ASSESSMENT OF WATER QUALITY IN WELLS LOCATED NEAR ABANDONED INDIGODYEING PITS IN ZARIA CITY, NIGERIA

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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 ANALYTICAL CHEMISTRY

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Declaration

I hereby declare that the work in this dissertation titled **"Assessment of Water Quality in Wells Located near Abandoned Indigo Dyeing Pits in Zaria City, Nigeria"**has been carried out by me in the Department of Chemistry. The information derived from the literature has been duly acknowledged in the text and a list of references provided.

_____ _____

Amina Kudu ABDULLAHI Date

Certification

This dissertation entitled **ASSESSMENTOF WATER QUALITY IN WELLS LOCATED NEAR ABANDONED INDIGO DYEING PITS IN ZARIA CITY, NIGERIA by**AMINA KUDU ABDULLAHI meets the regulations governing the award of the degree of Master of Science in Analytical Chemistry of Ahmadu Bello University, is approved for its contribution to knowledge and literary presentation.

Prof. V. O. Ajibola	_____	_____
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Member, Supervisory Committee	Signature	Date
Prof. V. O. Ajibola	_____	_____
Head of Department	Signature	Date
Prof. K. Bala	_____	_____
Dean, School of Postgraduate Studies	Signature	Date

Dedication

This work is dedicated to Almighty Allah, my parents and to my dearest sister, Barr. Fatima Abdullahi Kudu (Mrs. Yahaya) for her support throughout the course of this work.

Acknowledgement

All praises and thanks are due to Allah “the Exalted” Who in His Infinite mercies, granted me protection and the ability to do this work.

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Abstract

Assessment of water quality in wells located near three abandoned indigo dyeing centers in Zaria City, Nigeria was carried out. Physicochemical parameters (pH, temperature, electrical conductivity, turbidity, colour, total dissolved solid, hardness, alkalinity, Cl^- PO_4^{3-}, NO_3^-, SO_4^{2-}, dissolved oxygen, biochemical oxygen demand and chemical oxygen demand), heavy metals (Ni, Cr, Cu, Pb , Cd) and coliform test using standard method were used to study the well water quality in dry and wet seasons. The presence of dye residue in water was determined using FTIR and UV-Visible spectroscopy. The data obtained were compared with SON standard values and discussed. The result showed physical parameters (pH, temperature, turbidity, colour, and total dissolved solid) ranged from 7.92-8.75, 24.01-24.45°C, 1.33-281.33NTU, 5-30 hazen and 617.33-3186.37 mg/dm^3 for dry season and 7.40-8.57, 28.05-29°C, 1.33-66.33NTU, 5-20 hazen and 444.33-3563.33mg/dm^3 for wet season respectively. The result for chemical parameters (electrical conductivity, dissolved oxygen, biochemical oxygen demand, Cl^-, hardness, alkalinity, SO_4^{2-}, PO_4^{3-}, NO_3^-, chemical oxygen demand) ranged from 272.00-5840.00µ℧/cm, 0.30-0.77mg/dm^{3}0.13-0.63mg/dm^3, 2017.33-44613.46mg/dm^3, 276.36-2898.91mg/dm^3, 313.33-1663.33mg/dm^3, 73.3-438.33mg/dm^3, 0.70-12.67mg/dm^3, 10.83-119.20mg/dm^{3}and 8.00-56.67mg/dm^{3}for dry season and 933.99-4783.33µ℧/cm, 0.30-2.13mg/dm^3, 0.1-0.93mg/dm^3,1798.67-7277.03mg/dm^3, 538.95-3046.80mg/dm^3, 153.33-1160.00mg/dm^3, 42.67-351.67mg/dm^3, 0.43-17.37mg/dm^3,3.20-105.13mg/dm^{3}and 2.03-35.00mg/dm^3 for wet season respectively. Values obtained for metal analysis (Pb, Cd, Cu, Cr and Ni) ranged from not detected-0.09mg/dm^3, 0.01-0.02mg/dm^3, 0.04-0.11mg/dm^3, not detected-0.21mg/dm^3 and not detected-0.05mg/dm^3 for dry season and 0.11-0.19mg/dm^3, not detected-0.02mg/dm^3, 0.00-2.26mg/dm^3,0.00-0.18 mg/dm^{3}and0.01-0.04. Large numbers of bacteria were found in wet season than in dry, none of the sampled wells gave a result that fell within the permissible level for drinking water quality given by the SON (2007) for both seasons. Principal Component Analysis (PCA) was used to investigate the sources of pollution and the course of variation in the water samples for two seasons and Cluster Analysis (CA) was used to detect the similarities in the well water samples for the two seasons. The principal component analysis extracted important parameters which indicated the abandoned dyeing pits, pits toilet in close proximity to the well water, seasonal effects and domestic wastes to be the sources of pollution. Hierarchical Cluster Analysis grouped the sampled wells into three clusters for both seasons showing the similarities between sampling wells during the period under investigation. UV-Visible spectra of the extracts showed maximum absorption peaks at 465nm, 235nm and 220nm when, methanol, diethyl ether and n-hexane respectively were used for the extractions. The extracts showed the presence of C-H, C=O,C-C=C, CH_3 –C-H and N-H in FTIR spectra.

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CHAPTER ONE

1.0 INTRODUCTON

Water is absolutely essential to life. It is undoubtedly one of the most precious natural resource that exists on our planet. Humans may survive for several weeks without food, but barely few days without water because constant supply of water is needed to replenish the fluids lost through normal physiological activities, such as respiration, perspiration, urination (Murray, 2003). The essential role played by water in supporting human life, makes it a great potential for transmitting diseases and illnesses if contaminated (Yakasai*et al*., 2004). Adequate supply of safe and potable water assist in preventing the spread of gastrointestinal diseases, supports domestic and personal hygiene, and improves the standard of living (Ike and Ugodulunwa, 1999). Access to safe drinking water is a basic human need and a fundamental human right. Even at that, 1 billion people worldwide live without access to safe and potable drinking water and nearly 50% of them, suffer from health problems due to lack of safe drinking water sources and sanitation (Giwa*et al*., 2008).

Ground water is the most suitable fresh water resource with nearly balanced concentration of the salts for human consumption. It is generally less susceptible to contamination and pollution when compared to surface water bodies (Zaman, 2002). Over burden of the population pressure, unplanned urbanization, unrestricted exploration policies and dumping of the polluted water at inappropriate place enhance the infiltration of harmful compounds to the ground water (Sandeep and Shweta, 2009). Furthermore, the natural impurities in rainwater, which replenishes groundwater systems, get removed while infiltrating through soil strata (Veslind, 1993).

In the last few decades, there has been a tremendous increase in the demand for fresh water due to rapid growth of population and the accelerated pace of industrialization (Ramakrishnaiah, 2009). The quality of water is vital concern for mankind since it is directly linked with human welfare. Due to inadequate supply of pipe –borne water in towns and cities in Nigeria, many people have been sourcing their daily water need from wells in order to meet the daily water demand (Adejide and Ajibade, 2005). The major substitutes for pipe borne water are shallow hand dug wells in areas of low and average income (Akinleye,2008). Groundwater contamination is responsible for water related and water borne diseases. The source of ground water contamination could be natural through ground water -rock interaction or through anthropogenic sources which involve human activities. Ground water pollution which is man-made is worse than natural pollution as it eventually renders water unsuitable for use (Abimbola*et al*., 2005). Ground water pollution due to toxic organic compounds is a serious problem which has necessitated the legal regulations concerning disposal of chemicals into the natural environment being more and more restrictive (Pieter and Nazar, 2011).

In Zaria, due to scarcity of drinking water, people collect water from surface streams and shallow wells. Therefore majority of the populace rely heavily on untreated well water and boreholes (Musa *et al*., 2004).

1.1 Justification

Kaduna State was famous for its traditional indigo dyeing pits, during the trans Sahara trade in northern part of the country. Local industries like the dyeing industry, proved vital to Nigeria's socio-economic development, apart from providing employment to a good number of people, it serves as source of tourist attraction. These local industries used a local technology of dyeing and discharge of waste. Ideally citing industries should strike a balance between socio-

economic and environmental considerations. This was not the case with local dyeing industries in Zaria, they were mostly located within the city walls and surrounded by settlements. The mode of disposal was usually in pits dug for that purpose.

Previous studies, when the dyeing activities were functional have shown contamination of ground water in close proximity to the dye wastes well in Zaria (Ajibola and Rilwanu, 1998). The findings show environment-related ailments ranging from skin and eye problems to cancerous tumours and methaemoglobinaemia in children which were attributed to the disposal of dye wastes in these areas.Even though most of these dyeing pits have long been abandoned, their impacts on the settlements around them are still persisting.

1.2 Aim of Study

The overall aim of this study is to assess the water quality in wells located near abandoned indigo dyeing pits in Zaria City, Kaduna State, Nigeria.

1.3 Objectives of the Study

The above aim will be achieved by the following objectives:

i. To determine the level of some heavy metals (Ni, Cd, Cu, Pb, Cr) concentration in the well water during wet and dry seasons.
ii. To determine some physiochemical properties of well water during wet and dry seasons.
iii. To determine the level of coliform in the water samples.
iv. To determine qualitatively, the presence of dye residues using FTIR and UV-Visible Spectroscopies.

CHAPTER TWO

2.0 LITERATURE REVIEW

The characteristic qualities of five textile industries effluent in Kaduna, Nigeria was analysed and high level of chemical oxygen demand (COD), total suspended solids (TSS), ammonia (NH_3), biological oxygen demand (BOD) and sulphide (S^{2-}) that exceeded the federal environmental protection agency (FEPA) limit by several fold was reported (Yusuf and Sonibare, 2004). The effect of the effluents discharged from two textile industries on the well waters was investigated. The results showed that the effluents had high values of BOD5 (100–390mg/dm^3), COD (204–2000 mg/dm^3), pH and were highly coloured. These values were higher than the effluent limits stipulated by the Federal Ministry of Environment for textile industries. The well that was closest to point of discharge (a shallow well) showed the highest BOD5 (107 mg/dm^3) and total dissolved solids (TDS) while all the other wells showed acceptable results (Olayinka and Alo, 2004). Textile effluents have been found to contain a higher amount of metals especially chromium, copper, lead and cadmium. These effluents are ultimately leached into ground water and this leads to contamination due to accumulation of toxic metallic components (Malarkodi *etal*., 2007). Asia *et al*., (2009) studied the physicochemical properties and investigated some selected heavy metals in three effluent samples collected from textile factories in Kaduna, results shows that the heavy metals investigated have higher concentration than the Federal Environmental Protection Agency (FEPA) standards for effluent discharge. Physicochemical properties result also indicated that the effluents may not be able to undergo up to 50% substrate biodegradation, thus biological processes may not be feasible for the treatment of these effluents. Awomeso *et al.*, (2010), reported that dissolved oxygen at the points closest to the point of effluent discharge were found to be zero signifying that stream was heavily polluted

and may not likely support aquatic lives. Munnafi *et al.*, (2012) observed the pH values of water discharged from dyeing industry to be alkaline which ranged from 8.9-10.5 and 9.2-10, the studied water samples contain DO concentrations of less than 1mg/ dm^3 during rainy and dry seasons respectively. High levels were observed in the industrial effluent analysed for COD (73-345 mg/ dm^3), pH (7.6-9), TS (2100-6050 mg/ dm^3l), TDS (1990-5820 mg/ dm^3), DO (0-8 mg/ dm^3), total hardness (321-880 mg/dm^3), which exceeds the standard level of world health organization (WHO). The study revealed that there was an adverse impact on physicochemical characteristics of the receiving water bodies as a result of directly discharge of untreated effluents from dye industries. This poses a health risk to several rural communities which rely on the receiving water bodies primarily as their source of domestic water (Thoker *et al*., 2012*).* Ground water samples were analyzed for various water quality parameters like pH, EC, K, Ca, Mg, Na, Cl, $HCO3^-$, $CO3^-$ and SO_4^{2-}. The content of the element lies above the maximum permissible limit prescribed by World Health Organization (WHO). The analysis report shows contamination where dyeing industries are located (Gayathri *et al.*, 2013). Schuchismita and Ashraful (2015) conducted a review on the characteristics of textile effluent from 2005 to 2014 which reveals huge amount of effluent from dyeing industries with some physiochemical parameters such as temperature (25-65°C), pH (3.9-14), TDS (90.7 – 5980 mg/dm^3), DO (0-7 mg/ dm^3), COD (41-2430 mg/ dm^3), BOD (10 – 786 mg/ dm^3), TSS (24.9 – 3950 mg/ dm^3) and EC (250-63750µS/cm) were being discharge in water bodies every day. Abduljali and Sule (2013) studied the condition of hand dugs wells in Zaria city, reported that 40 percent of the headwall around the wells were inadequate, allowing surface water to enter the wells. About 70 percent of the wells (well-lining) were not adequately sealed and there is no provision of

concrete floor apron around 80 percent of the wells of 1m wide. This poses a risk to the well water quality.

2.1 Water Pollution Indicators

2.1.1 Heavy metals

The term heavy metal refers to any metallic chemical element that has a density greater than 4g/cm^3 or five times or more greater than water. Exposure to heavy metal causes serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Metals are particularly toxic to the sensitive, rapidly developing systems of fetuses, infants, and young children. (IARC,1990). These serious health effects depend on the nature and quantity of the metal ingested (Adepoju-Bello and Alabi, 2005). A strong relationship has been shown between contaminated drinking water with heavy metals and the incidence of chronic diseases such as renal failure, liver cirrhosis, hair loss and chronic anaemia (Wang *et al*., 2010 ; Salem *et al*., 2000).These diseases however may be related to the contamination of drinking water with heavy metals such as Cd, Cu, Cr, Ni and Pb. Renal failure is related to the contamination of drinking water with Cd and Pb; liver cirrhosis to the contamination with Cu and molybdenum; hair loss to the contamination with Cr and Ni; and chronic anemia to the contamination with Cd and Cu (Johri *et al*., 2010).

