

**EFFECT OF KADUNA PETROCHEMICAL REFINERY EFFLUENTS ON
WATER QUALITY AND PLANKTONS OF RIVER ROMI, KADUNA, NIGERIA**

BY

OLOFINBIYI, STELLA BOLA

**DEPARTMENT OF BIOLOGY,
FACULTY OF LIFE SCIENCES,
AHMADU BELLO UNIVERSITY,
ZARIA, NIGERIA.**

OCTOBER, 2016

EFFECT OF KADUNA PETROCHEMICAL REFINERY EFFLUENTS ON WATER
QUALITY AND PLANKTONS OF RIVER ROMI, KADUNA, NIGERIA

BY

OLOFINBIYI, STELLA BOLA
(M.Sc./SCIE/ 43988/2012/2013)

A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE
STUDIES, AHMADU BELLO UNIVERSITY, ZARIA

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD
OF
MASTER OF SCIENCE DEGREE IN BIOLOGY.

DEPARTMENT OF BIOLOGY,
FACULTY OF LIFE SCIENCES
AHMADU BELLO UNIVERTY,
ZARIA, NIGERIA

OCTOBER, 2016

DECLARATION

I declare that the work in this dissertation entitled “**EFFECT OF KADUNA PETROCHEMICAL REFINERY EFFLUENTS ON WATER QUALITY AND PLANKTONS OF RIVER ROMI, KADUNA, NIGERIA**” has been carried out by me in the Department of Biological Sciences, Ahmadu Bello University, Zaria, Nigeria. The information derived from the literature has been duly acknowledged in the text and in a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any Institution.

OLOFINBIYI, STELLA BOLA

Signature

Date

CERTIFICATION

This dissertation entitled EFFECT OF KADUNA PETROCHEMICAL REFINERY EFFLUENTSON WATER QUALITY AND PLANKTONS OF RIVER ROMI, KADUNA, NIGERIA meets the regulations governing the award of the degree of Master of Biology of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

Prof. J. K. Balogun

Chairman, Supervisory Committee
Department of Biology,
Ahmadu Bello University, Zaria

Signature

Date

Prof. S. J. Oniye

Member, Supervisory Committee
Department of Zoology,
Ahmadu Bello University, Zaria

Signature

Date

Prof. M. L. Balarabe

Head of Department,
Department of Biology,
Ahmadu Bello University, Zaria

Signature

Date

Prof. K. Bala

Dean, School of Postgraduate Studies,
Ahmadu Bello University, Zaria

Signature

Date

DEDICATION

I dedicate this work to Almighty God for seeing me through my studies, and to my lovely husband, Mr. Samuel Adetola.

ACKNOWLEDGMENTS

I give glory, honour, praise and adoration to Almighty God for seeing me through my study.

My sincere appreciation goes to my supervisors, Prof. J. K. Balogun and Prof. S. J. Oniye for their keen interest and tireless efforts towards the completion of this study. They have been a great tool in impacting knowledge and the requisite skills that has resulted to the successful completion of this research. I say a big thank you for having the privilege to learn from you.

I thank members of academic and non-academic staff of the Department of Biological Sciences, especially Dr. Y. Tanimu, Mal. Magaji of Hydrobiology Laboratory, Mal. Bashir of Multi User Research Laboratory in the Department of Chemistry. God bless you all.

The spiritual and financial support of my family cannot go un-noticed. My loving and caring husband, Mr. Samuel, A. for his patience and understanding; my children: Joy, Seun, David and Isaac for being there for me.

To my colleagues: Balli, G., Mr. Kamba, B., Tabat, L. J. and all those that I could not mention, I appreciate their efforts toward making this work a success.

ABSTRACT

This study aimed at determining the effect of Kaduna Refinery on water quality of River Romi, Kaduna, Nigeria. The study was conducted for a period of six months, February to July, 2015. Water samples and plankton samples were collected from five different selected sites along River Romi. Some physicochemical parameters such as temperature, pH, TDS and EC were measured with HANNA instruments. Other physicochemical parameters measured include: DO, BOD, COD, PO₄, NO₃, SO₄, total phosphorous, total nitrogen, hardness, alkalinity, oil and grease based on American Public Health Association (APHA) method; concentrations of each selected metal ion were read against the standards on a Buck Scientific model 200A Atomic Absorption Spectrophotometer (AAS). Analysis of Variance (ANOVA) and correlation analysis were used to analyse the data generated. The study revealed the following: temperature (27.78°C), pH (7.71), electrical conductivity (123.29µS/cm), TDS (61.99mg/L), DO (4.05mg/L), BOD (2.32mg/L), COD (419.07mg/L), PO₄ (0.13mg/L), NO₃ (2.31mg/L), SO₄ (6.94mg/L), total phosphorous (1.85mg/L), total nitrogen (20.98mg/L), hardness (186.87mg/L), alkalinity (54.80mg/L) and oil and grease (0.15mg/L). The concentration of heavy metals increased in this order: Nickel (0.15mg/L) < Lead (0.19mg/L) < Zinc (0.24mg/L) < Manganese (0.44mg/L) < Chromium (0.52mg/L). Phytoplankton species composition was higher than the zooplankton species. The highest number of species encountered was in *Stigonema* sp. (752) and the lowest was observed in *Closterium* sp. and *Pleurogaster* sp. with one each, while, zooplankton had highest and lowest number in *Paramaecium* sp. (49) and *Heliodiaptomus* sp. (6). Some surface water parameters had influence on the distribution of plankton species. These findings suggested that most of the

physicochemical parameters were above the acceptable limit of the portable water for domestic use which may be due to industrial effluent, house waste discharges and agricultural activities that are taking place in the vicinity of River Romi.

TABLE OF CONTENTS

Title	Page
Title Page	i
Cover Page.....	iii
Declaration Page	iv
Certification Page	v
Dedication	vi
Acknowledgements	vii
Abstract	viii
Table of Contents	ix
List of Figures.....	xii
List of Tables	xiii
List of Appendices	xiv
CHAPTER ONE	
1.0 INTRODUCTION.....	1
1.1 Background of the Study	1
1.2 Statement of the Research Problems	5
1.3 Justification	6
1.4 Aim and Objectives	6
1.5 Hypotheses	7
CHAPTER TWO	
2.0 LITERATURE REVIEW	8
2.1 Pollution of Water Bodies.....	8

2.2	Physicochemical Parameters.....	11
2.2.1	Determination of Oxygen	11
2.3	Toxic Effects of Pollutants on Plankton.....	12
2.3.1	Phytoplankton.....	12
2.3.2	Zooplankton.....	17
2.3.3	Effects of Pollution on Zooplankton.....	17
CHAPTER THREE		
3.0	MATERIALS AND METHODS	19
3.1	Study Area	19
3.2	Field Sampling Procedure.....	19
3.2.1	Station 1.....	21
3.2.2	Station 2.....	21
3.2.3	Station3.....	24
3.2.4	Station4.....	24
3.2.5	Station5.....	24
3.3	Determination of Physicochemical parameters.....	28
3.4	Laboratory Analysesof WaterSamples.....	28
3.4.1	Temperature	29
3.4.2	pH	29
3.4.4	Total Dissolved Solids	29
3.4.3	Electrical Conductivity	29
3.4.5	Hardness	29
3.4.6	Alkalinity	30
3.4.7	Nitrate	30

3.4.8	Total nitrogen	30
3.4.9	Phosphate	31
3.4.10	Sulphate.....	31
3.4.11	Determination of Dissolved Oxygen and Biochemical Oxygen Demand (BOD).....	31
3.4.12	Determination of Chemical Oxygen Demand.....	33
3.4.13	Determination of Oil and Grease	34
3.5	Determination of Heavy Metals	34
3.6	Plankton Sampling	35
3.7	Statistical Analyses	35
CHAPTER FOUR		
4.0	RESULTS	37
4.1	Monthly Variation of Physicochemical Parameters of River Romi, 2015	37
4.2	Physicochemical Parameters across Sampling Stations for February to July, 2015	42
4.3	Comparison of Physicochemical Parameters in the Dry and Wet Season	56
4.4	Principal Component Analysis (PCA) of Physicochemical Parameters	57
4.5	The Canonical Correspondence Analysis of Physicochemical Parameters and Phytoplankton	58
4.6	The Canonical Correspondence Analysis of Physicochemical Parameters and Zooplankton Organisms	61
4.7	The Canonical Correspondence Analysis of Physicochemical Parameters, Phytoplankton and Zooplankton	63
4.8	Heavy Metal Concentrations in River Romi	65
4.9	Distribution and Composition of Plankton Species in River Romi	67

4.9.1	Phytoplankton Species	67
4.9.2	Zooplankton Species.....	69
4.10	Correlation between Phytoplankton and Zooplankton Species Composition	71
CHAPTER FIVE		
5.0	DISCUSSION	73
CHAPTER SIX		
6.0	CONCLUSIONS AND RECOMMENDATIONS	83
6.1	Conclusions.....	83
6.2	Recommendations.....	83
	REFERENCES.....	85
	APPENDICES.....	95

LIST OF FIGURES

Figure	Page
3.1:Kaduna Town showing NNPC Refinery Complex and Sampling Stations (ST1-ST5) along River Romi	20
3.2: Station 1 of the Sampling Station.....	22
3.3: Station 2 of the Sampling Station.....	23
3.4: Station3 of the Sampling Station.....	25
3.5: Station4 of the Sampling Station.....	26
3.6: Station 5 of the Sampling Station.....	27
4.1:The Mean monthly variation of TDS, temperature, pH and EC of River Romi(2015)	38
4.2: The Mean monthly variation of COD, DO, BOD and PO ₄ of River Romi(2015)	40
4.3:The Mean monthly variation of total nitrogen (TN), sulphate, nitrate and total phosphorous of River Romi(2015)	42
4.4:The Mean monthly variation of hardness, alkalinity and oil and grease of River Romi(2015)	44
4.5: PCA biplotof the relationship between physicochemical parameters of River Romi.....	59
4.6: CCA analysis of the relationship between Physicochemical Parameters and Phytoplankton of River Romi, Kaduna, Nigeria	60
4.7: CCA analysis of the relationship between Physicochemical Parameters and Zooplankton Organisms of River Romi, Kaduna, Nigeria	62
4.8: CCA analysis of the association of Physicochemical Parameters with Phytoplankton and Zooplankton of River Romi, Kaduna, Nigeria	64
4.9: Heavy metal concentration in River Romi	66

LIST OF TABLES

Table	Page
4.1: Physicochemical values of River Romi in February, 2015.....	44
4.2: Physicochemical values of River Romi in March, 2015	46
4.3: Physicochemical values of River Romi in April, 2015.....	48
4.4: Physicochemical values of River Romi in May, 2015.....	50
4.5: Physicochemical values of River Romi in June, 2015	52
4.6: Physicochemical values of River Romi in July, 2015	56
4.7: Comparison of Physicochemical Parameters of River Romi in Dry and Wet Season (2015)	57
4.8: Distribution and Composition of Phytoplankton Species in River Romi, 2015.....	68
4.9: The Distribution and Composition of Zooplankton Species in River Romi, 2015.....	70
4.10: The Correlation of Phytoplankton and Zooplankton Species Composition.....	72

LIST OF APPENDICES

Appendix	Page
I: The February physicochemical parameters of River Romi.....	96
II: The March physicochemical parameters of River Romi.....	97
III: The April physicochemical parameters of River Romi.....	98
IV: The May physicochemical parameters of River Romi.....	99
V: The June physicochemical parameters of River Romi.....	100
VI: The July physicochemical parameters of River Romi.....	101

CHAPTER ONE

1.0

INTRODUCTION

1.1 Background of the Study

Pollution maybe considered as analogous to contamination. It can be defined as the presence of elevated concentrations of a substance in the air, water, soil resulting in a deleterious effect (Burgis and Symeons, 1987; Aderogba, 2011). As a result, there is growing appreciation nationally, regionally, and globally, that the management and utilization of natural resources need to be improved and that the amount of waste and pollutant generated by human activities need to be reduced on a large scale (Burgis and Symeons, 1987; Ugya and Umar, 2015).

One of the resources that is highly required to drive the world industrial revolution is crude oil. Nigeria joined the league of oil producing nations on August 3rd, 1956 when oil was discovered in commercial quantities at Oloibiri in Bayelsa state. Nigeria today is ranked as the leading oil and grease producer in Africa and the sixth largest exporter in the world (Cynthia, 2006).

Efforts to improve the standard of living of man through the control of nature and the development of new products have resulted in the pollution or contamination of the environment. Most of the world's air, water and land are now partially poisoned by chemical wastes from industrial processes, including those of crude oil and grease (Cynthia, 2006). The pollution exposes people to new risks, many species of plants and animals have become endangered or are at the verge of extinction; as a result of this

development, governments have passed laws to limit or reverse the threat of environmental pollution (Vivanet *al.*, 2012).

Wastes may be classified into solids, effluent treatment Solids and gaseous waste. Waste products from the Refinery are generally consist of oils, organic and inorganic chemicals (particularly acids), alkalis, hydrocarbons, sulphides, phenols and other sulfur-bearing compounds with suspended Solids (Al-amin, 2013). He further stressed that inhabitants of the surrounding Kaduna refinery and its environment are at the risk of exposure to the toxic wastes emitted into both water and air.

Environmental problems began to surface during and after the industrial revolution because of increase in human population hence placing a greater demand on resources, thus several environmental harmful technologies were used which began to overload the environment's ability to clean itself due to high pollution of air, water and land (Sharad and Mashal, 2005).Crude oil has had profound impact on the world than any single natural resource in recorded history and has become a very decisive element in defining the politics, rhetoric and diplomacy of states (ASTM, 2005).

The oil companies operating in Nigeria maintained that their activities are conducted to the highest environmental standards; but the Nigeria environmental laws, in most respects comparable to their international equivalents, are ineffectively enforced (Cynthia, 2006). Furthermore, due to rapid population growth, urbanization, industrialization and exploitation of natural resources, there has been a steady increase in the quantity, quality and diversity of discharge into the aquatic environment (FAO, 1991).These discharges

contain huge amount of heavy metals and organic metals which adversely affect the physicochemical properties of the receiving water bodies and consequently its biota.

Potential contaminants in refinery waste water originate from crude oil, the intake water, storm water, ballast water from the oil tankers sanitary water, process chemicals and catalyst, reaction products and chemical additives (John, 2002). Waste waters released from crude oil processing and petrochemical industries are characterized by the presence of large quantities of crude oil, polycyclic and aromatic hydrocarbons, phenols, metal derivatives, surface-active substances, sulfides, naphthylenic acids and other chemical (Suleimanov, 1995).Owing to ineffectiveness of purification systems, waste water may become seriously dangerous, leading to accumulation of toxic products in receiving water bodies with potentially serious consequences on the ecosystem (Beg *et al.*, 2001).

Accumulation of heavy metals with accompanying histopathology was observed in *Oreochromis niloticus* exposed to treated petroleum refinery effluent from the Nigerian National Petroleum Corporation, Kaduna (Onwumere and Oladimeji, 1990).Vivanet *al.* (2012) carried out a study on River Romi and reported that Kaduna refinery did not adhere to the minimum permissible levels for effluents discharge into the receiving water body. Almost all the physicochemical parameters measured were above the World Health Organisation (WHO) acceptable limits.In addition, it has been demonstrated that phenol is one of the major pollutants found in the refinery effluentsand was much higher than the 0.5mg/l minimum recommended for refinery effluent (Otokunefor and Obiukwu, 2004; Vivanet *al.*, 2012).

A major epidemic of water pollution was the “itai-itai disease” which affected a Japanese population that consumed fish and other foods harvested from coastal waters into which cadmium containing industrial effluent was being discharged. The disease was characterized by brittleness of bones, muscular weakness and loss of appetite (Hugh and Maduka, 2006). Sprague *et al.* (1978) conducted a two year study to examine the effect of sublethal concentrations of oil refinery effluent on aquatic organisms; and to determine whether a relatively rapid and simple test of sublethal effects could be developed for monitoring or assessing toxicity of oil refinery effluents. Testing showed that there was no acute effect, but chronic or sublethal effects to fish and invertebrates as the effluent concentration increased from 1 to 10%.

One of the most critical problems of developing countries is improper management of vast amount of wastes generated by various human activities. More challenging is the unsafe disposal of these wastes into the ambient environment, unfortunately, water bodies especially freshwater reservoirs are the most affected. Such activities have rendered these natural resources unsuitable for both primary and secondary usage (Fakayode, 2005). Industrial effluent contamination of natural water bodies has emerged as a major challenge in developing and densely populated countries like Nigeria, where estuaries and inland water bodies, which are the major sources of drinking water, are often contaminated by the activities of the adjoining populations and industrial establishments (Sangodoyin, 1995). These effluents can alter the physical, chemical and biological nature of the receiving water body (Sangodoyin, 1991).

Plankton communities are sensitive to changes in their environment and therefore plankton total biomass and many phytoplankton and zooplankton species are used as indicators of water quality (Reynolds *et al.*, 2002; Brettum and Andersen 2005). Phytoplankton communities give more information on changes in water quality than mere nutrient concentrations or chlorophyll-a concentration. Water quality is an ensemble of physical, chemical and biological characteristics of the given water. Eutrophication of freshwater is regarded as a water quality issue which results in the deterioration of the aquatic environment and impacts on water usage. Cyanobacteria have been recognised as a major symptom of eutrophication in fresh water as their blooms are prevalent in waters affected by cultural nutrient enrichment (Reynolds *et al.*, 2002).

With competing demands on limited water resources, industrial pollution remains one of the major problems facing Nigerian cities(Dejoux *et al.*, 1981). As societies throughout the world and Nigeria in particular become more aware of the issues involved in water pollution, public debate about environmental effects of effluents discharged into aquatic environments are on the increase (Calamari, 1985). Furthermore, the Federal Environmental Protection Agency (FEPA) and their state counter parts established to check environmental abuses,have little or no impact on pollution control in our cities over the years(Vivanet *al.*, 2012).

1.2 Statement of the Research Problem

Wastewaters released by crude oil-processing and petrochemical industries are characterized by the presence of large quantities of crude oil products, polycyclic and aromatic hydrocarbons, phenols, metal derivatives, surface-active substances, sulfides,

naphthylenic acids, heavy metals and other chemicals (Suleimanov,1995;Vivanet *al.*, 2012). Due to the ineffectiveness of purification systems, wastewaters may become seriously dangerous, leading to the accumulation of toxic products in receiving water bodies with potentially serious consequences on the ecosystem (Beg *et al.*, 2001; Beg *et al.*, 2003). The effect of Kaduna Refinery on the water quality of River Romi, needs to be reassessed.

1.3 Justification

Kaduna Petrochemical Refinery was established in 1974 to produce various petroleum by-products required by the country and particularly to supply the need of Northern Nigeria. Kaduna town has expanded in size and population, hence the extension to the Refinery area.As such, River Romi, which was of littleconsequence now serves the populace and Kaduna refinery in several ways.The effluents discharged by the Petrochemical Industry into this river could be one of the sources of pollution to the river (Romi).

1.4 Aim and Objectives

The aim of this study was to assess the impact of effluents from Kaduna Refinery on the physicochemical properties and planktons of River Romi, Kaduna State.

The specific objectives are:

- i. To determine the physicochemical parameters of River Romi
- ii. To determine the phytoplankton and zooplankton species composition of River Romi.

- iii. To determine the relationship between surface water physicochemical characteristics and planktons density of River Romi.

1.5 Hypotheses

- i. There is no significant difference in the physiochemical parameters of River Romi.
- ii. There is no significant difference in the composition of phytoplankton and zooplankton species of River Romi in all the sampling stations.
- iii. There is no significant relationship between surface water physicochemical characteristics and planktons density of River Romi.

CHAPTER TWO

2.0

LITERATURE REVIEW

2.1 Pollution of Water Bodies

According to Gore (1993) human beings are made up of water, in roughly the same percentage as water in the surface of the earth. Our tissues and membranes, brains, and hearts, our sweat and tears, all reflect the same recipe for life. Water is essential for the development and maintenance of the dynamics of every ramification of the society (UNDP, 2006).

Water is indeed life and thus is the most important natural resource, without which life would be non-existent. Availability of safe and reliable source of water is an essential prerequisite for sustained development (Asonye *et al.*, 2007). Common man-made pollutants include pesticides, chemical fertilizers, heavy metals, detergents, oil, sewage, plastics and other Solids (UNEP, 2011). Many of these pollutants accumulate in the deep oceans and sediments (Jacobsen *et al.*, 2010; Zarfl and Matthies, 2010), where they are consumed by small marine organisms and may be reintroduced to the global food chain. Some 20 per cent of marine pollution originates from direct disposal into the oceans; regular discharges of oily wastes from ships, accidental oil spills and untreated sewage disposal in enclosed areas such as the Mediterranean are threats to marine ecosystems (UNDP, 2011).

Increased industrial activities have led to pollution stress on surface waters both from industrial, agricultural and domestic sources (Ajayi and Osibanji, 1981; Al-Amin, 2013). Wastes entering these water bodies are both in solids and liquid forms. These are mostly

derived from Industrial, agricultural and domestic activities. As a result, water bodies which are major receptacles of treated and untreated or partially treated industrial wastes have become highly polluted. The resultant effects of this on public health and the environment are usually great in magnitude (Osibanjo *et al.*, 2011).

Over the last years, in many African countries a considerable population growth has taken place, accompanied by a steep increase in urbanization, industrial and agricultural land use. This has entailed a tremendous increase in discharge of a wide diversity of pollutants to receiving water bodies and has caused undesirable effects on the different components of the aquatic environment and on fisheries (Saad *et al.*, 1984).

Industries are the major sources of pollution in all environments. Based on the type of industry, various levels of pollutants can be discharged into the environment directly or indirectly through public sewer lines. Wastewater from industries include employees' sanitary waste, process wastes from manufacturing, wash waters and relatively uncontaminated water from heating and cooling operations (Glyn and Gary, 1996). High levels of pollutants in river water systems causes an increase in biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved Solids (TDS), total suspended Solids (TSS), toxic metals such as Cadmium (Cd), Chromium (Cr), Nickel (Ni) and Lead (Pb) and fecal coliform and hence make such water unsuitable for drinking, irrigation and aquatic life. Industrial wastewaters range from high biochemical oxygen demand (BOD) from biodegradable wastes such as those from human sewage, pulp and paper industries, slaughter houses, tanneries and chemical industry. Others include those from plating shops and textiles, which may be toxic and require on-site

physicochemical pre-treatment before discharge into municipal sewage system (Otokunefor and Obiukwu, 2005).

Organic pollution of inland water systems in Africa, in contrast to the situation in developed countries of the world, is often the result of extreme poverty, economic and social underdevelopment. According to Tolba (1982) and Lekwotet *al.* (2014) state that countries that the quality of water, and often the quantity, is lowest, sanitation and nutrition the worst and disease most prevalent.

Kuehn *et al.* (1995) observed that refinery effluent contaminated with aromatic hydrocarbon produces poor health and lethal toxicity in fishes. Onwumere and Oladimeji (1990) reported accumulation of heavy metals has adverse effect on the histopathology of *O. niloticus* exposed to treated petroleum refinery effluent from the Kaduna refining and petrochemical company. Drinking contaminated water can cause various diseases such as typhoid fever, dysentery, cholera and other intestinal diseases (Udoh, 1987; Adeyemi, 2004).

Industrial effluent characteristics provide basic information about the integrity of the aquatic habitat within such rivers and streams into which they are discharged. Most of these effluents pose inestimable harm to which the microbial entity is the most adversely affected. In Nigeria, there are many small to large cottage industrial establishments that discharge such harmful waste water effluents (Kanu and Achi, 2011).

2.2 PhysicochemicalParameters

The physicochemical indices of effluents from industries indicate that most of these industries partially conform to the recommended guidelines of FEPA (1991) guidelines. For instance, the total dissolved Solids (TDS) and Nitrate (NO_3) contents, are found to be very high in most of the effluents sampled in urban rivers of River Romi and may have adverse effect on humans and the aquatic habitat (Lekwotet *et al.*, 2013). The pH analyses from food and beverage effluents from the industries tend to be abnormally very acidic (Agedengbe *et al.*, 2003).

2.2.1 Determination of Oxygen

An important pollution index of industrial wastewaters is the oxygen function measured in terms of COD and BOD, while the nutrient status of wastewater is measured in terms of nitrogen and phosphorus. In addition, other important quality parameters include pH, temperature and total suspended Solids (Ezenobi and Okpokwasili, 2004; Phiri *et al.*, 2005).

Industrial effluents are characterized by abnormal turbidity, conductivity, COD; TSS and total hardness. The effluent total hardness concentrations of a chemical-biological treatment plant were found greater than the influents. The results are presented in terms of the relative flux as a function of time related to hydrodynamic conditions and pollution characteristics of wastewater (Ogunfowokan and Fakankun, 1998). Mean values of Phosphate phosphorous at most sampling sites were higher than 0.1 mg L^{-1} for subject to eutrophication and the characteristics of rivers and the nearby soils near them affect the equilibrium concentrations of N and P between the soil and the overlying water industrial

effluents are also known to exhibit toxicity toward different aquatic organisms. The coastal residential environment in any industrial effluent site is always under considerable stress due to the prevailing harsh environmental conditions, especially high temperature and salinity, restricted benthic fauna diversity and overall development of a fragile intertidal ecosystem. The fauna inhabiting the intertidal zone is most likely dominated by a few species probably living at their limit of tolerance (Awomeso *et al.*, 2010).

Organic pollution is always evident and the pollution is made worse by land-based sources such as the occasional discharge of raw sewage through storm water outlets, and industrial effluents from refineries, oil terminals and petrochemical plants (Adekunle and Eniola, 2008).

