Pb	Cr	Temperature	pH	Alkalinity	Hardness	DO	BOD	COD	Residual Chlorine	TS	TDS	TSS	Sulphate	Turbidity	EC	% Nitrogen
May	0.51	0.07	0.02	0.12	0.02	28.00	6.99	9.00	70.70	2.25	0.20	85.00	0.02	2.64	2.15	0.50	2.70	221.00	0.08	0.00
August	0.52	0.06	0.01	0.14	0.00	31.00	7.38	12.00	17.70	2.00	0.90	30.00	0.02	2.62	2.15	0.47	1.93	191.00	0.01	0.00
December	0.54	0.08	0.01	0.09	0.03	20.00	7.39	9.90	63.00	7.15	0.14	151.50	0.35	2.22	1.94	0.29	0.79	47.50	0.03	0.03

Table 4.12: Monthly Mean Concentration of Physical and Chemical Properties for Side-sediment Samples

	Zn	Ni	Cd	Pb	Cr	Residual Chlorine	Sulphate	EC	% Nitrogen
May	0.12	0.02	0.00	0.04	0.01	-	16	0.06	0.05
Aug	0.21	0.02	0.00	0.03	0.00	0.80	18.11	0.07	0.02
Dec	0.05	0.00	0.00	0.01	0.03	0.75	6.34	0.07	0.05

4.4.2. Principal Components Analysis

4.4.2.1. Principal Components from Correlation or Covariance Matrix

Correlation or covariance matrices may be used in principal component analysis; the mathematical derivation is the same in the choice of any of these matrices. If the correlation matrix is used, the components turn out to be eigenvectors of R. However, it is important to note that the eigenvalues and the eigenvectors of R will generally not be the same as those of S (covariance matrix). The use of the R matrix for analyzing involves a decision that variables have been considered equally important (Chatfield and Collins, 1980).

Principal components are generally changed by scaling. In other words, principal components depend upon the scales used to measure the variables. If, for example, one variable has a greater variance than all the others, then this variable will dominate the first principal component of the covariance matrix whatever the correlation structure, whereas if the variables are all scaled to have unit variance, then the first principal component will be quite different in kind (Chatfield and Collins, 1980).

After computing the variances (eigenvalues, or latent roots) and principal components (eigenvectors) of a correlation (or covariance) matrix, the usual procedure is to look at the first few components which, hopefully, account for a large proportion of the total variance. Chatfield and Collins (1980) stated that when analyzing a correlation matrix where the sum of the eigenvalues is equal to the number of variables, many social scientists use the rule that eigenvalues less than 1 may be disregarded. This arbitrary policy is a useful rule of thumb but has no theoretical justification.

In principal components analysis, the variables are rotated to obtain new variables (principal components or principal axes) and later the numbers of principal components are reduced by eliminating some relatively unimportant components. Sometimes the first few principal components selected are rotated to achieve a new set of components which can be more easily interpreted. A variety of rotation techniques (varimax, equamax, quartimax) may be used for this purpose. Varimax rotation is used in this work because it is the most widely used rotation in principal component analysis.

4.4.3 Scree Plot

The scree plot indicates point of inflection after the third factor, and then a stable line is formed. The first-two factors, with the eigenvalues of about 13.8 and 6.2 respectively, will be suitable to describe all the other components.

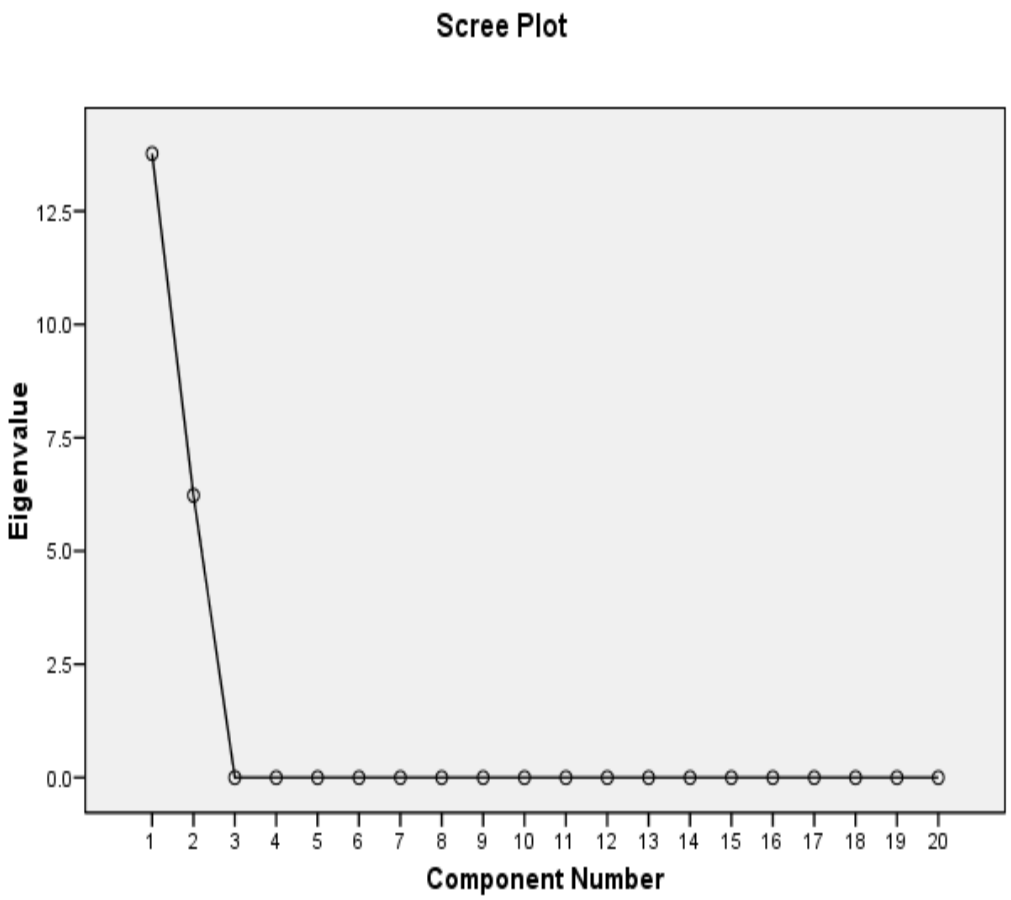


Fig. 4.8: Scree Plot

Table 4.13: Component Matrix for Water Samples

	Component	
	1	2
Dissolved oxygen	-1.00	-0.08
Total Nitrogen	-0.99	-0.12
Residual chlorine	-0.99	-0.12
TDS	0.99	0.12
Temperature	0.99	-0.15
TS	0.99	0.16
TSS	0.97	0.25
Turbidity	0.96	0.28
Pb	0.96	-0.28
COD	-0.94	0.34
Ni	-0.92	0.39
Zn	-0.90	-0.44
Sulphate	0.86	0.51
Cr	-0.83	0.56
EC	0.12	0.99
Alkalinity	0.34	-0.94
Cd	0.39	0.92
pH	-0.41	-0.91
Hardness	-0.49	0.87
BOD	0.66	-0.75
% Variance Extracted	68.85	31.15
Cumulative %	68.85	100.00

Extraction Method: Principal Component Analysis. a 2 components extracted.

The proportion of the total variables explained by each principal component is additive, with each new component contributing less than the proceeding one to the explained variance. In other words, the components are derived in decreasing order of importance in Table: 4.14. Twenty linear components (factors) were identified within the data set. Only two factors with eigenvalues greater than 1 were extracted and rotated. The eigenvalues of the first factor explained 68.85% of the total variance while the second factors explained only small amount of variance.

Subsequently, these components were rotated to eliminate medium-range loading (correlation) to make the interpretation of the component easier. Before rotation factor 1 account for considerable more variance than the others (68.85% compare to 31.15%) but after extraction if accounted for 67.85% while factor 2 account for 32.15%.