2.1.1.1*Copper*

Copper is among heavy metals that are essential to life but could be toxic at high concentration. It occurs in drinking water either from contaminated corroded copper pipes, or from fertilizers, septic systems, animal feedlots, industrial wastes, and food processing wastes (NSF, 2003). Immediate health effects from drinking water with very high levels of copper

include nausea, vomiting, diarrhea, and stomach cramps. Drinking water with high levels of copper for many years could cause liver or kidney damage (NSF, 2003).

2.1.1.2 *Lead*

Lead is very toxic element, which accumulates in the skeletal structure of man and animal (Akhilesh *et al.,* 2009). The possible long term effects of chronic exposure to lead present in drinking water are subject to considerable public concern (Zietz *et al*., 2007). Lead can be either inhaled or ingested. Symptoms of lead poisoning vary; they may develop gradually or appear suddenly after chronic exposure. Symptoms of lead poisoning include nausea, vomiting, fatigue, and high blood pressure and in more extreme cases, brain damage. These can be chronic or acute health effects. Some of the harmful effects of lead ingestion or inhalation are anaemia, high blood pressure, kidney damage, miscarriages, nervous system damage, brain damage, and behavioral and learning disruptions in children (Lenntech, 2011a). The most serious effects are seen in children under the age of six, where brain and nervous system development are still occurring. In these children, a small amount of lead can result in permanent damage and loss of function of the affected area of the brain. Complications may occur, such as learning disabilities, slowed growth, blindness, deafness, and, in extreme cases, convulsions and coma ending in death. Brain injury may also occur in adults after massive exposure (WHO, 2011).

2.1.1.3 *Chromiu*m

Chromium is an important industrial metal used in diverse products and processes (Nriagu, 1988). At many locations, Cr has been released to the environment via leakage, poor storage, or improper disposal practices. As chromium compounds were used in dyes and paints and the tanning of leather these compounds are often found in soil and groundwater at abandoned industrial sites (Palmer and Wittbrodt, 1991). Within the environment, Cr is found

primarily in two oxidation states Cr(Vl) and Cr(lll). Chromium (lll) is an essential human dietary element and is found in many vegetables, fruits, meats, grains and yeast. Chromium (Vl), however occurs naturally in the environment from the erosion of natural chromium deposits, and it can also be produced by industrial processes and it is relatively mobile in the environment and is acutely toxic, mutagenic and cancernogenic (Bianchi *et al*., 1984). Chromium (lll) has relatively low toxicity (Van *et al*., 1964) and deficiency in humans may cause heart conditions, disruptions of metabolisms and diabetes, and too much cancause health effects as well, for instance skin rashes (IARC, 1990).

2.1.1.4 *Cadmium*

Cadmium occurs naturally in the earth's crust as well as being introduced to the environment in fertilizers and pesticides (Lenntech, 2011b). Cadmium can be present in groundwater through contact with dissolved rocks and minerals. Other sources of cadmium in groundwater include mining and smelting operations, industrial operations, burning of fossil fuels, fertilizer application, sewage sludge disposal, corrosion of galvanized pipes, leaching of landfills (MPCA, 1999).

Cadmium is a highly toxic metallic pollutant that does not have any metabolic benefit (Watanabe, 1998). Cadmium buildup in the kidneys hinders their filtration systems. This problem can persist because cadmium does not exit the kidneys very quickly and will begin to accumulate. This can ultimately lead to kidney failure. Other adverse health effects from cadmium include stomach pains and infertility, and cadmium is considered a carcinogen. It can also harm the central nervous and immune systems as well as damage DNA. Inhalation of cadmium can lead to severe damage of the lungs and even death (Lenntech, 2011b).

2.1.1.5 *Nickel*

Nickel is abundant on Earth, most notably the planet's iron/nickel core. It is used in the manufacturing of many alloys and products such as stainless steel, ceramic paint, jewelry, kitchen ware, batteries, textiles and coins. Nickel is released into the environment by power plants, metal factories and waste incinerators. It is also used in fertilizers and enters groundwater from farm runoff (NPDWR, 1998). Nickel is necessary in many organisms' diets but can become carcinogenic and toxic in high doses. Toxicity of Ni is enhanced in the presence of some other metals in drinking water (Mandour and Azab, 2010).

2.1.2 pH

pH is a term used universally to express the intensity of the acid or alkaline condition of a solution. It is defined as the logarithm to base 10 of the reciprocal of the concentration or the logarithm of the hydrogen ion concentration with negative sign (Ademoroti, 1996).

Measurement of pH is one of the most important and frequently used tests in water chemistry. pH control is necessary at all stage of water classification and to ensure satisfactorily water classification and disinfections (WHO, 1996). It also affects other chemical reactions such as solubility and metal toxicity (Fakayode, 2005). The hydrogen ion concentration of water is a measure of its purity. Polluted water has pH values greater than 7.0 depending on type of pollutants. Water containing dye wastes has been reported to have high pH values (APHA, 1985)

Several methods are available for pH determination, some of these include use of electrometric method (Ademoroti, 1996) and bicarbonates and free carbon dioxide determinations (APHA, 1985).

2.1.3 Electrical conductivity

Electrical conductivity is a measure of water capacity to convey electric current. It signifies the amount of total dissolved salts (Sudhir and Amerjeet, 1999). The higher the conductivity the higher the concentration of ionic solids in water and by implication the more polluted is the water. Water that is not polluted will have very low conductivity values because ionic solids are likely to be absent. Conductivity values can be regarded as measure of the presence of ionic salts in water (Aderomoti, 1996).

2.1.4 Turbidity

Clarity of water is important in producing products for human consumption. The presence of colloidal solid gives liquid a cloudy appearance, which is aesthetically unattractive and may be harmful. Turbidity in water may be due to clay slit particles, discharge of sewage or industrial waste, to presences of large number of micro –organisms (Tebutt, 1998). Turbidity has been long known to hinder disinfection by shielding microbes, some of them perhaps pathogens (Hauser, 2001). Turbidity should normally be below 5 units and above 25units; undesirable level may possibly cause gastro intestinal irritation (WHO, 2000). Turbidity is measured by simple comparison of the interferences of light rays passing through a sample with that in a standard samples. The methods adopted for the measurement of turbidity are Bottle procedure, Jackson candle turbidimeter and Nephelometric method. (APHA, 1985; Ademoroti, 1996).

2.1.5 Temperature

This is the degree of hotness or coldness measured on several arbitrary scale .The Temperature of drinking water should be several degrees below the ambient temperature and too high temperature can result in flat tasty water probably due to loss of dissolve oxygen (APHA, 2005).

2.1.6 Colour

Hues in water may result from natural minerals such as iron and manganese, vegetables origins human materials and tannins or coloured waste discharged from a variety of industries which include mining, refining, textile, pulp and paper, chemical and food processing (Hammer, 1995).

2.1.7 Total dissolved solid

The total dissolved solids (TDS) is the term used to describe the inorganic salts and small amount of organic matter present in a solution in water .The principal constituents are usually calcium, magnesium, sodium, potassium, chlorides, sulphates, nitrates ions (Tebutt,1998). TDS in water supplies originates from natural source, sewage, urban and agricultural run-off and industrial waste water. Water with high dissolved solids generally is of inferior palatability and may induce a favourable physiological reaction in the transient consumer (WHO, 1996).

2.1.8 Water hardness

Hardness is the property of water which prevents the lather formation with soap and increases the boiling points of water. Hardness of water mainly depends upon the amount of calcium or magnesium salts or both. (Travedy and Geol, 1986). Hardness caused by calcium and magnesium usually results in excessive soap consumption and subsequent "scum" formation. Water with hardness above approximately 200 mg/dm^3 may cause scale deposition in the treatment works, distribution system and pipe work and tanks within buildings. Soft water, with a hardness of less than 100 mg/dm^3, may, have a low buffering capacity and so be more corrosive for water pipes (WHO, 2000 ; SON, 2007; WHO, 2008; WHO, 2011). Hardness in water may have some effects in reducing certain types of heart diseases and thus softening water may have a detrimental health effect (Tebutt, 1998).

2.1.9 Alkalinity

Alkalinity is a measure of the ability of a substance to neutralize acids. The key ions contributing to alkalinity are bicarbonate and carbonate (Devi and Premkumar, 2012). The main sources of these are from natural reactions between water and carbon dioxide, or as byproducts of naturally occurring reduction processes. Alkalinity in effluent is due to the presence of salts of weak acid such as ethanoic, propionic formic acids or the presence of ammonia and hydroxide ion (Ademoroti, 1996).

If water has an alkalinity below about 100mg/dm^3 as $CaCO_3$, it is poorly buffered and pH sensitive. This could be harmful to the plants and animals that live there. (SON, 2007; WHO, 2011). Alkalinity can be determined in water by titration (APHA, 1995).

2.1.10 Dissolved oxygen

Dissolved oxygen (DO) content plays a vital role in supporting aquatic life and is susceptible to slight environmental changes (Fakayode, 2005). It is also an important parameter indicating level of water quality and organic pollution in the water body (Wetzel and Likens, 2006). Oxygen affects a vast number of other water indicators, not only biochemical but aesthetic ones like the odour, clarity and taste. Consequently, oxygen is perhaps the most well-established indicator of water quality (Lenntech, 2013). If water is too warm, there may not be enough oxygen in it. When there are too many bacteria or aquatic animals in the area, they may overpopulate, using DO in great amounts. Oxygen levels also can be reduced through over fertilization of water plants by run-off from farm fields containing phosphates and nitrate. Under these conditions, the numbers and size of water plants increases, when the plants die, they become food for bacteria, which in turn multiply and use large amounts of oxygen (Lenntech,

2013). Dissolved oxygen can be determined by azide modification of the Winkler method (APHA, 2000) and can also be determined electrochemically (Bertram and Balance, 1996).

2.1.11 Chemical oxygen demand

Chemical oxygen demand (COD) is an important parameter in measuring quality and determining what organic load is present in the water. Chemical oxygen demand determines the oxygen required for chemical oxidation of organic matter. COD values convey the amount of dissolved oxidisable organic matter including the non-biodegradable matter present in it. All aquatic plants and animals contribute to chemical oxygen demand through their metabolism and excretion of waste products. Dissolution of dead organisms also contributes to the organic carbon, as well as surrounding humus and peat. Anthropogenic dispersal includes all organic substances released into the environment. High levels of COD in water often correlate with threats to human health including toxic algae blooms bacteria from organic wastes and sea food contamination (NSTC, 2003). High COD levels decrease the amount of dissolved oxygen available for aquatic organisms. Low (generally under $3mg/dm^3$) dissolved oxygen, or "hypoxia," causes reduced cell functioning, disrupt circulatory fluid balance in aquatic species and can result in death of individual organisms (NSTC, 2003).

2.1.12 Biochemical oxygen demand

Biochemical oxygen demand (BOD) is the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. The decomposition of organic matter and metabolic activities of bacteria results in utilization of a part of the dissolved oxygen. This depletion of oxygen is considered as a measure of the amount of degradable organic matter in the sample under analysis (Clair *et al*., 2003).

2.1.12 Chloride

Chloride occurs in all natural water in widely varying concentration. The chloride content normally increases as the mineral content increases. Upland and mountain supplies usually are quite low in chloride, whereas rivers and groundwater usually have considerable amount (Sawyer *et al*., 2003). Chloride in groundwater arise from both natural and anthropogenic sources, such as runoff containing inorganic fertilizers, landfill leachates, septic tank effluents, animal feeds, industrial effluents, irrigation drainage, and seawater intrusion in coastal areas. Chlorides are important in detecting the contamination of groundwater by waste water (Purandara *et al*., 2003). Chlorides increase the electrical conductivity and salinity of water and thus its corrosiveness (Hammer and Hammer, 1996).

2.1.13 Nitrates

Although nitrate occurs naturally in drinking water, elevated levels in groundwater usually result from human activities such as over use of chemical fertilizers and improper disposal of human and animal wastes. These fertilizers and wastes are sources of nitrogen, containing compounds which are converted to nitrates in the soil. Nitrates are extremely soluble in water and can move easily through soil into the drinking water supply. However, the ingestion of excessive amounts of nitrate can cause adverse health effects in very young infants and susceptible adults (MSU, 2003).The most common sources of nitrate are municipal and industrial wastewaters, refuse dumps, animal feed lots, and septic systems. Once nitrate is formed, its movement in soil and potential for contamination of ground, water depend on several factors including the soil characteristics, location and characteristics of the underground water formations (aquifers), and climatic conditions. Potential for nitrate contamination of drinking water also depend on the depth and construction of wells (MSU, 2003). The most significant

health effect associated with nitrate ingestion is methemoglobinemia in infants under six months of age. This condition results from the presence of high nitrate levels in the blood. Untreated, severe methemoglobinemia can result in brain damage and even death. (Johnson *et al*., 1987; Comly, 1987).