2.3 Toxic Effects of Pollutants on Planktons

2.3.1 Phytoplankton

Phytoplankton organisms of which their growth is facilitated by the presence of waste can result in decreased oxygen contents in the water. Oxygen deprivation promotes premature or unnatural aquatic species migration, which creates an imbalance in the aquatic ecosystem (Tanimu *et al.*, 2011). When the ecosystem loses its balance, a chain reaction of undesired effects, such as insufficient diet for some species and increased procreation of other species occur, inhibition of methionine production in some species by mercury may occur. It is important, therefore, when testing for effects of some pollutants that total volume or weight of living matter be measured, and not only cell numbers (Beg *et al.*, 2001).

Algal growth may be inhibited or stimulated by pollutants that affect nutrient relationships (Mohammad and Saminu, 2012). The mechanisms that affect the chemical state of a nutrient or its uptake and utilization of nutrient's physical and chemical conditions in water and algal species showed decrease in the phosphate concentration in the growth medium. The increase in copper concentration causes toxicity to *Chlamydomonas* sp. as measured by oxygen production and an increase in cell numbers (Meijer, 1972). Steeman-Nielsen *et al.* (1969) reported similar results and suggested that the toxic effect of copper could be due to binding to the cytoplasmic membrane, thus arresting cell division. Zarnowski (1972) demonstrated this to be true with iron and *Chlorella pyrenoidosa* and stated that phosphorus compounds cause oxidation and precipitation of iron from water. Sheih and Barber (1973) showed that mercury in low concentration (0.03 mM HgCl_2) as mercuric chloride stimulated the rate of potassium turnover in *C. pyrenoidosa* but did not affect the concentration of internal potassium. At higher concentrations (0.5 mM HgCl_2) mercury caused changes in permeability of the cell membrane that resulted in a net efflux of potassium. The stimulatory effect of low concentrations of heavy metals on algae is well known. DeFilippis and Pallaghy (1976) hypothesized that 1mM ZnCl_2 , 1 pM HgCl_2 , or 0.1 pM phenylmercuric acetate stimulated growth by preventing loss of carbon compounds from *Chlorella* sp. They suggested that heavy metals either interfere with production of glycollate or inhibit its secretory mechanism (Aneni and Hassan, 2003). Such actions by heavy metals are often related to ionic state. In sediments at low redox potential, Hg^{2+} is reduced to Hg^0 with the formation of dimethylmercury by methyl radical addition.

Organic mercurial compounds are sometimes more toxic than inorganic compounds. Harriss *et al.* (1970) showed that 0.1 ppb (pg/l) of methylmercury reduced photosynthesis (as ^{14}C uptake) and growth of the marine diatom *Nitzschia delicatissima*. However, dimethylmercury was less toxic; 1 ppb was required for an effect. The authors stated that the alga was sensitive to much lower concentrations of mercurial compounds than fishes. Davies and Gasse (1988) suggested that some algae detoxify mercury by reduction of Hg^{2+} to Hg^+ in the outer layers of the cell. Zingmark and Miller (1975) noted that net photosynthesis by *Amphidinium carteri* decreased to 92% by 100 ppb mercury. However, Hg^{2+} was reduced to HgO during the test. A very important aspect of uptake and toxicity of heavy metals to phytoplankton is the role of chelating agents. Plum and Lee (1973) showed that up to 20% of the iron content in a lake was associated with organic matter. Andren (1973) found that mercury in the water of three estuaries was associated with dissolved organic matter. Dissolved mercury was associated with dissolved organic matter of the humic and fulvic types. In a Norwegian lake, Benes *et al.* (1976) reported that sodium, calcium, aluminium, chromium, iron, zinc, manganese, mercury, and other elements were bound strongly to humus.

Perdue *et al.* (1976) described competition between metals for binding sites on dissolved organic matter as free colloidal particles of iron hydroxide, possibly associated with colloidal organic matter, and dissolved complexes of iron with naturally occurring organic substances, and that aluminium competes with iron for sites on molecules of dissolved organic matter. Hendrickson *et al.* (1974) demonstrated the high affinity of cadmium for dissolved organic matter from a lake in Wisconsin.

Formation of chelates implies that the amount of dissolved matter may, in some cases, regulate toxicity of metals because chelation decreases toxicity to a very great extent. Lomonosov (1969) showed that copper dichloride pyridinate inhibited growth of *Scenedesmus quadricauda* at 0.4 mg Cull. Copper chelates were much less toxic. Walsh *et al.* (1971) have found that when the marine unicellular alga *Dunaliella tertiolecta* is exposed to nickel in the presence of the chelator ethylenediaminetetraacetic acid (EDTA) its EC₅₀ was 9.1 ppm. When EDTA was excluded from growth media the EC₅₀ was 2.4 ppm.

The species that is most susceptible to the influence of pollution will be eliminated in competition with a species of lesser susceptibility. Dominance is determined by many factors and for any given species, may be related to temperature, salinity, irradiation and pollution among others. Mandelli (1969) reported that the growth of selected species of dinoflagellates and diatoms was inhibited by copper.

Walsh and Grow (1971) demonstrated a direct correlation between carbohydrate concentration in algal cells and concentration of urea herbicides in growth medium. If it is assumed that the coefficients of increase of different species are affected in different ways by pollutants in relation to environmental conditions, then changes in species composition of a community are to be expected. Hollister and Walsh (1973) reported the responses of 18 species of marine unicellular algae among four compounds that inhibit the Hill reaction. Bowes (1972) reported that DDT had no effect on growth of the marine alga *Dunaliella tertiolecta*, had slight effect on growth of *Cyclotella nana*, *Thalassiosira*

fluvilltilis, *Amphidinium carteri*, *Coccolithus huxleyi*, and *Porphyridium* sp., but caused a lag of nine days in growth of *Skeletonema costatum*.

Fisher *et al.* (1973) showed that estuarine clones of the algae *Thammsiosira pseudonana*, *Fragilarill pinnata*, and *Bellerochia* spp were more resistant to PCBs (polychlorinatedbiphenyls) than were oceanic clones. Dunstan *et al.* (1975) demonstrated effects of oil on marine phytoplankton and concluded that a significant effect of oil could be the stimulation of some species by aromatic compounds of low molecular weight, resulting in the alteration of natural phytoplankton community structure and its trophic relationships. These works suggest that, in mixed culture; the competitive exclusion principle of Gause (1934) would operate, causing species best adapted to the polluted condition to dominate.

Changes in structure of a marine algal community under stress from PCBs and DDT were demonstrated by Mosser *et al.* (1972) and Fisher *et al.* (1974). In untreated mixed cultures, *T. pseudonana* was dominant in number over *D. tertiolecta*. When treated with 1 ppb of PCBs or 10 ppb of DDT, the competitive success of *T. pseudonana* decreased while that of *D. tertiolecta* increased, even though the pollutant concentration had no effect on *T. pseudonana* in pure culture. Another important aspect of pollution is the fact that algae accumulate many compounds and heavy metals by absorption or by adsorption to the cell wall. In general, pollutants such as pesticides are not degraded to a large extent by algae. Butler *et al.* (1975) and are passed on to herbivores when eaten. Hollister *et al.* (1975) showed that four species of marine phytoplankton, when exposed to only 10 ppt (parts per trillion) of the insecticide mirex, concentrated it to over 100 ppb on cells.

Numerous other publications report uptake of pollutants by phytoplankton (Falchuk *et al.*, 1975; Stokes, 1975; DeFilippis and Pallaghy, 1976; Glooschenko and LoU, 1976). Uptake and accumulation of substances may prove to be the most important aspect of phytoplankton pollution dynamics. Since they are grazed upon by many animals, the phytoplankton may be a vital link in the transfer of pollutants from water to higher trophic levels, including man.

2.3.2 Zooplankton

Zooplankton comprises a very dynamic portion of the total plankton. There is greater species diversity among the zooplankton than phytoplankton, and composition varies strongly with seasonal production of meroplankton such as medusae, eggs, larvae, and juveniles of the benthos and nekton (Emongor *et al.*, 2005). Functionally, the zooplankton includes detritivores, herbivores, carnivores and omnivores, all of which excrete dissolved and particulate organic and inorganic materials that can serve as nutrients for saprovores, phytoplankton and coprovores. Organic and inorganic materials are lost from the water column when organisms die and settle to the bottom, where they enter geochemical cycles involving sediments (Anetor, 2003). Zooplankton population production is a function of the intrinsic rate of increase, natural mortality, mortality due to pollution, and rate of predation (Egborge and Fagade, 1999).

2.3.3 Effects of Pollution on Zooplankton

It is difficult to measure an effect of pollution on the rate of predation, but such an effect is theoretically probable. For example, if a compound such as chlorinated hydrocarbon insecticide was present, it could affect the efficiency of a prey arthropod in avoiding a

predatory fish. Since arthropods are generally more sensitive to the direct influence of such pollutants than fishes, their rates of population increase could be expected to decline because of increased predation and direct mortality due to insecticide (Imoobe and Adeyinka, 2010). Hansen (1974) studied the effect of 'Aroclor' 1254, a polychlorinated biphenyl (PCB), on settling of planktonic larvae (meroplankton). He used the composition of estuarine animal communities that developed while meroplankton was subjected to three concentrations of the pollutant for four months. Arthropods constituted over 75% of the organisms in untreated aquaria and aquaria that received 0.1 J/g/l of PCB. Two other aquaria that received 1.0 and 10 J/g/l were dominated by chordates, primarily tunicates. Just as important, however, is the fact that species diversity, as measured by the Shannon-Weaver index (Shannon and Weaver, 1963), was not affected, indicating that such an index cannot always measure pollution effects on planktonic larvae.

Conversely, temporal changes in zooplankton community composition may be modified if benthic and nektonic contributions to the meroplankton are affected by pollution. Numerous reports show that zooplanktonic species and meroplanktonic larvae are often much more sensitive to pollutants than adults (Ikomi and Anyanwu, 2010). Armstrong and Millemann (1974) showed that, for the mussel, *Mytilus edulis*, the developmental stage most sensitive to the insecticide 'Sevin' occurred shortly after fertilization, at the time of appearance of the first polar body and sensitivity decreased to insecticide.

CHAPTER THREE

3.0

MATERIALS AND METHODS

3.1 Study Area

River Romi is one of the tributaries of River Kaduna in Chikun Local Government Area. Kaduna Refinery and Petrochemical Company discharges its waste water into this river (River Romi). River Romi is located on latitude $10^{\circ}45'$ and longitude $7^{\circ}37'$ (Figure 3.1). The inhabitants of Angwan Romi village and its environs use water from River Romi to supplement their daily water demand (Emeaso, 2011).

3.2 Field Sampling Stations

Five sampling stations were chosen for the purpose of this study (Figure 3.1). Water samples and plankton samples were collected from five different selected sites along River Romi. The distance between one station and another was about 300 to 400m except the distance of station one from refinery outlet. Station 1 was 2m to the refinery outlet, station 2 was 400m away from station 1 and it was the meeting between refinery effluent and River Romi, stations 3, 4 and 5 were approximately 300 apart along the river course. Collection of samples was done twice a month from February to July, 2015.

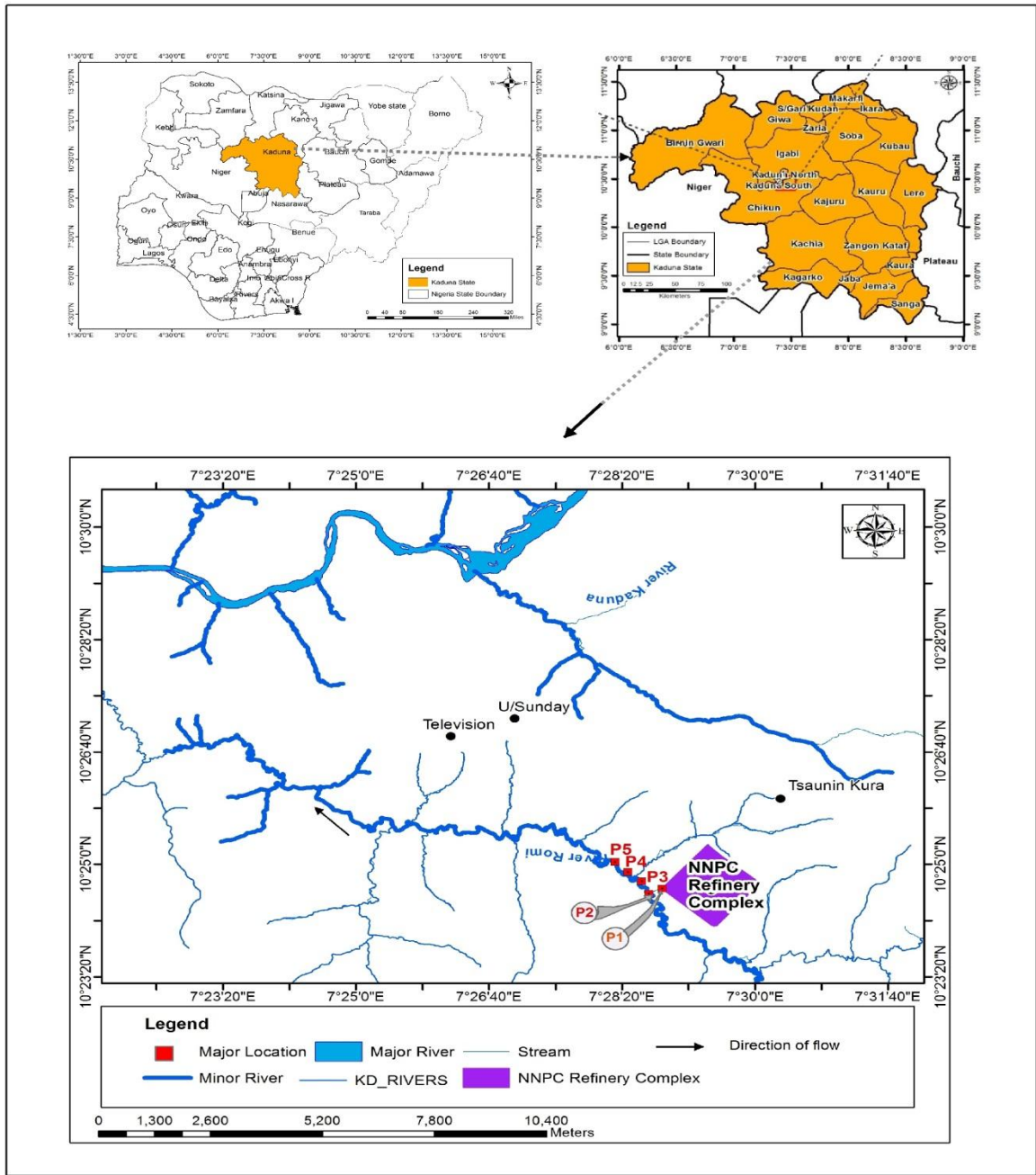


Figure 3.1: Kaduna Town showing NNPC Refinery Complex and Sampling Stations (ST1-ST5) along River Romi

3.2.1 Station1

Station 1 (ST1) is 2m away after Nigeria National Petroleum Corporation (NNPC) Refinery (Figure 3.2). It is a station in which waste water from Refinery empties into the concrete drainage system that flows into River Romi. Common features of the station include grasses, trees such as *Parkia biglobosa* providing shade to the station. An obvious bio-activity at station 1 is little calves roaming about within a Fulani settlement.

3.2.2 Station 2

This is a meeting station between Refinery drainage and the River Romi that is 400m away from the first sampling station (Figure 3.3). The area is covered by climbers: John's wort (*Hypericum tomentosum*), pea (*Melilotus alba*), tall grasses; Rock mountain maple (*Acer glabrum*), western juniper (*Juniperus occidentalis*) and the bottom is rocky. Water flows all day and throughout the year at this station. Human activity at this station is mainly watering of farm crops using pumping machine (irrigation) during dry season and continues with the farming activities during wet season. Herdsmen use the river as a source of water for their animals.



Figure 3.2: Station 1 of the Sampling Station



Figure 3.3: Station 2 of the Sampling Station

3.2.3 Station 3

Station 3 is down the River Romi and it is about 400m away from station 2. The station is also characterized by climbers; pea (*Melilotusalba*), covering the station half-way, grasses; Rock mountain maple (*Acer glabrum*), and some tree species; desert parsley (*Lomatium dissectum*), mountain alder (*Alnus incana*) (Figure 3.4). Irrigation farming was the common human activity seen around this station. Garden egg, sugar cane, okra, pepper among others were crops that were farmed at this station.

3.2.4 Station 4

At this station, the water level of the River has increased to the brim. It is characterized by tall grasses; elephant grass (*Aegilops cylindrical*) some macrophytes such as *Melilotusalba* floating on the surface of the water. It is about 400m away from station 3 (Figure 3.5). This station is mostly predominated by activities such as loading the sand into trucks that has been gathered by mainly women and young male children from the nearby village.

3.2.5 Station 5

The width and depth of the water in River Romi has increased as the tributaries increase (Figure 3.6). The station is muddy and is also 400m away from station 4; some species of big trees; desert parsley (*Lomatium dissectum*), mountain alder (*Alnus incana*) also covered the station half-way. The station is characterized by irrigation activities where farmers used the water during drying season. The most common farm produced here include: Garden egg (*Solanum macrocarpon*), Sugarcane (*Saccharum officinarum*), maize (*Zea mays*), okra (*Abelmoschus esculentus*), yam (*Deioscorea rotundata*) among others.



Figure 3.4: Station 3 of the Sampling Station



Figure 3.5: Station 4 of the Sampling Station



Figure 3.6: Station 5 of the Sampling Station

3.3 Determination of Physicochemical Parameters

The physicochemical parameters of River Romi that were taken on the field include; surface water temperature, pH, Total Dissolved Solids (TDS) and Electrical Conductivity (EC) using HANNA instrument (model: HI9932). Water samples were taken to the Hydrobiology Unit of Department of Biological Sciences for further analysis.

3.4 Laboratory Analyses of Water Samples

All water samples were analyzed for levels of pH, temperature, Total Dissolved Solids (TDS), Electrical Conductivity (EC), Biochemical oxygen demand (BOD), Chemical Oxygen Demand (COD), Dissolved Oxygen (DO), Phosphates, Nitrates, Sulphates, Total phosphorous, Total nitrogen, alkalinity, Hardness, and oil and grease.

The pH, TDS, EC and temperature were determined using HANNA Instrument microprocessor conductivity meter (model HI98129) at the station of sample collection. Physicochemical properties such as Nitrates, Phosphate and Sulphates were determined with the aid of an HACH DR/5000 spectrophotometer. Other parameters such as Biochemical Oxygen Demand and Chemical Oxygen Demand were determined using the following procedures given by the American Society for Testing and Materials (ASTM, 1995). Heavy metal samples were digested using Nitric acid in Hydrobiology Laboratory, Department of Biological Sciences, A. B. U., Zaria. It was further analysed to determine some selected heavy metals (Pb, Mn, Cr, Ni and Zn) using Atomic Absorption Spectrometry (AAS) at the Multipurpose Research Laboratory, Department of Chemistry, ABU, Zaria.

3.4.1 Temperature

Temperature of the water at each sampling station was measured in degree centigrade (°C). It was determined by dipping a Hanna instrument model HI98129 into the water for at least 1-2 minutes, the reading was recorded after stabilizing (APHA, 2005).

3.4.2 pH

The pH was determined using a pH meter (HANNA combo pH/EC meter HI 98129). The meter was calibrated using two buffers (pH 7 and 10) according to the manufacturer's directions. The pH was taken directly from the meter by dipping the HANNA instrument into water at each sampling station.

3.4.3 Total dissolved Solids

Total Dissolved Solids (TDS) of the water measured in milligramme per litre (mg/L) was also determined by dipping a HANNA instrument (model HI98129) into the water at each sampling station for some minutes (at least 1-2 minutes). The reading was taken immediately.

3.4.4 Electrical Conductivity (EC)

The electrical conductivity was determined using (Hanna combo pH/EC meter HI 98129) by placing a conductivity probe into the water at every sampling station. The electrical conductance obtained in micro second per centimetre ($\mu\text{s}/\text{cm}$) was recorded directly from the meter after 3 minutes.

3.4.5 Hardness

Twenty-five (25) ml of the water sample was measured and 25ml of distilled water was added. Then 2ml of buffer solution of pH 10.4 was added, followed by 0.1g of

eriochrome black T dye and titrated with EDTA (0.01M). The titre values were multiplied by 40 as $\text{CaCO}_3 \text{ L}^{-1}$. Hardness is measured in milligramme per litre (mg/L).

3.4.6 Alkalinity

Fifty millilitre (50 ml) of water sample was measured into clean conical flask. Two (2) drops of methyl orange were added. It was shaken vigorously and titrated with 0.02M H_2SO_4 until the colour change from yellow to orange. Alkalinity is measured in milligramme per litre (mg/L).

Where,

V_T (ml) = Volume of acid used for titration,

M = Molarity of the acid.

$$\text{Total Alkalinity as mg/l CaCO}_3 = \frac{V_T \times M \times 100,000}{\text{volume of sample}}$$

3.4.7 Nitrate

Cadmium reduction method was used to analyze samples of nitrate (NO_3^-) content. Cadmium metal reduces nitrates in the sample to nitrites. Nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt. The salt complex with gentisic acid to form amber coloured solution. Test result was measured at 430nm using HACH DR 2400 spectrophotometer (APHA, 2005). Nitrate is measured in milligramme per litre (mg/L).

3.4.8 Total nitrogen

One hundred milliliter (100 ml) of water sample from each sampling station was poured into a dry metallic crucible and kept in an oven at 100°C till dryness. It was removed and allowed to cool after which 2ml of phenol disulphonic acid was added and swirled round

uniformly in the crucible and left to stand for 10 minutes. Ten(10) ml of distilled water was added, followed by 5ml of strong ammonia solution, then allowed to cool. Change in graduation was taken at 430nm wavelength. Total nitrogen is measured in milligramme per litre (mg/L).

3.4.9 Phosphate

One hundred (100) ml of water sample was transferred into a conical flask, 1ml of ammonium molybdate reagent and 1 drop of stannous chloride was added and allowed to stand for 12 minutes. The colour changes were determined at 600nm. Phosphate is measured in milligramme per litre (mg/L).

3.4.10 Sulphate

Five series of standard solutions with concentration that ranged from 1-5mg/L were prepared and analysed with water samples (measured in mg/L). To each 10ml of standard, 1ml of BaCl₂ gelatin was added. The mixtures were allowed to stand for 45 minutes. The respective absorbance of the solutions at 420nm was determined. A blank without sample was prepared and read at the same wavelength (APHA, 2005).

3.4.11 Determination of Dissolved Oxygen and Biological Oxygen Demand (BOD)

- i. Preparation of diluents water (aerated water): Distilled water was placed into a Winchester bottle and aerated for 1 hour then followed by addition of 1ml of each of the following solutions: Phosphate buffer solution, Magnesium sulphate solution, Calcium chloride solution and Ferric chloride solution. The aerated water was used for the determination of dissolved oxygen (mg/L) before incubation.

- ii. Dissolved Oxygen before incubation: The BOD–bottle was half filled with the aerated water; 2mls of the water sample was added and made up to the mark with aerated water. Also 2mls of Manganous sulphate, 2mls of alkaline iodide-sodium azide solution were added simultaneously well below the surface of the liquid. The stopper of the bottle was then replaced to exclude air bubbles and the solution mixed by inverting the bottle several times. After achieving a clear solution, 2mls of conc. Sulphuric acid was added and mixed with the solution (ASTM, 1995).
- iv. Dissolved Oxygen (DO) after incubation: Half of the aerated water was placed into BOD bottle and 2mls of the sample was added made up to the brim with the aerated water. The cap of the bottle was replaced without leaving air bubbles and stored in the thermostatic chamber (incubator) at controlled temperature of 20°C for 5 days.
- v. Procedure for the analysis (titrimetric method): A 50ml burette was filled with 0.025N Sodium thiosulphate solution and titrated against 200ml of the sample, until a colour change of golden yellow to pale yellow was obtained. Then 2mls of starch indicator were added and the titration process continued until the colour changed from blue to colourless. The same process was repeated for the incubated samples.
- vi. Calculation of the result for Biological Oxygen Demand

One ml of 0.025N of Sodium thiosulphate is equivalent to 0.2mg of oxygen

DO in parts per million (ppm) was calculated as:

$$DO = T \times 0.2 \times 1000/V$$

$$BOD \text{ in ppm} = (D1-D2) \times T/V$$

Where,

T = Titre Value of 0.025N Sodium thiosulphate required for titration of sample.

V = volume of sample

D1 = Dissolved OSxygen of diluted water sample before incubation.

D2= Dissolved Oxygen of diluted water after incubation

3.4.12 Determination of Chemical Oxygen Demand

i. Procedure for the analysis of Chemical Oxygen Demand (COD) measure in mg/L:

50ml of distilled water was measured into a reflux flask as blank. Ten millilitre of the sample was measured into a reflux flask and made up to 50ml with distilled water. The reflux flask was kept in an ice bath. One gramme Mercuric sulphate was added with 5mls of Sulphuric acid and many boiling stones were then placed in each of the flask. 25mls of 0.25N Potassium dichromate was added to the sample and the blank. These were refluxed for 2hrs. The 300ml of distilled water was then added to each flask and allowed to cool to room temperature. Ten drops of Phenolphthalein indicator were added and titrated with 0.25N ferrous ammonium solution to a colour change of bluish green till reddish colour was obtained at end station (ASTM, 1995).

ii. Calculation of COD:

The COD in the sample was calculated in milligrams per liter as follows;

$$\text{COD mg/I} = (A-B) \times N \times 8000/S$$

Where, A=Ferrous ammonium sulphate required for titration of blank solution.

B=Ferrous ammonium sulphate solution required for the titration of sample

N = normality of the Ferrous ammonium solution

S = Volume (ml) of sample used for test.