Since all the communality are larger than 0.7 in the final case, it may be assumed that all variables were describe to an acceptable level. In general, component loading (Correlation coefficient) larger than 0.6 may be taken into consideration in the interpretation (Mahloch, 1974)

Table 4.14: Rotated Component Matrix for Water Samples

	Rotated Component		Communalities	
	1	2	Initial	Initial
TS	1.00	0.00	1.00	1.00
Total Nitrogen	-1.00	0.04	1.00	1.00
TDS	1.00	-0.04	1.00	1.00
Residual chlorine	-1.00	0.04	1.00	1.00
Dissolved oxygen	-1.00	0.09	1.00	1.00
TSS	1.00	0.09	1.00	1.00
Turbidity	0.99	0.12	1.00	1.00
Zn	-0.96	-0.29	1.00	1.00
Temperature	0.95	-0.30	1.00	1.00
Sulphate	0.93	0.36	1.00	1.00
Pb	0.90	-0.44	1.00	1.00
COD	-0.87	0.49	1.00	1.00
Ni	-0.84	0.54	1.00	1.00
Cr	-0.73	0.69	1.00	1.00
Alkalinity	0.18	-0.98	1.00	1.00
EC	0.28	0.96	1.00	1.00
Hardness	-0.34	0.94	1.00	1.00
BOD	0.53	-0.85	1.00	1.00
Cd	0.54	0.84	1.00	1.00
pH	-0.56	-0.83	1.00	1.00
% Variance Rotated	67.85	32.15		
Cumulative %	67.85	100.00		

Extraction Method: Principal Component Analysis. 2. Rotation Method: Varimax with Kaiser Normalization. 3. a Rotation converged in 3 iterations.

4.4.4. Component Matrix

Principal component analysis shows the relationship between variable (variable-directed), while others are primarily concerned with the relationship between samples (individual-directed or sample-directed) and component arranged in the order of importance.

From Table 4.14, the first components are more desirable since they are with larger variances and so they give more information about the data. All factors showed significant at first rotated component except alkalinity (0.18), EC (0.28), Cd (0.54), pH (-0.56) and Hardness (-0.34), which showed significant at second rotated component with values for alkalinity (-0.98), EC (0.96), Cd (0.84), pH (-0.83) and hardness (0.94). In the first rotated component, the variables TDS, TS, TSS, turbidity, sulphate, temperature, BOD and Pb show a significant relationship. Positive relationship among these components show that the lead pollution and sulphate can be attributed to the particles, while the negative relationship between DO and BOD, TS, TSS and TDS, implies that the introduction of these particulate matters have been from a domestic discharge. TDS, temperature, TSS, TS are important factors that affect the level of DO, percentage nitrogen and Cl in the water samples.

COD, Ni, Zn, Cr, and Cl, have negative relationships, it implies that chemical sources rather than domestic sources, have been responsible for the level of Zn, Ni, Cr, and Cl, in the samples. This could be chemical substance uses for agricultural purposes in the environment. From the second rotated component, it can be deduced that Cd, Hardness, Cr, EC have significant positive relationship. The low EC in the original data obtained could have been dictated by the low level of Cd and hardness measured in the samples.

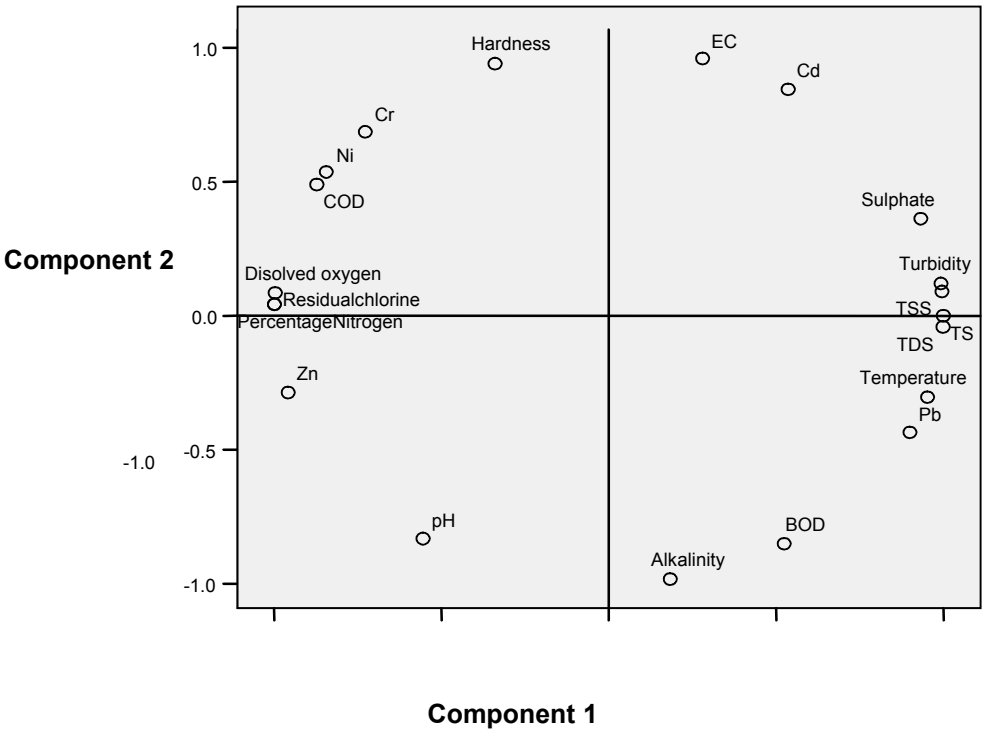


Fig. 4.9: Component Plot in Rotated Space

4.4.5. Hierarchical Cluster Analysis for Water Samples

4.4.5.1 Dendrogram

The dendrogram confirms what was inferred from the component matrix, two clusters were formed at a rescaling distance of about 20 with great relationship between the variables at short rescale distance. Residual chloride, percentage nitrogen, DO, Zn, Ni, COD, Cr and hardness form cluster 1 at a rescaled distance of 6, while alkalinity, BOD, pH, Cd, EC, Pb, temperature, TSS, TS, TDS, sulphate, turbidity, all form cluster 2. Hardness and pH are singletons which belong to cluster 1 and cluster 2 respectively.

The same or similar sources could be responsible for the level of Cl and Zn in the sample. The COD, Ni, Cr form a cluster at a close distance and they all form cluster with hardness at a close distance. A chemical source or agricultural run-off, from zinc-based fertilizers, could be the source of Cl and Zn to the dam.

Alkalinity, BOD, pH, Cd, EC, Pb, temperature, TSS, TS, TDS, sulphate, turbidity, all formed cluster with temperature and Pb also at a close distance. The correlation between TDS and EC shows that there are no significant relationship, it could be inferred that the particles may be colloidal of organic origin that do not conduct electricity.

BOD and alkalinity show a very high correlation and are related at a very short distance. It could be deduced that the high alkalinity could have resulted from domestic waste discharge into the dam. The pH is a singleton that is related to both BOD and alkalinity at about 8 rescaled value distance. These three components show high value in August during raining season, when there are more run-offs with domestic waste into the dam.