2.1.14 Sulphate

Sulphate can be found in almost all natural water. The origin of most sulfate compounds is the oxidation of sulphite ores, the presence of shales, or the industrial wastes. Health concerns regarding sulphate in drinking water have been raised because of reports that diarrhea may be associated with the ingestion of water containing high levels of sulphate, particular concern are groups within the general population that may be at greater risk from the laxative effects of sulfate when they experience an abrupt change from drinking water with low sulphate concentrations to drinking water with high sulphate concentrations (EPA, 1999). One such potentially sensitive population is infants receiving their first bottles containing tap water, either as water alone or as formula mixed with water. A series of three case histories from Saskatchewan, Canada suggested that infants may experience gastroenteritis, including diarrhea and dehydration, upon their first exposure to water that contains high levels of sulphate. (Chien *et al*,.1968). The presence of sulfate in drinking-water can also result in a noticeable Taste (WHO, 2004).

2.1.15 Phosphate

In natural and wastewaters, phosphorus occurs almost solely as dissolved phosphate and it is the most significant form of phosphorus in natural water. Orthophosphate is the most thermodynamically stable form of phosphate, and is the form commonly identified in laboratory analysis and also used by plants. Furthermore, polyphosphates in water are unstable and

eventually convert to orthophosphate (Chapman, 1992). Natural sources of phosphorus in both surface and groundwater include atmospheric deposition, natural decomposition of rocks and minerals, weathering of soluble inorganic materials, decaying biomass, runoff, and sedimentation. Anthropogenic sources include; fertilizers, wastewater and septic system effluent, animal wastes, detergents, industrial discharge, phosphate mining, drinking water treatment, forest fires, synthetic material development surface (Mueller,1995). Naturally occurring levels of phosphates in surface and ground water bodies are not harmful to human health, animals or the environment. Conversely, extremely high levels of phosphates can cause digestive problems. Furthermore, excessive amounts of phosphates in water bodies can lead to eutrophication, a condition of accelerated algal production (Sheila, 2005).

2.1.16 Bacteriological analysis

The principal means through which pathogenic microorganism reach water supplies are faecal, soil and vegetation. The main diseases transmitted by faecal contamination are typhoid fever, salmonellose, cholera, bacillary and amoebic dysentery. The vital agents of infection in hepatitis and poliomyelitis are faecal organisms which can also spread in contaminated water (Ademoroti, 1996).

The testing for the presence of E.coli is pre-eminently the test for safe guarding the bacterial quality of water. The presence of *E.coli* in water usually indicates pollution by faecal contamination. Other coliform bacteria will usually be present as well, but if *E. coli* is absent then the inference is that pollution primarily arises from the soil and vegetation (APHA, 1985).

2.2 Instruments

2.2.1 Principle of atomic absorption spectroscopy

The principle governing the use of AAS technique depends on the absorption of electromagnetic radiation by an atom. The measurement of reduction intensity of radiation on passing through an absorbing medium can be correlated to the concentration of the absorbing sample as embodied in the Beer-Lambert's law (Christian, 2011). Acetylene, nitrous oxide, or mixture of air acetylene and nitrous oxide produces flame, which is of a sufficiently high temperature to ensure the presence of free atoms of most elements. When a sample solution is passed through the flame via a nebulizer, a fine spray mist droplets that settle and are then passed down the drain tube. The remaining solution is carried by the air fuel mixture as a mist to the burner head were the solvent evaporates and the solute dissociates into atoms. The source of light is hollow cathode lamp containing the element under consideration, the lamp produces radiation of appropriate wavelength for absorption by the free atoms of the sample (Christian, 2011). The number of atoms, of the metal present in the ground state determines the extent of absorption of the radiation emitted from the cathode tube. The amount of absorption of the atoms in the ground state is a measure of the concentration of the metal ions in solution. This device, produce a signal, which allow for the measure of light intensity and hence of absorption caused by the sample (Christian, 2011).The advantages of the atomic absorption spectrophotometer method of analysis are the high degree of sensitivity, accuracy and its cheap cost .

2.2.2 Principle of ultraviolet–visible spectroscopy

Ultraviolet–visible spectrophotometry (UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. The absorption or reflectance

in the visible range directly affects the perceived colour of the compounds involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions (Christian, 2011).

UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugatedorganic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied (Dana*et al.,* 1994)

The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV/Vis spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken more accurately, from a calibration curve. The Beer-Lambert Law is useful for characterizing many compounds but does not hold as a universal relationship for the concentration and absorption of all substances (Christian, 2011).

2.2.3 Principle of fourier transform infra-red spectroscopy

Infrared spectroscopy (IR spectroscopy) deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemical compounds. Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of

their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates.

Fourier transform infrared (FTIR) spectrophotometer measures and records infrared spectra. The infrared light is guided through an interferometer and then through the sample (or vice versa). A moving mirror inside the apparatus alters the distribution of infrared light that passes through the interferometer. The signal directly recorded, called an "interferogram", represents light output as a function of mirror position. A data-processing technique called Fourier transform turns this raw data into the desired result (the sample's spectrum): Light output as a function of infrared wavelength (or equivalently, wave number). As described above, the sample's spectrum is always compared to a reference (Christian, 2011).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Description of the Study Area

Zaria Local Government Area is located in North Western Nigeria on longitude $11^0$04'N and latitude $7^0$42'E(Figure 3.1). The study area is located on a plateau at a height of about 0.67 km above the mean sea level and more than 643.71 km away from the sea and possesses a Tropical Savanna climate with distinct wet and dry seasons(Hore, 1970). It is the home of numerous artisans, from traditional crafts like leather work, dyeingand cap making, to tinkers, print shops and furniture makers. Zaria is also the centre of a textile industry that for over 200 years has made elaborately hand-embroidered robes that are worn by men throughout Nigeria and West Africa (Maiwada and Renne, 2007).

3.2 Sample Collection

3.2.1 Sampling locations

Samples of well water were collected in February 2013 for dry season and August 2013 for wet season, from three locations where dyeing activities took place in Aguwar Mallam Sule, Anguwar Limanci and Anguwar Karfe between 6am and 9am (Figure 3.2). The points were determined with a hand held Global positioning System (GPS, Germin 72 model) and listed in Tables 3.1- 3.3. Some of the abandoned pits are shown in Plates I-II. Nine Samples each were collected from the hand-dug wells in the vicinity of the abandoned waste dyeing pits for both seasons. Two samples were also collected from hand-dug wells in Anguwar Rimin Tsiwa where there are no dyeing activity took place, those served as controls. This gave a total of twenty nine samples collected for each season.

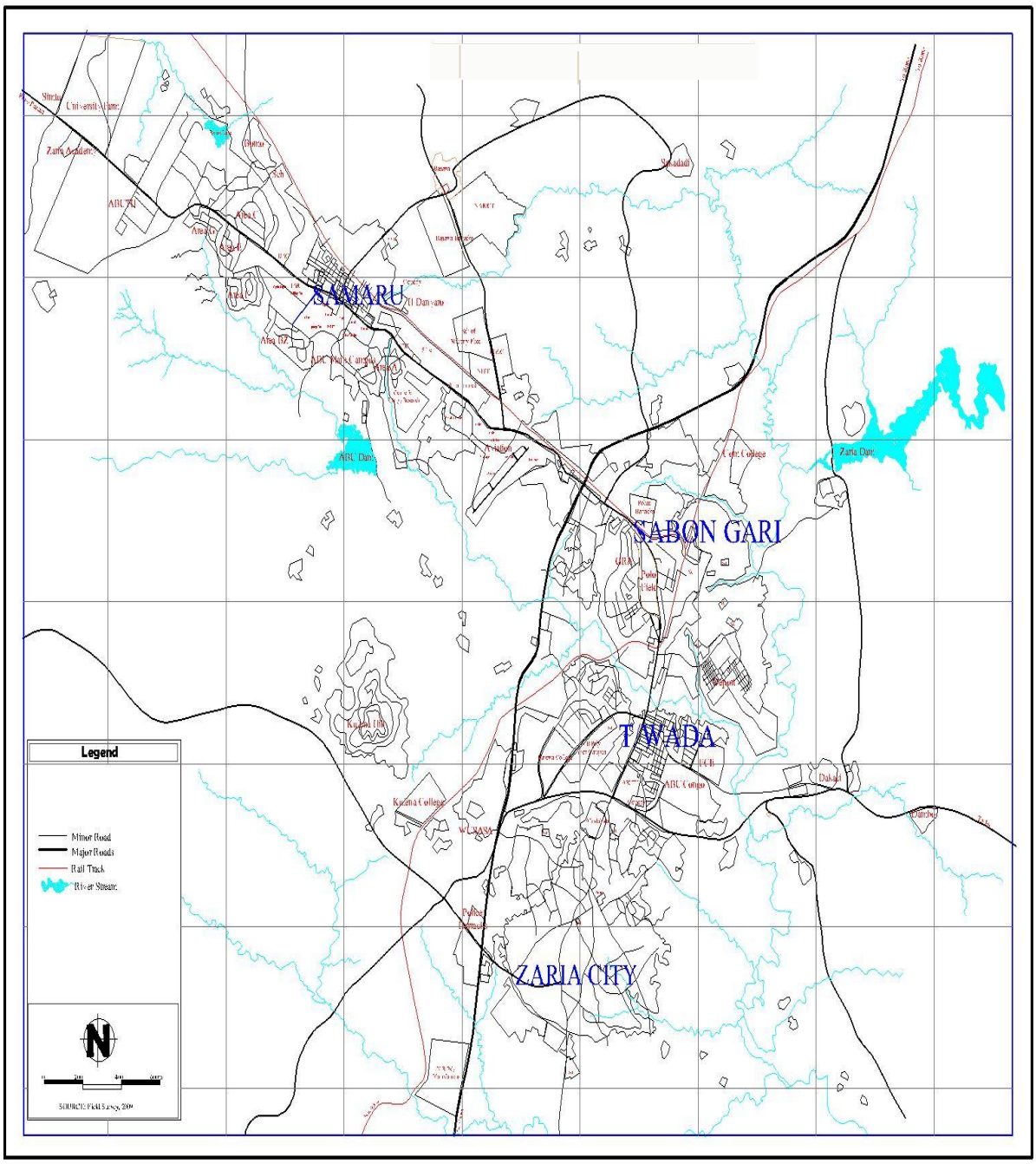

Figure 3. 1: Map of Zaria showing the Urban Areas

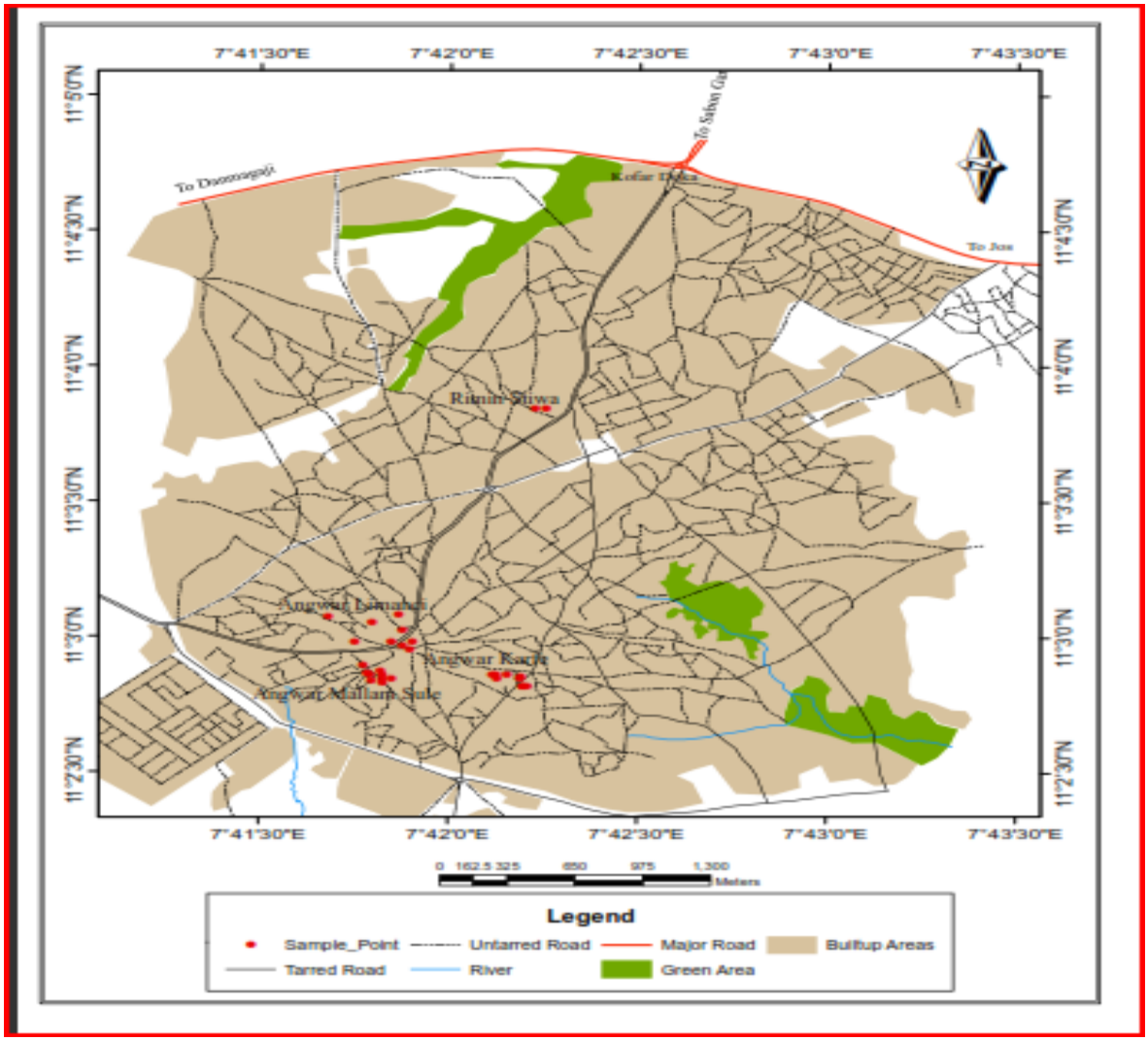

Figure 3. 2: Map of Zaria City showing Sampling Points

Table 3. 1: Sampling Points at Anguwar Mallam Sule

S/NO	Sampling Point	GPS Coordinate
1	S1	NW 32 P 0357618 1221561 East to 192
2	S2	SW 32 P 0357632 1221522 East to 192
3	S3	SW 32 P 0357683 1221509 East to 192
4	S4	NW 32 P 0357729 1221535 East to 192
5	S5	WE 32 P 0357685 1221558 East to 192
6	S6	NE 32 P 0357684 1221537 East to 192
7	S7	NE 32 P 0357674 1221584 East to 192
8	S8	SW 32 P 0357606 1221567 East to 192
9	S9	NW 32 P 0357590 1221626 East to 192