3.4.13 Determination of Oil and Grease

Oil and grease was determined using the following procedure:

One hundred millilitre (100ml) of water sample was measured into separating funnel. It was followed by the addition of 5ml of concentrated H_2SO_4 . The mixture was agitated for 2 minutes and allowed the water to drain off. Two hundred millilitre (20ml) of petroleum ether was added to the solution and agitated for 3min. It was placed in a water bath and allowed to evaporate to dryness. Further elimination of water in the sample was done by placing it in an oven for 30 minutes. It was then transferred to a desiccator and allowed to cool; the weight of sample was measured.

3.5 Determination of Heavy Metals

Water samples previously acid-treated with a 1:3:1 mixture of Hydrogen tetroxochlorate acid (HClO_4), Nitric acid (HNO_3) and sulphuric acid (H_2SO_4) pre-concentrated were used to determine selected cations in water. Serially diluted mixed standard solutions containing 1.00mg of the metal ion in 1 ml of the solution were prepared by pipetting volumes of commercially purchased stock solutions (BDH Chemicals), into a single 250ml standard flask. The concentrations of each metal ion, such as; Lead(Pb), Manganese(Mn), Chromium(Cr), Nickel (Ni), and Zinc(Zn) were

read against the standards on a Buck Scientific model 200A Atomic Absorption Spectrophotometer (AAS) Model 200A equipped with air-acetylene.

3.6 Plankton Sampling

Planktons were collected using hand trawling method. This involved trawling horizontally 55 µm mesh size plankton net for 2 minutes for a distance of 1 meter in the littoral zone (i.e. at the shore). The net content of the plankton net was emptied into a 120ml plastic bottle, containing 4% formalin and Lugol solution. The sample was then taken to the Laboratory for identification and enumeration of phytoplanktons and zooplanktons.

A drop of water sample was placed onto the glass slide and covered with cover slip. The sample was viewed under the binocular microscope for identification and enumeration. The numbers of planktons were enumerated by counting the same species encountered per slide. Planktons were identified at magnifications of x10, x40 and x100 using keys by Perry (2003). Enumeration of plankton was carried out following the drop count method (counting same species per slide) and was reported as units or organisms per drop. The identification of plankton was carried out by the use of keys and identification guides as described by Palmer (1969), Sournia (1978), and, Verlencar and Desai (2004).

3.7 Data Analyses

Data generated were analysed using Analysis of Variance (ANOVA) to compare the differences between means of physicochemical parameters and heavy metals using SPSS version 20. Duncan Multiple Range Test was used to separate means that differed.

Pearson correlation analysis was used to establish the relationship between physicochemical parameters as well as species number in the sampling stations. Principal Component Analysis (PCA) was used to establish the relationship between physicochemical parameters. Canonical Correspondence Analysis (CCA) was used to find the relationship between physicochemical parameters and planktons. All data analyses were tested at 0.05 level of significant.

CHAPTER FOUR

4.0

RESULTS

4.1 Monthly Variation of Physicochemical Parameters of River Romi, 2015

The monthly variation in physicochemical parameters of River Romi is shown in Figure 4.1-4.4. There was significant difference in all the physicochemical parameters in sampling months except sulphate. Temperature ($^{\circ}\text{C}$) was significantly highest ($p < 0.05$) in the month of April (31.91); February (30.97) and March (30.66) did not differ significantly ($p < 0.05$) but were significantly higher than May (29.84), June (29.00) and July (27.50) (Figure 4.1). The pH in the months of April (8.87) and May (8.80) did not differ significantly ($p > 0.05$) but were significantly higher than pH in the months of February (8.38), March (8.13), July (7.97) and June (29.00). Total dissolved solids (mg/L) differed significantly among the months of February (282.77), March (117.80) and April (217.73); on the contrary, May (70.10), June (59.63) and July (56.23) did not differ significantly (Figure 4.2). Similar trend was observed in the level of EC ($\mu\text{S}/\text{cm}$), February (664.54), March (354.57), and April (417.17) differ significantly; while May (139.07), June (117.50) and July (113.30) did not show significant decrease in EC level (Figure 4.1). The concentration of DO (mg/L) February (5.77) was significantly highest; there was no significant different between March (5.00) and June (4.93); similarly, April (2.70) and July (3.72) did show significant variation (Figure 4.2). Month of July (3.06) had the highest BOD (mg/L), while March (1.51) and April (1.34) had the least (Figure 4.2). There was no significant different in COD (mg/L) between June (437.30) and February (438.97); similarly, COD in April (417.00) and July (427.33) did not differ significantly (Figure 4.2).

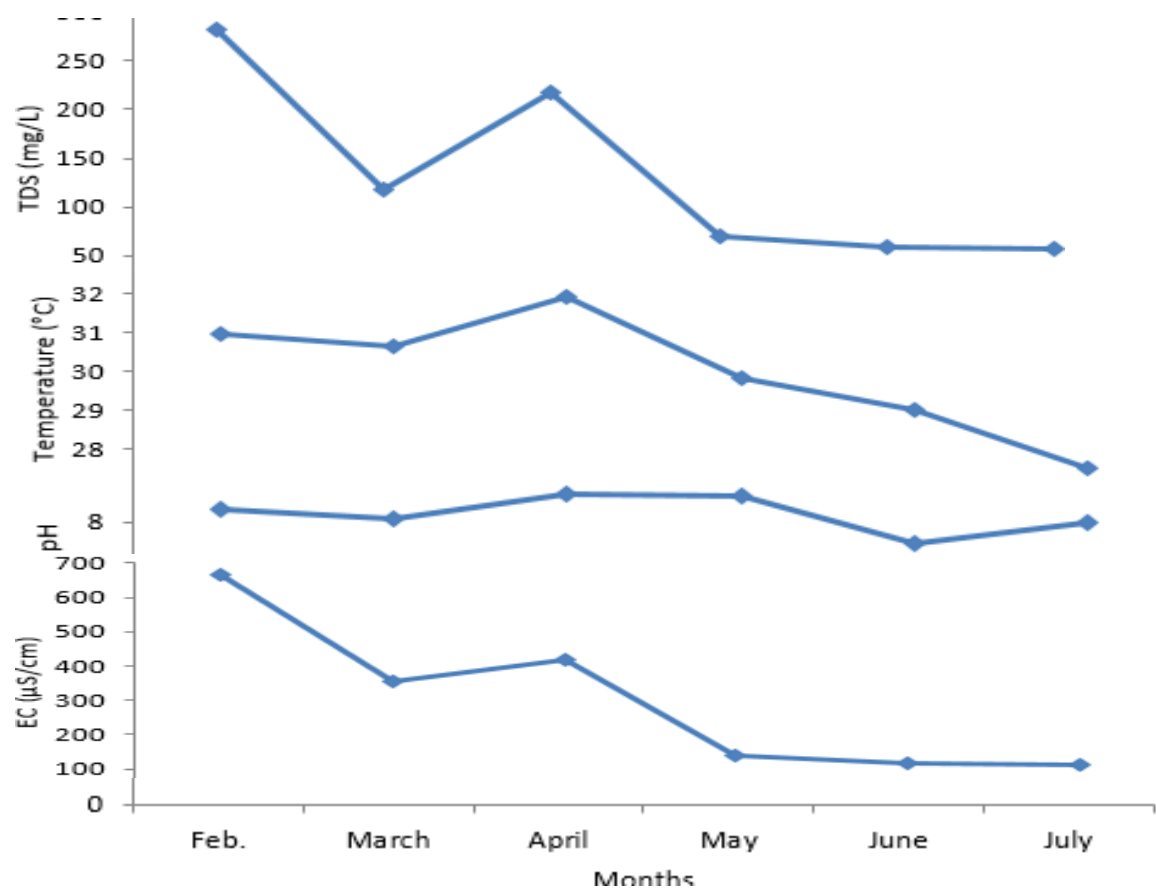


Figure 4.1: The Mean monthly variation of TDS, temperature, pH and EC of River Romi (2015)

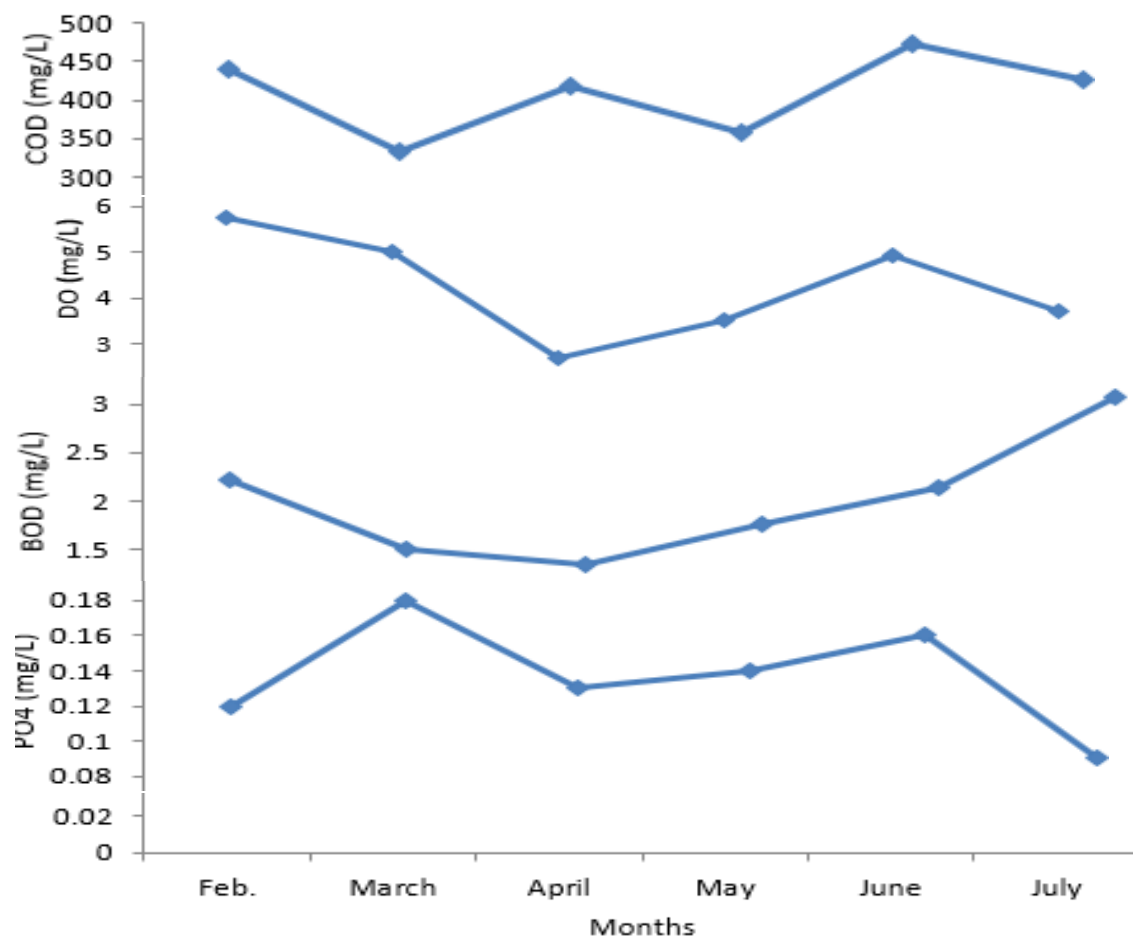


Figure 4.2: The Mean monthly variation of COD, DO, BOD and PO₄ of River Romi (2015)

Phosphate (mg/L) concentration was significantly highest in March (0.18) but was comparable to April (0.13), May (0.14), June (0.16), while July had the least PO₄ level (Figure 4.2). There was no significant different in NO₃ (mg/L) concentration among the months of February (2.33), May (2.35), June (2.44) and April (2.30) but were significantly higher than March (2.12) and July (2.13). There was no significant difference in SO₄ level among the sampling months (Figure 4.3). Total phosphorous (mg/L) did not differ significantly ($p < 0.05$) in the months of May (2.01) and June (3.02); similarly, February (1.10), March (1.06) and April (1.31) did not exhibit significant different. There was no significant difference in total nitrogen (mg/L) in February (22.36), March (20.36), May (21.36), June (20.89) and July (20.68), while April (17.28) had the least. There was no significant variation in hardness between May (210.10) and June (209.50) but were significantly higher than February (177.40) (Figure 4.3); hardness in March (144.60), April (148.60) and July (141.00) did not differ significantly. There was no significant reduction in alkalinity (mg/L) level from February (131.23) to March (128.50) but decreased significantly in April (86.70), May (71.43), June (49.77) and July (43.20) (Figure 4.4). Oil and grease (mg/L) was significantly highest in March (128.25), while February (0.39), April (0.23), May (0.23), June (0.04) and July (0.18) did not differ significantly (Figure 4.4).

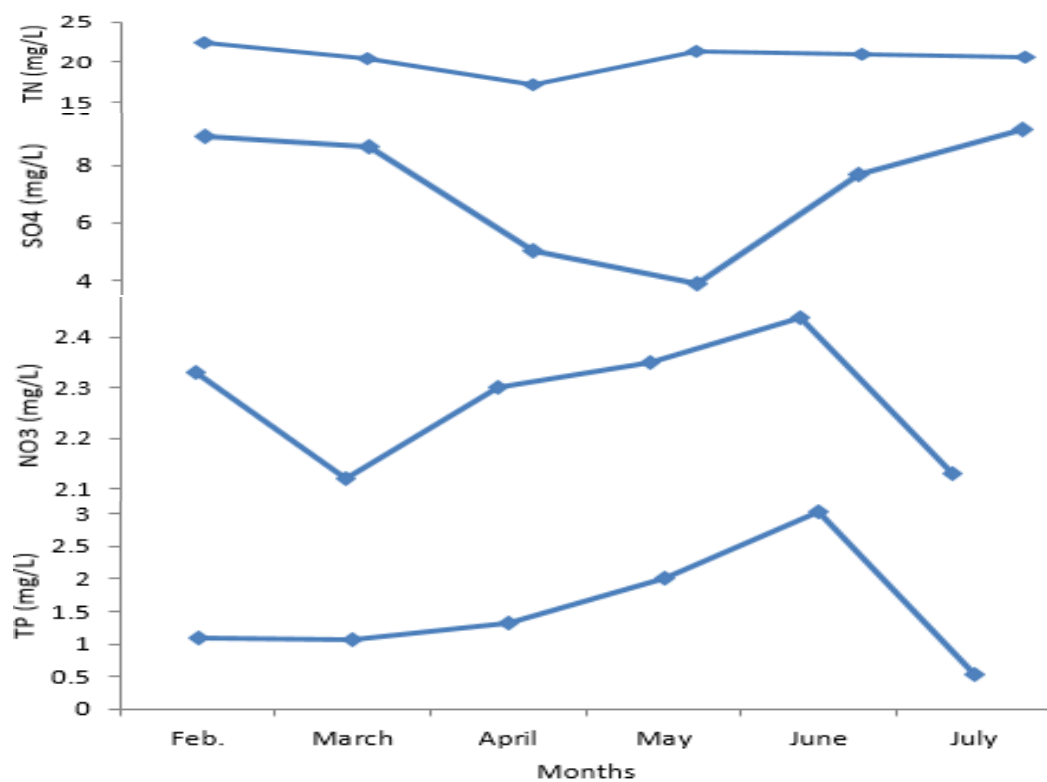


Figure 4.3: The Mean monthly variation of total nitrogen (TN), sulphate, nitrate and total phosphorous of River Romi (2015)

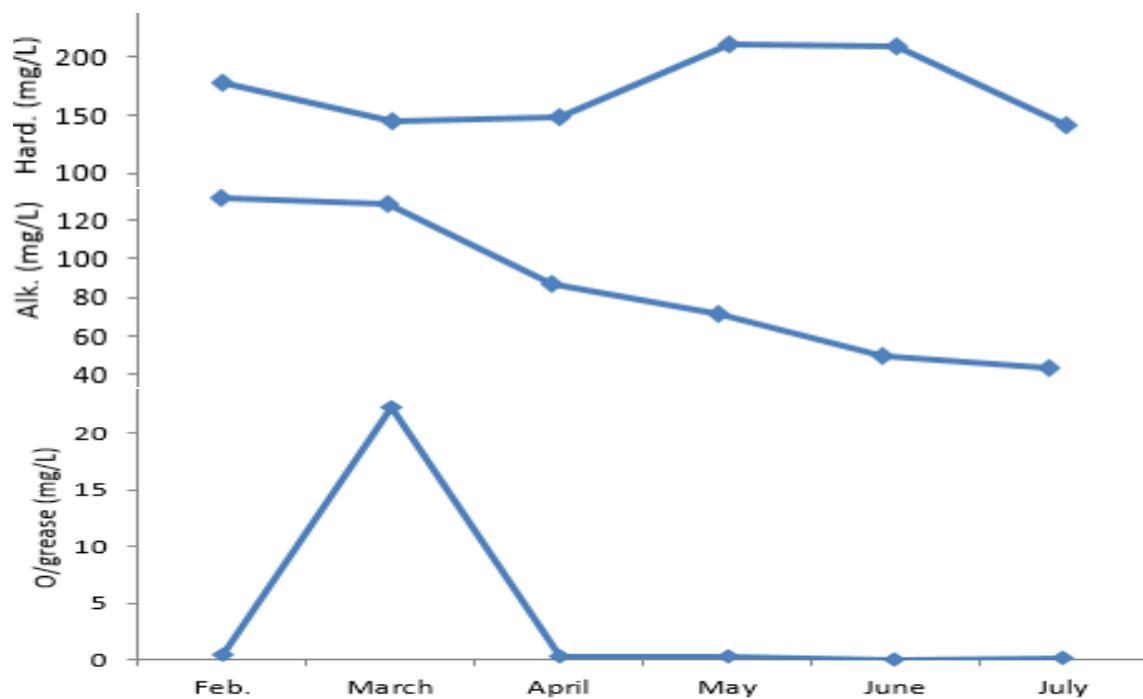


Figure 4.4: The Mean monthly variation of hardness, alkalinity and oil and grease of River Romi (2015)

4.2 Physicochemical Parameters across Sampling Stations for February to July, 2015

The results of physicochemical parameters from the month of February to July are shown in Table 4.1. There was significant ($p \leq 0.05$) difference in temperature across the stations which ranged from 29.00°C at ST2 to 31.98°C at ST1. There was no significant ($p > 0.05$) difference between ST1 (31.98°C) and ST3 (31.65°C) as well as ST4 (30.27°C) but they differed from ST5 (31.07°C) and ST2 (29.00°C). In the same way, ST4 and ST5 did not differ significantly ($p > 0.05$); also the temperature at ST5 and ST2 did not differ from each other. The pH of the sampling stations ranged from 7.80 at ST4 to 8.98 at ST3. There was no significant ($p > 0.05$) difference in pH at stations ST2 (8.81), ST3 (8.89); but pH values differed significantly from ST1 (7.91) to ST4 (7.80). While, ST5 (8.41) was comparable to both groups. The TDS level did not differ significantly ($p > 0.05$) between ST1 (306.00mg/L) and ST2 (307.83mg/L); but differed from ST3 (266.00mg/L) and ST4 (257.00mg/L). Electrical conductivity did not differ significantly ($p > 0.05$) across all the stations except at ST5 (611.33 μ S/cm) (Table 4.1). Dissolved Oxygen (DO) did not differ significantly ($p > 0.05$) across all the sampling stations. Biological Oxygen Demand (BOD) at ST1 (2.55mg/L) was significantly ($p > 0.05$) higher than the other stations. In the same vein, Chemical Oxygen Demand (COD) was significantly highest at ST1 (465.00). There was no significant difference in COD between ST2 (440.00mg/L) and ST3 (441.00mg/L) but differed from ST4 (431.00mg/L) and ST5 (417.17mg/L). The level of phosphate across the stations were slightly more in ST4 (0.13mg/L) and P (0.14mg/L) than the others. Parameters such as Phosphate, Sulphate as well oil and grease did not differ significantly ($p > 0.05$) within the sampling stations for the month of March.

Table 4.1: Physicochemical values of River Romi in February, 2015

Parameters	ST1 (Mean±SE)	ST2	ST3	ST4	ST5	Average
Temp.	31.98 ^a ±0.06	29.00 ^c ±0.06	31.65 ^a ±0.69	30.27 ^{ab} ±0.29	31.07 ^{bc} ±0.35	30.97±0.21
pH	7.91 ^b ±0.19	8.81 ^a ±0.27	8.98 ^a ±0.38	7.80 ^b ±0.08	8.41 ^{ab} ±0.14	8.38±0.13
EC	696.33 ^a ±2.88	665.50 ^a ±20.95	680.00 ^a ±10.36	669.67 ^a ±8.61	611.33 ^b ±18.23	664.57±7.84
TDS	306.00 ^a ±1.52	307.83 ^a ±11.10	266.00 ^b ±19.85	257.00 ^b ±8.81	277.00 ^{ab} ±12.85	282.77±6.41
DO	5.38 ^a ±0.53	6.18 ^a ±0.40	5.45 ^a ±0.61	5.73 ^a ±0.21	6.12 ^a ±0.37	5.77±0.19
BOD	2.55 ^a ±0.06	2.34 ^{ab} ±0.12	2.03 ^c ±0.12	2.18 ^{bc} ±0.05	1.99 ^c ±0.12	2.22±0.06
COD	465.00 ^a ±4.28	440.00 ^b ±6.83	441.67 ^b ±5.43	431.00 ^{bc} ±1.00	417.17 ^c ±8.21	438.97±3.75
Phosphate	0.11 ^{bc} ±0.02	0.13 ^{ab} ±0.03	0.11 ^{bc} ±0.01	0.10 ^c ±0.01	0.14 ^a ±0.02	0.12±0.23
Nitrate	2.25 ^b ±0.04	2.36 ^b ±0.05	2.76 ^a ±0.04	1.93 ^c ±0.02	2.35 ^b ±0.16	2.33±0.06
Sulphate	9.47 ^{ab} ±0.43	9.17 ^{ab} ±0.21	9.67 ^a ±0.72	8.39 ^b ±0.11	8.43 ^{ab} ±0.12	9.03±0.19
TP	0.95 ^b ±0.03	0.92 ^b ±0.04	0.92 ^b ±0.02	0.92 ^b ±0.09	1.78 ^a ±0.19	1.10±0.07
TN	20.97 ^c ±0.50	23.64 ^b ±0.59	19.39 ^d ±0.04	20.60 ^c ±0.07	27.22 ^a ±0.17	22.36±0.54
Hardness	168.33 ^a ±7.15	185.83 ^a ±10.21	165.67 ^a ±3.97	178.00 ^a ±10.20	189.17 ^a ±2.86	177.40±3.57
Alkalinity	153.33 ^a ±21.41	126.50 ^a ±3.90	123.50 ^a ±2.61	125.17 ^a ±3.19	127.67 ^a ±2.51	131.23±4.63
Oil and grease	0.27 ^b ±0.08	0.07 ^b ±0.04	0.45 ^{ab} ±0.15	0.42 ^{ab} ±0.20	0.72 ^a ±0.14	0.39 ±0.07

Key:

Temp. = Temperature, TDS = Total Dissolved Solids, EC = Electrical Conductivity, DO = Dissolved Oxygen, BOD = Biological Oxygen Demand, COD = Chemical Oxygen Demand, TP = Total phosphorous, TN = Total nitrogen.

The nitrate level was significantly ($p \leq 0.05$ mg/L) higher at ST3 (2.76mg/L); while ST1 (2.25mg/L), ST2 (2.36mg/L) and ST5 (2.35mg/L) did not differ significantly ($p > 0.05$) but differed from ST4 (1.93mg/L). Sulphate was slightly more in ST3 (9.67mg/L) compared to other stations but differed significantly ($p \leq 0.05$) from ST4 (8.39mg/L). Total Phosphorous (TP) at ST5 (1.78mg/L) was the only station that showed significant ($p \leq 0.05$) difference. The Total Nitrogen (TN) across the sampling stations differed significantly ($p \leq 0.05$) in this increasing order ST5: (27.22mg/L) > ST2 (23.64mg/L) > ST1 (20.97mg/L) > ST3 (19.36mg/L). Hardness and alkalinity did not differ significantly ($p > 0.05$) across all the sampling stations. The level of oil and grease increased slightly among the sampling stations with ST5 (0.72mg/L) significantly ($P \leq 0.05$) higher than ST1 (0.27mg/L) and ST2 (0.07mg/L) (Table 4.1).

Table 4.2 shows the physicochemical parameters of River Romi, Kaduna State for the month of March. Temperature, pH and Electrical conductivity did not differ significantly ($p > 0.05$) across all the sampling stations of the river. Dissolved oxygen varied slightly within the sampling stations with ST2 (4.17mg/L) having the least and the highest was 5.95mg/L at ST3. The DO did not differ significantly ($P > 0.05$) across the sampling stations except at ST2 and ST3. Biological Oxygen Demand differed significantly ($p \leq 0.05$) across all the sampling stations in this order: ST1 (2.00mg/L) > ST3 (1.60mg/L) > ST5 (1.45mg/L) > ST2 (1.27mg/L) > ST4 (1.22mg/L). The COD did not differ significantly ($p > 0.05$) from one station to another; ST5 (371.67mg/L) from ST1 (325.83mg/L), ST2 (342.50mg/L) and ST4 (326.67mg/L) except at ST3 (300.00mg/L).