Dendrogram using Average Linkage (Between Groups)

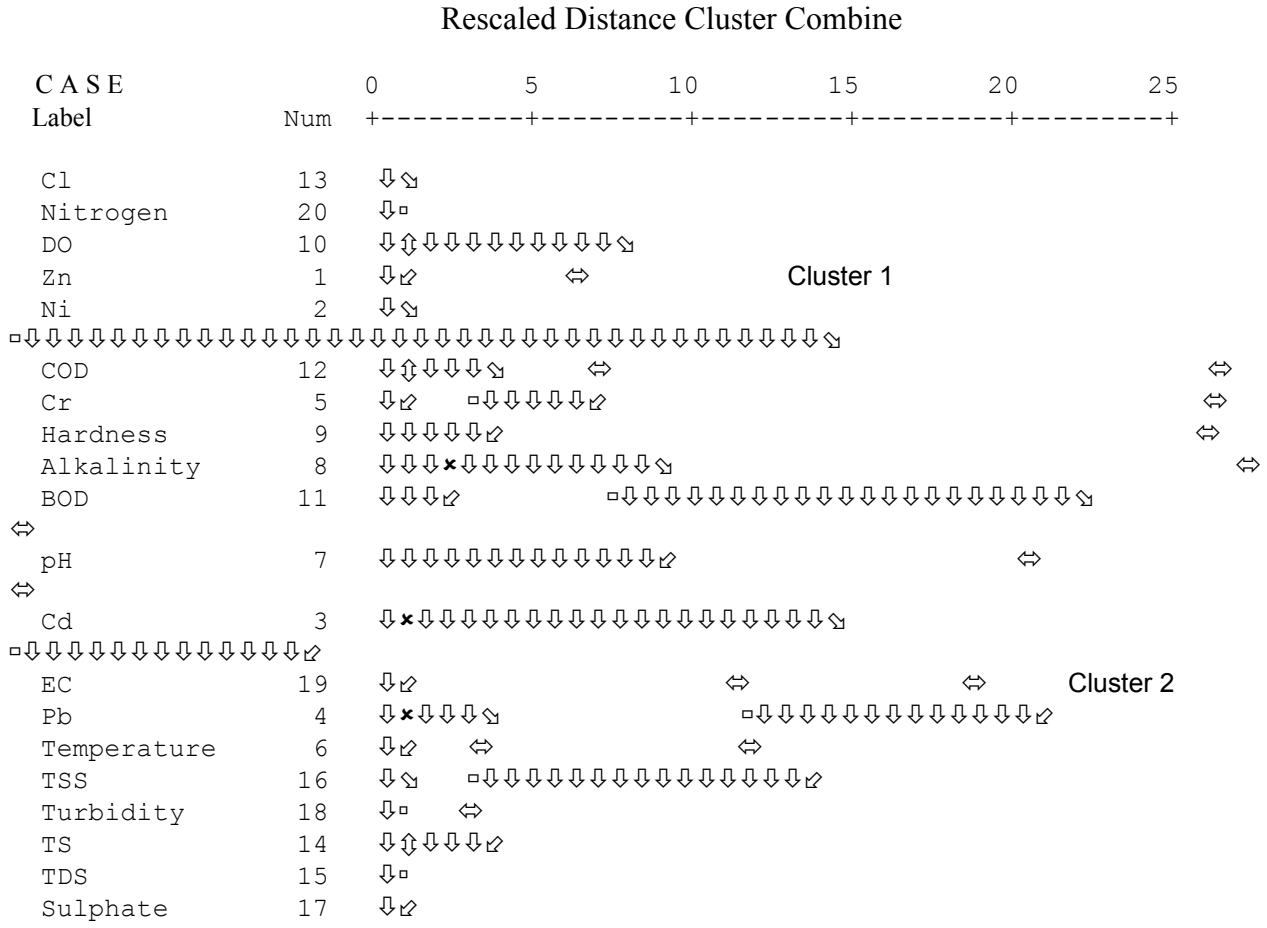


Fig. 4.10: Hierarchical Cluster Analysis for Water Samples

4.4.6. Hierarchical Cluster Analysis for Side-sediments Samples

Two Clusters were formed; the pH, percentage nitrogen, Cr, formed the cluster 1, while Zn, Cl, Ni, Pb, form the cluster 2 with Cd and EC as singleton members of the cluster. The pH and percentage nitrogen are related at a very close distance, and both are related to Cr.

Zn and residual chlorine are both related at close distance, probably zinc-based fertilizer from agricultural, deposited by water sides as the water level reduced or the construction activities at the dam which involve the use of Zn and cadmium galvanized iron, would like wise contribute the zinc and cadmium pollution level in the side-sediments.

Dendrogram using Average Linkage (Between Groups)

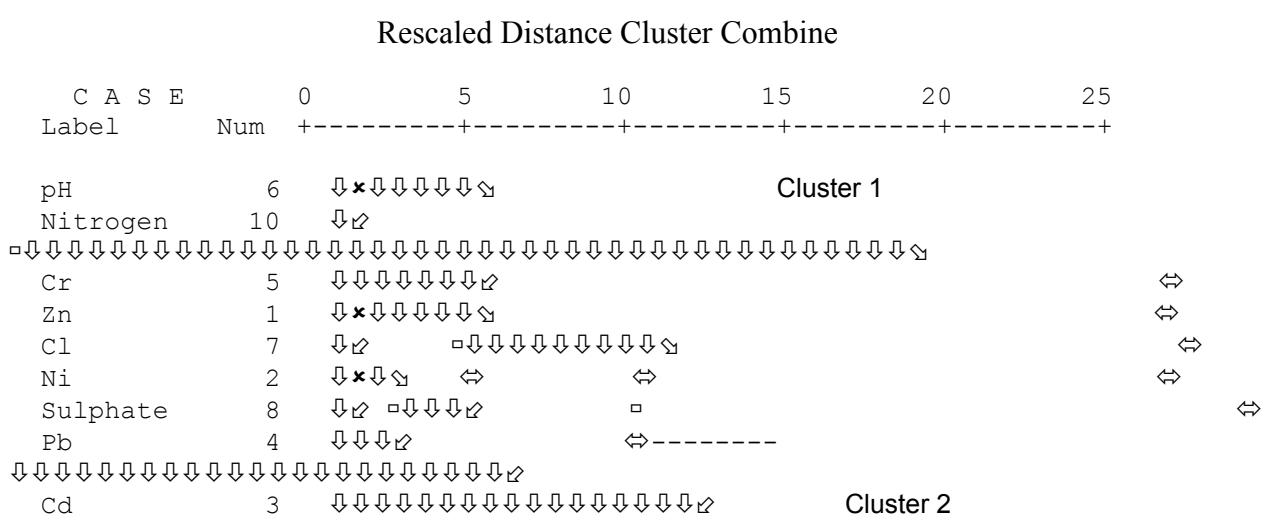


Fig. 4.11: Hierarchical Cluster Analysis for side-sediments

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The pH range for the side-sediments and water could influence the mobility rate of the metal within the sites of sampling and also between the suspended particles and water. The temperature of the samples varies with the highest value in August. The seasonal variation in dissolved oxygen contents is related to temperature and biological activities.

The results obtained from this study showed that side-sediments, suspended solids and water filtrate taken in August during raining season have the highest trace metals concentration. This could be as a result of run-off which enters into the dam during rainy season contains domestic, municipal waste and agriculture waste which contaminated the side-sediments and water.

Trace metals in suspended solids, side-sediments, and water from Galma dam are not evenly distributed. Concentration of nickel, zinc, chromium and cadmium were found to be higher in dissolved species whereas lead were higher in the undissolved species which was in agreement with the result obtained from similar analysis carried out by Wufem *et al., (*2007) on Gubi dam water Bauchi State of Nigeria . Generally for all trace metals determined, samples taken in August showed higher concentration for the suspended solids, side-sediments and water samples.

Concentration of trace metals in the suspended solids is in the order of Zn > Pb > Ni > Cr > Cd , the range of the trace metals in the side-sediments is in the order of Zn > Pb > Ni > Cr > Cd while for water samples, is in the order of Zn > Pb > Ni > Cr > Cd.

The physicochemical parameters and level of trace metals concentration range for Zn, Pb, Cd, and Ni were found to be consistent with the World Health Organization standard for drinking water (WHO, 1993) and recommended maximum concentration of trace metals for irrigation water.

Evaluation of Result from Multivariate Analysis

From the twenty components in the table for component matrix, the first-two components were sufficient to explain the dam monitored. As can be seen in the Table 4.14, these components explain 100% of the total variable of the original data set.