KEY:

S1 – S9: Sampling point at Anguwar Mallam Sule from well 1 -9

Table 3. 2: Sampling Points at Anguwar Limanci

S/NO	Sampling Point	GPS Coordinates		
1	M1	SW 32 P 0357825	1221788	East to 192
2	M2	NW 32 P 0357728	1221788	East to 192
3	M3	NE 32 P 0357780	1221752	East to 192
4	M4	NW 32 P 0357814	1221726	East to 192
5	M5	NE 32 P 0357780	1221864	East to 192
6	M6	SW 32 P 0357834	1221784	East to 192
7	M7	NW 32 P 0357856	1221785	East to 192
8	M8	SW 32 P 0357867	1221779	East to 192
9	M9	NW 32 P 0357856	1221772	East to 192

KEY:

M1 – M9: Sampling point at Anguwar Limanci from well 1 -9

Table 3. 3: Sampling Points at Anguwar Karfe and Anguwa Rimi Tsiwa

S/NO	Sampling point	GPS Coordinates	
1	K1	NW 32 P 0358355	1221458 East to 192
2	K2	E 32 P 0358355	1221482 East to 192
3	K3	N 32 P 0358341	1221539 East to 192
4	K4	W 32 P 0358348	1221542 East to 192
5	K5	NW 32 P 0358381	1221494 East to 192
6	K6	NW 32 P 035823	1221530 East to 192
7	K7	NW 32P 0358229	1221563 East to 192
8	K8	N 32P 0358281	1221564 East to 192
9	K9	N 32 P 0358304	122570 East to 192
10	T1	NW 32 P 0358421	1223376 East to 192
11	T2	W 32P 0358471	1223370 East to 192

KEY:

K1 – K9: Sampling point at Anguwar Karfe from well 1 -9

T1 – T2: Sampling point at Rimin Tsiwa from well 1 - 2

Plate I: Abandoned DyeingPits around Residential Areas at Anguwar Limanci Sampling Area

Plate II: Abandoned Dyeing Pits around Residential Areas at Anguwar Mallam Sule Sampling Area

Plate III: Drinking Well Water Polluted by Leachates from Dye Waste Pits at Anguwar Mallam Sule, Sampling Area.

3.2.2. Water sampling techniques

Water samples were obtained from wells using plastic buckets between 6am and 9am. The sample was stored in well labelled, clean polyethylene bottles at 4^0C in refrigerator to minimize physiochemical changes (Ademoroti, 1996). Parameters with extremely low stability such as pH, electrical conductivity, and temperature, were measured in situ. Thereafter the samples were transported to the laboratory for further analysis. The time lapse between sample collection and analysis did not exceed one week.

3.3 Preparation of Solutions

3.3.1 Manganous sulphate solution (2.16M)

This was prepared by dissolving 48g $MnSO_4.4H_2O$ in 50$cm^3$of deionised water in a beaker and was transferred into 100cm^3 volumetric flask and made up to mark.

3.3.2 Alkali iodide-azide reagent

This was prepared by dissolving 50g NaOH and 13.5g NaI in 50cm^3 of deionised water in a beaker and diluted to mark in 100cm^3 volumetric flask. This was then transferred into a beaker NaN_3 (1g) initially dissolved in 4cm^3 distilled water was added to the solution and mixed thoroughly (APHA, 1995).

3.3.3 Sodium thiosulphate solution (0.0125M)

This was prepared by dissolving 12.41g $Na_2S_2O_3.5H_2O$ in 200cm^3 of deionised in a beaker and diluted to mark in 1000cm^3 volumetric. 250cm^3stock of$Na_2S_2O_3$was transferred into 1000cm^3volumetric flask and was diluted to mark with deionized water.

3.3.4 Potassium dichromate digestion solution (0.0417M)

$K_2Cr_2O_7$ was first dried at 103^0C for 2 hours in a ventilated oven, 12.26g was weighed and dissolved in 200cm^{3}of deionised water in a beaker then was transferred into 1000cm^3 volumetric flask and made up to mark with deionised water (APHA, 1995).

3.3.5 Standard ferrous ammonium sulphates solution (0.025M)

This was obtained by dissolving 98g Fe $(NH_4)_2(SO_4)_2.6H_2O$ in 200cm^3 of deionised water in a beaker. Concentrated H_2SO_4(20cm^3) was then added to the solution. It was allowed to cool and transferred to 1000cm^{3}volumetric flask and diluted to mark (APHA, 1995).

3.3.6 Standard EDTA solution (0.01 M)

This was prepared by dissolving 3.723g EDTA sodium salt in 200cm^3 of deionised water in a beaker in1000cm^3 volumetric flask and was diluted to mark.

3.4 Determination of Physico-chemical Parameters of Water Samples

3.4.1 Temperature measurement

Measurements of the water samples temperature were taken at the time of sampling using a mercury thermometer (0-100°C).

3.4.2 Measurement of pH

The pH was determined using a digital pH meter (JENWAY 3505). The probe was rinsed thoroughly with distilled water before use on sample. The probe of the pH meter was inserted in the water sample and the pH values were recorded.

3.4.3 Determination of conductivity

The electrical conductivity measurement was determined using digital TDS/conductivity meter (HACH) Sension 5. The probe was rinsed thoroughly with distilled water before use on the sample. The probe of the TDS/conductivity meter was inserted in sample at the time of sampling and the conductivity values were recorded

3.4.4 Determination of turbidity

The turbidity measurement was determined using a digital meter (HACH DR/890) colorimeter. The sample cell was filled with 10cm^3 of deionized water and was placed in cell holder of the HACH-DR/ 890 data logging, micro-processor controlled spectrophotometer and was used as blank. Another Sample bottle was filled with 10cm^3 of the sample then inserted into the instrument and the reading was obtained and recorded.

3.4.5 Determination of total dissolved solid

The total dissolved solids measurement was determined using a digital TDS/conductivity meter (HACH) Sension 5. The probe was rinsed thoroughly with distilled water before use on sample. The probe was inserted in the sample and TDS values were recorded.

3.4.6 Determination of dissolved oxygen (azide modification method)

Dissolved Oxygen was determined by filling bottles of 300cm^3 capacity with the water sample. Manganous sulphate (2cm^3)and alkali-iodide-azide (2cm^3) solutions were added to each bottle by inserting a pipette just below the surface of the liquid. The bottles were stoppered to avoid the introduction of air and inverted several times to mix the content of the bottles. They were then left to stand for two minutes, after which 2cm^3 H_2SO_4 was added to the samples and mixed to dissolve the precipitate formed. Sample (200cm^3)was then measured into a clean

250cm^{3}conical flask and titrated against sodium thiosulphates solution ($Na_2S_2O_3.5H_2O$) using starch indicator until the solution turned colourless.

Calculation

$$\text{DO } (\text{mg}/dm^3) = \frac{16000 \times M \times V}{Vi(cm^3)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

where M = Molarity of thiosulpahte used (mol/dm^3),V = volume of thiosulphate used for titration (cm^3) and V_1 = Volume of aliquot taken for titration (cm^3)

3.4.7 Determination of biochemical oxygen demand

The samples were transferred into bottles of 300 capacities as in section 3.4.6 and incubated at 20^{o}C in the dark for 5 days. Initial dissolved oxygen (DO_0) of the water sample was determined using the azide modification method (as described above for dissolved oxygen). Determination of final dissolved oxygen was carried out after incubation (for 5days) using the same azide modification method.

Calculation:

$$\text{BOD } \left(\frac{\text{mg}}{dm^3}\right) = \frac{DO_0 - DO_5}{B} \quad \ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

where DO_0 = initial dissolved oxygen (immediately after preparation) , DO_5 = final dissolved oxygen (after 5days of incubation) and B = Fraction of sample used.

3.4.8 Determination of chemical oxygen demand

This was carried out by weighing $HgSO_4$ (0.4g) and placed in a refluxing flask. Sample (20cm^3)was transferred into the refluxing flask. $K_2Cr_2O_7$ (10cm^3) standard solution and H_2SO_4 - Ag_2SO_4 solution (30cm^3) were added and resulting solution was thoroughly mixed by gentle

swirling. The mixture was refluxed for 2hours, cooled and the condenser was washed with about 25cm^{3}of distilled water into the flask. The mixture was diluted to 150cm^3 with distilled water and cooled to room temperature. About three drops of (0.10-0.15cm^3) ferroin indicator was added. The mixture was titrated with $Fe(NH_4)_2(SO_4)_2$ until colour changed from blue-green to reddish brown as end point. In the same manner a blank containing 20cm^{3}distilled water was prepared.

Calculation

$$\text{COD mg}/dm^3 = \frac{(a-b)\times M\times 8000}{Vol\ (cm^3)} \quad \text{.....3.3}$$

where COD = Chemical Oxygen Demand, a = cm^{3}Fe $(NH_4)_2$ $(SO_4)_2$used as blank, b = vol cm^{3}Fe $(NH_4)_2(SO_4)_2$used for sample and M = Molarity of Fe $(NH_4)_2$ $(SO_4)_2$

3.4.9 Determination of total hardness

The sample was shaken thoroughly and 25cm^3 was taken into 100cm^3 measuring cylinder and diluted to 50cm^3 with distilled water. This was transferred into a conical flask, Buffer solution (1cm^3) and two to three drops of Eriochrome Black –T indicator were added to the flask. The mixture was then titrated with 0.01M EDTA until the colour changed from wine red to blue

Calculation:

$$\text{Hardness mg/dm}^3 = \frac{V\times M\times 1000}{vol(cm^3)} \quad \text{.....3.4}$$

where M = Molarity of EDTA Used and V =Volume (cm^3) of EDTA used.

3.4.10 Determination of alkalinity

Sample (25cm^3)was transferred into a conical flask and 2 drops of phenolphthalein indicator was added to develop a pink colour. It was then titrated with 0.02M H_2SO_4 until pink colour disappeared (pH 8.3). The volume of H_2SO_4 required was noted. Two drops of methyl orange were added to the same flask, and the titration was continued until yellow colour changed to orange. The volume of H_2SO_4 required at this endpoint was also noted and recorded.

Calculations:

$$\text{Total alkalinity } \left(\frac{\text{mg}}{dm^3}\right) = \frac{\text{V}\times\text{M}\times 1000}{vol(cm^3)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.5$$

where V = Total volume (cm^3) of acid used = A+B A = volume (cm^3) of H_2SO_4 required to bring the pH to 8.3 and B = volume (cm^3) of H_2SO_4 required to bring the pH to 4.5

3.4.11 Determination of chlorides

The water sample (50cm^3)was taken in a conical flask and titrated against 0.014M standard Silver nitrate solution. An indicator of potassium chromate (1cm^3) was added. Titration was carried out until the colour of water sample changed from yellow to brick red.

Calculation:

$$\text{Chloride } (\text{mg}/dm^3) = \frac{A\times M\times 35450}{vol\ (cm^3)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.6$$

Where A = cm^3 of titrant used and M = Molarity of silver nitrate solution (0.0141 M).

3.4.12 Determination of phosphates (molybdovanadate method)

Two sample cells were rinsed with 6M $HNO_3$and washed with water and oven dried. The Cells were then filled with 25cm^3water sample and deionized water respectively. Molybdovanadate reagents (1cm^3) were added to each of the sample cells. The solutions in the cells were allowed to stand for five minutes after thorough mixture. The sample cell containing deionized water was placed in the cell holder of digital meter (HACH-DR/ 890) colorimeter and was used as blank. Thereafter, sample cell containing the water sample was inserted in the cell holder of the colorimeter and reading was obtained.

3.4.13 Determination of sulphate (turbidimetric method)

A 10cm^3 sample cell was filled with deionized water and was placed in the cell holder of digital meter (HACH-DR/ 890) colorimeter and was used as blank. Another10cm^3 sample cell was filled with sample, and then a content of sulfa ver 4 sulphate reagent powder pillow was emptied into it. This was allowed to stand for five minutes after thorough mixture. The cell was inserted into the cell holder of digital meter (HACH-DR/ 890) colorimeter and reading was obtained.

3.4.14 Determination of nitrate (cadmium reduction method)

A 10cm^3 sample cell was filled with deionized water and was placed in the cell holder of digital meter (HACH-DR/ 890) colorimeter and was used as blank. Another10cm^3 sample cell was filled with sample, and then a content of nitra ver 4 nitrate reagent powder pillow was emptied into it. This was allowed to stand for five minutes after thorough mixture. The cell was inserted into the cell holder of digital meter (HACH-DR/ 890) colorimeter and reading was obtained.