Table 4.2: Physicochemical values of River Romi in March, 2015

Parameters	Station 1	Station 2	Station 3	Station 4	Station 5	Average
Temperature	31.56 ^a ±0.77	30.82 ^a ±0.69	30.82 ^a ±0.72	30.78 ^a ±0.69	29.33 ^a ±1.13	30.66±0.37
PH	8.18 ^a ±0.43	8.25 ^a ±0.41	8.07 ^a ±0.39	8.06 ^a ±0.40	8.08 ^a ±0.38	8.13±0.17
EC	400.67 ^a ±96.31	355.17 ^a ±76.41	338.33 ^a ±69.17	336.00 ^a ±67.41	342.33 ^a ±69.05	354.57±32.05
TDS	200.50 ^a ±47.94	177.83 ^a ±39.01	171.83 ^a ±35.72	169.50 ^a ±33.71	169.33 ^a ±34.37	177.80±16.14
DO	4.78 ^{ab} ±0.20	4.17 ^b ±0.61	5.95 ^a ±0.77	5.04 ^{ab} ±0.32	5.08 ^{ab} ±0.34	5.00±0.23
BOD	2.00 ^a ±0.06	1.27 ^{cd} ±0.09	1.60 ^b ±0.06	1.22 ^d ±0.06	1.45 ^{bc} ±0.09	1.51±0.06
COD	325.83 ^{ab} ±5.23	342.50 ^{ab} ±17.12	300.00 ^b ±13.17	326.67 ^{ab} ±25.78	371.67 ^a ±10.22	333.33±7.91
Phosphate	0.10 ^a ±0.00	0.10 ^a ±0.00	0.26 ^a ±0.15	0.26 ^a ±0.15	0.18 ^a ±0.01	0.18±0.04
Nitrate	2.18 ^{ab} ±0.09	2.07 ^{ab} ±0.11	2.19 ^{ab} ±0.08	1.75 ^b ±0.37	2.40 ^a ±0.11	2.12±0.09
Sulphate	8.98 ^a ±0.16	8.38 ^a ±0.13	8.51 ^a ±0.10	8.97 ^a ±0.37	8.40 ^a ±0.11	8.65±0.10
T/phosphate	0.92 ^b ±0.03	0.95 ^b ±0.02	0.83 ^b ±0.05	0.95 ^b ±0.2	1.63 ^a ±0.07	1.06±0.06
T/nitrate	19.66 ^b ±0.23	19.50 ^b ±0.26	20.01 ^b ±0.13	20.21 ^b ±0.30	22.41 ^a ±0.25	20.36±0.22
Hardness	128.83 ^c ±3.21	139.50 ^{bc} ±2.78	132.33 ^{bc} ±2.60	141.50 ^b ±4.24	180.00 ^a ±4.34	144.60±3.77
Alkalinity	140.83 ^a ±4.65	127.33 ^{bc} ±4.19	122.00 ^c ±3.06	135.17 ^{ab} ±1.96	117.17 ^a ±4.21	128.50±2.23
Oil and grease	23.75 ^a ±10.44	21.87 ^a ±9.78	21.52 ^a ±9.40	19.18 ^a ±8.74	24.91 ^a ±11.04	22.25±4.13

Key:

Temp. = Temperature, TDS = Total Dissolved Solids, EC = Electrical Conductivity, DO = Dissolved Oxygen, BOD = Biological Oxygen Demand, COD = Chemical Oxygen Demand, TP = Total phosphorous, TN = Total nitrogen.

There was no significant difference between nitrogen content of ST1 (2.18) and ST5 (2.40); also it did not differ significantly between ST2 (2.07) and ST3 (2.19) except at ST4 (1.75) which was significantly ($p \leq 0.05$) lower than the other stations. Total phosphorous in station 5 (1.63) was significantly ($p \leq 0.05$) higher than all the other sampling stations (ST1-0.92, ST2-0.95, ST3-0.83 and ST4-0.95). Similarly, Total Nitrogen (TN) showed significant ($p \leq 0.05$) level of increase at ST5 (22.41), while sampling stations 4, 3, 2 and 1 did not differ significantly. The hardness of water was significantly ($p \leq 0.05$) highest at ST5 (180.00); while ST4 (141.50) did not differ from ST2 (139.50) and ST3 (132.33) but differed significantly ($p \leq 0.05$) from ST1 (128.83) which did not differ from the last two stations. The alkalinity contents of ST4 (135.17) and ST1 (140.83) were similar ($p > 0.05$); likewise those of ST3 (122.00) and ST5 (117.17).

The physicochemical indices of River Romi for the month of April are shown in Table 4.3. Some physicochemical parameters of the river did not vary significantly ($p > 0.05$) across the sampling stations, while others varied. Parameters such as Temperature, total dissolved Solids, electrical conductivity, dissolved oxygen, chemical oxygen demand, phosphate, nitrate, sulphate, total nitrogen, hardness and alkalinity did not differ significantly ($p > 0.05$) across the sampling stations even though there was slight increase in concentration for each afore-mentioned parameter. The pH at ST1 (8.85), ST2 (9.16), ST3 (9.06) and ST4 (8.91) did not differ significantly ($p > 0.05$) from each other but they were significantly ($p \leq 0.05$) higher than ST5 (8.33).

Table 4.3: Physicochemical Values of River Romi in April, 2015

Parameters	Station 1	Station 2	Station 3	Station 4	Station 5	Average
Temperature	31.95a±0.10	32.30a±0.29	31.91a±0.45	32.20a±0.28	31.20a±0.73	31.91±0.19
PH	8.85a±0.20	9.16a±0.06	9.09a±0.03	8.91a±0.15	8.33b±0.18	8.87±0.08
EC	401.50a±23.19	424.00a±18.41	431.17a±19.07	427.50a±29.90	401.17a±5.31	417.17±8.13
TDS	200.33a±8.26	212.00a±10.21	214.83a±10.60	231.50a±21.20	230.00a±20.62	217.73±6.69
DO	3.40a±0.42	2.45bc±0.16	3.18ab±0.43	2.06c±0.10	2.38bc±0.14	2.70±0.15
BOD	1.68ab±0.10	0.96c±0.14	1.80a±0.41	1.08bc±0.08	1.18bc±0.08	1.34±0.11
COD	425.00a±17.65	405.00a±11.76	423.33a±14.53	431.67a±13.27	400.00a±7.30	417.00±5.99
Phosphate	0.13a±0.01	0.13a±0.01	0.13a±0.01	0.14a±0.04	0.14a±0.02	0.14±0.05
Nitrate	2.14a±0.09	2.14a±0.09	2.34a±0.19	2.41a±0.06	2.47a±0.16	2.30±0.06
Sulphate	5.96a±0.15	5.92a±0.93	5.52a±0.16	1.38b±0.17	6.21a±0.78	5.00±0.41
TP	0.77b±0.16	0.85b±0.14	0.80b±0.17	3.21a±0.84	0.90b±0.19	1.31±0.24
T/nitrate	17.87a±3.41	15.90a±2.65	17.49a±4.07	15.53a±2.78	19.62a±3.77	17.28±1.43
Hardness	143.33a±9.81	144.67a±6.48	135.00a±7.57	161.00a±9.74	159.00a±6.98	148.60±3.88
Alkalinity	84.50a±18.56	109.50a±14.43	84.17a±15.42	73.00a±9.14	82.33a±11.21	86.70±6.29
Oil and grease	0.33 ^a ±0.09	0.00b±0.00	0.42a±0.07	0.42a±0.00	0.42a±0.06	0.23±0.04

Key:

Temp. = Temperature, TDS = Total Dissolved Solids, EC = Electrical Conductivity, DO = Dissolved Oxygen, BOD = Biological Oxygen Demand, COD = Chemical Oxygen Demand, TP = Total phosphorous, TN = Total nitrogen.

On the other hand, ST2 (2.45) differed significantly from there two groups. Biological oxygen demand varied significantly from ST3 (1.80) to ST2 (0.96) and ST1 (1.68). The

BOD level at ST4 (1.08) and ST5 (1.18) did not differ significantly ($p>0.05$) from each other and from ST1 and ST2. Total phosphate at ST4 (3.21) was significantly ($p\leq 0.05$) higher than those at ST1 (0.77), ST2 (0.85), ST3 (0.80) and ST5 (0.90). The Oil and grease level varied slightly along the different stations in River Romi. There was no significant ($p>0.05$) difference among ST1 (0.33), ST3 (0.42), ST5 (0.42) and ST5 (0.42) but differed significantly ($p\leq 0.05$) from ST2 (0.00).

Table 4.4 shows the physicochemical indices of River Romi for the month of May. There was slight increase in values of parameters such as temperature, dissolved oxygen, biological oxygen demand, sulphate, and alkalinity but they did not differ significantly ($p>0.05$) in the corresponding sampling stations. At ST1(8.22), pH was significantly ($P\leq 0.05$) higher than the ones observed at ST2 (7.85), ST3(7.70), ST4 (7.61) and ST5 (7.62). Total dissolved solids did not differ significantly ($p>0.05$) at ST1, ST2, ST3 and ST4 but differed significantly ($p\leq 0.05$) from ST5. The electrical conductivity at ST1 (145.50), ST2 (146.22), ST3 (143.00) and ST4 (141.17) were significantly ($p\leq 0.05$) different from ST5 (119.00). The COD at ST2(521.67) was significantly highest, followed by ST5 (410.00) while ST3 (369.33) did not differ significantly ($p>0.05$) from both ST5 and ST1 (280.17). Also, ST1 did not differ significantly ($p>0.05$) from ST4 (201.67). Phosphate level of the sampling stations recorded significant ($p\leq 0.05$) concentration at ST1 (0.20) but did not differ significantly at ST4 (0.14) and ST3 (0.14).

Table 4.4: Physicochemical Values of River Romi in May, 2015

Parameters	Station 1	Station 2	Station 3	Station 4	Station 5	Average
Temperature	30.28a±0.42	29.90a±0.68	29.90a±0.71	30.14a±0.77	28.97a±0.97	29.84±0.32
PH	8.22a±0.14	7.85b±0.01	7.70b±0.07	7.61b±0.15	7.62b±0.13	7.80±0.06
EC	145.50a±4.11	146.22a±2.01	143.33a±1.76	141.17a±1.60	119.00b±11.75	139.07±3.04
TDS	73.67a±1.86	72.00a±0.68	72.00a±1.13	72.50a±1.26	60.33b±5.99	70.10±1.52
DO	3.64a±0.09	3.47a±0.10	3.33a±0.30	3.47a±0.19	3.63a±0.21	3.51±0.08
BOD	1.68a±0.20	1.50a±0.10	1.87a±0.07	1.90a±0.07	1.88a±0.21	1.77±0.07
COD	280.17cd±2.76	521.67a±4.77	369.33bc±5.58	201.67d±4.66	410.00b±82.22	356.57±25.51
Phosphate	0.20a±0.01	0.10c±0.01	0.08c±0.00	0.14bc±0.01	0.16b±0.04	0.14±0.01
Nitrate	2.53a±0.07	2.33bc±0.09	2.16c±0.06	2.40b±0.03	2.35b±0.02	2.35±0.03
Sulphate	4.62a±1.40	3.61a±0.93	4.97a±1.13	2.67a±0.32	3.55a±0.62	3.88±0.43
T/phosphate	1.60b±0.23	4.35ab±1.66	0.62b±0.15	1.13b±0.10	2.35ab±0.65	2.01±0.41
T/nitrate	23.57a±0.09	20.46b±0.21	20.46b±0.59	21.15b±0.06	20.96b±0.41	21.36±0.25
Hardness	220.00ab±3.65	234.67a±16.28	189.00b±2.94	201.00ab±6.79	205.83ab±18.01	210.10±5.59
Alkalinity	70.67a±3.93	77.17a±2.59	68.67a±3.52	73.17a±4.51	67.50a±5.20	71.43±1.80
Oil and grease	0.33a±0.05	0.00b±0.00	0.45a±0.04	0.05b±0.23	0.03a±0.11	0.23±0.04

Key:

Temp. = Temperature, TDS = Total Dissolved Solids, EC = Electrical Conductivity, DO = Dissolved Oxygen, BOD = Biological Oxygen Demand, COD = Chemical Oxygen Demand, TP = Total phosphorous, TN = Total nitrogen.

The phosphate levels at ST2(0.10), ST3 (0.08) and ST4 did not vary significantly. Nitrates were observed to be highest at ST1 (2.53) and differed statistically from other sampling stations; ST4 (2.40), ST5 (2.35) and ST2 (2.33) had similar levels of concentration ($p>0.05$) while ST3 (2.16) was significantly least. There was no significant ($p>0.05$) difference in total phosphorous levels among the sampling stations except at ST5(2.35). The same trend was maintained for the total nitrogen in which the significant ($p\leq0.05$) difference was observed at ST5 (0.62). Oil and grease were recorded in the samples at different proportions except at ST2 and ST3. There was no significant ($p>0.05$) difference among ST1 (0.33), ST3 (0.45) and ST5 (0.03); similarly, there was no significant ($p>0.05$) difference between ST2 (0.00) and ST4 (0.00).

The physicochemical values of River Romi for the month of June are shown in Table 4.5. The level of dissolved oxygen and oil and grease did vary along the sampling stations. Temperature at ST1 (30.10) and ST3 (29.10) did not differ significantly ($p>0.05$) from each other; also at ST2 (28.82), ST4 (28.87) and ST5 (28.10) they did not differ significantly ($p>0.05$). The pH was lowest at ST3 (7.24) and ST4 (7.24) and did not differ significantly ($p>0.05$); similarly, ST2 (97.39) and ST5 (7.340) did not differ significantly ($p>0.05$), while ST1 (7.61) was significantly ($p\leq0.05$) highest. The total dissolved solids did not differ significantly ($p>0.05$) among ST2 (57.00), ST3 (61.50) and ST4 (62.50); but there was significant ($p\leq0.05$) increase and decrease at ST1 (96.17) and ST5 (21.00), respectively. Electrical conductivity at ST2 (115.17), ST3 (122.83) and ST4 (122.83) did not differ significantly ($p>0.05$); while ST1 (185.50) was significantly ($p\leq0.05$) highest and ST5 (42.00) was the lowest.

Table 4.5: Physicochemical Values of River Romi in June, 2015

Parameters	Station 1	Station 2	Station 3	Station 4	Station 5	Average
Temperature	30.10a±0.14	28.82b±0.44	29.10a±0.26	28.87b±0.22	28.10b±0.45	29.00±0.18
PH	7.61a±0.04	7.39b±0.02	7.24c±0.02	7.24c±0.04	7.34ab±0.03	7.36±0.03
EC	185.50a±22.33	115.17b±4.37	122.00b±1.88	122.83b±0.95	42.00c±4.07	117.50±9.50
TDS	96.17a±11.57	57.00b±2.25	61.50b±1.29	62.50b±1.06	21.00c±2.48	59.63±4.97
DO	4.72a±0.37	5.10a±0.41	4.95a±0.56	5.02a±0.56	4.85a±0.44	4.93±0.20
BOD	1.78ab±0.28	2.60a±0.23	2.40ab±0.27	2.23ab±0.39	1.63b±0.07	2.13±0.13
COD	436.00c±3.18	637.17a±2.32	330.00d±6.83	470.00b±23.20	493.33b±5.58	473.30±19.00
Phosphate	0.12c±0.01	0.15b±0.01	0.15b±0.01	0.16b±0.01	0.22a±0.01	0.16±0.01
Nitrate	2.69a±0.05	2.51b±0.03	2.20c±0.05	2.58ab±0.03	2.24c±0.02	2.44±0.04
Sulphate	14.57a±5.38	3.00b±0.07	3.57b±0.05	2.88b±0.06	14.29a±5.39	7.66±1.75
TP	9.60a±0.78	1.37b±0.02	1.27b±0.04	1.35b±0.03	1.51b±0.02	3.02±0.63
TN	22.08a±0.22	19.69c±0.36	20.63b±0.22	21.60a±0.10	20.47b±0.18	20.89±0.19
Hardness	189.50bc±3.05	231.33ab±6.04	170.00d±8.13	208.83bc±17.28	247.83a±10.18	209.50a±6.68
Alkalinity	79.00a±1.69	53.50b±1.54	43.83c±2.36	28.50d±1.26	44.00c±2.30	49.77±3.19
Oil and grease	0.00 ^a ±0.00	0.00a±0.00	0.00a±0.00	0.10a±0.05	0.10a±0.05	0.04±0.02

Key:

Temp. = Temperature, TDS = Total Dissolved Solids, EC = Electrical Conductivity, DO = Dissolved Oxygen, BOD = Biological Oxygen Demand, COD = Chemical Oxygen Demand, TP = Total phosphorous, TN = Total nitrogen.

There was significant ($p > 0.05$) difference of BOD across all the sampling stations except ST5 (1.63) in which there was slight decrease in value. The COD for the sampling stations increased significantly ($p \leq 0.05$) in this order: ST2 (637.17) > ST5 (493.33) > ST4 (470.00) > ST1 (436.00) > ST3 (330.00). The phosphate level was significantly ($p \leq 0.05$) highest at ST5 (0.22) but did not differ significantly ($p > 0.05$) among ST2 (0.15), ST3 (0.15) and ST4 (0.16) and reduced significantly ($p \leq 0.05$) at ST1 (0.12). At ST1 (2.69) and ST4 (2.58), the concentration of nitrate did not differ significantly ($p > 0.05$); similar trend was obtained at ST2 (2.51) and ST4 but differed significantly ($P \leq 0.05$) from ST3 (2.20) and ST5 (2.24). There was no significant ($p > 0.05$) difference in the amount of sulphate at ST1 (14.57) and ST5 (14.29); the same level of significant ($p > 0.05$) difference was observed among ST2 (3.00), ST3 (3.57) and ST4 (2.88). Total phosphorous did not vary significantly ($p > 0.05$) at all the sampling stations except at ST1 (9.60) that was significantly ($p \leq 0.05$) highest. Total nitrogen did not vary significantly ($p > 0.05$) between ST1 (22.08) and ST4 (21.60) but they differed significantly ($p \leq 0.05$) from ST3 (20.63) and ST5 (20.47) in which the later was significantly ($p \leq 0.05$) higher than ST2 (19.69).

The hardness of water varied significantly ($p \leq 0.05$) across all the sampling stations in this order from highest to the lowest: ST5 (209.50) > ST2 (231.33) > ST4 (208.83) > ST1 (189.50) ST3 > (170.00). Alkalinity was highest at ST1 (79.00), followed by ST2 (53.50). At ST3 and ST5 the level of alkalinity did not differ significantly ($p \leq 0.05$) but it differed from ST4 (28.50).

The physicochemical parameter for the month of July at various sampling stations is shown in Table 4.6. Some parameters such as temperature, phosphate and sulphate did not differ significantly ($p>0.05$) across all the sampling stations. The pH was significantly highest at ST1 (8.31) and ST5 (8.66) followed by ST2 (7.74) and ST4 (7.65) while ST3 (7.47) was significantly ($p\leq 0.05$) least. Station 1 had significantly higher TDS than ST2, ST3, ST4 and ST5. At ST1 (164.17), the electrical conductivity was significantly ($p\leq 0.05$) higher than the other sampling stations; while ST2 (9112.83), ST3 (119.33) and ST4 (116.50) were significantly ($p>0.05$) the same but differed significantly ($p\leq 0.05$) from ST5 (53.67).

The DO (mg/L) differed significantly in this order across the sampling stations: ST1 (4.03) > ST3 (3.93) > ST2 (3.73) > ST5 (3.53) > ST4 (3.35). Biological oxygen demand was highest at ST5 (3.40) in which it did not differ significantly from ST4 (3.05) and ST1 (3.15). In the same way, ST2 (2.93) and ST3 (2.77) did not differ statistically ($p>0.05$) from each other as well as from ST1 and ST5. The COD at ST1, ST2, ST3 and ST5 did not differ significantly but differed from ST4 (403.33). Nitrate level at all the sampling stations did not differ statistically from each other except at ST4 (1.40). Total phosphate differed significantly between ST2 (0.69) and ST4 (0.41) only; while other stations did not differ statistically from each other and other stations. The total nitrogen level of ST1 (21.75), ST2 (21.03) and ST5 (21.13) did not differ significantly ($p>0.05$) from each other; while ST4 (19.99) did not differ significantly ($p>0.05$) from ST3 (19.50). The hardness of water at ST1 (178.00) was significantly ($p\leq 0.05$) higher than ST2 (129.50) and ST3 (115.00) but not at ST4 (142.00) and ST5 (140.50).

Table 4.6: Physicochemical Values of River Romi in July, 2015

Parameters	Station 1	Station 2	Station 3	Station 4	Station 5	Average
Temperature	28.50 ^a ±0.08	27.33 ^a ±0.51	27.13 ^a ±0.29	26.97 ^a ±0.22	27.55 ^a ±1.14	27.50±0.26
PH	8.31 ^a ±0.01	7.74 ^{bc} ±0.02	7.47 ^c ±0.02	7.65 ^{bc} ±0.08	8.66 ^a ±0.56	7.97±0.13
EC	164.17 ^a ±13.97	112.83 ^b ±8.77	119.33 ^b ±6.25	116.50 ^b ±4.65	53.67 ^c ±11.49	113.30±7.66
TDS	80.83 ^a ±7.46	55.67 ^b ±4.06	59.50 ^b ±3.40	58.00 ^b ±2.73	27.17 ^c ±5.78	56.23±3.79
DO	4.03 ^a ±0.11	3.73 ^{bc} ±0.07	3.93 ^{ab} ±0.09	3.35 ^d ±0.13	3.53 ^{cd} ±0.07	3.72±0.06
BOD	3.15 ^{ab} ±0.09	2.93 ^b ±0.26	2.77 ^b ±0.06	3.05 ^{ab} ±0.13	3.40 ^a ±0.10	3.06±0.07
COD	438.33 ^a ±4.77	433.33 ^a ±7.15	430.00 ^a ±5.77	403.33 ^b ±5.58	431.67 ^a ±8.33	427.33±3.52
Phosphate	0.11 ^a ±0.01	0.08 ^a ±0.01	0.08 ^a ±0.00	0.07 ^a ±0.02	0.09 ^a ±0.02	0.09±0.01
Nitrate	2.40 ^a ±0.08	2.21 ^a ±0.04	2.10 ^a ±0.02	1.40 ^b ±0.33	2.51 ^a ±0.09	2.13±0.10
Sulphate	5.04 ^a ±1.56	2.36 ^a ±0.56	29.86 ^a ±25.65	4.37 ^a ±1.21	4.66 ^a ±1.46	9.26±5.16
T/phosphate	0.53 ^{ab} ±0.08	0.69 ^a ±0.06	0.53 ^{ab} ±0.09	0.41 ^b ±0.07	0.51 ^{ab} ±0.10	0.54±0.04
T/nitrate	21.75 ^a ±0.78	21.03 ^{ab} ±0.35	19.50 ^c ±0.22	19.99 ^{bc} ±0.33	21.13 ^{ab} ±0.16	20.68±0.23
Hardness	178.00 ^a ±5.27	129.50 ^b ±5.18	115.00 ^b ±14.95	142.00 ^{ab} ±25.06	140.50 ^{ab} ±7.28	141.00±6.93
Alkalinity	59.00 ^a ±10.31	42.83 ^{ab} ±9.08	44.17 ^{ab} ±8.24	39.50 ^{ab} ±8.30	30.50 ^b ±2.14	43.20±3.78
Oil and grease	0.28 ^a ±0.06	0.10 ^b ±0.05	0.35 ^a ±0.08	0.10 ^b ±0.05	0.07 ^b ±0.03	0.18±0.03

Key:

Temp. = Temperature, TDS = Total Dissolved Solids, EC = Electrical Conductivity, DO = Dissolved Oxygen, BOD = Biological Oxygen Demand, COD = Chemical Oxygen Demand, TP = Total phosphorous, TN = Total nitrogen.

Alkalinity at ST1 (59.00) was significantly higher than ST5 (30.50) but did not differ significantly ($p>0.05$) from ST2 (42.83), ST3 (44.17) and ST4 (39.50). The level of oil and grease at ST1 (0.28) and ST3 (0.35) did not differ significantly ($p>0.05$); similarly, ST2 (0.10), ST4 (0.10) and ST5 (0.07) similar levels ($p>0.05$).

4.3 Comparison of Physicochemical Parameters in the Dry and Wet Seasons

The physicochemical parameters for the dry and wet seasons in River Romi are shown in Table 4.7. There was variation in physicochemical indices in the two seasons but not significant ($p>0.05$) except for alkalinity concentration. Temperature was slightly higher in the dry season (31.18°C) than the wet season (28.78°C); similar trend was observed in pH of 8.46 and 8.04 for dry and wet seasons respectively. Total dissolved solids (206.10mg/L and 61.99mg/L), EC (478.76mg/L and 123.29mg/L) and DO (4.49mg/L and 4.05mg/L), were higher in dry season than wet. On the contrary, BOD was higher in wet season (2.32mg/L) than the dry season (1.69mg/L).

Chemical oxygen demand (mg/L) and PO_4 (mg/L) in dry season (396.43 and 0.14) was higher than that of wet season (55.74 and 0.13). Nitrate (mg/L), total phosphorous (mg/L), total nitrogen (mg/L) and hardness (mg/L) were higher in wet season (2.31, 1.85, 20.98 and 186.87) than dry season (2.25, 1.16, 20.00 and 156.87), respectively. Sulphate (mg/L) was higher in dry season (7.56) than wet season (6.93). Alkalinity in dry season (115.87) was significantly ($p\leq 0.05$) higher than dry season (54.80). Oil and grease was higher in dry season (7.62mg/L) than wet season (0.15mg/L).

Table 4.7: Comparison of Mean Physicochemical Parameters of River Romi in Dry and Wet Seasons (2015)

Parameters	Dry Season (Mean±SE)	Wet Season (Mean±SE)	P-value
Temperature	31.18±0.65	28.78±1.19	0.142
pH	8.46±0.38	8.04±0.72	0.426
TDS	206.10±83.10	61.99±7.23	0.087
EC	478.76±163.91	123.29±13.83	0.055
DO	4.49±1.60	4.05±0.77	0.695
BOD	1.69±0.47	2.32±0.67	0.420
COD	396.43±	55.74	0.759
PO ₄	0.14±0.03	0.13±0.04	0.529
NO ₃	2.25±0.11	2.31±0.16	0.730
SO ₄	7.56±2.23	6.93±2.76	0.839
Total phosphorous	1.16±0.13	1.85±1.25	0.475
Total nitrogen	20.00±2.56	20.98±0.35	0.528
Hardness	156.87±17.89	186.87±39.72	0.289
Alkalinity	115.87±24.96	54.80±14.77	0.027
Oil and grease	7.62±12.67	0.15±0.10	0.417

4.4 Principal Component Analysis (PCA) of Physicochemical Parameters

The relationships among physicochemical parameters of River Romi are shown in Figure 4.5. There was positive correlation between TP, BOD, pH, DO, SO_4 , NO_3 and OG; but higher relationships were established between TP, BOD, DO, pH and SO_4 . Similarly, there were positive correlation between Alkalinity, temperature, TDS, EC, and COD. Conversely, TP, BOD, pH, DO, SO_4 , NO_3 and Oil and grease correlated negatively with TN, PO_4 and hardness. Similarly, COD, EC, TDS, temperature and alkalinity correlated negatively with TN, PO_4 and hardness.