As can be seen in the Table 4.14, the variance of the principal component and the rotated components are nearly the same for all components. Principal component analysis of the water from dam showed that domestic waste, industrial waste, and agricultural run-off in raining seasons, are the main cause of variation in the water quality in Zaria dam.

5.2 Recommendations

Intermittent monitoring of the dam's surrounding side-sediments, water and plants will help to ensure that the cadmium concentration do not pose an increased health threat to the population that depend on the dam as the water sources. The growth of phytoplankton around the dam could also help in reducing the Cd level in the dam water.

Availability of information on the activities around the dam would have made the interpretation of the components easier since some activities might have lasted for short periods and not for the entire duration of the observation periods. Limited numbers of data (insufficient data), improper frequency of observation of data, and error in analyzing the quality variables in the laboratory or in situ may have contributed to the difficulties that arose in the interpretation of principal components.

For this reason, it is worthwhile to stress that more systematical observed data should be used in analysis. More frequently observed (in a certain time period) data or data observed as frequently as necessary may help obtain more meaningful principal components.

REFERENCES

Abu, R.D. (2006). *Assessment of the Magnitude of Saltation in the Zaria Dam (Galma Reservoir)*, Unpublished M.Sc. Thesis. Department of Geography, Ahmadu Bello University, Zaria. PP. 22

Achi, M.M. (2010). *Assessment of Heavy Metal Contamination of Soil and Vegetation in the Vicinity of Automobile Mechanic Workshop in Kaduna and Jos Cities,* Unpublished M.Sc. Thesis. Department of Chemistry A.B.U Zaria, Nigeria, PP. 68 - 69.

Adefemi, S.O. and Awokunmi, E.E. (2010). *Determination of Physicochemical Parameters and Heavy Metals in Water Samples from Itaogbolu Area of Ondo State, Nigeria,* African Journal of Environmental Science and Technology, 4(3): 145 – 148

Adefemi, S.O., Asaolu, S.S. and Olaofe, O. (2007). *Assessment of the Physicochemical Status of Water Samples from Major Dams in Ekiti State, Nigeria.* Pakistan Journal of Nutrition. 6(6): 657- 659.

Adeyeye, E.I. and Ayejumo, O.O. (2002). *Assessment of the Physicochemical Status of a Textile Industry's Effluent and its Environment.* Pakistan Journal of Science and Industrial Research, 45, 10 - 16.

Adewoye, R.A. (1998). *Saving and Oceans; Opportunity for Nigeria Chemist: Plenary Address at 21st Annual International Conference of Chemical Society of* Nigeria; at University of Ibadan.

Akpoveta, O.V., Osakwe, S.A., Okoh, B.E. and Oyuta, B.O. (2010). *Physicochemical Characteristics and Levels of some Heavy Metals of Soils around Metal scrap Dumps in some parts of Delta State Nigeria,* Journal of Applied Science Environmental Management, 14(4): 57-60.

Alabaster, J.S. and Lloyd, R. (1980). *Water Quality Criteria for Fish (Second edition*) London, Butterworth.

Allen, R.J. (1973). *Reconnaissance Geochemistry using Lake Sediments of a 36,000 Mile Area of the Northwestern Canadian Shield,* London. Geological Survay of Canada, PP. 72-80

American Public Health Association, (APHA), (1992). *Standard Method for the Examination of Water and Wastewater*, 14th Edition, APHA Inc. New York

Aribike, D.A. (1996). *Environmental Impacts of Industrialization on Nigeria:* A Treatise Proceeding of the 26th Annual Conference of the Nigerian Society of Chemical Engineers.

Asaolu, S.S. (1998). *Chemical Pollution Studies of Coastal Water of Ondo State.* Unpublished PhD Thesis, Federal University of Technology Akure, Nigeria.

Asaolu, S.S., Ipinmoroti, K.O., Adeyinowo, C.E., and Olaofe, O. (1997). *Interrelationship of Heavy Metals Concentration in Water, Sediments as Fish Samples from Ondo State Coastal Area Nigeria*, Africa Journal of Science 1, 55-61

Aston, S.R. and Thornton, I. (1973). *The Application of Regional Geochemical Reconnaissance Survey in the Assessment of Water Quality as Estuarine Pollution,* Water Research, 9, PP. 189-195

Aston, S.R. and Thornton, I. (1977). *Regional Geochemical Data in Relation to Seasonal Variation in Water Quality.* Science of the Total Environment, 7, 247-260.

Becker, A., Klock, W., Friese, K., Schreck, P., Treutler, H.C., Spettel B. and Duff M.C. (2001) *Lake Suber See as a Natural Sink for Heavy Metals from Copper Mining.* Journal of Geochemistry Exploration 74(1-3): 205-217.

Borgmann, U. (1983). *Metal Speciation and Toxicity of Free Metals Ions to Aquatic biota. In Nriagu J.O (ed) Aquatic Toxicity,* Advance in Environmental Science and Technology, 13, John Wiley and Sons, New York. PP. 47 – 73

Campbell, P.G.C. (1995). *Interaction between Trace Metals and Aquatic Metals and Aquatic Organism: A Critique of the Free-ion Activity Models*. In: Tessier, A., Turner, D.R. (Eds.),

Metal Speciation and Bioavailability in Aquatic Systems. John Wiley & Sons,, John Wiley and Sons, New York, PP. 28-30.

Cerda, V., Estela J.M., Miro M. (2004). *Determination of Total Nitrogenin Natural Waters by Means of Persulphate Oxidation.* Analytica Chimica Acta. Talanta, 63, 201

Chapman, D. and Kimstach, V. (1992). *Selection of Water Quality Variables: in Water Assessment* (Ed. Champman, D) UNESCO, WHO and UNEP. PP. 59 - 126.

Chatfield, C. and Collin, A.J., (1980). *Introduction to Multivariate Analysis. Published in USA by Chapman and Hallin, Association with Methuen Incoporation.* 733 Third Avenue, New York NY. 10017, ISBN 0-412-16030-7

Csuros, M. and Csuros, C. (2002). *Environmental Sampling and Analysis for Metals,* CRC Press LLC, Florida, USA, PP. 71-72

Dee, A.K, (1989). *Environmental Chemistry*, Second edition. Wiley Eastern Publication, PP. 164-272.

Department of Water Affair and Forestry (DWAF). (1996). *South African Water Quality Guideline*. second edition, 1; Domestic Use.

Deuzuane, J. (1979). Handbook *of drinking water quality*. Indiana University Press PP. 3 - 17.

Dix, H.M. (1983). *Environmental Pollution Control.* first edition, John Willey and sons, New York, PP. 120.

Donat, J.R. (1994). *Speciation of Cu and Ni in South San. Francisco Bay; a Multimethod Approach*. Analytical Chimaca Acta 284(3): 547-571 Retrieved December 2010 from http://academic.research.microsoft.com

Egila, J.N., Nimyel, D.N. (2002). *Determination of Trace Metals Specification in Sediments from some Dam in Plateau State*. Journal of Chemical Society of Nigeria 27: 21-75.

EPA United State Environmental Protection Agency (1976). *National Recommended Water Quality Criteria.* Retrieved October 2, 2010 from http://water.epa.gov

Ewa, I.O.B., Ebele, S., and Umar, I.M. (2002). *Trace Elements from Effluents Discharged into the Kaduna River Basin Environment.* Journal of Trace and Microprobe Techniques 20, 261

Fakayode, S.O. (2005). *Impart of Industrial Effluent on Water Quality of the Receiving Alero River in Ibadan,* Ajeam-Ragee, 10, 1 - 13

Florence, T.M. (1981). *Development of Physicochemical Speciation Produce to Investigate the Toxicity of Lead, Copper, Cadmium, Zinc, Towards Aquatic Biota.* Talanta. 345-364.