3.5 Elemental Analysis By Atomic Absorption Spectrophotometer

3.5.1 Sample pre -treatment

Water sample ($100cm^3$) was transferred into an evaporating dish. Concentrated69% HNO_3 ($5cm^3$)was added to sample and then the sample was evaporated to reduce to half of the volume. The evaporated sample was transferred to a $125cm^3$ conical flask and was allowed to cool. Afterwards, $5cm^3 HNO_3$ + $10cm^3$ 70% $HClO_4$ was added to the cooled sample. It was then heated on a hot plate and was kept boiling till a cleared solution was produced. The solution was cooled and diluted to $50cm^3$ with distilled water. It was brought to boil to expel chlorine and oxide of nitrogen, after which it was filtered into $100cm^3$ volumetric flasks. It was then cooled and made up to $100cm^3$mark. Aliquot of the solution was taken for metal determination.

3.5.2 Preparation of standard solution for cadmium

Standard cadmium stock solution was prepared by dissolving 0.16309g $CdCl_2$ in $1000cm^3$ volumetric flask with deionised water and diluted to mark, $1cm^3$ = 0.1mg of Cd. Aliquot of standard 0.00, 0.05, 0.10, 0.15, 0.20, 0.25 cm^3 were transferred in each $10cm^3$ volumetric flask and diluted to mark to obtain 0.00, 0.05, 0.10, 0.20, 0.25mg/dm^3 respectively.

3.5.2 Preparation of standard solution for chromium

Standard Chromium stock solution was prepared by dissolving 0.28282g $K_2Cr_2O_7$ in $1000cm^3$ volumetric flask with deionised water and diluted to mark, $1cm^3$ = 0.1mg of Cr. Aliquot of standard 0.00, 0.05, 0.10, 0.15, 0.20, 0.25 cm^3 were transferred in each $10cm^3$ volumetric flask and diluted to mark to obtain 0.00, 0.05, 0.10, 0.20, 0.25mg/dm^3 respectively.

3.5.3 Preparation of standard solution for lead

Standard lead stock solution was prepared by dissolving 0.1598g of Pb $(NO_3)_2$ in 1000cm^3 volumetric flask with deionised water and diluted to mark,1cm^3 = 0.10mg of Pb. Aliquot of standard 0.00, 0.05, 0.10, 0.15, 0.20, 0.25cm^3 were transferred in each 10cm^3 volumetric flask,two drops of 6M HNO_3 were addedand diluted to mark to obtain 0.00, 0.05, 0.10, 0.20, 0.25 mg/dm^3 respectively.

3.5.4 Preparation of standard solution for copper

Standard Copper stock solution was prepared by dissolving 0.3929g $CuSO_4.5H_2O$ in 1000cm^3 volumetric flask with deionised water and diluted to mark, 1cm^3 = 0.1mg of Cu. Aliquot of standard 0.00, 0.05, 0.10, 0.15, 0.20, 0.25cm^3 were transferred in each 10cm^3 volumetric flask and diluted to mark to obtain 0.00, 0.05, 0.10, 0.20, 0.25 mg/dm^3 respectively.

3.5.5 Preparation of standard solution for nickel

Standard Nickel stock solution was prepared by dissolving 0.4479g $NiSO_4.6H_2O$in 1000cm^3 volumetric flask with deionised water and diluted to mark, 1cm^3 =0.1mg of Ni. Aliquot of standard 0.00, 0.05, 0.10, 0.15, 0.20, 0.25cm^3 were transferred in each 10cm^3 volumetric flask, and diluted to mark to obtain, 0.00, 0.05, 0.10, 0.20, 0.25 mg/dm^3 respectively.

3.6 Determination of Coliform Bacteria

3.6.1 Preparation of media eosin methylene blue agar (EMB)

EMB agar (36g) was dissolved in 1000$cm^3$of distilled water in a beaker and was stirred with a magnetic stirrer for fifteen minutes. The solution was transferred into 1000cm^3 conical flask, covered with cotton wool and aluminum foil and autoclaved for fifteen minutes at 121°C. 20$cm^3$of the solution was transferred into a petri dish and was allowed to fix.

3.6.2 Serial dilution

Six test tubes were filled with 9$cm^3$of sterile distilled water each. The sample (1cm^3) was measured using sterile pipette and transferred into one of test tubes, then another sterile pipette was used to draw the mixed sample in and out for ten times in the test tube. Afterwards, 1cm^3 of mixed sample from the first test tube was transferred into the next test tube using a sterile pipette. The same procedure was repeated for the remaining test tubes using sterile pipettes, 1$cm^3$of the sixth test was discarded. The third test tube was chosen for inoculation, one drop of the mixed sample from third dilution was transferred onto the prepared EMB gel in a petri dish using sterile pipette. The sample was evenly spread with a sterile bent glass rod. The petri dish was covered and incubated at 37^0C for twenty four hours. The number of colonies formed on the solution were counted and recorded as the bacteria growth.

3.7 Spectrophotometric Analysis of Dye Residue in Water Sample

n-hexane and diethyl ether50cm^3eachwere transferred into two different separatory funnel containing the 100$cm^3$of sample. The mixtures were separated into organic and aqueous layers in the separatory funnels. Organic layer was collected from the funnels and another 50cm^3 of n-hexane and diethyl ether were added to the separate separatory funnels for separation. Organic layers were collected for the second time.

Another 100cm^3 of sample was heated in two separate beakers to dryness. Methanol (50cm^3) was transferred into the one beaker containing dry residue to extract the dye residue and was filtered. The residue from the second beaker was termed dry residue. The aliquot of the extracts were taken for FTIR and UV-Visible spectrophotometric analysis, the dry residue was subjected to FTIR analysis only.

3.7.1 Uv-visible spectrophotometric determination of dry residue

Sample cell filled with the solvent was placed in the cell compartment of UV-Visible spectrophometer (6405 UV-Visible Spectrophotometer Jenway) and was used as blank. Another sample cell was filled with the extract and placed in cell compartment. The absorbance of maximum wave length for each extract were taken at wavelength regions between 200-700nm.

3.8.2 FTIR spectrophotometric determination of dry residue

The analysis was carried out by mixing each extract ($1cm^3$) with nujol separately, onto the face of a KBr plateand the second window was placed on top. The mixture was evenly distributed with a gentle circular and back-and-forth rubbing motions, the sandwiched plates were placed in the FTIR spectrometer (SHIMADZU 84005 FTIR Spectrophotometer) a spectrum was obtained for each extract. The dry residue sample (1.5mg) was ground for five minutes in a mortal. KBr (300mg) was gradually added and mixed with the sample. The mixture was pressed into pellet for mounting in FTIR Spectrophotometer to obtain spectral in the range of400-$4000cm^{-1}$.

3.8 Statistical Treatment of Results

All results were obtained in triplicates and the results are expressed as the mean values with standard deviations (Appendix 1-6). The application of multivariate statistical techniques which include Principal Component Analysis (PCA) and Cluster Analysis (CA) were used to interpret data. In terms of PCA and CA the data were log transformed using $(\text{Log } x)^2$because the parameters are in widely different and result are presented in Table 4.7-12. All statistical analyses were performed using the Statistical Package for the Social Sciences (SPSS) Version 20.0 Software.

3.8.1 Principal component analysis

Is a variable reduction technique which reduces analytical data of each sample and inter-correlates them into a smaller set of factors that are interpretable. This method consists of data standardization, factor extraction and rotation of factor axes. PCA starts by building a correlation matrix for the data and rearranges them in a manner that better explains the structure of the underlying system that produced the data. This is followed by the generation of a new group of variables from initial data set (factors or principal components) that are linear combination of the original variables (Chatfield and Collins, 1980). Then, the components loadings matrix is rotated according to some rotation techniques namely, varimax, equamax or quartimax. The idea is that each variable should be heavily loaded on as few components as possible. One of the most commonly used techniques for accomplishing this transform is the varimax rotation and it is used for the work. This technique tends to eliminate medium-range correlations between components and original variable thus simplifying the decision as to which of the original variables to include in the components extracted. PCA reduces the large data matrix into two smaller matrices called principal component (PC) loading and PC scores which are obtained through, the process of eigen analysis. In order to determine the number of components to be retained the Kaiser criterion is followed. The components which best describe the variance of the analyzed data (eigenvalue>1) and can be reasonably interpreted are accepted for further analysis. Because PCA is simply the generation of pairs of eigenvalues and eigenvectors, the data do not need to be normally distributed (Johnson and Wichem, 2002). The first factor or component has the highest eigenvector sum and represents the most important source of variation in the data,i.e explains the biggest part of the variance. The last factor is the least important process contribution to the chemical variation. Factor loading on the factor are interpreted as correlation coefficients

between the variable and the factors. Components loading show how the factor characterizes the variable.

High factor loadings (close to 1 or -1) indicate strong relationship (positive or negative) between the variables and the factor describing the variable. The measure of how well the variance of a particular variable is described by a particular set of factors is called communality. Finally, factor scores are calculated for each sample and plotted as a scatter diagram. Extreme positive factor scores(>+1) reflect sampling stations most affected by the process and extreme negative (<-1) scores reflect those unaffected by the process explained by the factor. Near zero scores reflect sampling station affected to an average degree by the process.

3.8.2 Cluster analysis

Cluster analysis is a pattern recognition technique that reveals intrinsic structure of a data set without making a prior assumption about the data in order to classify the objects to the system into relatively similar or homogeneous groups. The agglomerative hierarchical cluster analysis which is the most common approach where cluster are formed sequentially, starting with the most similar pair of objects and forming higher clusters step by step was used. It was performed according to Ward's Method with squared Euclidean distances to detect the multivariate similarities in the well water samples and a distance can be represented by the difference between analytical values from both the samples. The method uses an analysis of variance approach to evaluate the distances between clusters, attempting to minimize the sum of squares of any two clusters that can be formed at each step. The different measures for similarity with respect to distance between parameters and different algorithms for finding a cluster are applied and displayed in form of a dendrogram. The dendrogram provides a visual summary of the clustering process, presenting a picture of the groups and its proximity with a dramatic

reduction in dimensionality of the original data. In this study hierarchical clustering analysis was used to group similar sample into cluster based on their similarities in terms of physiochemical parameter for the two seasons (Ward, 1963).

CHAPTER FOUR

4.0 RESULTS

4.1 Descriptive Summary of Data

The mean concentration, Standard deviation, maximum and minimum values of the physicochemical parameters analysed for sampling location S M and K for dry and wet seasons are shown in Tables 4.1-4.6. The values were compared with the control and SON (2007) standard for drinking water quality.

4.2 Statistical Treatment of Data

Tables 4.7-4.12 presented result obtained from transformation of datafor principal component analysis and cluster analysis for sampling location of S, M and K for both seasons. Table 4.13-4.18 displayed result obtained from principal components analysis for sampling locations S, M and K for both seasons, showing the components extracted for each sites in both seasons. Figure 4.1-4.2 illustrated the spartial clustering of the sampling location during dry and wet Season respectively on the dendogram.

4.3 Coliform Test

A comparison of coliform count values for all wells sampling location for both seasons is shown in Table 4.19.

4.4 Spectroscopic Studies of Dye residue in Water

Figures 4.3-4.5 showed uv-visible absorption spectral of methanol, diethyl ether and n-hexane. Figures 4.6-4.9 showed the IR spectral of dry water residue, methanol, diethyl ether and n-hexane respectively, in range of 4000-400cm^{-1}.

Table 4. 1: Descriptive Summary of Data for Site S during Dry Season

Parameters	Minimum	Maximum	Mean	Std. Deviation	Control	SON
pH	8.11	8.75	8.45	0.23	7.81	6.5-8.5
Temp(^{0}C)	24.15	24.33	24.2	0.07	23.90	30
Cond (µ℧/cm)	272.00	5840.00	2579.22	2258.22	931.00	750
Col (Hazen)	5.00	30.00	12.77	7.94	5.00	15
TDS (mg/dm^3)	1195.67	2670.00	1887.51	567.82	365.33	500
Tur(NTU)	2.33	281.33	63.37	88.50	12.00	5
DO (mg/dm^3)	0.40	0.77	0.52	0.12	1.00	5
BOD (mg/dm^3)	0.13	0.30	0.20	0.05	0.13	3
Cl(mg/dm^3)	14538.13	44613.4	23332.2	10027.05	2013.00	250
TH (mg/dm^3)	1014.45	1967.51	1419.79	331.72	670.04	500
ALK (mg/dm^3)	603.33	1663.33	1001.48	395.57	323.33	150
SO_4^{2-}(mg/dm^3)	95.00	438.33	271.51	110.438	36.00	100
PO_4^{3-}(mg/dm^3)	.90	12.67	5.2152	3.17692	1.80	6.5
NO_3^-(mg/dm^3)	30.90	119.20	54.15	29.73	12.57	50
COD(mg/dm^3)	13.33	56.67	28.62	12.55	8.50	10-20
Pb(mg/dm^3)	BDL	0.06	0.03	0.02	BDL	0.01
Cd (mg/dm^3)	0.01	0.02	0.01	BDL	0.01	0.003
Cu (mg/dm^3)	0.06	0.11	0.08	0.02	0.03	1.0
Cr(mg/dm^3)	0.06	0.21	0.11	0.05	0.03	0.05
Ni (mg/dm^3)	BDL	0.05	0.04	0.08	0.02	0.02