4.5 The Canonical Correspondence Analysis (CCA) of Physicochemical Parameters and Phytoplankton

Physicochemical parameters and phytoplankton interaction in various ways is shown in Figure 4.6. There was positive correlation among TDS, EC, TP, temperature, hardness, alkalinity, BOD, PO_4 and TN. The relationship among hardness, EC, alkalinity was strongly positive. Cyanophyta (13 species) correlate positively with hardness, EC, TDS alkalinity, temperature, TP, BOD, TN, and PO_4 . The following parameters: oil and grease, NO_3 , SO_4 , DO and pH correlated positively with each other. They also correlated positively with Bacillariophyta (20 species). There was negative correlation among COD, Euglenophyta (1 species) and Cyanophyta (13 species). There was positive correlation of TDS, EC, TP, temperature, hardness, alkalinity, BOD, PO_4 and TN with Oil and grease, NO_3 , SO_4 , DO and pH.

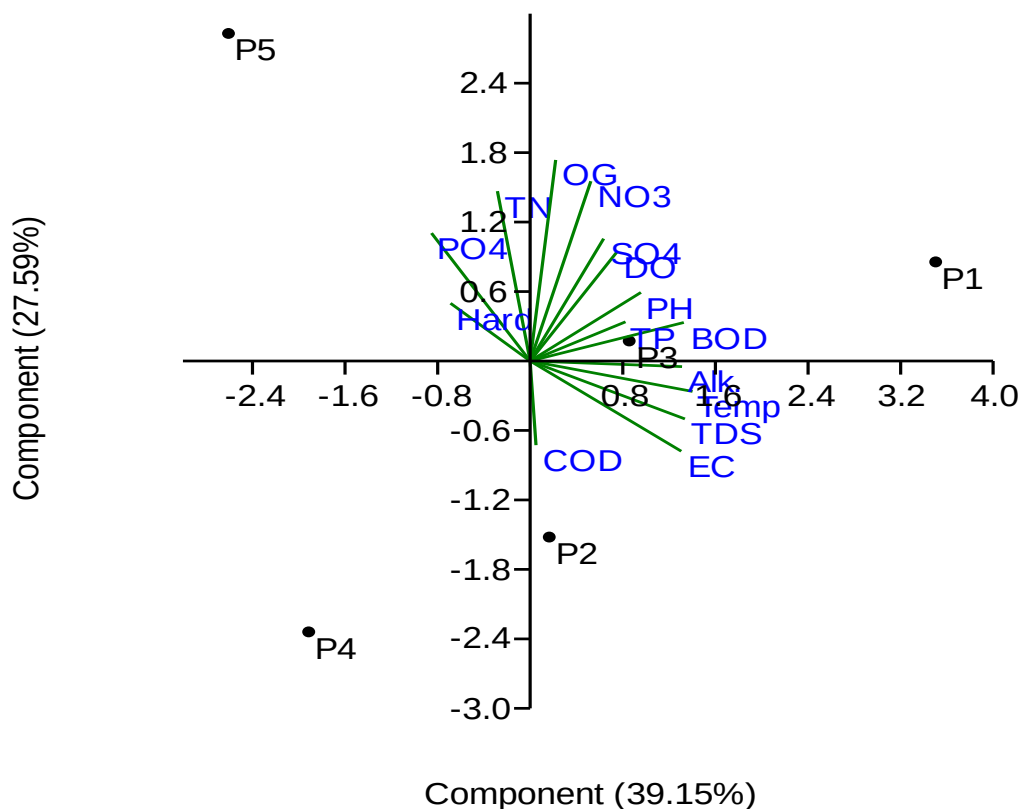


Figure 4.5: PCA biplot of the relationship between physicochemical parameters of River Romi

Key:

Temp = Temperature, TDS = Total dissolved solids, EC = Electrical conductivity, DO = Dissolved oxygen, BOD = Biological oxygen demand, COD = Chemical oxygen demand, PO4 = Phosphate, NO3 = Nitrate, SO4 = Sulphate, TP = Total phosphorous, TN = Total nitrogen, Hard = Hardness, Alk. = Alkalinity, OG = Oil and grease.

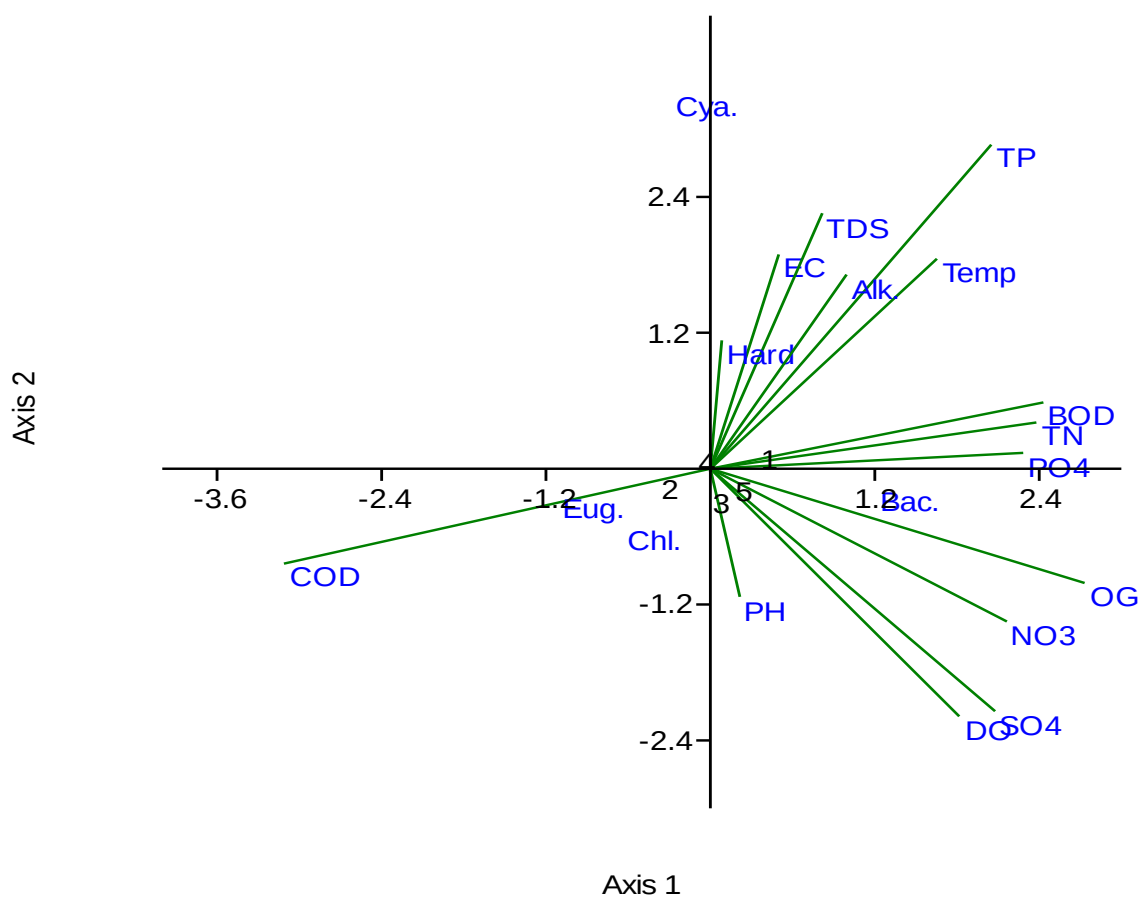


Figure 4.6: CCA analysis of the relationship between Physicochemical Parameters and Phytoplankton of River Romi, Kaduna, Nigeria

Key:

Temp = Temperature, TDS = Total dissolved solids, EC = Electrical conductivity, DO = Dissolved oxygen, BOD = Biological oxygen demand, COD = Chemical oxygen demand, PO4 = Phosphate, NO3 = Nitrate, SO4 = Sulphate, TP = Total phosphorous, TN = Total nitrogen, Hard = Hardness, Alk. = Alkalinity, OG = Oil and grease, Bac. = Bacillariophyta, Chl. = Chlorophyta, Cya. = Cyanophyta, Eug. = Euglenophyta.

Total Dissolved Solids, EC, TP, temperature, hardness, alkalinity, BOD, PO_4 and TN correlated negatively with COD. Similarly, Oil and grease, NO_3 , SO_4 , DO and pH correlated negatively with COD.

4.6 The Canonical Correspondence Analysis(CCA) of Physicochemical Parameters and Zooplankton

Figure 4.7 shows the relationship among physicochemical parameters and zooplankton. There was correlation between physicochemical parameters and Zooplanktons. There was positive correlation among alkalinity, TP, pH, TDS, EC, temperature, NO_3 , TN, OG, BOD, DO and SO_4 . The correlation among TN, EC, OG, DO and SO_4 was positively strong. Rotifers (11 species) correlated positively with alkalinity, TP, pH, TDS, EC, temperature, NO_3 , TN, OG, BOD, DO and SO_4 but it was strongly positive with TN. There was positive correlation between Copepoda (6 species) and PO_4 . While, COD and hardness correlated negatively. Alkalinity, TP, pH, TDS, EC, temperature, NO_3 , TN, OG, BOD, DO and SO_4 correlated positively with Copepoda and PO_4 , but the former correlated negatively with COD and hardness. In the same way, Copepoda and PO_4 correlated negatively with COD and hardness. Protozoans correlated negatively with Alkalinity, TP, pH, TDS, EC, temperature, NO_3 , TN, OG, BOD, DO and SO_4 .

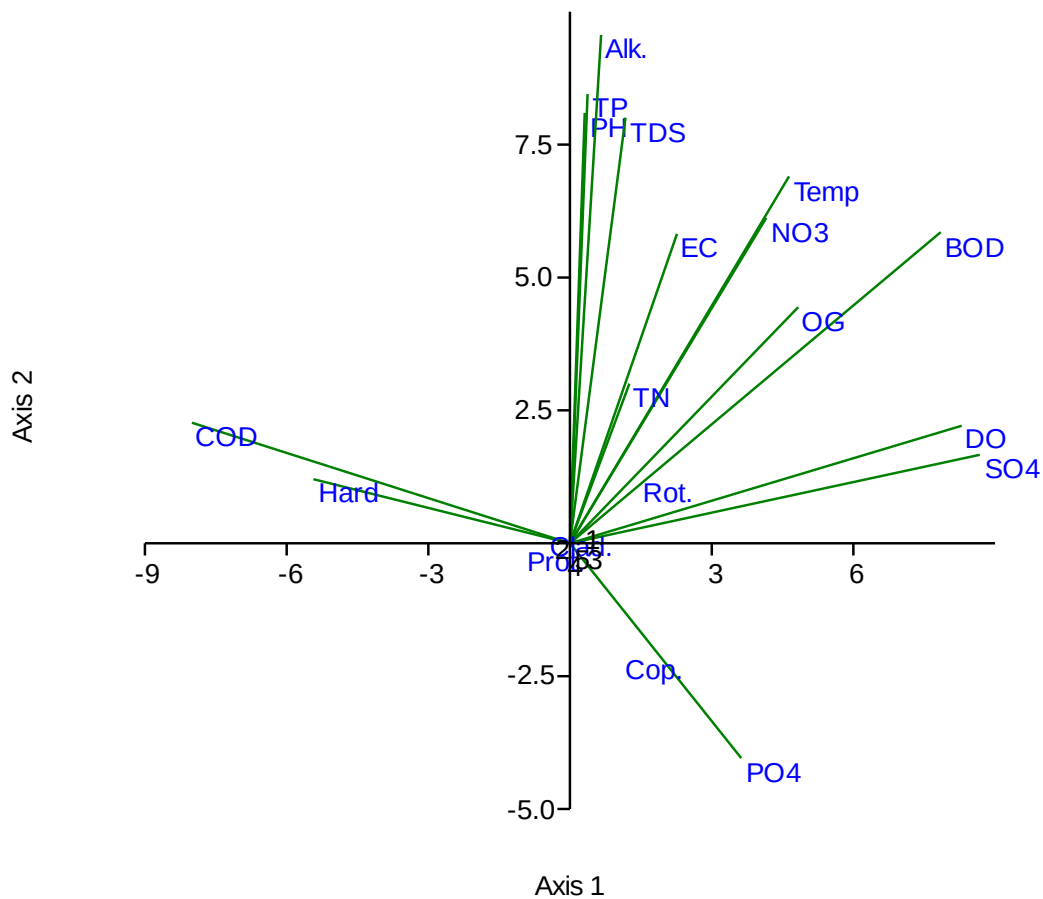


Figure 4.7: CCA analysis of the relationship between Physicochemical Parameters and Zooplankton of River Romi, Kaduna, Nigeria

Key:

Temp = Temperature, TDS = Total dissolved solids, EC = Electrical conductivity, DO = Dissolved oxygen, BOD = Biological oxygen demand, COD = Chemical oxygen demand, PO4 = Phosphate, NO3 = Nitrate, SO4 = Sulphate, TP = Total phosphorous, TN = Total nitrogen, Hard = Hardness, Alk. = Alkalinity, OG = Oil and grease, Prot. = Protozoan, Clad. = Cladoceran, Cop. = Copepoda, Rot. = Rotifers.

4.7 The Canonical Correspondence Analysis(CCA) of Physicochemical Parameters, Phytoplankton and Zooplankton

The physicochemical parameters, phytoplankton and zooplankton interacted in different ways. Alkalinity, TP, TDS, EC, TN, temperature, NO_3 , OG, BOD, DO and SO_4 correlated positively with each other. There was strong and positive correlation among TN, EC and OG. There was positive correlation among PO_4 , Bacillariophyta, Copepods and Chlorophyta. Protozoan, Cyanophyta and Euglenohyta correlated negatively. In the same way, COD, hardness and Cladocera also correlated negatively. Alkalinity, TP, TDS, EC, TN, temperature, NO_3 , OG, BOD, DO and SO_4 correlated positively with PO_4 , Bacillariophyta, Copepods and Chlorophyta. The following parameters Alkalinity, TP, TDS, EC, TN, temperature, NO_3 , OG, BOD, DO and SO_4 correlated negatively with Protozoan, Cyanophyta and Euglenohyta. Similarly, PO_4 , Bacillariophyta, Copepods and Chlorophyta correlated negatively with Protozoan, Cyanophyta and Euglenohyta. It also correlated negatively with COD, hardness and Cladocera. Alkalinity, TP, TDS, EC, TN, temperature, NO_3 , OG, BOD, DO and SO_4 correlated negatively with COD, hardness and Cladocera.

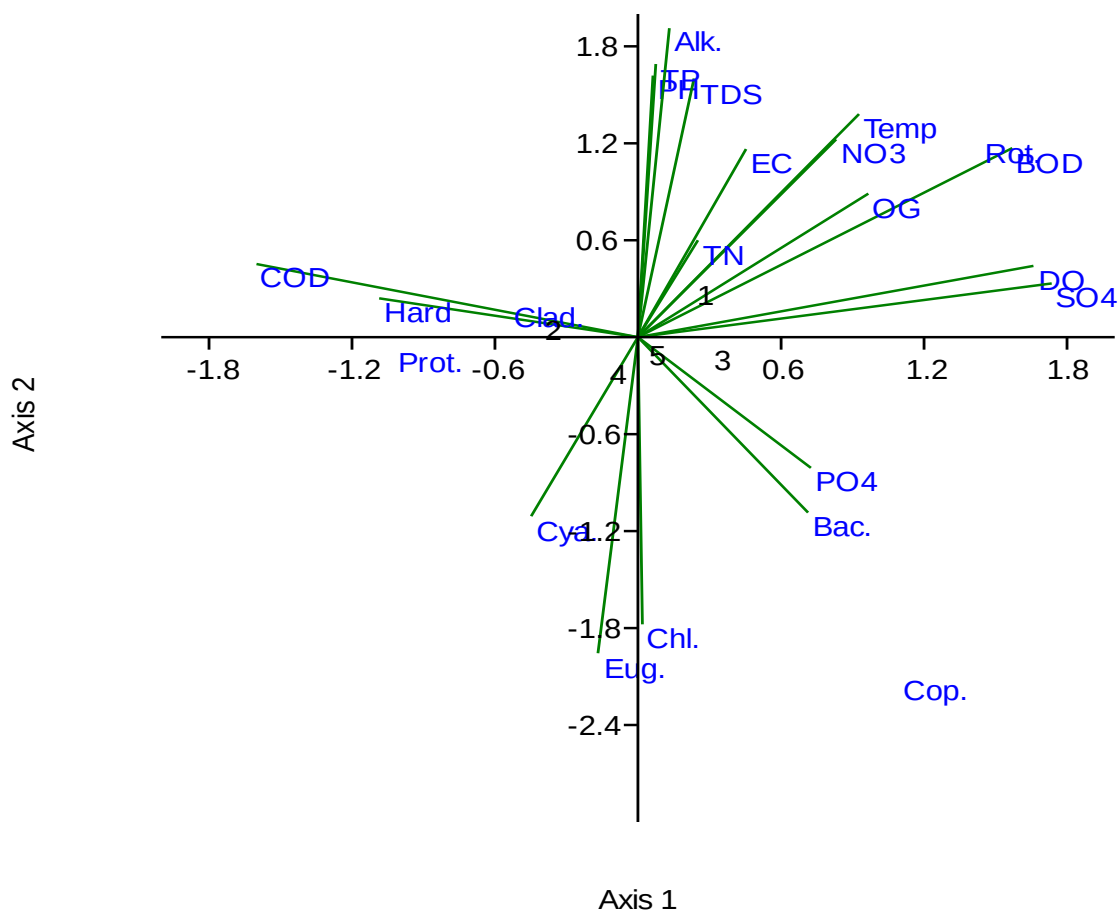


Figure 4.8: CCA analysis of the association of Physicochemical Parameters with Phytoplankton and Zooplankton of River Romi, Kaduna, Nigeria

Temp = Temperature, TDS = Total dissolved solids, EC = Electrical conductivity, DO = Dissolved oxygen, BOD = Biological oxygen demand, COD = Chemical oxygen demand, PO₄ = Phosphate, NO₃ = Nitrate, SO₄ = Sulphate, TP = Total phosphorous, TN = Total nitrogen, Hard = Hardness, Alk. = Alkalinity, OG = Oil and grease, Bac. = Bacillariophyta, Chl. = Chlorophyta, Cya. = Cyanophyta, Eug. = Euglenophyta, Prot. = Protozoan, Clad. = Cladoceran, Cop. = Copepoda, Rot. = Rotifers.

4.8 Heavy Metals Concentrations in River Romi

The pooled concentration of heavy metals of River Romi is shown in Figure 4.9. There were variations in concentrations of heavy metals per sampling month. Zinc (0.53mg/L) had the highest concentration in the month of February, followed by Cr (0.37mg/L), Ni (0.36mg/L), Pb (0.24mg/L) and Mn (0.22mg/L). All the heavy metals investigated were present in March. The highest and the lowest heavy metals were found in Cr (0.26mg/L) and Ni (0.14mg/L), respectively. Zinc (0.23mg/L) was higher than Pb (0.18mg/L) and Mn (0.18mg/L). In the month of April, Mn (0.32mg/L) had the highest followed by Zn (0.27mg/L), Cr (0.25mg/L), Pb (0.15mg/L), while Ni (0.12mg/L) was the least. The concentration of the sampled heavy metals was significantly ($p \leq 0.05$) highest in Ni (5.85mg/L). It was followed by Cr (0.50mg/L), Mn (0.3mg/L), Pb (0.28mg/L) and Zn (0.19mg/L) was the least. Manganese (0.77mg/L) had the highest concentration while Ni (0.13mg/L) recorded the least. Chromium (0.37mg/L) and Pb (0.31mg/L) were almost of the same value, while Zn had 0.21mg/L. The level of Pb in the month of July was very minimal. Manganese (0.79mg/L) had the highest concentration followed by Cr (0.40mg/L), Ni (0.16mg/L) and Zn (0.01mg/L).

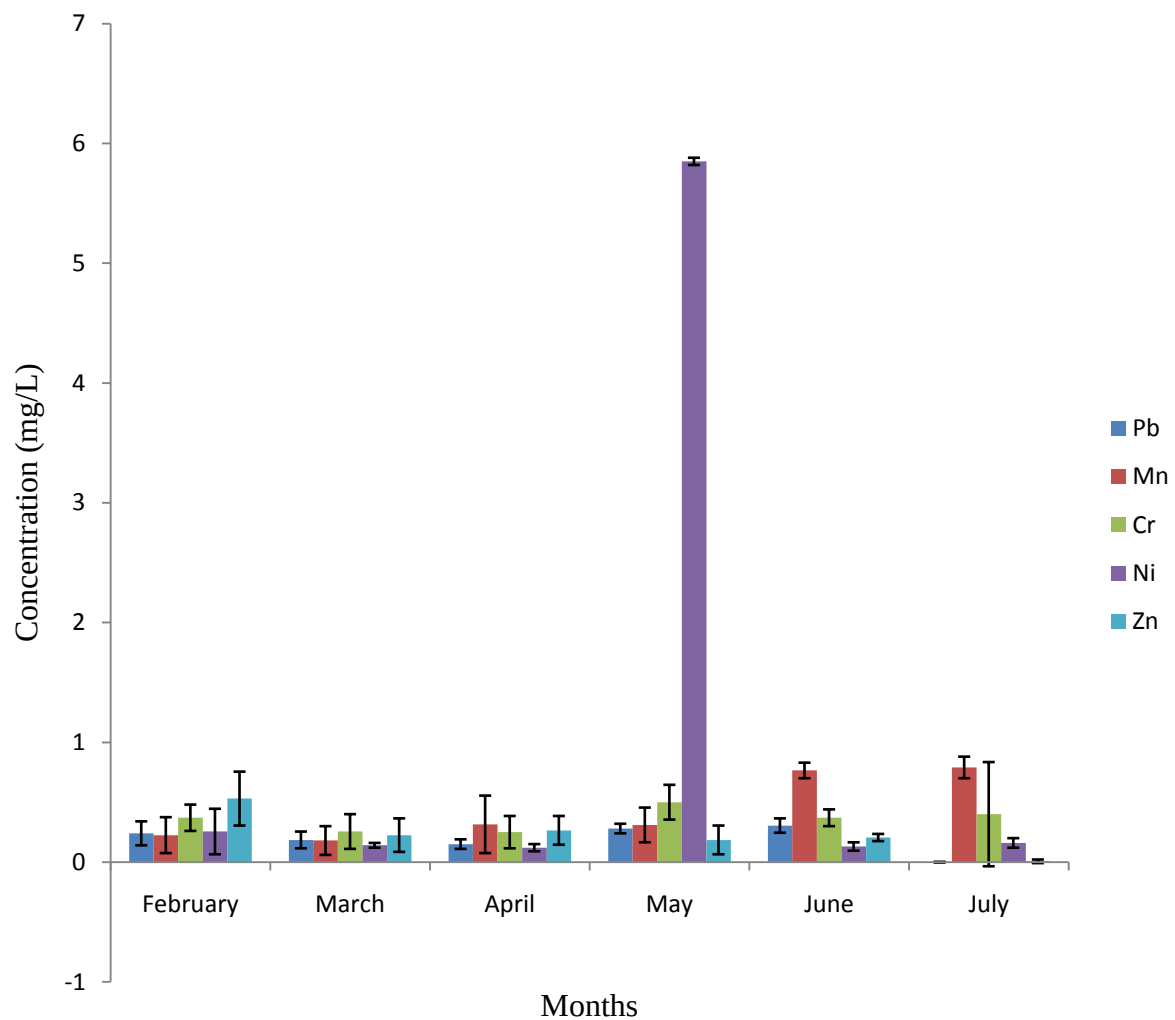


Figure4.9: Concentration of heavy metals in River Romi

4.9 Distribution and Composition of Plankton Species in River Romi

4.9.1 Phytoplankton Species

The distribution and composition of phytoplankton species in River Romi are shown in Table 4.8. Fifty three (53) species of phytoplankton were observed in this study at different sampling stations in various quantities. *Stigonemasp.* was the most abundant during the sampling period and was found in all the sampling stations. The variations in the abundantmost species were found to be 165, 14, 257, 207 and 121 in ST1, ST2, ST3, ST4 and ST5, respectively. The most second abundant species was *Aphanothece* sp. with a total of 428 distributed in all the sampling stations and the months. Species such as *Oscillatoria* (309), *Eunotia* (272), *Diadesmis* (210), *Coelosphaerina* (143) and *Pseudo-Nitzschia* (124) species were found to be in decreasing order of abundance. There was one species of *Closterium* and *Pleurogaster* in ST4 and ST2, respectively. Also species of *Desmidium* (2) was found in ST3, while *Pleurogaster* (1) was observed ST2. In the same way, *Opicytlum*, *Pleurogaster*, *Protococcus* and *Staurastrum* species were recorded to be three each. A total of four were found for the species of *Anabaena*, *Tetraedon* and *Zygnema*, while *Stitococcus* and *Microcystis* were recorded to be seven and eight respectively. The following species were found to be > 10: *Centropyxis* (10), *Chroococcus* (11), *Ctenophora* (12), *Aulacoseira* (13), *Dactylococcus* (14), *Cylindrotheca* and *Oedogonium* were 15 each. Other species ranged between 16 and 125 that were distributed in various amounts among the sampling stations (ST1, ST2, ST3, ST4 and ST5) along the River Romi.