Fernandez, G.O., Hidalgo, M., Margui, E., Carvalho, M.L. and Queralt, I. (2008). Heavy Metals' Content of Automotive Shredder Residues (ASR): Evaluation of Environmental Risk. Environmental Pollution 153, 476 – 482.

Gaur, V.K., Gupta, S.K., Pandey, S.D., Gopal, K. and Misia, V. (2005). *Distribution of Heavy Metals in Sediments and Water of River Gomti.* Environmental Monitory and Assessment. 102 (1-3): 419-533.

Hess, R. and Schmid, B. (2002). *Zinc Supplement Overdose can have Toxic Effect*. *Journal* of *Pediatric Hematology*/*Oncology* 24, 582-584.

Harte, J., Holdren, C., Schneider, R and Shirley, C. (1991). *Toxics A to Z: A Guide to Everyday Pollution Hazards*. University of California Press, Berkeley.

Hill, S.J., Arowolo, T.A., Butler, O.T., Cook, J.M., Cressor, M.S., Harrington, C., and Mile, D.L. (2004) *Spectrometry*. Journal of Analytical Atomic 19, 301

Holmbeck-Pelham, S.A. and Rasnussen T.C. (1997). *Characterization of Temperature and Spatial Variation of Turbidity in the Upper Chattahochee River*. K.J. Hatcher, (Ed) proceeding of the 1997 Georgia water Resources conference. March 20-22, 1997, Athens, Georgia.

Hendershot,. W.H, Mendes L., Landande H., Courchone F. and Savaole S. (1992). *Soil and Stream Water Chemistry during Spring Snowmelt*. Nordic Hydrology 23(1): 13 - 26

Ipinmoriti, K., Oshodi, O. (1993*). Determination of Trace Metal in Fish Associated Wanted and Soil Sediments Fresh Fish Pond.* Discovery Innovate 5, 138. Retrieved October 18, 2010, from http://www.ajol.info

Iwegbue, C.M.A., Emuh F.N., Iirimah, N.O., Egun, A.C. (2006). *Fractionation, Characterization and Speciation of Heavy Metals in Composts and Composts-amended Soils.* African Journal of Biotechnology 6(2): PP. 069 – 078. Retrieved October 2, 2010 from http://www.acedemicjournals.org/AJB

Kagaya, S., Hosomori, Y., Arai, H., and Hagsagawa, K. (2003). *Determination* of *Cadmium in River Water by Electrothermal Atomic Absorption Spectrometry after Internal Standardization-assisted Rapid Co-precipitation with Lanthanum Phosphate.* Analytical Sciences. 19, 1061

Kazantzis, G. (1987). "Cadmium." In Lawrence Fishbein, Arthur Furst, and Myron A. Mehlman, eds., *Genotoxic and Carcinogenic Metals: Environmental and Occupational Occurrence and Exposure.* Advances in Modern Environmental Toxicology, 11, Princeton, N.J.: Princeton Scientific Publishing Co.

Karpuzcu, M. and Senes, S. (1987). *Design of Monitoring Systems for Water Quality by Principal Component Analysis and a Case Study.* Proceedings of the International Symposium on Environmental Management. Environment '87. 1, 673 - 690.

Lee, S.K., and Choi, H.S. (2001). *Spectrometric Determination of Cadmium.* Bull Korean Chemical Society. 22, 463

Mahloch, J.L. (1974). *Multivariate Techniques for Water Quality Analysis.* Journal of Environmental Engineering, Division of America Society of Civil Engineer. 100, No. EE5, 1119-1132.

Mazlum, N., Ozer, A., and Mazlum, S. (1999). *Interpretation of Water Quality Data by Principal Component Analysis.* Turkish Journal of Engineering and Environmental Science 23, 19-26

Melaku, S., Wondimu, T., Dams, R. and Moens, L. (2004). *Simultaneous Determination of Trace Elements in Tinishu Akaki River Water Sample, Ethiopia by ICP. MS,* Journal of Analytical Science and Spectrometry 49(6): 374 - 375,

Merian, E. (1991). *Metals and their Compounds in the Environment Occurrences*, Analysis and Biological Relevance UCH, Weinhein, New York, Basel Cambridge.

Miro, M., Estela, J.M. and Cerda, V. (2004). Flow Injection Wetting-film Extration System for Flame Atomic Absorption Spectrometric Determination of Cadmium in Environmental Waters. Talanta. 63, 201

Mohan, B.S. and Hosetti, B.B. (1998). *Lead Toxicity to Salvinia Natans Grown in Macrophyte Ponds.* Journal of Ecotoxicology and Environmental Monitory 81**,** 3-7.

O'Neil, P. (1993). *Environmental Chemistry*, Chapman and Hall, London PP. 193

Oluduro, A.O. and Adewoye, B.I. (2007). Efficiency *of Moringa Oleifera Seed Extract on the Microflora of Surface and Ground Water*. Journal of Plant Science, 6, 453-488.

Onyari, M.J., Muohi, A.W., Omondi, G. and Mavuti, K.M. (2003). *Heavy Metals in Sediments from Makupa and Port-Reitz Creek Systems: Kenyan Coast*. Environment International. 28(7): 639 - 647.

Pane, E.F., Richards, J.G. and Wood C.M. (2003). *Acute Water Borne Nickel Toxicity in the Rainbow Trout (Oncorhynchus Mykiss) occurs by a Respiratory rather than Ion Regulatory Mechanism*. Aquatic Toxicology 63(1): 65 - 82.

Poikane, R., Carstensen, J., Dahllof, I. and Aigars, J. (2005). *Distribution of Particulate Trace Metals in the Water Column and nephcloid layer of the Gulf of Riga Chemosphere* 60(2): 216 - 225.

Pollution Prevention and Abatement Handbook, World Bank Group, 1998.

Schetagne, R. (1985). *The Use of Multivariate Methods in the Interpretation of Water Quality Monitoring Data of a Large Northern Reservoir.* Proceedings of the Workshop Held at the Canada Centre for Inland Waters, October 7 – 10 1985. Statistical Aspects of Water Quality Monitoring, 31 – 43

Schüürmann, G. and Markert B. (1998). Ecotoxicology: *Ecological Fundamentals, Chemical Exposure, and Biological Effects,* JohnWiley & Sons, Inc. and Spektrum Akademischer Verlag, PP. 900

Tabatabai, M.A. (1982). *Methods of Measurement of Sulphur in Soil, Plant Materials and Waters*, Agronomy Department, Iowa State University, Ames IA, USA. Retrieved October 2, 2010 from http://www.iastate.edu/

Teo, K.C. and Chen, J. (2001). *Determination of Cobalt and Nickel in Water Sample by Flame Atomic Absorption Spectrometry after Cloud Point Extraction*. Analytica Chimica Acta 434(2): 325-330.

Townsend, A.T., O'Sullivan, J., Feathertone, A.M., Butler, E.C.V. and Mackey D.J. (2001). Journal of Environmental Monitoring 3, 113