BDL: Below Detection Level

Table 4. 2: Descriptive Summary of Data for Site S during Wet Season

Parameters	Minimum	Maximum	Mean	Std. Deviation	Control	SON
pH	8.14	8.57	8.28	0.14	7.55	6.5-8.5
Temp(^{0}C)	28.47	29.00	28.77	0.18	27.90	30
Cond (µ℧/cm)	1736.33	4783.33	3132.59	948.58	1151.67	750
Col (Hazen)	5.00	20.00	9.44	5.83	5.00	15
TDS (mg/dm^3)	873.00	2486.67	1632.51	502.90	575.33	500
Tur (NTU)	2.33	66.33	14.11	19.89	1.00	5
DO (mg/dm^3)	0.63	2.13	1.28	0.54	2.70	5
BOD (mg/dm^3)	0.13	0.63	0.41	0.18	0.40	3
Cl (mg/dm^3)	2409.67	7277.03	5304.78	1529.28	2415.75	250
TH (mg/dm^3)	538.95	3046.80	1303.36	783.25	942.95	500
ALK (mg/dm^3)	376.67	1160.00	620.74	259.04	289.78	150
SO_4^{2-}(mg/dm^3)	42.67	351.67	192.18	100.46	41.67	100
PO_4^{3-}(mg/dm^3)	0.43	17.37	5.94	5.33	2.40	6.5
NO_3^-(mg/dm^3)	4.43	105.13	49.84	34.19	10.67	50
COD(mg/dm^3)	3.67	35.00	11.71	10.66	1.67	10-20
Pd (mg/dm^3)	0.12	0.19	0.13	0.02	0.03	0.01
Cd (mg/dm^3)	BDL	0.01	0.01	BDL	0.01	0.003
Cu (mg/dm^3)	BDL	2.26	0.25	0.75	BDL	1.0
Cr(mg/dm^3)	0.06	0.18	0.11	0.04	0.04	0.05
Ni (mg/dm^3)	0.01	0.04	0.02	0.00	0.02	0.02

BDL: Below Detection Level

Table 4.3: Descriptive Summary of Data for Site M during Dry Season

Parameter	Minimum	Maximum	Mean	Std. Deviation	Control	SON
pH	8.11	8.44	8.23	0.10	7.81	6.5-8.5
Temp(^{0}C)	24.07	24.45	24.24	0.13	23.90	30
Cond (µ℧/cm)	816.00	3826.00	2472.00	1021.82	931.00	750
Col (Hazen)	5.00	15.00	7.22	3.63	5.00	15
TDS (mg/dm^3)	663.33	3186.67	1544.29	680.30	365.33	500
Tur(NTU)	1.33	53.67	22.88	19.75	12.00	5
DO (mg/dm^3)	0.30	0.73	0.52	0.14	1.00	5
BOD (mg/dm^3)	0.13	0.63	0.22	0.16	0.13	3
Cl(mg/dm^3)	16042.42	41620.00	22122.6	8119.65	2013.00	250
TH (mg/dm^3)	1266.03	2898.91	2066.63	515.78	670.04	500
ALK (mg/dm^3)	313.33	953.33	574.81	226.76	323.33	150
SO_4^{2-}(mg/dm^3)	77.33	356.67	193.48	99.13	36.00	100
PO_4^{3-}(mg/dm^3)	0.70	6.30	2.6519	1.72	1.80	6.5
NO_3^-(mg/dm^3)	36.63	46.20	42.1889	4.21	12.57	50
COD(mg/dm^3)	12.67	35.67	25.03	6.78	8.50	10-20
Pb(mg/dm^3)	0.01	0.05	0.02	0.01	BDL	0.01
Cd (mg/dm^3)	0.01	0.02	0.01	BDL	0.01	0.003
Cu (mg/dm^3)	0.04	0.08	0.06	0.02	0.03	1.0
Cr(mg/dm^3)	BDL	0.05	0.01	0.02	0.03	0.05
Ni (mg/dm^3)	0.02	0.04	0.03	0.01	0.02	0.02

BDL: Below Detection Level

Table 4.4: Descriptive Summary of Data for Site M during Wet Season

Parameter	Minimum	Maximum	Mean	Std. Deviation	Control	SON
pH	7.48	8.05	7.83	0.23	7.55	6.5-8.5
Temp(^{0}C)	28.08	28.93	28.64	0.31	27.90	30
Cond (µ℧/cm)	933.33	3964.33	2707.70	993.28	1151.67	750
Col (Hazen)	5.00	10.00	6.66	2.50	5.00	15
TDS (mg/dm^3)	444.33	3563.33	2707.70	993.28	575.33	500
Tur (NTU)	1.33	10.00	4.00	3.04	1.00	5
DO (mg/dm^3)	0.30	0.73	0.52	0.14	2.70	5
BOD (mg/dm^3)	0.13	0.93	0.37	0.28	0.40	3
Cl (mg/dm^3)	1798.67	5522.96	3693.14	1203.54	2415.75	250
TH (mg/dm^3)	740.89	2036.88	1450.74	471.60	942.95	500
ALK (mg/dm^3)	153.33	813.33	528.51	195.61	289.78	150
SO_4^{2-}(mg/dm^3)	52.00	241.00	145.07	74.54	41.67	100
PO_4^{3-}(mg/dm^3)	0.47	5.60	3.48	1.88	2.40	6.5
NO_3^-(mg/dm^3)	18.00	55.33	41.93	11.25	10.67	50
COD(mg/dm^3)	2.03	9.90	5.1537	2.44632	1.67	10-20
Pb (mg/dm^3)	0.13	0.16	0.14	0.01	0.03	0.01
Cd (mg/dm^3)	0.01	0.02	0.01	BDL	0.01	0.003
Cu (mg/dm^3)	BDL	BDL	BDL	BDL	BDL	1.0
Cr(mg/dm^3)	BDL	0.12	0.07	0.03	0.04	0.05
Ni (mg/dm^3)	0.03	0.04	0.04	0.01	0.03	0.02

BDL: Below Detection Level

Table 4.5: Descriptive Summary of Data for Site K during Dry Season

Parameters	Minimum	Maximum	Mean	Std. Deviation	Control	SON
pH	7.92	8.46	8.20	0.19	7.81	6.5-8.5
Temp(^{0}C)	24.01	24.12	24.08	0.04	23.90	30
Cond (µ℧/cm)	1336.67	2666.67	1955.55	529.84	931.00	750
Col (Hazen)	5.00	15.00	9.44	3.90	5.00	15
TDS (mg/dm^3)	617.33	1195.67	887.85	247.34	365.33	500
Tur (NTU)	1.67	93.33	43.77	32.98	12.00	5
DO (mg/dm^3)	0.37	0.83	0.58	0.17	1.00	5
BOD (mg/dm^3)	0.13	0.43	0.20	0.11	0.13	3
Cl (mg/dm^3)	2017.33	15526.40	10042.69	4060.53	2013.00	250
TH (mg/dm^3)	276.36	2114.68	1448.44	570.00	670.04	500
ALK (mg/dm^3)	316.67	710.00	505.18	132.47	323.33	150
SO_4^{2-}(mg/dm^3)	73.33	242.67	150.62	49.91	36.00	100
PO_4^{3-}(mg/dm^3)	1.73	8.47	6.02	2.26	1.80	6.5
NO_3^-(mg/dm^3)	10.83	34.63	20.62	7.38	12.57	50
COD(mg/dm^3)	8.00	34.33	18.00	7.79	8.50	10-20
Pb (mg/dm^3)	BDL	0.09	0.03	0.02	BDL	0.01
Cd (mg/dm^3)	0.01	0.01	0.01	BDL	0.01	0.003
Cu (mg/dm^3)	0.04	0.10	0.06	0.02	0.03	1.0
Cr(mg/dm^3)	0.01	0.11	0.06	0.03	0.03	0.05
Ni (mg/dm^3)	0.01	0.04	0.03	0.01	0.02	0.02

BDL: Below Detection Level

Table 4.6: Descriptive Summary of Data for Site K during Wet Season

Parameters	Minimum	Maximum	Mean	Std. Deviation	control	SON
pH	7.40	8.31	7.84	0.29	7.55	6.5-8.5
Temp(^{0}C)	28.05	28.40	28.16	0.09	27.90	30
Cond (µ℧/cm)	1497.00	2503.33	2062.51	379.93	1151.67	750
Col (Hazen)	5.00	5.00	5.00	0.00	5.00	15
TDS (mg/dm^3)	575.00	1274.33	967.51	379.93	575.33	500
Tur(NTU)	2.00	10.67	4.33	2.95	1.00	5
DO (mg/dm^3)	0.83	1.90	1.28	0.41	2.70	5
BOD (mg/dm^3)	0.10	0.90	0.36	0.32	0.40	3
Cl(mg/dm^3)	2215.49	4367.06	3377.29	724.12	2415.75	250
TH (mg/dm^3)	925.74	2155.11	1355.73	372.85	942.95	500
ALK (mg/dm^3)	186.67	543.33	371.85	136.13	289.78	150
SO_4^{2-}(mg/dm^3)	47.33	208.00	110.88	52.41	41.67	100
PO_4^{3-}(mg/dm^3)	1.83	7.83	4.28	2.17434	2.40	6.5
NO_3^-(mg/dm^3)	3.20	33.03	11.33	9.33	10.67	50
COD(mg/dm^3)	2.33	11.33	6.17	3.37	1.67	10-20
Pb(mg/dm^3)	0.11	0.14	0.12	0.01	0.03	0.01
Cd (mg/dm^3)	0.01	0.02	0.01	BDL	0.01	0.003
Cu (mg/dm^3)	BDL	0.47	0.05	0.15	BDL	1.0
Cr(mg/dm^3)	0.07	0.16	0.11	0.03	0.04	0.05
Ni (mg/dm^3)	0.02	0.03	0.03	0.01	0.03	0.02

BDL: Below Detection Level

Table 4.7: Transformed Data for Site S during Dry Season

S/N	Parameter	SD1	SD2	SD3	SD4	SD5	SD6	SD7	SD8	SD9
1	pH	0.88	0.90	0.89	0.89	0.87	0.86	0.88	0.89	0.88
2	TEMP	1.92	1.92	1.92	1.92	1.92	1.91	1.92	1.92	1.92
3	EC	14.17	14.19	11.95	7.06	12.70	7.64	5.93	7.34	12.31
4	COLOUR	1.69	2.18	0.49	1.00	1.38	1.00	0.49	1.00	1.00
5	TDS	11.74	11.49	9.82	11.19	10.55	9.47	9.72	11.49	10.18
6	TUR	6.00	4.30	2.62	1.19	1.36	2.60	0.14	1.75	2.48
7	DO	0.13	0.16	0.03	0.11	0.05	0.13	0.01	0.07	0.13
8	BOD	0.77	0.40	0.40	0.28	0.77	0.40	0.40	0.40	0.77
9	Cl^-	18.41	20.72	18.32	18.41	18.41	17.57	21.6	18.86	17.33
10	TH	10.61	10.85	9.62	10.37	9.91	9.80	9.04	9.66	9.06
11	ALK	10.20	10.38	7.73	9.66	8.08	8.23	8.44	8.58	8.50
12	PO_4^{3-}	0.51	1.22	0.52	0.28	0.51	0.45	0.00	0.61	0.32
13	SO_4^{2-}	6.76	6.98	4.99	3.91	6.10	5.64	5.44	5.67	6.49
14	NO_3^-	3.65	4.31	2.66	2.53	2.22	2.35	2.49	3.34	2.40
15	COD	2.45	3.07	1.27	1.87	1.65	1.87	1.99	2.02	2.31
16	Pb	2.57	1.84	3.33	7.28	1.45	3.13	2.41	1.51	1.95
17	Cd	3.33	3.84	4.19	4.0	4.19	5.30	4.0	4.16	4.0
18	Cu	0.99	0.93	1.11	1.33	0.98	1.49	1.44	1.33	1.51
19	Cr	0.65	0.46	0.99	1.09	0.86	1.05	1.22	0.99	1.59
20	Ni	1.67	1.63	7.28	0.00	0.00	2.57	6.37	2.02	9.0

Table 4.8: Transformed Data for Site S during Wet Season

S/N	Parameter	SW1	SW2	SW3	SW4	SW5	SW6	SW7	SW8	SW9
1	pH	0.84	0.86	0.83	0.85	0.85	0.84	0.83	0.87	0.83
2	TEMP	2.13	2.13	2.12	2.12	2.14	2.14	2.13	2.13	2.13
3	EC	13.54	13.37	11.93	11.98	12.12	10.50	11.65	11.97	12.01
4	COL	1.38	1.69	0.49	0.49	1.38	0.49	0.47	0.49	1.00
5	TDS	13.54	13.37	11.93	11.97	12.12	10.50	11.65	11.97	12.01
6	TUR	1.11	3.32	0.32	0.14	1.14	0.75	1.17	0.49	0.75
7	DO	0.003	0.003	0.003	0.006	0.11	0.02	0.10	0.04	0.04
8	BOD	0.13	0.04	0.14	0.13	0.04	0.08	0.19	0.77	0.77
9	Cl^-	14.65	14.92	13.39	12.70	13.99	11.44	13.95	14.56	13.78
10	TH	9.95	10.32	12.14	10.49	9.11	7.87	8.18	7.46	8.85
11	ALK	8.71	9.39	7.11	8.16	7.65	6.64	7.07	7.12	7.11
12	PO_4^{3-}	0.26	1.54	0.43	0.76	0.06	0.13	0.63	1.05	0.08
13	SO_4^{2-}	5.79	6.45	3.05	2.66	5.73	4.58	5.52	4.97	5.71
14	NO_3^-	2.98	4.09	2.34	3.34	1.35	0.42	3.64	3.44	1.59
15	COD	2.45	3.07	1.27	1.87	1.65	1.87	1.99	2.02	2.31
16	Pb	0.79	0.52	0.79	0.88	0.86	0.82	0.81	0.83	0. 88
17	Cd	4.00	4.19	4.40	6.7	4.00	3.44	4.94	4.19	3.84
18	Cu	3.56	3.84	0.13	4.63	2.62	5.30	0.00	6.37	0.00
19	Cr	1.18	0.54	1.25	1.44	0.98	0.84	0.75	1.13	0.80
20	Ni	2.51	1.87	3.22	3.84	3.23	3.44	4.19	3.13	3.04