Table 4.8: Distribution and Composition of Phytoplankton Species in River Romi, 2015

S/N	Taxon	ST1	ST2	ST3	ST4	ST5	Total	SD	Diversity index
Bacillariophyta									
1	<i>Amphora</i> sp.	12	29	19	4	4	68	10.64	1.34
2	<i>Melosira</i> sp.	3	1	45	2	0	50	19.49	0.48
3	<i>Gomphonema</i> sp.	6	1	1	4	22	34	8.76	1.05
4	<i>Nitzschia</i> sp.	8	5	14	3	3	33	4.62	1.43
5	<i>Tabellaria</i> sp.	8	6	8	20	4	31	6.26	1.45
6	<i>Acanthidium</i> sp.	0	3	0	8	46	57	19.62	0.60
7	<i>Navicula</i> sp.	5	4	6	4	10	21	2.49	1.54
8	<i>Eunotia</i> sp.	45	35	64	70	58	272	14.26	1.58
9	<i>Synedra</i> sp.	0	0	0	0	2	2	0.89	0.00
10	<i>Ctenophora</i> sp.	0	9	0	1	2	12	3.78	0.72
11	<i>Mastogloia</i> sp.	10	5	3	0	1	18	3.96	1.14
12	<i>Pseudo-nitzschia</i> sp.	28	38	26	11	21	124	9.88	1.54
13	<i>Cylindrotheca</i> sp.	0	0	9	3	3	15	3.67	0.95
14	<i>Diadesmis</i> sp.	1	102	74	1	33	210	44.91	1.06
15	<i>Tryblionella</i> sp.	0	1	0	0	1	2	0.55	0.69
16	<i>Stauroseiralla</i> sp.	20	4	47	13	3	86	17.95	1.21
17	<i>Pleurogaster</i> sp.	0	1	0	0	0	1	0.45	0.00
18	<i>Pleurosigma</i> sp.	0	1	2	0	0	3	0.89	0.64
19	<i>Centropyxis</i> sp.	0	1	3	4	2	10	1.58	1.28
20	<i>Aulacoseira</i> sp.	9	3	2	2	2	13	3.05	1.38
Cyanophyta									
1	<i>Stigonema</i> sp.	165	14	257	207	121	752	92.49	1.42
2	<i>Aphanothece</i> sp.	58	55	41	100	173	428	53.70	1.47
3	<i>Oscillatoria</i> sp.	39	15	110	59	74	309	35.92	1.45
4	<i>Calothrix</i> sp.	1	12	1	2	1	16	4.83	1.00
5	<i>Nostoc</i> sp.	13	15	8	1	9	40	5.40	1.43
6	<i>Chroococcus</i> sp.	0	7	1	1	2	11	2.78	1.03
7	<i>Anabaena</i> sp.	0	0	0	1	3	4	1.30	0.56
8	<i>Protococcus</i> sp.	0	0	0	2	1	3	0.89	0.64
9	<i>Stichococcus</i> sp.	1	2	2	1	1	7	0.55	1.55
10	<i>Microcystis</i> sp.	0	0	0	1	7	8	3.05	0.38
11	<i>Gloeocapsa</i> sp.	16	8	0	0	45	69	18.66	0.87
12	<i>Phormidium</i> sp.	4	5	8	30	8	53	10.77	1.30
13	<i>Coelosphaerium</i> sp.	0	13	34	96	43	143	36.98	1.18
Euglenophyta									
1	<i>Phacus</i> sp.	2	1	8	11	0	22	4.83	1.21
Chlorophyta									
1	<i>Trentepohlia</i> sp.	21	3	2	7	3	36	7.95	1.21
2	<i>Sphaerocystis</i> sp.	6	1	3	0	3	13	2.30	1.23
3	<i>Oocystis</i> sp.	2	0	0	10	5	17	4.22	0.92
4	<i>Scenedesmus</i> sp.	3	9	2	1	27	41	10.85	1.04
5	<i>Closterium</i> sp.	0	0	0	1	0	1	0.45	0.00
6	<i>Oedogonium</i> sp.	0	1	9	5	0	15	3.94	0.85
7	<i>Zygnema</i> sp.	0	0	4	0	0	4	1.79	0.00
8	<i>Ulothrix</i> sp.	4	10	8	3	12	31	3.85	1.49
9	<i>Tetraedon</i> sp.	0	0	4	0	0	4	1.79	0.00
10	<i>Mougeotia</i> sp.	14	9	20	1	12	50	6.98	1.41
11	<i>Cladophora</i> sp.	1	0	2	2	49	54	21.37	0.41
12	<i>Chaetophora</i> sp.	0	0	1	0	18	19	7.95	0.21
13	<i>Ophiocytium</i> sp.	1	2	0	0	0	3	0.89	0.64
14	<i>Coelastrum</i> sp.	20	4	47	13	3	86	8.76	1.21
15	<i>Coenocystis</i> sp.	4	0	0	16	0	20	6.93	0.50
16	<i>Geminella</i> sp.	5	2	15	0	1	23	6.11	0.96
17	<i>Desmidium</i> sp.	0	0	2	0	0	2	0.89	0.00
18	<i>Dactylococcus</i> sp.	0	3	1	4	6	14	2.39	1.24
15	<i>Staurostrum</i> sp.	1	2	0	0	0	3	0.89	0.64

Phytoplankton species diversity was highest in *Navicula* and *Pseudo-nitzschia* with 1.54 each; *Synedra*, *Pleurogaster*, *Zygnema* and *Desmidium* had 0.00 species diversity.

4.9.2 Zooplankton Species

The distribution and composition of zooplankton in River Romi is shown in Table 4.9. Zooplanktons were not recorded in large quantity compared to phytoplanktons in all the sampling stations and months. *Microcystis* (58) was the dominant zooplankton species that was distributed in all the sampling stations. *Paramecium* (49) was the second most dominant; followed by *Paracyclops* (36). The following species were found in the order: *Simocephalus* (34) > *Daphnia* (33) = *Ceriodaphnia* (33). The least predominant of the species was *Heliodiatomus* (6) of which 2 and 4 were recorded in ST1 and ST5, respectively. *Macrothrix* (8) was found equally distributed in all the sampling stations except ST2 with more. Similarly, *Bosmina* species was found to be 2 each in ST1, ST3, ST4 and ST5. *Diaphanosoma* (12) was among the species that was recorded in few number which was distributed between ST1 (4), ST2 (2) and ST3 (6). In the same way, *Eubranchipus* recorded a total of 14 that was distributed within the three sampling stations namely; ST1 (4), ST2 (2) and ST4 (8). Other species were *Cyclops* and *Eurycerus* which were found to be 18 each, *Nauplius* (22), *Diaptomus* and *Onychocamptus* were also 24 each, *Thecamoeba* (25) and *Polyphemus* (31). The highest zooplankton species diversity was found in *Diatomus* (2.00), while *Spirotomum* (0.36) had the least.

Table 4.9: The Distribution and Composition of Zooplankton Species in River Romi, 2015

S/N	Taxon	S T 1	ST2	ST3	ST4	ST5	Total	SD	Diversity inde
Protozoan									
1	<i>Paramecium</i> sp.	6	18	7	6	12	49	16.67	0.75
2	<i>Spirotomum</i> sp.	2	44	0	8	2	16	16.73	0.36
Cladocera									
3	<i>Daphnia</i> sp.	5	10	1	11	6	33	11.37	1.43
4	<i>Simocephallus</i> sp.	2	16	0	4	12	34	12.69	1.14
5	<i>Ceriodhaphnia</i> sp.	5	2	6	12	8	33	11.28	1.48
6	<i>Bosmina</i> sp.	2	0	2	2	2	8	2.73	1.39
7	<i>Diaphnosoma</i> sp.	4	2	6	0	0	12	4.56	1.01
8	<i>Macrothrix</i> sp.	2	4	2	0	0	8	3.01	1.04
9	<i>Eurycercus</i> sp.	6	2	0	2	8	18	6.57	1.22
10	<i>Microcyclops</i> sp.	2	10	14	8	24	58	20.30	1.40
11	<i>Onychocamptus</i> sp.	4	2	2	6	10	24	8.39	1.42
12	<i>Heliodiaptomus</i> sp.	2	0	0	0	4	6	2.53	0.64
13	<i>Polyphemus</i> spp	4	5	4	6	12	31	10.56	1.51
Copepoda									
14	<i>Diaptomus</i> sp.	2	4	0	12	6	24	8.85	2.00
15	<i>Eubbranchipus</i> sp.	4	2	0	8	0	14	5.47	0.96
16	<i>Cyclops</i> sp.	7	0	0	7	4	18	6.66	1.07
17	<i>Nauplius</i> sp.	1	2	4	0	6	22	7.97	1.24
18	<i>Paracyclops</i> sp.	0	0	0	2	28	36	15.84	0.66
19	<i>Thecamoebasp.</i>	6	0	0	2	28	36	15.84	0.66
		4	1	0	8	12	25	9.31	1.14

4.10 Correlation between Phytoplankton and Zooplankton Species Composition

The correlation between the phytoplankton and zooplankton species composition are shown in Table 4.10. There was weak correlation ($r = 0.260$) between station 2 and station 1. Station 3 was positively correlated ($r = 0.895$) with station 1 and moderately correlated ($r = 0.369$) with station 2. Station 4 was also correlated ($r = 0.878$) with station 1 and station 3 (0.852). Station 5 exhibited positive correlation ($r = 0.716$) with station 1, station 2 ($r = 0.486$), station 3 ($r = 0.635$) and station 4 ($r = 0.784$). The zooplankton species composition did not correlate significantly across all the sampling stations. The correlation ($r = -0.125$) between station 2 and station 1 was low and negatively correlated. There was no correlation ($r = 0.007$), between station 3 and station 1, while station 3 and station 2 ($r = 0.349$) were positively and moderately correlated. Station 4 and 1 were negatively correlated ($r = -0.123$), while station 4 and station 2 ($r = 0.248$) as well as station 3 ($r = 0.100$) were positively but weakly correlated. Station 5 correlated positively with station 1 (0.115), 2 (0.282) and 3 (0.382), while stations 4 (0.084) did not correlate with station 1 (0.115), 2 (0.282) and 3 (0.382).

Table 4.10: The Correlation of Phytoplankton and Zooplankton Species Composition

Stations	Station 1	Station 2	Station 3	Station 4	Station 5
Station 1	1				
Station 2	0.260	1			
Station 3	0.895 ^{**}	0.369 ^{**}	1		
Station 4	0.878 ^{**}	0.269	0.852 ^{**}	1	
Station 5	0.716 ^{**}	0.486 ^{**}	0.635 ^{**}	0.784 ^{**}	1
Station	Station 1	Station 2	Station 3	Station 4	Station 5
Station 1	1				
Station 2	-0.125	1			
Station 3	0.007	0.349	1		
Station 4	-0.123	0.248	0.100	1	
Station 5	0.115	0.282	0.382	0.084	1

^{**} = Significant at $p \leq 0.01$

CHAPTER FIVE

5.0 DISCUSSION

The physicochemical parameters and plankton diversity of River Romi changed throughout the sampling station along the river's course within the months of study. These variations are related to various effluents regularly released into the aquatic environment as observed in dry and wet seasons. For instance, temperature of water at sampling station 1 to 5 varied, particularly at station 1 when the river received effluent in February. This might be as a result of low water level at that station leading to heating up of water.

The temperature of River Romi from February to April differed significantly ($p \leq 0.05$) across the sampling stations. There was decrease in temperature along the sampling stations from May to July. The change in the temperature observed across the sampling stations for the separate seasons might be due to differences in the depth of water as the wet season is characterized by rainfall, thus, could lead to decrease in temperature. High temperature recorded in this study agreed with the findings of Lekwotet *al.* (2014) who noted slightly higher temperatures in the dry season in all the stations than in the rainy season in River Romi, Kaduna State Nigeria. The pH level of water in February to April was slightly alkaline (8.46) in all the sampling stations, but in May to July (wet season) the pH reduced to 7.71. The pH of River Romi is within the WHO recommendation of 6.5 to 8.5, but some sampling stations that had higher pH was associated with relatively still nature of water as well as industrial waste, sewage, waste dumping through leaching into

the soil which ultimately increased the soil alkalinity and consequently the pH increase (WHO, 1997, 1999).

The Total Dissolved Solids (TDS) was high during the first three months of this study, which corresponded to the dry season, while the last three months (wet/rainy season) was low. The difference might be due to evaporation during the dry season which led to concentration of dissolved substances in water, while the low level during the rainy season of TDS could be due to increase in volume of water as a result of rainfall, thereby, leading to dilution and subsequent reduction in TDS. Similar observation was made by Oniye *et al.* (2007) in River Galma and Kubanni, Zaria, Augustus (2011) in Iffie River Delta State and Ewa *et al.* (2011) Omoku Creek, Rivers State of Nigeria.

The average Electrical Conductivity (EC) of water in the River exhibited an increase from February, decrease in March and then slightly increases in April. In contrast, the average EC during the rainy season was lower than the dry season. The high value of EC recorded in dry season (February to April) might be due to high accumulation of organic matter and elemental materials in water which could have led to more ions responsible for high EC values. On the other hand, the low level of EC recorded in the wet season (May to July) could be due to increased volume of water from rainfall, which invariably reduced the contribution of ions (via dilution) in the sampling stations. This result is in contrast with the report of Augustus (2011) where water samples analyzed in Ubeji River in June to September (wet season), showed higher conductivity.

Dissolved Oxygen (DO) was very high at the beginning of the dry season (February and March) and decreased abruptly in April. This decrease might be attributed to the microbial activities which are often associated with utilization of oxygen and production of gases such as NH_3 , NO_2 , etc. in rivers which is often associated with the increase in temperature as experienced in April. Marcus and Ekpete (2014) reported that, in organically rich waters where there depletion of dissolved oxygen typically occurs in the bottom layer because there is little or no photosynthetic activity or little or no mixing with oxygen-rich surface layer. In the wet months, the DO level was averagely 4.05 mg/L which was far less than the one recorded in the first two months of dry season. The reduction in the DO level might be linked to the volume of water during the wet season which might have led to reduction in microbial activity and the amount of oxygen in the body of the water body.

The level of Biological Oxygen Demand was very low in the dry season except in February that was slightly higher. The low level of BOD could be linked to microbial activities and limited run offs during dry season. In the wet season, the level of BOD increased. Increase in BOD level might be associated with influx of water due to rainfall and low activities of microbes. Kaduna refinery industry that discharges liquid effluents into the River Romi as regards to organic waste disposal might be responsible for the high BOD recorded in this study. This is in agreement with the reports of Davies *et al.* (2008) in River Omoku Creek, Rivers State that obtained similar range of BOD.

The levels of COD are within the limits of WHO recommended values with few stations exceeding the value in all the months which could be attributed to organic contamination entering the system from municipal and industrial effluents due to urban life and industrial establishments. These organic materials eventually get broken down by bacteria, which require oxygen for the decomposition process, leading to depletion of DO, hence the low DO content of the water. Quinby-Hunt *et al.* (1986) reported that a low DO indicates high COD values. The decomposition of organic substances as well as the self-purification capacity of the water body might have led to low DO recorded. Low dissolved oxygen level in this study agrees with the findings of Sa'eed and Mahmoud (2014), who reported an average DO of 3.73 mg/L in Fagge Local Government of Kano State.

The water analyses during the two seasons were found to have similar phosphate (PO_4^{3-}) level throughout the study with the exception of the least value of PO_4^{3-} recorded in July. Farming activities around River Romi might be responsible for the introduction of phosphate through fertilizers applied by farmers. The slight decrease in PO_4^{3-} level in July might be due to increase in volume of water in the river that could dilute the leached phosphate from the farming activities. Total phosphorous also showed variation in this study. Sources of phosphates include septic tanks overflow, runoff from feedlots, run-off from agriculture and waste water treatment plants (Ezemoronye and Amogu, 1998). In addition, detergents with phosphates were a prime source before manufacturers developed phosphate-free alternatives. Phosphorus gets into water in both urban and

agricultural settings (Ezemoronye and Amogu, 1998). Phosphorus tends to attach to soil particles and, thus, moves into surface-water bodies from runoff. A United State Geological Survey (USGS) study on Cape Cod, Massachusetts showed that phosphorus could also migrate with ground-water flows. Since groundwater often discharges into surface water, such as through streambanks into rivers, there is a concern about phosphorus concentrations in groundwater affecting the water quality of surface water (Agatha, 2011).

The nitrate (NO_3^-) level of River Romi did not differ significantly ($p > 0.05$) across all the sampling stations and the months for the two seasons. This implies that the microbial activities were limited throughout during the sampling period, hence, resulted in reduced decomposition in the river. Nitrate is a by-product of the aerobic decomposition of organic nitrogenous matter. Total nitrogen reduced slightly from February to April in the dry season and then increased in May. Normally only little amounts are found naturally, but an increase in nitrate levels can come from many man-made sources such as septic systems, fertilizer runoff and improperly treated wastewater (EPA, 1976; EPA, 1994; WHO, 1997). As nitrates increase, they act as a plant (algae and macrophytes) nutrient and cause an increase in plant growth. Upon the death and decomposition of micro and macrophytes, dissolved oxygen will be depleted. Water hardness, alkalinity, pH (associated with buffering capacity) and nutrients such as nitrates, carbonates, and phosphates, are some of the other important chemical characteristics governing the nature

and quantity of wastes in the different phases of a natural aquatic system (EPA,1976; EPA, 1994).

The concentrations of sulphate in all the sampling stations in all the sampled months were within the acceptable limit except in February and July where high values of sulphate were recorded. The deviation of the values from the trend might be due to wastes from industrial and the farming activities which were at their peak in July. Sulphate doses of 1000 to 2000 mg have a cathartic effect on humans, resulting in purgation of the alimentary canal (Sa'eed and Mahmoud, 2014). Water containing magnesium sulphate at a concentration of 1000 mg/L acts as a purgative in normal humans, but concentrations below this are apparently physiologically harmless to the general population (Health Canada, 1993).

Water hardness was very high throughout the sampling months. This could be attributed to high level of calcium and magnesium present in the river which might have found its way into the River Romi from homes and industries. During the dry season, River Romi is in influent condition, so the river flow is maintained by groundwater discharge. Usually, there is a direct hydraulic connection between the river system and the upper portion of the shallow aquifers. This makes the water inappropriate for washing as it requires large amount of detergent to obtain maximum foam. Based on classification of water conducted by Roxanne and Tom (2012), softness and hardness water were measured as follows in mg/L: 0-60 soft, 60 – 120 moderately soft, and 121 – 180 moderately hard and above 180 are hard. Thus, considering this classification, it can be

deduced that almost all the water samples analyzed in their study in Kano were hard, but safe for drinking and other domestic purposes (Sa'eed and Mahmoud, 2014).

Alkalinity level decreased progressively from February to July. The reduction might be due to the decrease in mineral salts contents with increase in rainfall. The Alkalinity value in water provides an idea of natural mineral salts present in the water. The main compounds that could have contributed to alkalinity levels include bicarbonates, hydroxides, phosphates and borates (Wania, 2002). The alkalinity levels assessed in the water samples of Fagge River in Kano by Sa'eed and Mahmoud (2014) in dry season were all higher than those recorded in this study. The oil/grease level was generally low in all the months except in March that had the highest value. The higher value of oil and grease recorded might have resulted from industrial effluents of Kaduna refinery that always end up in River Romi. The values obtained for oil and grease were within WHO acceptable limit of not more than 10.00mg/L, except for the month of March (Beg *et al*, 2003).

Electrical conductivity was positively correlated with temperature. Increase in temperature could have been responsible for high EC recorded in this study. This is because heat will activate the ions which will in turn tend to collide faster (Zabel, 1993). The same reason might go for the effect of temperature on TDS. In the same way, TDS was positively correlated with EC. Electrical conductivity is mostly dependent on quantity of TDS in water. Sulphate concentration was strongly and positively correlated with DO. This implies that DO is a principal determining factor for the concentration of

sulphate which might have resulted from the oxidation of sulphur element. This finding is in contrast to the study of Uzoekwe and Oghosanine (2011) who reported negative correlation in the physicochemical parameters of Ubeji Creek, Warri, Southern Nigeria.

There was positive correlation between Bacillariophyta species composition and PO_4 concentration. This could insinuate that PO_4 concentration plays a role in the growth of Bacillariophyta organism (Stokes, 1975). Chlorophyta was negatively correlated with both TDS and alkalinity. Excess dissolved solids could have lead to decrease in chlorophyta species composition and vice versa. The species composition of cyanophyta was negatively quantified by pH level; high or low pH might stress the species composition. The composition of protozoans and cladocerans were negatively correlated with temperature, EC, TDS and BOD. Presence of the mentioned physicochemical parameters could reduce the composition of the protozoans and cladocerans. Copepod observed in this study was negatively correlated with alkalinity. High or low alkaline has a drastic effect on copepods abundance. This study is in contrast with the findings of Iloba and Ruejoma (2014) who reported that alkalinity and pH favoured zooplankton growth and abundance in the river as seen from the positive correlation with pH. The positive significant influence of conductivity on the abundance of protozoa and Cladocera could be due to ionic and nutrient enrichment of the river from the surrounding environment (Iloba and Ruejoma, 2014).

The heavy metals were found to be in various concentrations in all the sampling stations except in July where Pb was not recorded. The absence of Pb in the month of July could

be attributed to the volume of water in the river that would have led to dilution of the heavy metal concentration beyond detectable level. The absence of Pb in this study is in agreement with Mohamed *et al.* (2010) who worked on some surface water bodies of Nile Delta in Egypt during wet season in Egypt and recorded low level of lead. The level of Pb decreased progressively from February to April in the dry season. There was increase in Pb contents from May to June, while in July no Pb was recorded. The average concentration of Pb in the two seasons was low (0.19 mg/L). This finding is in agreement with the report of Emeaso (2011) who reported that heavy metal concentration decreased downstream for Pb.

The average concentration of Mn was high in April during dry season while lower value was recorded in June. On the average, dry months had lower levels of Mn compared to that of rainy season. The high level of Mn in the rainy season on average might be associated with chemical and metal discharges in the municipal waste and industrial effluents that enters the river. The Cr level was slightly higher in February during the dry season, while during the rainy season higher value was obtained in July. The higher level of Cr metal concentration in rainy season than in dry season on the average might be associated with generated domestic wastes and washing off of the earth's crust by rain. There was a decrease in quantity of Ni from the first month of dry season to rainy season except in July where higher value was recorded. High level of Ni in July might be attributed to other relevant occupational activities like steel making, welding, cutting, glass and ceramic production etc. as rainfall was high during that sampling month (Vilia-

Elena, 2006). Likewise Zn level decreased the same way Ni from February to July when very low value was obtained. The mean concentration of Ni in the dry month was lower than the one observed in rainy season, the reverse was the case for Zn. The high level of Zn in the dry season might be associated with evaporation that could result in the concentration of the metal. The concentration of heavy metals such as Pb and Zn in all the sampling stations and within the sampling months were all within the permissible limit recommended by Food and Agriculture Organization (1985). Similarly, Mn was within the FAO (1985) limit in March and June; also Ni concentration, except in February that was observed to be above the FAO limit of 0.2mg/L. In contrast, the concentrations of Cr in all the sampling stations were far above the FAO limit of heavy metals (0.5mg/L). This might have originated from corrosion of brass fittings of submersible pumps used in ground water wells as reported by FAO (1997). It could also be due to passage of effluent from Refinery Channel into River Romi, or from sewage and other industrial wastes or refuse which may include lead battery that could ultimately leach into the ground thereby contaminating the water. The presence or absence of Pb, Ni, V and Cd in the refinery wastewater is an indication that the process of wastewater quantity, quality and composition may change with changing logistics during the routine shifts run by the refinery (UNEP, 1992).

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The receiving water body and wastewater from the Kaduna Refinery have shown to result in appreciable concentrations of chemical contaminants (including trace metals) in the water. It can therefore be concluded that

- i. All the physicochemical parameters were within the WHO permissible limits of petrochemical effluent parameters except EC in February ($664.54 \mu\text{scm}^{-1}$) and April ($417.17 \mu\text{scm}^{-1}$), TDS in February (282.77g/mL) COD in all the sampling months and oil and grease in March (22.25g/mL). All the heavy metals were above the WHO acceptable limits making the water unfit for drinking.
- ii. The highest number of phytoplankton was found in *Stigonemasp.* (752) and the lowest was observed in *Closteriumsp.* and *Pleurogastersp.* with one each, while, zooplankton had highest and lowest number in *Paramaeciumsp.* (49) and *Heliodiaptomussp.* (6)
- iii. The plankton distribution and abundance were influenced by some physicochemical parameters of the River.

6.2 Recommendations

The state of River Romi is under pollution that needs to be addressed. Based on the findings of this study, it is recommended that:

- i. Kaduna Refinery and other companies along the catchment area of River Romi need to maximize purification of their effluents as some heavy metals were found to be above WHO acceptable limits.
- ii. Environmental protection agency need to intensify monitoring and mitigation of River Romi as it serves as source of water supply to the community along the river course.
- iii. Further studies need to carry out to ascertain the level of heavy metals in the benthic stratum as well as the effects on benthic organisms.

CONTRIBUTION TO KNOWLEDGE

Title: Effect of Kaduna Petrochemical Refinery Effluents on Water Quality and Planktons of River Romi, Kaduna, Nigeria

Name: Olofinbiyi, Stella Bola

Registration Number: M.Sc./SCIE/ 43988/2012/2013

Programme: MSc. Biology

The study has contributed to the scientific knowledge as follows:

- i. Almost all the physicochemical parameters of River Romi were within the WHO limits except EC (664.54 μ S/cm) in February, COD (438.97mg/L) in February and oil/grease (128.25mg/L), while Ni (5.85mg/L) was the highest heavy metal recorded in May.
- ii. The most dominant species of phytoplankton was *Stigonema* sp. (752), while *Microcyclops* sp. (58) was the highest zooplankton.
- iii. Phosphate, Bacillariophyta, Copepods and Chlorophyta correlated negatively with Protozoan, Cyanophyta and Euglenohyta.