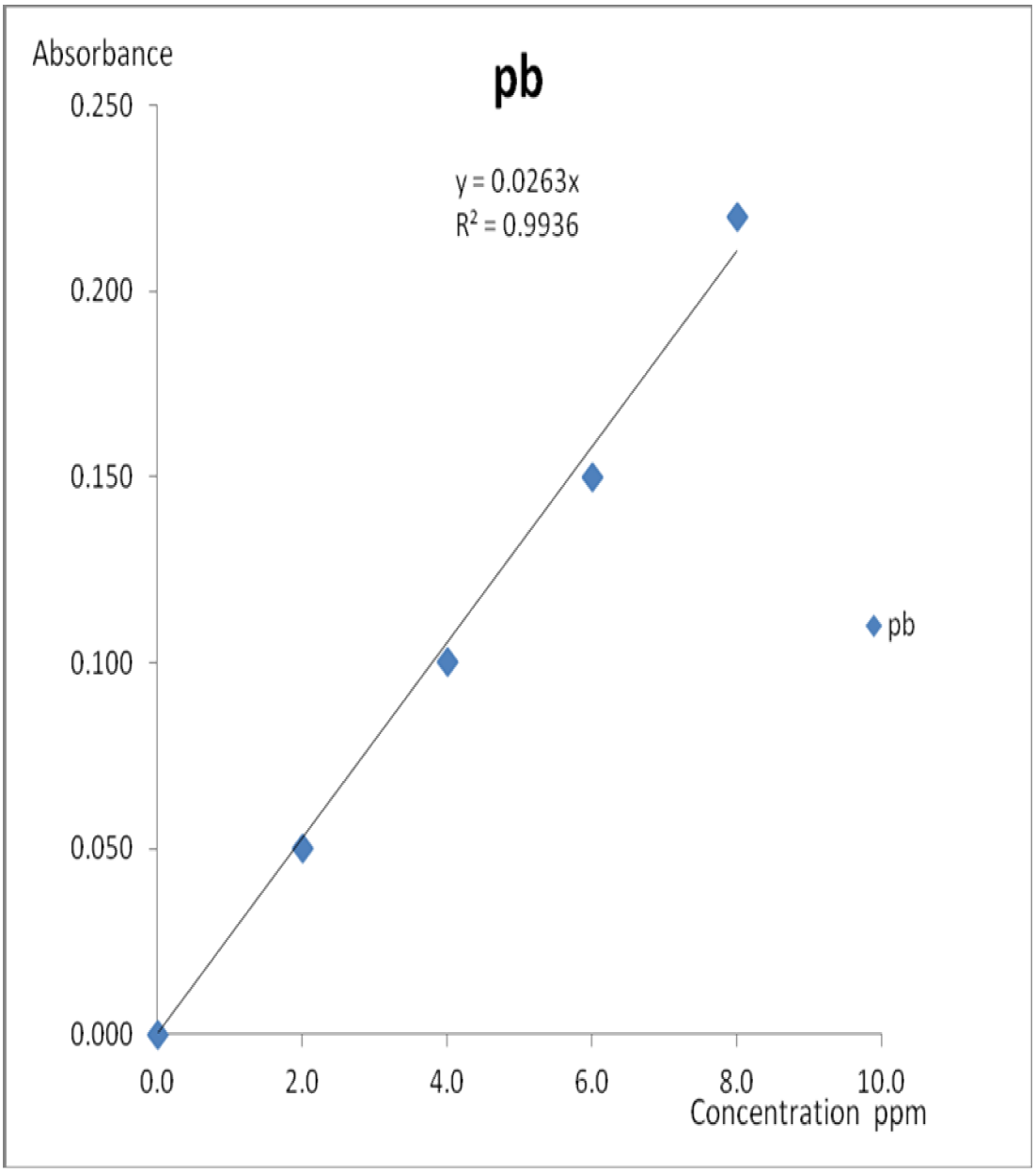
Tyler, T.G. (1981). *Heavy metals in soil biology and biochemistry in Paul E.A and Ladd JN (Ed) Soil Chemistry*, Marcel Dekker, New Yolk, PP. 33

United States Environmental Protection Agency (USEPA) (1986). *Quality Criteria for water*. United States Environmental Protection Agency Office of water. Regulations and Standards. Washington DC, 20460.

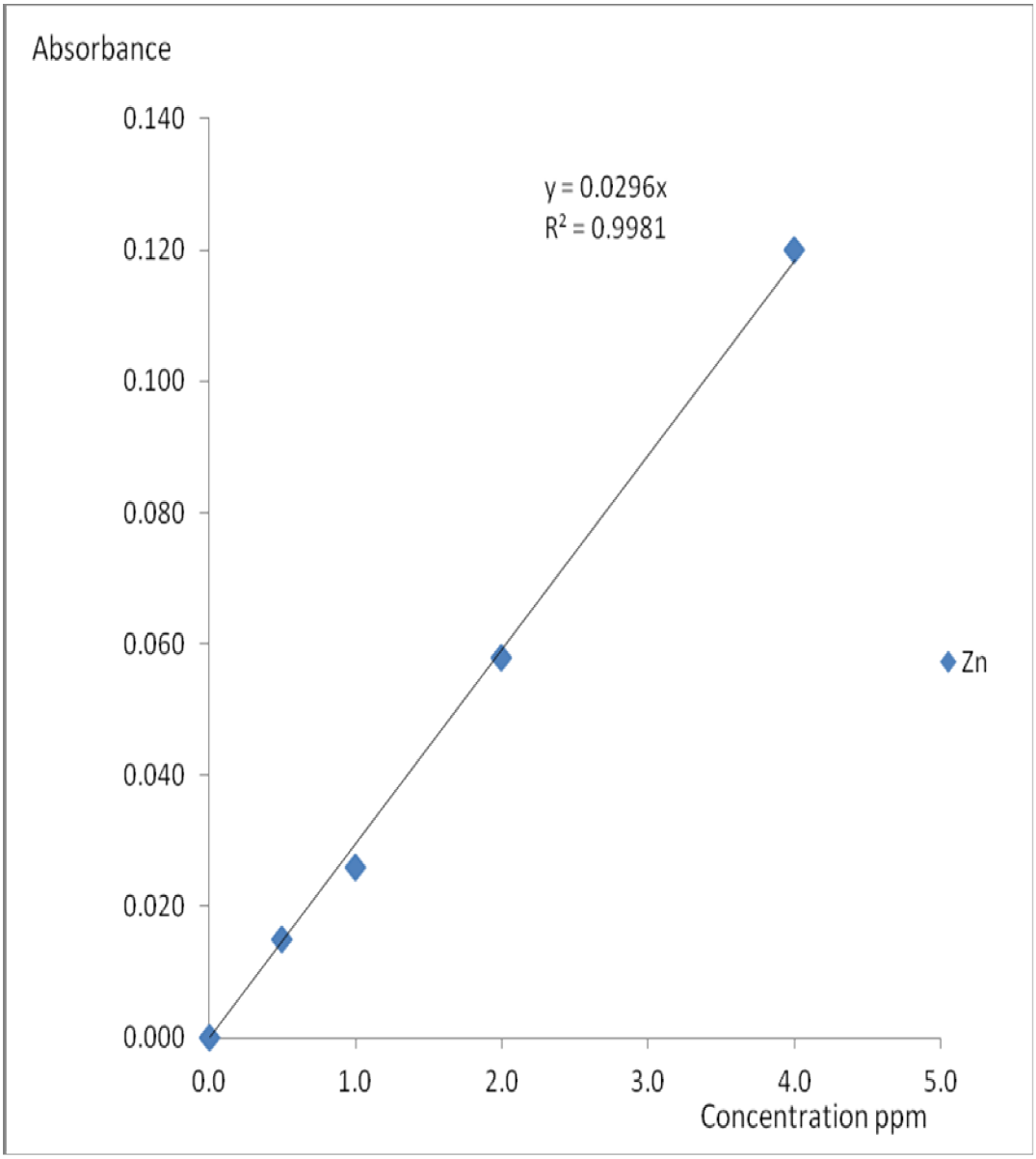
Wetzel, R.G. and Likens, G.E. (2006). *Limnological Analysis*. Third edition. Springer-Verlag, New York, PP. 391.

Wufem, B.M., Ibrahim, A.Q., Gin, N.S., Shibdawa, M.A. and Adamu, H.M., (2007). *Level of Heavy Metals in Gubi Dam Water Bauchi.* Global Journal of Environmental Sciences. 8(2): 29 - 37.