Table 4.9: Transformed Data for Site M during Dry Season

S/N	Parameter	MD1	MD2	MD3	MD4	MD5	MD6	MD7	MD8	MD9
1	pH	0.86	0.84	0.83	0.83	0.84	0.83	0.83	0.84	0.84
2	TEMP	1.93	1.92	1.91	1.92	1.91	1.92	1.93	1.92	1.91
3	EC	12.27	8.48	11.94	11.87	12.44	11.64	12.84	9.93	9.94
4	COL	1.38	1.00	0.49	1.00	0.49	0.49	0.49	0.49	0.49
5	TDS	10.03	12.27	9.66	9.56	9.78	10.03	10.31	10.31	7.96
6	TUR	2.24	1.84	0.02	1.22	0.82	0.41	1.60	2.99	2.99
7	DO	0.11	0.05	0.27	0.13	.02	0.16	0.07	0.03	0.04
8	BOD	0.77	0.76	0.77	0.77	0.23	0.77	0.40	0.77	0.04
9	Cl^-	19.20	19.57	17.68	18.12	17.91	18.62	18.01	18.01	21.34
10	TH	10.26	11.62	11.21	11.06	11.21	9.63	11.10	11.99	10.19
11	ALK	8.64	8.88	6.23	7.11	6.86	8.28	7.11	7.45	6.79
12	PO_4^{3-}	0.28	0.64	0.06	0.22	0.31	0.02	0.07	0.02	0.18
13	SO_4^{2-}	6.51	4.60	5.45	6.27	4.68	5.79	4.60	3.57	3.86
14	NO_3^-	2.77	2.45	2.49	2.74	2.53	2.49	2.77	2.74	2.76
15	COD	2.41	1.80	1.89	1.85	2.08	1.91	1.85	2.33	1.22
16	Pb	2.16	1.95	3.23	1.76	2.51	4.64	2.32	3.13	3.56
17	Cd	3.69	3.84	3.44	3.69	3.33	3.69	3.56	3.23	3.69
18	Cu	1.20	1.31	2.08	1.67	1.23	1.24	1.67	1.63	1.84
19	Cr	1.74	0.00	3.69	1.72	0.00	6.36	3.69	3.04	2.16
20	Ni	1.92	1.95	1.99	1.90	2.68	2.19	2.23	3.13	2.02

Table 4.10: Transformed Data for Site M during Wet Season

S/N	Parameter	MW1	MW2	MW3	MW4	MW5	MW6	MW7	MW8	MW9
1	pH	0.82	0.82	0.76	0.76	0.81	0.78	0.80	0.82	0.81
2	TEMP	2.13	2.13	2.13	2.14	2.13	2.12	2.13	2.10	2.10
3	EC	11.95	12.95	11.60	11.64	12.75	8.82	11.71	10.18	12.62
4	COL	1.00	1.00	0.49	0.49	1.00	0.49	0.49	0.49	0.49
5	TDS	11.95	12.95	11.60	11.64	12.75	8.82	11.71	10.18	12.62
6	TUR	1.00	0.85	0.09	0.14	0.36	0.18	0.14	0.02	0.23
7	DO	0.11	0.05	0.27	0.13	0.02	0.16	0.07	0.03	0.04
8	BOD	0.33	0.00	0.77	0.07	0.04	0.13	0.77	0.77	0.77
9	Cl^-	12.99	14.00	12.57	12.91	13.72	10.59	12.94	12.39	11.11
10	TH	2.50	1.58	3.04	2.65	2.91	2.62	2.97	2.39	2.67
11	ALK	8.07	8.47	7.02	6.97	7.50	4.78	8.02	6.79	7.65
12	PO_4^{3-}	0.22	0.55	0.54	0.16	0.44	0.04	0.56	0.11	0.18
13	SO_4^{2-}	5.49	4.12	5.13	5.67	3.88	5.63	3.55	2.94	3.93
14	NO_3^-	2.50	1.58	3.04	2.65	2.91	2.62	2.97	2.39	2.67
15	COD	2.41	1.80	1.89	1.85	2.08	1.91	1.85	2.33	1.22
16	Pb	0.78	0.67	0.72	0.75	0.66	0.62	0.62	0.69	0.68
17	Cd	3.04	3.69	4.19	4.19	4.00	4.00	4.19	4.00	4.19
18	Cr	.88	1.43	1.23	1.43	6.36	1.06	1.43	1.33	.93
19	Ni	1.84	2.05	2.12	1.99	1.90	2.12	2.19	2.46	2.32

Table 4.11: Transformed Data for Site K during Dry Season

S/N	Parameter	KD1	KD2	KD3	KD4	KD5	KD6	KD7	KD8	KD9
1	pH	0.83	0.82	0.81	0.83	0.84	0.82	0.86	0.85	0.86
2	TEMP	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91
3	EC	11.12	9.98	11.41	10.07	9.77	11.67	11.74	10.92	10.07
4	COL	1.00	0.49	0.49	0.49	1.00	1.38	1.38	1.00	1.00
5	TDS	9.04	7.94	9.34	8.04	7.79	9.43	9.47	8.65	7.84
6	TUR	2.24	1.36	.05	1.24	3.43	2.61	3.74	3.88	2.62
7	DO	0.01	0.09	0.19	0.13	0.01	0.07	0.13	0.02	0.02
8	BOD	0.13	0.77	0.40	0.77	0.77	0.77	0.23	0.77	0.77
9	Cl^-	10.92	15.24	15.65	16.01	16.01	17.57	16.65	17.48	15.45
10	TH	11.06	9.74	10.89	5.96	9.76	10.52	10.69	9.81	9.07
11	ALK	0.86	0.48	0.06	0.65	0.58	0.77	0.83	0.78	0.31
12	PO_4^{3-}	1.24	1.56	1.84	0.82	1.24	1.56	1.84	1.24	2.36
13	SO_4^{2-}	5.69	5.06	4.67	3.90	3.48	4.56	4.64	5.15	4.83
14	NO_3^-	2.01	1.61	1.54	2.08	2.37	1.07	1.62	1.38	1.49
15	COD	2.19	3.56	2.89	3.44	5.75	2.19	1.10	3.69	2.96
16	Pb	4.00	4.19	4.00	4.00	4.00	4.19	4.19	4.00	3.84
17	Cd	1.39	1.43	1.53	1.55	1.53	1.29	.97	1.57	1.84
18	Cu	1.19	1.01	1.39	2.96	1.18	3.23	.96	5.29	1.09
19	Cr	1.84	5.29	2.57	3.44	3.04	2.02	2.02	3.13	2.19
20	Ni	1.84	5.29	2.57	3.44	3.04	2.02	2.02	3.13	2.19

Table 4.12: Transformed Data for Site K during Wet Season

S/N	Parameter	KW1	KW2	KW3	KW4	KW5	KW6	KW7	KW8	KW9
1	pH	0.76	0.82	0.82	0.82	0.78	0.76	0.81	0.80	0.85
2	TEMP	2.10	2.10	2.10	2.10	2.10	2.10	2.10	2.10	2.11
3	EC	11.01	11.13	11.41	10.42	10.29	11.55	11.53	11.08	10.08
4	COL	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49
5	TDS	11.01	11.13	11.41	10.42	10.29	11.55	11.53	11.08	10.08
6	TUR	.14	0.09	0.32	0.23	0.27	1.06	0.18	0.27	0.82
7	DO	0.00	0.00	0.07	0.01	0.05	0.00	0.00	0.00	0.08
8	BOD	.23	1.00	1.00	0.13	0.49	0.49	1.00	0.00	0.00
9	Cl^-	13.25	12.33	13.25	12.15	12.00	12.20	12.99	12.20	11.19
10	TH	10.05	8.80	9.79	9.96	8.80	11.11	10.15	9.58	9.39
11	ALK	7.48	7.48	6.71	6.53	6.04	5.16	5.33	6.34	7.30
12	PO_4^{3-}	0.28	0.80	0.20	0.41	0.16	0.68	0.66	0.19	0.07
13	SO_4^{2-}	1.35	1.28	2.31	1.21	1.14	0.26	0.27	0.44	0.54
14	NO_3^-	1.24	1.56	1.84	0.82	1.24	1.56	1.84	1.24	2.36
15	COD	1.24	1.56	1.84	0.82	1.24	1.56	1.84	1.24	2.36
16	Pb	0.90	0.88	0.85	0.80	0.74	0.76	0.79	0.71	0.76
17	Cd	2.89	4.00	4.40	4.19	4.00	4.00	4.40	4.19	4.00
18	Ni	5.37	4.81	4.38	3.55	2.81	3.90	4.74	3.46	3.37

Table 4.13: Principal Component Analysis Result for Site S during Dry Season

Variables	PC1	PC2	PC3	PC4	Communalities
Hardness	**0.93**	0.21	0.25		0.99
Cr	**-0.91**	-0.37			0.97
Ni	**-0.85**		0.17	-0.22	0.82
Phosphate	**0.84**	0.13		0.20	0.78
Color	**0.76**		0.36	**0.50**	0.98
Sulphate	**0.76**	0.45		0.42	0.98
Cu	**-0.70**	**-0.65**	-0.26		0.99
Alkalinity	**0.64**	0.32	0.35	**0.54**	0.92
DO	**0.56**	-0.42	0.53	0.41	0.95
TDS	**0.55**	0.34	0.25	**0.54**	0.78
Temperature	0.17	**0.94**			0.93
pH	0.30	**0.83**	-0.12	0.15	0.82
Cd		**-0.78**	-0.45	-0.37	0.95
Chloride		**0.63**	**-0.56**	0.33	0.82
BOD	-0.24		**0.90**	0.25	0.95
EC	0.40	0.33	**0.78**		0.90
Turbidity	**0.67**	0.11	**0.72**		0.98
Pb			0.10	**-0.92**	0.88
COD	0.45	0.11	0.25	**0.79**	0.91
Nitrate	0.41		**0.58**	**0.67**	0.96
Eigenvalue	10.72	3.27	2.33	2.00	
Total Variance %	53.61	16.36	11.688	10.01	
Cumulative %	53.61	69.95	81.673	91.69	

Table 4.14: Principal Component Analysis Result for Site S during Wet Season

Variables	PC1	PC2	PC3	Communalities
TDS	**0.96**	0.16		0.978
EC	**0.96**	0.16		0.978
Chloride	**0.91**	0.14		0.987
Alkalinity	**0.80**	0.29		0.993
Sulphate	**0.77**		0.30	0.998
Colour	**0.68**	**0.60**	-0.14	0.999
Cr		**-0.98**	-.010	0.973
Tur	0.45	**0.84**		0.978
Pb	-0.40	**-0.77**		0.989
Nitrate	0.44	**0.76**	0.21	0.991
Ni	**-0.64**	**-0.72**		0.985
Temp	-0.15	**0.68**	0.28	0.981
Cd	0.18	**-0.68**		0.959
COD	**0.52**	**0.63**	0.34	0.934
Cu	-0.19		**0.92**	0.927
pH	0.31		**0.90**	0.937
Hardness	0.35	-0.22	**-0.77**	0.975
BOD		-0.31	**0.71**	0.999
DO				0.915
Phosphate	0.43	0.25	0.45	0.927
Eginevalue	8.75	4.27	2.36	
%TotalVariance	43.76	21.37	16.80	
% cumulative	43.76	65.13	81.94	

Table 4.15: Principal Component Analysis Result for Site M during Dry Season

Variables	PC1	PC2	PC3	PC4	Communalities
DO	**0.95**		-0.18		0.96
Turbidity	**-0.87**		0.15	0.31	1.00
Sulphate	**-0.77**			**0.60**	0.99
Nitrate	**0.72**	-0.25	0.39	0.37	0.98
BOD	**0.65**	**0.59**	0.41		0.95
Cd	0.15	**-0.90**	0.22	0.20	0.97
Hardness	-0.18	**0.84**	-0.44	0.20	0.99
Ni	-0.47	**0.75**	0.10	-0.37	0.98
Chloride	-0.46	**-0.72**		0.10	0.99
COD	0.17	**0.70**	**0.62**	0.20	0 .99
TDS	0.19	**0.67**	0.41	-0.15	0.99
Alkalinity			**0.98**		0.99
Cu		0.12	**-0.95**		0.97
pH	-0.37		**0.60**	0.41	0.80
Cr	0.29		0.16	**-0.92**	1.00
Phosphate		-0.43	0.19	**0.87**	0.99
Pb	0.10	-0.19	0.12	**-0.85**	0.99
Colour	0.18	-0.16	**0.53**	**0.80**	0.98
EC	0.45	-0.10	0.11	0.15	0.98
Temperature		0.11	**0.60**	0.12	0.97
Eginevalue	5.66	5.36	4.26	2.90	
%Total Variance	28.33	26.84	2 1.33	14.54	
Cumulative %	28.33	55.18	76.51	91.05	