REFERENCES

- Adekunle, A. S. and Eniola, I. T. K. (2008). Impact of Industrial Effluents on Quality of Segment of Asa River within an Industrial Estate in Ilorin, Nigeria. *New York Science Journal*, 1 (1): 17-21.
- Aderogba, K. A. (2011).Significance of Kaduna River to Kaduna Refinery and Petrochemicals Complex: Some Checks and Balances.*International Multidisciplinary Journal, Ethiopia*, 5 (22): 83-98.
- Adeyemi, O. T. (2004). Oil Exploration and Environmental Degradation: The Nigerian Experience. *Environmental Informatic Archives*,(2): 389-393.
- Agatha, A. N. (2011). Water quality and micro-organisms of leachate-contaminated pond.*American Journal of Scientific and Industrial Research*, 2(2): 205-208.
- Agedengbe, K., Akinwole, A. O. and Babatunde, A .O. (2003). Effluents Characteristics of Selected Industries in Western Nigeria and Implications for re-use in Agricultural Production. *Journal of EnvironmentalExtension*, 4: 79-82.
- Ajayi, S.O. and Osibanji, O. (1981) Pollution studies on Nigeria Rivers 11; Water quality of some Nigerian Rivers. *Environmental Pollution Series*, 2: 87-95.
- Al-Amin, M. A. (2013). Energy Production and Environmental Concerns in Nigeria: The Case of Kaduna Petroleum Refinery on its Host Community.*Journal of Energy Technologies and Policy*, 3(10): 67-77.
- American public health association (APHA) (1998). *Standard Methods for the Examination of water and Wastewater* 20th edition. American Public Health Association, American Water Works Association and Water Environment Federation (APHA-AWWA-WEF), Published by the American Public Health Association, Washington D.C. Pp. 23-32.
- American Society for Testing Material(1995). Standard Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor. Retrieved on 09/11/16 from <http://www.astm.org/DATABASE.CART/HISTORICAL/F1249-90R95.htm>
- American Society for Testing Material (2005). *Annual book for ASTM standards*. American Society for Testing Materials. 285P.
- Andren, A. W. (1973). The geochemistry of mercury in three estuaries from the Gulf of Mexico. *Ph.D. Dissertation*, University of Florida, Gainesville. 140 P.

- Aneni I. T. and Hassan, A. T. (2003). Effect of pollution on seasonal abundance of plankton in Kudeti and Onireke Stream Ibadan, Nigeria. *The Zoologist*, 2 (2): 76-83.
- Anetor, J. I., Adeniyi, F. A. A., and Olaleye, S. B. (2003). Molecular Epidemiology: A Better Approach for the Early Detection of Pathophysiologic Response to Environmental Toxicants and Diseases. *African Journal of Biomedical Research*. 6: 113-118.
- Armstrong, D. A. and Millemann, R. E. (1974). Effects of the insecticide 'Sevin' and its first hydrolytic product, I-naphthol, on some early developmental stages of the bay mussel *Mytilus edulis*. *Marine Biology (Berl.)*, 28: 11-15.
- Asonye, C. C., Okolie, N. P., Okenwa, E. E. and Iwuayanwu, U. G. (2007). Some Physico-Chemical Characteristics and Heavy Metal Profiles of Nigeria Rivers, 6(5): 617-24. Available online at <http://www.academicjournals.org/AjB>.
- Augustus, O. A. (2011). Effects of Warri Refinery Effluents on Water Quality from the Iffie River, Delta State, Nigeria. *American Review of Political Economy*, 1: 45-56.
- Awomeso, J. A., Taiwo, A. M., Gbadebo, A. M. and Arimoro. A. O. (2010). Waste disposal and pollution management in urban areas: A workable remedy for the environment in developing countries. *American Journal of Environmental Sciences*, 6(1): 26 – 32.
- Barnes, K.H., Meyer, J.L and Freeman, B.J. (1998). Sedimentation and Georgia's fishes: An analysis of existing information and future research. 1997 Georgia Water Resources. Conference, March 20-22, 1997, University of Georgia, Athens, Georgia.
- Beg, M. U., Al-Muzaini, S., Saeed, T., Jacob, P.G., Beg, K. R., Al-Bahloul, M., Al-Matrouk, K., Al-Obaid, T. and Kurian, A. (2001). Chemical contamination and toxicity of sediment from a coastal area receiving industrial effluents Kuwait. *Archives of Environmental Contamination and Toxicology*, 41: 289–297.
- Beg, M. U., Saeed, T., Al-Muzaini, S., Beg, K. R. and Al-Bahloul, M. (2003). Distribution of petroleum hydrocarbon in sediment from coastal area receiving industrial effluents in Kuwait. *Ecotoxicology and Environmental Safety*, 54: 47–55.
- Benes, P., Gjessing, E. T., and Steinnes, E. (1976). Interactions between humus and trace elements in freshwater. *Water Resource*, 10: 711-716.

- Bowes, G. W. (1972). Uptake and metabolism of 2, 2-bis-(p-chlorophenyl)- 1,1,1-trichloroethane (DDT) by marine phytoplankton and its effect on growth and electron transport. *Plant Physiology*, 49: 172-176.
- Brettum, P. and Andersen, T. (2005). *The use of phytoplankton as indicators of water quality*. NIVA report, SNO 4818-2004.
- Burgis, M. J. and Symoens, J. J. (1987). African wetlands and shallow water bodies/Zones humides et lacs peu profonds d'Afrique. Directory/Repertoire. *Travellers Document Institute de French Rech Sciety Développement Cooperate*, (211):650-653.
- Butler, G. L., Deason, T. R., and O'Kelley, J. C. (1975). Loss of five pesticides from cultures of twenty-one planktonic algae. *Bulletin of Environmental Contamination and Toxicology*, 13: 149-152.
- Calamari, D. (1985). Review of the state of aquatic pollution of West and Central African inland waters. *CIFA Occas.Pap*, (12):26.
- Colby, R. S. (1967). Calculating synergistic and antagonistic responses of herbicide combinations. *Weeds*, 15: 20-22.
- Cynthia, A. J. (2006). The crude truth about pollution and global warming (<http://www.renewamerica.us/columns/janak>) 1060819.
- Davies, B. and Gasse, F. (1988). African wetlands and shallow water bodies/Zones humides et lacs peu profonds d'Afrique. Bibliography/Bibliographie. *Trav.Doc.Inst.Fr.Rech.Sci.Dév.Coop.*, (211): 498-502.
- Davies, O. A., Ugwumba, A. A. A. and Abolude, D. S. (2008) Physico-chemical Quality of Trans-Amadi (Woji) Creek Port Harcourt, Delta, Niger Delta, Nigeria. *Journal of Fisheries International*, 3(3): 92-97.
- DeFilippis, L. F. and Pallaghy, C. K. (1976). The effect of sublethal concentrations of mercury and zinc on *Chlorella*. I. Growth characteristics and uptake of metals. *Z. Pflanzenphysiol.*, 78:197-207.
- Dejoux, C., Deelstra, H. and Wilkinson, R. (1981). Pollution. In The ecology and utilization of African inland waters, ed. J. Symoens, M. Burgis and J. Gaudet. *UNEP Report on Processing Series*, (1):149-161.

- Dunstan, W. M., Atkinson, L. P., and Natoli, J. (1975). Stimulation and inhibition of phytoplankton growth by low molecular weight hydrocarbons. *Marine Biology*, 31: 305-310.
- Egborge, A. B. M. and Fagade, S. O. (1999). Notes on the hydrobiology of the Wikki warm spring, Yankari Game Reserve, Nigeria. *Poland Archieve of Hydrobiology*, 23: 313-322.
- Emeaso, O. I. (2011). *Pollution and self-purification studies of River Romi, Chikun Local Government Area Kaduna State*. A thesis submitted to the postgraduate school in partial Fulfillment of the requirements for the award of the Degree of Master of Science in Water Resources and Environmental. Pp. 28-87.
- Emongor, V., Nkegbe, E., Kealotswe, B., Koorapetse, I., Sankwase, S., and Keikanetswe, S. (2005). Pollution indicators in Gaborone industrial effluent. *Journal of Applied Science*, 5: 147-150.
- EPA (1976). *Quality criteria for water*, US EPA. 440/9-76-023; Environmental Protection Agency, Washington DC.
- EPA (1994). Drinking water regulations and health advisories. 822-R-94-001.
- Ewa, E. E., Iwara, A. I., Adeyemi, J. A., Eja, E.I., Ajake, A.O. and Otu, C. A. (2011). Impact of Industrial Activities on Water Quality of Omoku Creek. *Sacha Journal of Environmental Studies*, 1(2): 8-16.
- Ezemoronye, O. U and Amogu, N. (1998). Microbiological Studies of Effluents from the Nigerian Fertilizer and Paper Mill Plants. *International Journal of Environmental Studies*, 54:213-221.
- Ezenobi, N. O. and Okpokwasili, G. C. (2004). Bacterial flora and physico-chemical characteristics of Hospital sewage in Port Harcourt City. *Nigerian Journal of Microbiology*, 18(2): 277-283.
- Fakayode, S. O. (2005). Impact assessment of industrial effluent on water quality of the receiving Alaro river in Ibadan Nigeria. *AJEAM-RAGEE* 10: 1-13.
- Falchuk, K. H., Fawcett, D. W. and Vallee, B. L. (1975). Role of zinc in cell division of *Euglena gracilis*. *Journal of Cellular Science*, 17: 57-58.
- FEPA (1991). *National Environmental Protection (Effluent Limitation) Regulations*. under section 40.

- Fisher, N. S., Carpenter, E. J., Remsen, C. C., and Wurster, C. F. (1974). Effects of PCB on interspecific competition in natural and gnotobiotic phytoplankton communities in continuous and batch cultures. *Microbiology Ecology*, **1**: 39-50.
- Fisher, N. S., Graham, L. B., Carpenter, E. J., and Wurster, C. F. (1973). Geographic differences in phytoplankton sensitivity to PCBs. *Nature*, 241: 548-549.
- Food and Agriculture Organization (1985). Water quality guidelines for agriculture, surface irrigation and drainage. *Food and Agriculture Organization Review*, 1: 29-31.
- Food and Agriculture Organization (1991). African Fisheries and the Environment. Food and Agriculture Organisation of the United Nations Regional Office for Africa Accra. RAFR/91/02.26pp.
- Food and Agriculture Organization (1997). Expert Committee on Food Additives, World Health Organization, Geneva. *WHO Technical Report series (FAO) Rome*, 1(2): 20-26.
- Gause, G. F. (1934). *The Struggle for Existence*, Williams and Wilkins, Baltimore. 163 P.
- Glooschenko, V. and Lott, J. N. A. (1976). Effects of chlordane on the green alga *Scenedesmus quadricauda*. *Abst. Thirty-ninth Annual Meeting, American Society of Limnology and Oceanography*, Savannah, Georgia.
- Glyn, H. J. and Gary, W. H. (1996). *Environmental Sciences and Engineering*. Prentice Hall International Inc. 778P.
- Gore, A. L. (1993). *Earth in the Balance Ecology and the Human Spirit*, New York: Penguin Book. Pp. 105-119.
- Hansen, D. J. (1974). 'Aroclor' 1254. Effect on composition of developing estuarine animal communities in the laboratory. *Contributions in Marine Science*, 18: 19-33.
- Harris, R. C., White, D. B. and Macfarlane, R. B. (1970). Mercury compounds reduce photosynthesis by plankton. *Science*, 170: 736-737.
- Health Canada (1993). Guidelines for Canadian drinking water quality. Water treatment principles and applications. *A manual for the production of drinking water*. Environmental Health Directorate, Health Protection Branch, Ottawa. Pp. 233-251.

- Hendrickson, W. A., Pähler, A., Smith, J. L., Satow, Y., Merritt, E. A. and Phizackerley R. P. (1974). Crystal structure of core streptavidin determined from multiwavelength anomalous diffraction of synchrotron radiation. *Current Issue*, 86(7):2190-2194.
- Hollister, T. A. and Walsh, G. E. (1973). Differential responses of marine phytoplankton to herbicides: oxygen evolution. *Bulletin of Environmental Contamination and Toxicology*, 9: 291-295.
- Hollister, T. A., Walsh, G. E. and Forester, J. (1975). Mirex and marine unicellular algae: accumulation, population growth and oxygen evolution. *Bulletin of Environmental Contamination and Toxicology*, 14: 753-759.
- Hugh, C. and Maduka, C. (2006). Water Pollution and Man's Health. *The Internet Journal of Gastroenterology*. 4(1): 348-356.
- Hunt, S. and Hedgecott, S. (1992). Revised environmental quality standards for nickel in water. WRC report to the Department of the Environment DoE 2685/1.
- Ikomi, R. B. and Anyanwu, E. D. (2010). Zooplankton of Ogba River, Benin City, Nigeria. *Bioscience Research Communication*, 22 (5): 225-228.
- Iloba, K. I. and Ruejoma, M. G. O. (2014). Physico-Chemical Characteristics and Zooplankton of Ekpan River, Delta State, Nigeria. *International Journal of Applied Biological Research*, 6(1): 8-30.
- Imoobe, T. O. T. and Adeyinka, M. L. (2010). Zooplankton-based assessment of the trophic state of a tropical forest river. *International Journal of Fisheries and Aquaculture*, 2(2): 064-070.
- Jacobson, I. M., Cacoub, P., Dal Maso, L., Harrison, S. A. and Younossi, Z. M. (2010). Manifestations of chronic hepatitis C virus infection beyond the liver. *Clinical Gastroenterol Hepatology*, 8(12):1017-1029.
- Jeje, C. Y. and Fernando, C. H. (1992). Zooplankton associations in the middle Niger-Sokoto basin (Nigeria: West Africa). *International Review of Hydrobiology*, 77 (2): 237-253.
- John, D. C. (2002). *The Green Lane Environment Canada*. Retrieved from <http://www.atl.ec.gc.ca/epb/progs/petrol.html>.
- Kanu, I. and Achi, O.K. (2011). *Industrial Effluents and Their Impact on Water Quality of Receiving Rivers Ona*.

- Kuehn, R. L., Berlin, K. D., Hawkins, W. E. and Ostrander U. K. (1995). Relationships among Petroleum Refining, water and sediment contamination and fish health – *Journal of Toxicology and Environmental Health*, 46:101-105.
- Lekwot, V.E., Yakubu M.T., Michael K.B., Ya'u H., Ishaya M., Shehu B.M (2014) Effects of emissions from Kaduna Refining and Petrochemical Company (KRPC) on soil fertility in Rido area of Kaduna Metropolis, Nigeria. *International Journal of Environmental Monitoring and Analysis*, 2(2): 117-122
- Lomonosov, M. V. (1969). The toxicity of copper complexes towards *Scenedesmus quadricauda*. *Mikrobiologiya*, 38: 729-731.
- Mandelli, E. F. (1969). The Inhibitory effect of copper on marine phytoplankton. *Contr. Science Univer., Tex.* (14):47-57.
- Marcus, A. C. and Ekpete, O. A. (2014). Impact of Discharged Processed Wastewater from an Oil Refinery on the Physicochemical Quality of a Receiving Waterbody in Rivers State, Nigeria. *IOSR Journal of Applied Chemistry*, 7(12): 1-8.
- Marine Pollution Monitoring Management Group (1998). National monitoring programme survey of the quality of UK coastal waters Marine pollution monitoring management Group, Aberdeen.Pp. 35-71. ISBN 09532838 36.
- Meijer, C. L. C. (1972). The effect of phosphate on the toxicity of copper for an alga (*Chlamydomonas* sp.) (in Dutch). *TNO-nieuws*, 27: 468-473.
- Mohamed, M. E., Ahmed, A. El Barbary, Mohamed, M. Y. and Eman A. M. (2010). Heavy metal concentrations in surface river water and bed sediments at Nile Delta in Egypt. *Suo*, 61(1): 1–12.
- Mohammad, M. A. and Saminu, M. Y. (2012). A water Quality and Phytoplankton of Salanta River Kano, Nigeria. *Journal of Biological Science and Bioconservation*, 4: 65-73.
- Mosser, J. L., Fisher, N. S., and Wurster, C. F. (1972). Polychlorinated biphenyls and DDT alter species composition in mixed cultures of algae. *Science*, 176: 533-535.
- Ogunfowokan, A. O. and Fakankun, O. A. (1998). Physico-chemical characterization of effluents from beverage processing plants in Ibadan, Nigeria. *International Journal of Environmental Studies*, 54: 145–152.
- Onwumere, B. G. and Oladimeji, A. A. (1990). Accumulation of Metals and Histopathology in *Oreochromis niloticus* exposed to treated NNPC Kaduna

- (Nigeria) Petroleum refinery effluent. *Journal of Ecotoxicology and Environmental Safety*, 19:123–134.
- Osibanjo, O., Daso, A. P. and Gbadebo, A. M. (2011). The impact of industries on surface water quality of River Ona and River Alaro in Oluyole Industrial Estate, Ibadan, Nigeria. *African Journal of Biotechnology*, 10(4): 696-702.
- Otokunefor, T. V. and Obiukwu, C. (2005) Impact of refinery effluent on the physicochemical properties of a water body in the Niger Delta. *Applied Ecology and Environmental Research*, 3: 61-72.
- Palmer, C. M. (1969). A composite rating of algae tolerating organic pollution. *Journal of Phycology*, 5(1): 78-82.
- Perdue, E. M., Beck, K. C. and Reuter, J. H. (1976). Organic complexes of iron and aluminum in natural waters. *Nature*, 260:418-420.
- Perry, R. (2003). A Guide to the marine plankton of southern California. <http://www.msc.ucla.edu/oceanglobe>.
- Phiri, O. Mumba, P. Moyo, B. H. Z. and Kadewa, W. (2005). Assessment of the impact of industrial effluents on water quality of receiving rivers in urban areas of Malawi. *International Journal of Environmental Science and Technology*, 2:237-244.
- Plum, R. H., Jr. and Lee, G. F. (1973). A note on the iron-organic relationship in natural water. *Water Resource*, 7: 581-585.
- Quinby-Hunt, M.S., Lughlin, M.D. and Quintanilha, A.T. (1986) Instrumentation for environmental monitoring, 2nd ed., John Wiley and Sons, New York. pp. 155-184; 338-374.
- Reynolds, C., Huszar, V., Kruk, C., Naselli-Flores, L. and Melo, S. (2002). Towards a functional classification of the freshwater phytoplankton. *Journal of Plankton Research*, 24: 417-428.
- Roxanne, J. and Tom, S. (2012). Driving Water quality testing and interpreting your Results Revised Ed. Manual. Pp. 53-82.
- Sa'eed, M. D. and Mahmoud, A. M. (2014). Determination of Some Physicochemical Parameters and Some Heavy Metals in Boreholes from Fagge L.G.A of Kano Metropolis Kano State- Nigeria. *World Journal of Analytical Chemistry*, 2 (2): 42-46.

- Saad, M. A. H., El-Rayis, O., and Ahdy, H. (1984). Status of nutrients in Lake Mariut, a delta lake in Egypt suffering from intensive pollution. *Marine Pollution Bulletin*, 15 (1): 408-411.
- Sangodoyin, A. Y. (1991). Groundwater and Surface Water Pollution by Open Refuse Dump in Ibadan, Nigeria. *Journal of Discovery and Innovations*, 3 (1): 24-31.
- Sangodoyin, A. Y. (1995). Characteristics of control of industrial effluents-generated pollution. *Environmental Management and Health*, 6: 15-18.
- Shannon, C. E. and Weaver, W. (1963). *The Mathematical Theory of Communication*, University of Illinois Press, Urbana.
- Sharad, M. and Mashal, C. (2005). *Space and Urban Environment*. Retrieved from doc. <http://www.janaagraha.org/Indiausp>.
- Sheih, Y. J. and Barber, J. (1973). Uptake of mercury by *Chlorella* and its effect on potassium regulation. *Planta*, 109: 49-60.
- Slowey, J. F., Jeffrey, L. M., and Hood, D.W. (1967). Evidence for organic complexed 'copper in sea water. *Nature*, 214, 377-378.
- Sprague, J. B., Rowe, D. W., Westlake, G. F., Heming, T. A., Brown I. T. (1978). *Sub lethal effects of treated liquid refinery effluent from a petroleum refinery on fresh water organisms*. Report prepared by Sprague Associates, Ltd., Guelph, Ontario for the Petroleum Association for Conservation of the Canadian Environment. Ottawa, ON. 297p.
- Steeman-Nielsen, E., Kamp-Nielsen, L. and Wium-Anderson, S. (1969). The effect of deleterious concentrations of copper on the photosynthesis of *Chlorella pyrenoidosa*. *Physiologia Plantarum*, 22: 1121-1133.
- Stokes, P. (1975). Uptake and accumulation of copper and nickel by metal-tolerant strains of *Scenedesmus*. *Verhandlungen des Internationalen Verein Limnologie*, 19: 2128-2137.
- Sournia, A. (1978). Phytoplankton manual. In "Monographs on Oceanographic Methodology 6," UNESCO, Paris. 337p.
- Suleimanov, R.A. (1995). Conditions of waste fluid accumulation at petrochemical and processing enterprises and prevention of their harm to water bodies. *Meditina Truda I Promishlennaia Ekologiya*, 12: 31-36.

- Tanimu, Y, Bako, S.P., Adakole, J.A. and Tanimu, J. (2011). Phytoplankton as Bioindicators of Water quality in Saminaka Reservoir, Northern-Nigeria. *Proceedings of the 2011 international symposium on environmental science and technology*. Dongguan, Guandong province, China. Published by Science press USA: 318-322.
- Tolba, M. K. (1982). Development without destruction. Evolving environmental perceptions. Dublin, Tycooly, *Nat.Resour.Environ.Ser.*, (12):197.
- Tsay, S.-F., Lee, J.-M., and Lynd, J. Q. (1976). The interactions of eu++ and CNwith araquat phytotoxicity to a *Chlorella*. *Weed Science*, 18:596-598.
- Udoh, R. K. (1987). *Geographical Regions of Nigeria*, Ibadan, Nigeria. Heinemann Education Publishers, Ibadan. Pp. 23-34.
- Ugya, A.Y. and Umar, S.A.(2015). A Review on the Pollution and Phytoremediation of Romi Stream *IOSR Journal of Pharmacy and Biological Sciences (IOSR-JPBS)*, 10(2): 25-29.
- UNEP (2011). Emerging Issues in Our Global Environment. *Marine Environmental Research*, 70(2): 250-252.
- United Nations Development Program (2006). *Niger Delta Human Development Report*, Abuja, Nigeria, UNDP.
- Uzoekwe, S. A. and Oghosanine, F.A. (2011). The effect of refinery and petrochemical effluent on water quality of Ubeji Creek Warri, Southern Nigeria. *Ethiopian Journal of Environmental Studies and Management*, 4(2): 107-116.
- Verlencar, X.N. and Desai, S. (2004). Phytoplankton Identification Manual. National Institute of Oceanography. Dona paula, Goa India. Pp33.
- Vilia- Elena, S. (2006). Parkinson's disease and exposure to manganese during welding. *TechD.Welding Allied Process*. 2: 106 – 111.
- Vivan, E. L, Adamu, C. I. and Ayuba, K. N. (2012). Effects of effluent discharge of Kaduna refinery on the water quality of river Romi. *Journal of Research in Environmental Science and Toxicology*. Vol 1(3): 41-46.
- Walsh, G. E. and Grow, T. E.(1971). Depression of carbohydrate in marine algae by urea herbicides. *Weed Science*, 19: 568-570.

- Wania, F., G. L. Daly (2002). **Estimating the contribution of degradation in air and deposition to the deep sea to the global loss of PCBs.** *Atmosphere and Environment*, 36: 5581-5593.
- World Health Organization (1997). Expert committee food additives world health organization, Geneva. *WHO Technical Report series (FAO)* Rome, 1(2): 20-26.
- World Health Organization (1999a). *Guidelines for drinking quality water* WHO, Geneva. Pp. 160-220.
- World Health Organization (1999b). *Guidelines for safe disposal of unwanted pharmaceuticals in and after emergencies*. Essential Drugs and Other Medicines Department, World Health Organization, Avenue Appia 20, CH-1211 Geneva 27, Switzerland. Pp. 31-87.
- Zabel, T.F. (1993). Diffuse source of pollution by heavy metals. *Journal of the Institution of Water and Environmental Management* 20(1):232-267.
- [Zarfl, C.](#) and [Matthies, M.](#) (2010). Are marine plastic particles transport vectors for organic pollutants to the Arctic? [*Marine Pollution Bulletin*](#), 60(10):1810-1814.
- Zarnowski, J. (1972). The effect of ethylenediamine-tetraacetic acid on the growth of *Chlorella pyrenoidosa* and its role in the dynamics of metabolism and accessibility of iron and calcium. *Acta Hydrobiology*, 14: 353-373.
- Zingmark, R. G. and Miller, T. G. (1975). The effects of mercury on the photosynthesis and growth of estuarine and oceanic phytoplankton. *Belle W. Baruch Library in Marine Science*, 3: 45-57.