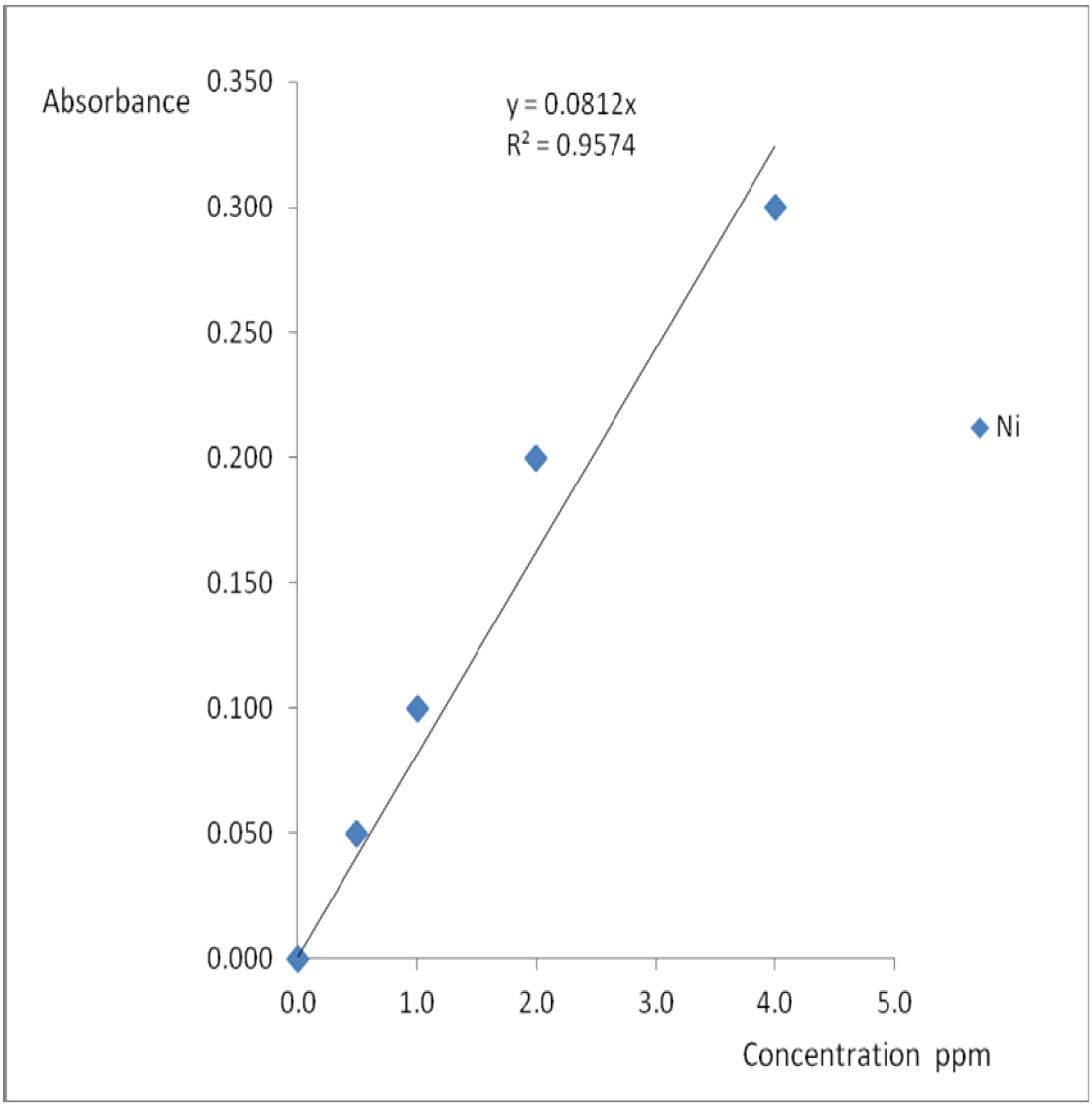
Wufem, B.M., Ibrahim, A.Q., Gin, N.S., Mohammed, M.A., Ekanem, E.O. and Shibdawa, M.A. (2007). *Speciation of Heavy Metals in Sediment of Gubi Dam, Bauchi State, Nigeria.* Global Journal of Environmental Sciences. 8(2): 55



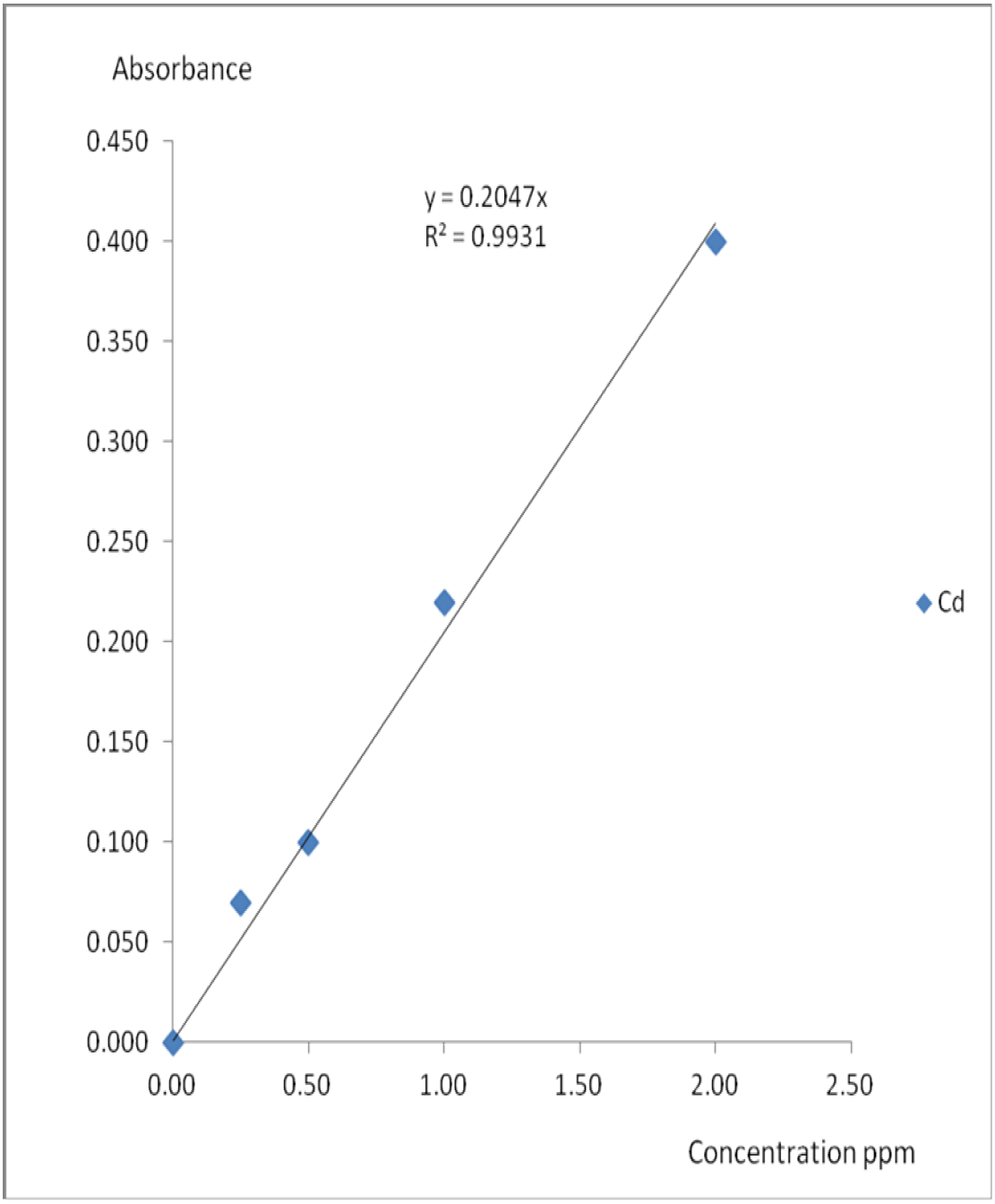
Appendix I: Calibration Curve for the Determination of Pb