APPENDICES

Appendix I: The Physicochemical parameters of River Romi in February

Temp	PH	EC	TDS	DO	BOD	COD	PO4	NO3	SO4	TP	TN	Hard	Alk.	OG
31.9	8.32	702	302	4.3	2.3	450	0.11	2.23	8.5	0.96	22.07	152	119	0.1
31.9	8.35	704	304	4.1	2.7	460	0.13	2.43	8.4	0.88	22.09	148	120	0.14
31.8	8.32	702	302	4.2	2.5	470	0.1	2.23	8.6	1.06	22.05	158	118	0.08
32.2	7.49	689	309	6.7	2.6	470	0.1	2.19	10.44	0.94	19.8	184	121	0.4
32.1	7.47	689	309	6.4	2.5	480	0.13	2.2	10.42	0.92	19.6	186	219	0.6
32	7.51	692	310	6.6	2.7	460	0.1	2.21	10.46	0.96	20.2	182	223	0.3
29.9	9.21	615	307	4.5	1.9	330	0.097	2.39	8.64	0.842	19.803	124	139	0.2
29.9	9.28	618	306	4.2	2	340	0.098	2.41	8.62	0.863	20.1	130	138	0.1
29.8	8.86	615	310	4.4	2.1	315	0.099	2.33	8.6	0.851	20	122	136	0.9
33.4	7.2	180	90	5.4	1.8	320	0.097	1.961	9.28	0.959	18.954	136	126	47
33.6	7.3	186	98	5	2	340	0.089	2.032	9.32	0.986	18.921	140	146	47.1
32.8	7.21	190	92	5.2	2.2	310	0.109	1.982	9.4	0.992	20.184	121	160	47.2
32	8.87	427	214	4.5	2	430	0.11	2.386	5.64	0.95	24.71	120	125	0.2
32.3	8.78	430	219	4.2	1.8	460	0.18	2.402	5.64	0.92	26.8	118	118	0.12
32.1	7.92	490	222	4.3	1.9	490	0.1	2.181	5.7	1.4	24.9	128	134	0.18
31.8	9.1	357	180	2.3	1.5	390	0.13	1.98	6.36	0.49	10.28	164	48	0.7
31.9	9.2	358	189	2.5	1.5	380	0.16	2.06	6.42	0.32	10.36	172	42	0.3
31.6	9.2	347	178	2.6	1.4	400	0.12	1.84	6	0.56	10.16	158	40	0.5
29.4	8.07	138	69	3.6	1.3	280	0.15	2.38	7.76	2.01	23.76	212	60	0.4
29.6	8.07	140	69	3.33	1.1	287	0.18	2.4	7.8	2	23.72	214	64	0.5
29.1	8.9	132	71	3.5	1.4	288	0.2	2.36	7.69	2.3	23.78	210	62	0.2
31.1	8	154	76	3.7	2.1	270	0.21	2.65	1.48	1.07	23.31	228	79	0.2
31.3	8	156	78	3.8	1.9	276	0.26	2.69	1.53	1.09	23.4	226	78	0.4
31.2	8.3	153	79	3.9	2.3	280	0.2	2.7	1.46	1.1	23.42	230	81	0.3
30.5	7.53	236	122	4.1	1.2	440	0.1	2.68	2.52	11.35	22.54	180	80	0
30.5	7.56	238	122	3.7	1	430	0.12	2.7	2.56	11.4	22.7	186	86	0
30.2	7.5	232	122	3.9	1.3	450	0.11	2.72	2.54	11.31	22.48	183	80	0
29.8	7.67	133	68	5.5	2.5	430	0.12	2.67	26.4	7.84	21.59	196	76	0
29.8	7.69	133	70	5.7	2.3	434	0.14	2.87	26.8	7.88	21.63	194	78	0
29.8	7.7	141	73	5.4	2.4	432	0.1	2.47	26.6	7.82	21.56	198	74	0
28.3	8.32	130	65	3.6	3.1	430	0.11	2.23	1.56	0.36	19.99	168	36	0.2
28.3	8.35	136	68	4.1	2.9	430	0.13	2.43	1.58	0.34	20.01	172	34	0.1
28.6	8.32	133	60	3.9	3	430	0.14	2.23	1.54	0.38	20	164	38	0.3
28.4	8.26	193	97	4.4	3.1	440	0.08	2.37	8.56	0.7	23.48	188	82	0.2
28.6	8.28	197	99	4	3.5	440	0.09	2.39	8.48	0.8	23.5	198	84	0.4
28.8	8.32	196	96	4.2	3.3	460	0.08	2.75	8.52	0.6	23.49	178	80	0.5

Appendix II: The Physicochemical parameters of River Romi in March

Temp	PH	EC	TDS	DO	BOD	COD	PO4	NO3	SO4	TP	TN	Hard	Alk.	OG
26.4	7.76	94	46	3.6	2.3	420	0.1	2.14	1.12	0.55	20.09	116	22	0
26	7.8	96	42	4	2.6	440	0.1	2.12	1.14	0.57	20.8	118	26	0
26.2	7.76	90	54	3.8	2.2	410	0.11	2.16	1.1	0.56	20	120	20	0
28.6	7.7	131	63	3.5	3.5	440	0.06	2.24	3.6	0.82	21.78	140	62	0.1
28.6	7.7	132	65	3.7	3.7	430	0.07	2.34	3.4	0.84	21.8	142	66	0.3
28.2	7.73	134	64	3.8	3.3	460	0.06	2.31	3.8	0.81	21.68	141	61	0.2
29.7	7.32	122	61	4.2	2.1	630	0.14	2.46	2.84	1.31	20.18	244	50	0
29.7	7.36	128	64	4	2	630	0.16	2.48	2.86	1.35	21	242	52	0
30	7.34	124	60	4.4	2.2	640	0.12	2.41	2.83	1.33	20.14	248	51	0
27.8	7.44	106	52	5.9	3	640	0.16	2.56	3.16	1.42	18.95	216	56	0
27.8	7.46	103	55	6	3.1	640	0.14	2.58	3.18	1.38	18.8	218	60	0
27.9	7.4	108	50	6.1	3.2	643	0.18	2.54	3.12	1.44	19.05	220	52	0
28.6	7.83	141	70	3.5	1.2	520	0.1	2.11	5.58	0.65	20.18	196	71	0
28.6	7.88	150	70	3.2	1.3	540	0.14	2.15	5.78	0.7	20.16	196	78	0
28	7.8	140	73	3.2	1.4	510	0.09	2.13	5.72	0.58	20.2	203	68	0
31.5	7.85	146	74	3.5	1.6	520	0.08	2.52	1.8	8.07	21.04	270	80	0
31.5	7.85	149	73	3.6	1.8	510	0.09	2.58	1.6	8.17	21.17	272	82	0
31.2	7.86	152	72	3.8	1.7	530	0.1	2.48	1.2	7.9	21.09	271	84	0
32.5	9.08	463	231	2.7	1.3	420	0.12	2.282	4.28	1.02	21.69	130	138	0
32.5	9.08	470	233	2.9	1.1	430	0.16	2.296	4.3	1.22	22	124	160	0
32.8	9.4	462	240	2.8	1.4	350	0.09	2.4	4.4	1.18	21.8	150	121	0
31	9.02	382	190	2.1	0.62	420	0.1	1.89	4.84	0.5	9.9	156	76	0
32	9.2	388	190	2	0.64	400	0.12	2.02	8.9	0.72	9.82	142	82	0
33	9.18	379	188	2.2	0.7	410	0.16	1.92	8.82	0.48	10.2	166	80	0
29.2	9.16	524	260	2.7	1	350	0.097	2.287	8.001	0.924	18.954	136	119	0
29.4	9.18	528	270	2.9	1.2	355	0.098	2.29	8.1	1.002	18.865	130	120	0
29.3	9.14	526	265	2.8	1.1	260	0.091	2.31	8.44	0.94	18.984	142	121	0
32.3	7.3	186	93	5.4	1.4	350	0.101	1.896	8.32	0.913	19.897	144	124	43.9
32.8	7.3	179	90	5.8	1.6	360	0.099	1.706	8.9	0.943	19.968	136	136	43.9
31.9	7.4	188	89	5.3	1.3	380	0.091	1.922	8.5	0.992	20.345	149	144	43.4
29.9	9.4	618	325	5.2	2.3	420	0.09	2.45	8.72	0.83	24.61	164	133	0
29.8	9.4	618	352	5.4	2.7	430	0.1	2.47	8.68	0.85	22.8	172	143	0
30.2	9.43	620	312	5.3	2.6	440	0.11	2.46	8.7	0.81	26.19	155	123	0
29.8	8.2	712	286	7.2	1.91	440	0.15	2.27	9.64	0.99	22.73	208	119	0.1
29.8	8.2	714	287	7	2.3	440	0.17	2.3	9.66	1.01	22.75	204	121	0.2
29.9	8.23	711	285	7	2.22	470	0.14	2.22	9.62	1	22.74	212	120	0.14

Appendix III: The Physicochemical parameters of River Romi in April

Temp	PH	EC	TDS	DO	BOD	COD	PO4	NO3	SO4	TP	TN	Hard	Alk.	OG
33.1	8.1	708	310	3.92	2.4	430	0.11	2.66	11.2	0.92	19.33	157	123	0.1
33.3	8.1	700	320	4.3	2.1	450	0.12	2.68	11.5	0.84	19.43	156	133	0.16
33.2	8.2	701	300	4.08	2.3	420	0.1	2.67	11.1	0.98	19.23	158	113	0.12
30.1	9.83	656	221	6.89	1.7	450	0.09	2.84	8.04	0.93	19.43	172	123	0.8
30.2	9.86	656	223	6.7	1.8	450	0.11	2.82	8.14	0.9	19.45	178	125	0.6
30	9.8	659	222	6.8	1.9	450	0.1	2.86	8.03	0.96	19.44	173	124	0.9
29.1	8.94	495	248	4	1.5	330	0.1	2.02	8.46	0.938	19.808	132	126	0.5
29.12	8.9	495	251	4.3	1.4	340	0.101	2.12	8.42	0.921	19.906	130	128	0.7
29.4	8.98	490	256	4.4	1.6	310	0.998	1.92	8.26	0.948	19.707	140	130	0.3
32.3	7.2	184	91	7.5	1.8	260	0.107	2.409	8.72	0.702	20.557	138	110	42
32.4	7.4	186	93	7.8	1.6	270	0.123	2.3	8.3	0.781	19.889	132	118	42.5
32.6	7	182	92	7.7	1.7	290	0.104	2.376	8.89	0.709	20.201	122	120	43.1
33.2	9.13	477	236	4	2.7	430	0.13	2.791	5.08	1.15	26.5	128	117	0.4
32.89	9.18	480	232	4.3	2.6	420	0.18	2.86	5.18	1.2	26.89	130	118	0.6
32.6	9.12	462	246	4.1	2.8	490	0.12	2.599	5.3	1.18	26.4	118	120	0.2
30.8	9.03	389	194	2.2	0.98	400	0.11	1.9	5.88	0.35	8.39	148	50	0.4
30.9	9.08	379	195	2.1	0.77	390	0.1	1.92	5.98	0.42	8.49	120	58	0.6
31.09	8.98	400	186	2.4	0.92	410	0.14	1.94	5.7	0.52	8.28	166	42	0.3
28.3	7.65	141	70	2.8	1.8	370	0.07	2.06	7.48	0.27	19.14	184	76	0.6
28.6	7.64	141	76	2.5	1.6	376	0.08	2.08	7.52	0.4	19.12	183	74	0.5
28.1	7.4	140	70	2.7	1.9	390	0.09	2.1	7.46	0.2	19.16	187	79	0.4
31.4	7.82	141	70	4	2	360	0.089	2.23	2.44	0.94	21.78	196	60	0.3
31.8	7.86	146	71	4	2.1	370	0.078	2.41	2.48	0.96	21.8	200	63	0.5
31.2	7.8	151	75	4	1.8	350	0.092	2.08	2.42	0.95	21.78	184	60	0.4
29.9	7.21	125	63	3.7	1.9	330	0.14	2.3	3.48	1.19	19.99	156	41	0
29.9	7.3	126	63	3.6	1.7	340	0.12	2.33	3.46	1.2	20.08	148	40	0
29	7.2	127	66	3.8	1.8	350	0.16	2.3	3.44	1.18	21.4	152	42	0
28.5	7.22	118	58	6.2	2.93	310	0.15	2.03	3.68	1.35	20.65	188	45	0
28.6	7.22	116	58	6.1	3	310	0.17	2.14	3.7	1.4	21.05	190	40	0
28.7	7.28	120	61	6.3	3.07	340	0.13	2.08	3.66	1.31	20.6	186	55	0
26.5	7.48	105	52	4.1	2.6	420	0.08	2.07	1.48	0.34	18.95	148	27	0.4
26.7	7.4	110	53	4	2.9	430	0.07	2.08	1.38	0.32	19.05	139	20	0.5
26.3	7.5	102	51	4.2	2.8	410	0.09	2.04	158	0.36	19	157	32	0.3
27.7	7.47	130	65	3.6	2.9	430	0.08	2.12	6	0.7	19.99	84	60	0.6
27.7	7.47	133	67	3.8	2.6	440	0.09	2.14	6.2	0.76	20.01	80	58	0.1
27.9	7.5	136	69	3.9	2.8	450	0.07	2.16	6.1	0.7	20	82	68	0.2

Appendix IV: The Physicochemical parameters of River Romi in May

Temp	PH	EC	TDS	DO	BOD	COD	PO4	NO3	SO4	TP	TN	Hard	Alk.	OG
26.5	7.58	105	52	3.4	2.9	380	0.09	0.97	1.68	0.56	18.95	196	21	0.1
26.7	7.58	106	52	2.8	2.5	400	0.11	0.2	1.7	0.58	19.08	198	20	0.2
26.3	7.78	108	52	3.6	3.4	410	0.1	0.93	1.66	0.54	20.01	200	22	0.3
27.5	7.48	127	64	3.6	3	400	0.03	2.08	7.08	0.25	20.65	88	58	0
27.5	7.48	130	66	3.5	3.2	410	0.05	2.12	7.12	0.27	20.8	86	56	0
27.3	8	123	62	3.2	3.3	420	0.02	2.1	7	0.26	20.45	84	60	0
29.2	7.16	121	60	3.6	1.5	410	0.15	2.6	2.76	1.29	21.31	168	26	0
29.3	7.18	120	67	3.8	1.2	415	0.17	2.63	2.74	1.31	21.63	173	28	0
29.5	7.14	122	62	3.9	1.4	435	0.13	2.66	2.78	1.28	21.3	170	24	0
28.4	7.32	123	61	6	3.1	500	0.15	2.56	3	1.4	21.78	248	31	0.3
28.6	7.36	125	61	6.5	3	540	0.19	2.46	3.08	1.42	21.68	242	30	0.1
28.2	7.3	126	64	6.3	3.2	520	0.14	2.58	2.92	1.38	21.88	252	32	0.2
28.3	7.2	140	70	2.9	1.6	190	0.14	2.35	3.36	1.36	21.03	188	83	0
28.3	7.8	140	78	3.1	1.8	192	0.16	2.45	3.46	1.4	21.06	179	86	0
28.7	7.1	138	74	3.5	2	198	0.12	2.3	3.32	1.28	21.01	193	80	0
31.92	7.86	140	70	3.3	2	200	0.1	2.42	1.96	0.92	21.22	216	62	0.1
31.82	7.89	140	72	3.8	2.1	210	0.18	2.48	1.98	0.94	21.4	220	66	0.08
31.8	7.82	149	71	4.2	1.9	220	0.12	2.4	1.94	0.9	21.18	210	62	0.12
32.7	9.12	471	234	2	1.2	400	0.097	2.434	0.96	1.01	21.5	140	94	0
32.8	9.11	490	236	1.7	1	400	0.11	2.463	0.8	1.22	22.8	150	96	0
32.8	9.13	463	330	1.98	1.4	480	0.11	2.66	1.7	1.82	20.9	132	89	0
31.1	8.97	381	191	2.1	0.9	420	0.1	2.21	1.6	5.03	9.34	180	51	0
31.8	8.96	362	198	2.2	0.98	430	0.32	2.41	1.8	5.18	9.2	172	48	0
32	8.2	398	200	2.4	1	460	0.08	2.3	1.4	5	9.46	192	60	0
29	8.92	490	245	4.2	1.2	270	0.098	2.56	8.24	0.889	19.52	148	132	0
29	8.7	480	248	4.42	1.1	260	0.099	2.46	8.22	0.92	19.628	152	136	0
29.8	9.2	490	241	4.4	1.3	280	0.99	2.68	8.081	0.889	19.5	150	131	0
32.3	7.16	186	94	5.6	1.4	380	0.094	0.987	10.04	1.001	20.56	128	131	31.4
32.3	7.18	180	96	6	1	370	0.099	0.863	9.88	1.001	21.08	141	143	43.9
32.3	7.2	190	92	5.6	1.3	400	0.154	0.966	9.37	0.988	20.96	130	138	39.8
30.8	7.58	689	276	6.2	2.3	430	0.09	1.98	8.12	0.92	20.65	155	118	0
30.9	7.58	680	276	6.1	2.1	430	0.11	1.96	8.22	0.96	20.85	159	120	0
31.02	7.68	696	278	6.3	2.2	430	0.1	1.94	8.17	0.9	20.35	154	119	0
29.6	7.97	650	238	5.1	2	430	0.09	1.9	8.6	0.91	20.56	200	130	0.7
29.7	7.97	653	238	5.4	2.3	430	0.11	1.89	8.4	0.92	20.58	210	138	0.6
29.6	8	650	236	5.3	2.2	436	0.1	1.91	8.8	0.9	20.6	190	126	1.2

Appendix V: The Physicochemical parameters of River Romi in June

Temp	PH	EC	TDS	DO	BOD	COD	PO4	NO3	SO4	TP	TN	Hard	Alk.	OG
30.2	8	568	298	5.6	1.96	400	0.14	2.7	8.16	2.12	27.35	188	131	0.38
30.2	8.2	568	320	5	1.6	410	0.12	2.72	8.2	2.16	28	176	136	0.4
30.5	8.15	576	296	5.4	1.8	390	0.16	2.71	8.17	2.11	27.15	190	132	0.52
31.8	8.7	651	249	7	2	440	0.14	1.98	8.68	1.2	26.97	192	122	1
31.8	8.73	652	251	6.6	2.4	433	0.16	2.01	8.7	1.89	27	196	124	1.2
31.9	8.7	653	248	7.1	2.2	430	0.12	2	8.69	1.21	26.87	193	121	0.8
26.7	8.92	495	245	4.18	1.4	390	0.165	2.49	8.4	1.556	21.878	172	111	0.2
26.8	8.92	505	245	4.38	1.3	385	0.175	2.59	8.48	1.721	22.008	181	110	0.4
26.9	8.92	490	249	4.5	1.2	395	0.165	2.69	8.3	1.5	21.761	176	114	0.1
31.7	7.26	188	93	6.2	1.6	340	0.158	2.423	8.44	1.685	22.73	188	127	49.6
31.9	7.3	186	93	5.4	1.8	340	0.208	2.004	7.98	1.882	22.92	198	133	49.8
32	7.14	190	92	5.8	1.4	380	0.2	2.204	8.8	1.428	23.17	170	108	49.4
32.6	7.93	401	200	2.7	1	410	0.12	2.763	7.92	1.23	28.01	160	106	0.3
32.7	7.8	410	300	2.5	1.1	430	0.18	2.781	7.8	1.31	27.92	180	120	0.5
33.1	8.4	422	290	2.8	1.2	390	0.2	2.901	8.08	1.42	28.24	130	92	0.4
29.6	8.85	386	193	2.3	1	390	0.12	2.1	4.48	0.49	11.13	152	58	0.6
29.2	8.78	391	197	1.9	1.3	400	0.14	2.12	4.32	0.61	11.42	170	56	0.2
30	8.22	400	200	2.1	1.5	380	0.1	2.16	4.63	0.35	11.01	162	62	0.5
26.7	7.1	147	73	3.1	1.4	490	0.25	2.32	4.96	3.76	21.88	164	77	0.8
26.7	7.9	150	76	3.2	1.3	480	0.28	2.4	4.8	3.86	21.78	162	79	0.2
27	7.4	138	72	3.3	1.6	520	0.19	2.3	5.04	3.8	21.98	171	81	0.2
31.2	7.77	93	46	4	2.2	480	0.07	2.35	2.16	0.87	19.99	244	58	0.4
31.2	7.7	95	47	3.8	2.3	490	0.08	2.42	2.2	0.89	20.01	246	56	0.1
31	7.86	91	48	4.4	2.5	460	0.06	2.28	2.14	0.9	20.1	248	54	0.1
29	7.22	50	25	4	1.5	490	0.21	2.25	2.24	1.58	19.99	268	43	0.2
29	7.22	51	25	3.7	1.5	510	0.25	2.3	2.3	1.54	19.89	273	40	0.1
29.3	7.26	52	29	3.9	1.6	480	0.23	2.24	2.22	1.52	20.4	266	40	0.3
27	7.45	31	15	6	1.5	480	0.2	2.24	26	1.47	20.84	228	47	0
27.3	7.48	33	15	5.6	1.9	490	0.23	2.26	25.9	1.49	20.82	240	40	0
27	7.4	35	17	5.9	1.8	510	0.2	2.14	27.1	1.45	20.88	212	54	0
25	7.4	27	14	3.5	3.6	420	0.14	2.7	1.4	0.74	20.84	156	26	0
24.9	7.4	27	16	3.3	3.5	410	0.12	2.72	1.38	0.76	20.64	160	24	0
25.1	7.43	30	13	3.4	3	430	0.16	2.71	1.42	0.72	20.92	154	28	0
30.1	9.91	79	40	3.6	3.2	430	0.03	2.31	7.92	0.27	21.41	124	35	0.2
30.2	9.9	79	42	3.8	3.6	430	0.04	2.32	7.82	0.3	21.6	126	37	0.1
30	9.92	80	38	3.6	3.5	470	0.05	2.3	8.02	0.28	21.39	123	33	0.1

Appendix VI: The Physicochemical parameters of River Romi in July

Temp	PH	EC	TDS	DO	BOD	COD	PO4	NO3	SO4	TP	TN	Hard	Alk.	OG
30.20	8	568	298	5.6	1.96	400	0.14	2.7	8.16	2.12	27.35	188	131	0.38
30.50	8.73	652	251	6.6	2.4	435	0.16	2.01	8.7	1.89	27	196	124	1.2
31.90	8.7	653	248	7.1	2.2	438	0.12	2	8.69	1.21	26.87	193	121	0.8
30.90	8.7	651	249	7	2	440	0.14	1.98	8.68	1.2	26.97	192	122	1
31.80	8.73	652	251	6.6	2.4	433	0.16	2.01	8.7	1.89	27	196	124	1.2
31.40	8.7	653	248	7.1	2.2	430	0.12	2	8.69	1.21	26.87	193	121	0.8
26.70	8.92	495	245	4.18	1.4	390	0.165	2.49	8.4	1.556	21.878	172	111	0.2
26.50	8.92	505	245	4.38	1.3	385	0.175	2.59	8.48	1.721	22.008	181	110	0.4
26.90	8.92	490	249	4.5	1.2	395	0.165	2.69	8.3	1.5	21.761	176	114	0.1
31.70	7.26	188	93	6.2	1.6	340	0.158	2.423	8.44	1.685	22.73	188	127	49.6
31.90	7.3	186	93	5.4	1.8	340	0.208	2.004	7.98	1.882	22.92	198	133	49.8
32.40	7.14	190	92	5.8	1.4	380	0.2	2.204	8.8	1.428	23.17	170	108	49.4
32.60	7.93	401	200	2.7	1	410	0.12	2.763	7.92	1.23	28.01	160	106	0.3
32.70	7.8	410	300	2.5	1.1	430	0.18	2.781	7.8	1.31	27.92	180	120	0.5
33.50	8.4	422	290	2.8	1.2	390	0.2	2.901	8.08	1.42	28.24	130	92	0.4
29.60	8.85	386	193	2.3	1	390	0.12	2.1	4.48	0.49	11.13	152	58	0.6
29.20	8.78	391	197	1.9	1.3	400	0.14	2.12	4.32	0.61	11.42	170	56	0.2
39.50	8.22	400	200	2.1	1.5	380	0.1	2.16	4.63	0.35	11.01	162	62	0.5
26.90	7.1	147	73	3.1	1.4	490	0.25	2.32	4.96	3.76	21.88	164	77	0.8
26.70	7.9	150	76	3.2	1.3	480	0.28	2.4	4.8	3.86	21.78	162	79	0.2
27.50	7.4	138	72	3.3	1.6	520	0.19	2.3	5.04	3.8	21.98	171	81	0.2
31.20	7.77	93	46	4	2.2	480	0.07	2.35	2.16	0.87	19.99	244	58	0.4
31.20	7.7	95	47	3.8	2.3	490	0.08	2.42	2.2	0.89	20.01	246	56	0.1
31.20	7.86	91	48	4.4	2.5	460	0.06	2.28	2.14	0.9	20.1	248	54	0.1
29.10	7.22	50	25	4	1.5	490	0.21	2.25	2.24	1.58	19.99	268	43	0.2
29.80	7.22	51	25	3.7	1.5	510	0.25	2.3	2.3	1.54	19.89	273	40	0.1
29.30	7.26	52	29	3.9	1.6	480	0.23	2.24	2.22	1.52	20.4	266	40	0.3
27.65	7.45	31	15	6	1.5	480	0.2	2.24	26	1.47	20.84	228	47	0
27.03	7.48	33	15	5.6	1.9	490	0.23	2.26	25.9	1.49	20.82	240	40	0
27.30	7.4	35	17	5.9	1.8	510	0.2	2.14	27.1	1.45	20.88	212	54	0
24.50	7.4	27	14	3.5	3.6	420	0.14	2.7	1.4	0.74	20.84	156	26	0
24.09	7.4	27	16	3.3	3.5	410	0.12	2.72	1.38	0.76	20.64	160	24	0
25.01	7.43	30	13	3.4	3	430	0.16	2.71	1.42	0.72	20.92	154	28	0
30.10	9.91	79	40	3.6	3.2	430	0.03	2.31	7.92	0.27	21.41	124	35	0.2
30.20	9.9	79	42	3.8	3.6	430	0.04	2.32	7.82	0.3	21.6	126	37	0.1
30.10	9.92	80	38	3.6	3.5	470	0.05	2.3	8.02	0.28	21.39	123	32	0.2