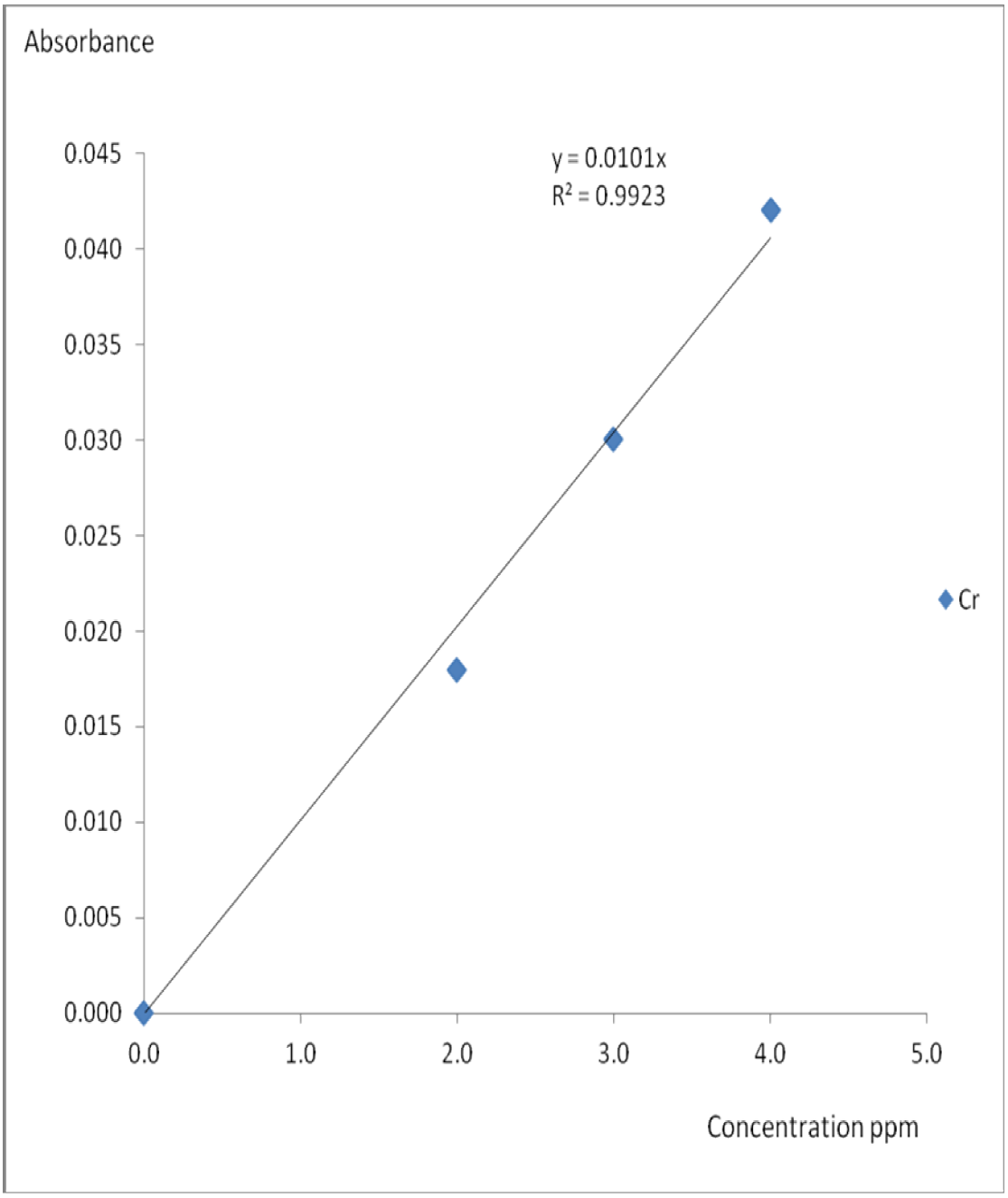
Appendix II: Calibration Curve for the Determination of Zn



Appendix III: Calibration Curve for the Determination of Ni



Appendix IV: Calibration Curve for the Determination of Cd



Appendix V: Calibration Curve for the Determination of Cr

Appendix VI: A Typical Sewage Analysis (Tebbutt, 1998)

		Source	
Characteristics (mg/L)	Crude	Settled	Final effluent
BOD	300	175	20
COD	700	400	90
Ammonia nitrogen	40	40	5
Nitrate nitrogen	<1	<1	20
Suspended solids	400	200	30
Total organic carbon	200	90	30

Appendix VII: WHO Drinking Water Quality Guidelines (WHO, 1993)

Parameters	Guide Level	Note
1.Inorganic		
Cadmium	0.003	
Chromium	0.05	
Copper	2	Depends on local conditions
Cyanide	0.07	
Fluoride	1.5	
Lead	0.01	
Manganese	0.5	
Mercury	0.001	Sum of conc./GL should not > 1 or both
Nitrate	50	
Nitrite	3	
Nickel	0.02	

Appendix VIII: Bathing Water Quality Standards (Tebbutt, 1998)

Parameter (mg/L)	Guide Limit (90^{th} percentile)	Mandatory Limit (95^{th} percentile)
Cadmium	0.0025	0.0025
Mercury	0.003	0.003
Dissolved oxygen	80-120% saturation	
Faecal coliforms (MPN/100ml)	100	2000
Total coliforms (MPN/100ml)	500	10,000
Salmonella (MPN/Litres)	-	0
Faecal streptocci (MPN/100ml)	100	-
Eternoviruses (MPN/10 Litres	-	0

Directive 76/110EE

Appendix IX: Effect and Drinking Water Standard for some Water Quality Parameters

PARAMETERS	UNITS	MAXIMUM PERMITTED	ECOLOGICAL OR HEALTH EFFECT
Dissolved Oxygen	mg/L	5.0mg/L average	High level of dissolved oxygen are necessary for fish respiration
Temperature	^{o}F or ^{o}C	90°	Fish suffer metabolic stress at high temperature
pH	-	6.5 -8.5	pH affect the solubility of other water quality
Residual chlorine	mg/L	0.2 - 0.25	
Total Nitrogen	mg/L	4.00	Micronutrient affects the aquatic productivity and trophic state
Conductivity	µS/cm	1000	None
Nitrate (NO_3)	mg/L	50	Cyanosis and asphyxia (blue -baby syndrome) in infant under 3 month
Nitrite (NO_2)	mg/L	0.2	Causes blue -baby syndrome and cyanosis in infants
Phosphorus		No effective standard	Macronutrient affects the aquatic productivity and trophic state
Hardnesss (as $CaCO_3$)	mg/L	150	
Total Dissolved Solid	mg/L	500	General indicator of ion concentration. Affect taste
Fecal Caliform	col/ml	200col/100ml (May - Oct), 1000col/100ml (Nov - April), 4000col/100ml (any time)	Facal coliform do not pose health threat but serve as indicator for bacteria that can cause illness in humans and aquatic life
Sulphate (SO4)	mg/L	100	None
BOD			
COD			
Suspended Solid			
METALS: Cadmium, Chromium, Lead,	mg/L		Heavy -metals cause a variety of product including interfering with vitamin uptake, neurological disorders and disruption of renal funtion. These problems result chronic and cumulative exposure

Appendix X: Recommended Maximum Concentrations of Trace Elements in Irrigation Water

	For water continuously used on soil (mg/L)	For water used up to 20yrs on five-textured soil, pH 6.0-8.5 (mg/L)
Aluminum (Al)	5.00	20.00
Cadmium (Cd)	0.01	0.05
Chromium (Cr)	0.10	1.00
Cobalt (Co)	0.05	5.00
Copper (Cu)	0.20	5.00
Fluoride (F)	1.00	15.00
Iron (Fe)	5.00	20.00
Lead (Pb)	5.00	10.00
Lithium (Li)	2.50	2.50
Manganese (Mn)	0.20	10.00
Nickel (Ni)	0.20	2.00
Vanadium (V)	0.10	1.00
Zinc (Zn)	2.00	10.00