Table 4.16: Principal Component Analysis Result forSite M during Wet Season

Variables	PC1	PC2	PC3	Communalities
pH	0.27	**-0.77**	-0.10	0.95
Temperature	0.07	0.44	**0.57**	0.92
EC	**0.96**	-0.13	0.15	0.99
Colour	0.42	-0.26	**0.58**	0.95
TDS	**0.96**	-0.13	0.15	0.99
Turbidity	0.42	0.02	0.36	0.92
DO	-0.21	**0.87**	-0.12	0.90
BOD	0.06	-0.07	**-0.91**	0.97
Chloride	**0.51**	-0.15	0.28	0.90
Hardness	-0.06	0.16	-0.07	0.96
Alkalinity	**0.87**	-0.20	-0.11	0.97
Phosphate	**0.54**	-0.00	0.00	0.92
Sulphate	-0.06	0.16	-0.07	0.96
Nitrate	-0.14	**0.85**	0.41	0.99
COD	-0.35	-0.11	0.10	0.97
Pb	0.39	0.46	-0.07	0.81
Cd	-0.14	-0.01	-0.20	0.93
Cr	0.15	**-0.50**	**0.64**	0.94
Ni	-0.28	-0.35	**-0.77**	0.98
Eginevalue	6.60	3.744	3.11	
% Variance	34.75	19.70	16.41	
Cumulative%	34.75	54.45	70.87	

Table 4.17: Principal Component Analysis Result for Site K during Dry Season

Variable	PC1	PC2	PC3	PC4	Communalities
Ni	**0.84**	-0.37	0.22		0.92
TDS	**-0.83**		0.41	0.25	0.96
Con	**-0.83**		0.38	0.34	0.97
BOD	**0.74**		-0.18	0.43	0.95
Pb	**0.74**		-0.27	-0.24	0.77
Turbidity		**0.96**	0.12	0.11	0.97
pH		**0.82**	-0.18		0.74
Colour	-0.41	**0.80**	0.28	0.20	0.95
DO	-0.32	**-0.73**	0.29		0.89
Cd			**0.97**	0.13	0.99
Cu	0.43	-0.13	**-0.86**	0.11	0.97
Temperature	0.39		**-0.74**	-0.29	0.95
Sulphate	0.21		-0.17	**-0.91**	0.99
Alkalinity	0.33	-0.35	-0.12	**-0.83**	0.98
Cr		0.12	-0.15	**0.68**	0.95
Nitrate	-0.24			0.28	0.95
Chloride	0.16	0.12	0.22	**0.61**	0.96
Hardness	-0.36	0.15	0.37		0.73
COD	-0.17			0.25	0.97
Phosphate	-0.16	0.61	0.36		0.96
Eigenvalue	6.781	3.62	2.86	2.433	
% Variance	33.90	18.10	14.33	12.164	
Cumulative%	33.903	52.008	66.34	78.506	

Table 4.18: Principal Component Analysis Result for Site K during Wet Season

Variable	PC1	PC2	PC3	Communalities
EC	**0.90**			0.94
TDS	**0.90**			0.94
Temperature	**-0.85**	0.45		0.97
BOD	**0.83**	0.23		0.87
Chloride	**0.81**	-0.25	0.38	0.94
COD		**0.98**		0.96
Nitrate		**0.98**		0.96
Pb	0.39		**0.86**	0.94
Cd	0.26	0.26	**-0.81**	0.93
Alkalinity	-0.36	0.10	**0.74**	0.92
Ni	**0.61**		**0.74**	0.97
Hardness	0.33			0.80
pH	-0.20	**0.56**	-0.17	0.83
Turbidity	-0.27	**0.51**	-0.30	0.86
Phosphate	**0.57**			0.87
Sulphate	0.24	-0.11	0.38	0.89
DO	-0.28	**0.58**	-0.16	0.97
Eigenvalue	6.01	3.48	3.10	
% Variance	35.37	20.52	18.26	
Cumulative%	35.37	55.89	74.16	

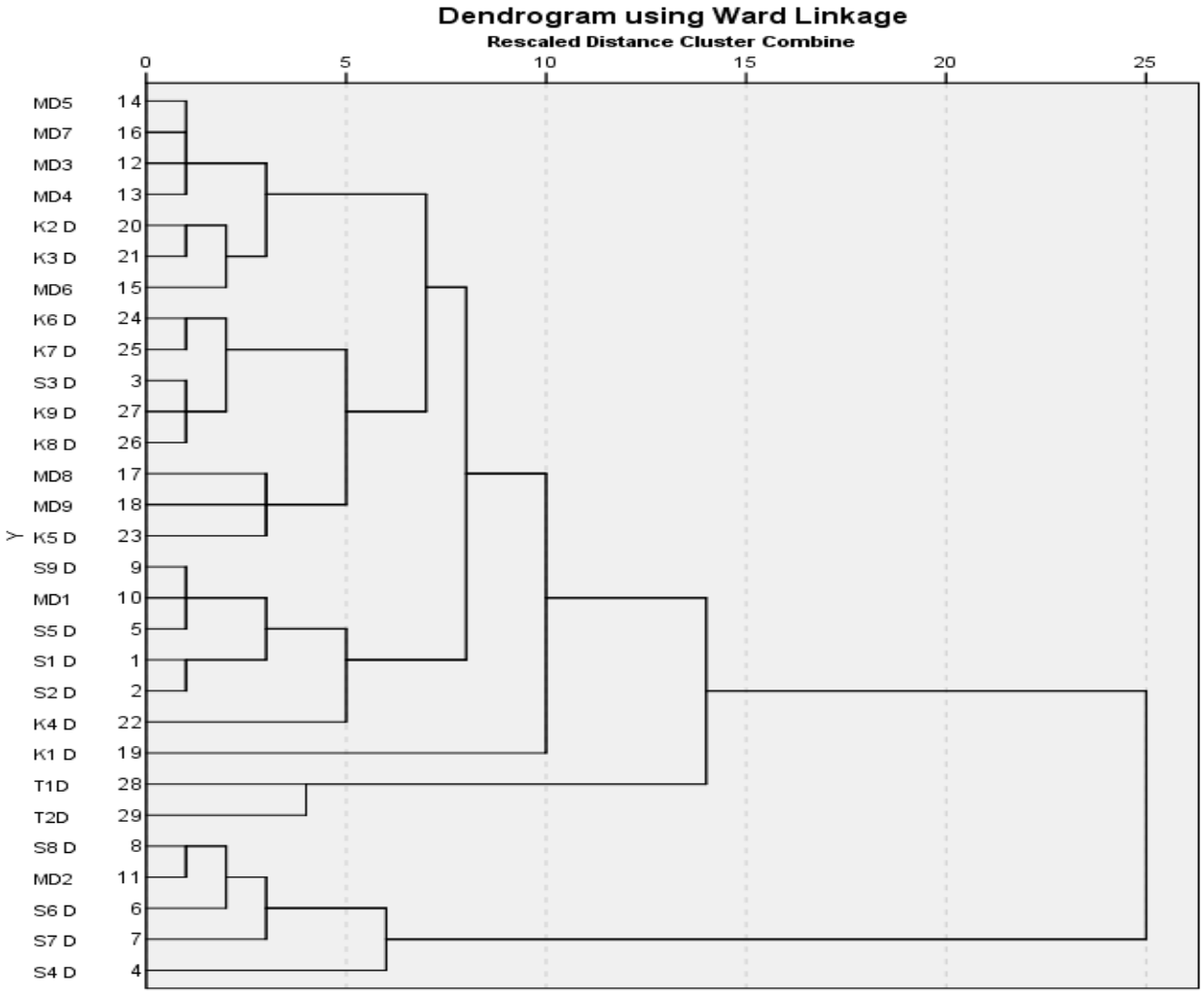

Figure 4. 1: Dendogram showing Spartial Clustering during Dry Seasonfor all Sampling Locactions

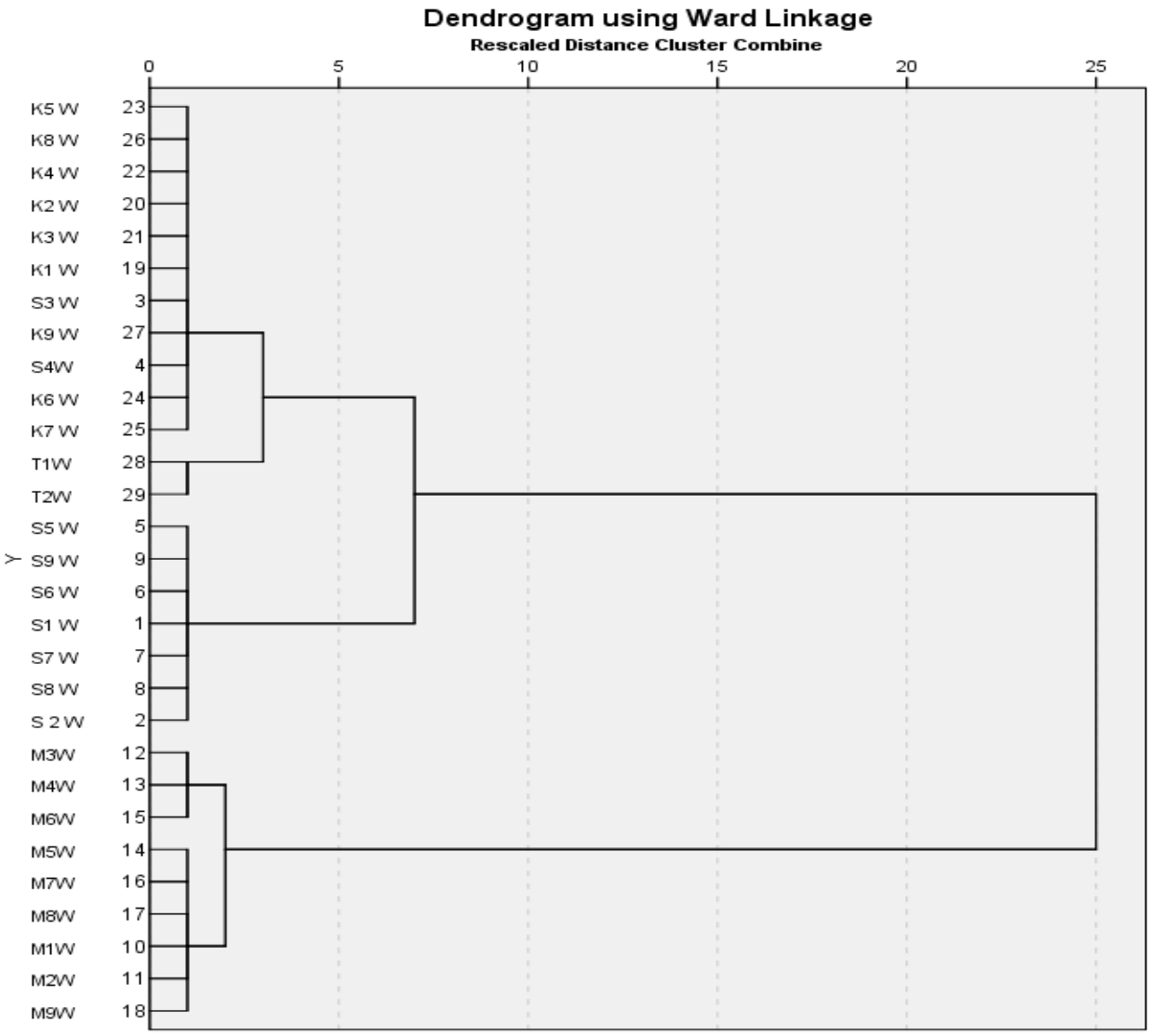

Figure 4. 2: Dendogram showing Spartial Clustering during Wet Season for all Sampling Locations

Table 4.19: Coliform Count Test Values

	Dry Season	Wet Season
S1	40×10^4/ 100 cm^3	123×10^4/ 100cm^3
S2	48×10^4/ 100 cm^3	234×10^4/ 100 cm^3
S3	34×10^4/ 100 cm^3	121×10^4/ 100 cm^3
S4	42×10^4/ 100 cm^3	123×10^4/ 100 cm^3
S5	23×10^4/ 100 cm^3	125×10^4/ 100 cm^3
S6	34×10^4/ 100cm^3	98×10^4/ 100 cm^3
S7	27×10^4/ 100 cm^3	54×10^4/ 100 cm^3
S8	43×10^4/ 100 cm^3	43×10^4/ 100 cm^3
S9	21×10^4/ 100 cm^3	87×10^4/ 100 cm^3
M1	44×10^4/ 100 cm^3	47×10^4/ 100 cm^3
M2	23×10^4/ 100 cm^3	31×10^4/ 100 cm^3
M3	22×10^4/ 100 cm^3	34×10^4/ 100 cm^3
M4	32×10^4/ 100 cm^3	44×10^4/ 100 cm^3
M5	14×10^4/ 100 cm^3	66×10^4/ 100 cm^3
M6	23×10^4/ 100 cm^3	54×10^4/ 100 cm^3
M7	43×10^4/ 100 cm^3	67×10^4/ 100 cm^3
M8	34×10^4/ 100 cm^3	34×10^4/ 100 cm^3
M9	13×10^4/ 100 cm^3	24×10^4/ 100 cm^3
K1	13×10^4/ 100 cm^3	65×10^4/ 100 cm^3
K2	23×10^4/ 100 cm^3	32×10^4/ 100 cm^3
K3	43×10^4/ 100 cm^3	121×10^4/ 100 cm^3
K4	29×10^4/ 100 cm^3	72×10^4/ 100 cm^3
K5	14×10^4/ 100 cm^3	54×10^4/ 100 cm^3
K6	42×10^4/ 100 cm^3	89×10^4/ 100 cm^3
K7	12×10^4/ 100 cm^3	58×10^4/ 100 cm^3
K8	45×10^4/ 100 cm^3	50×10^4/ 100 cm^3
K9	32×10^4/ 100 cm^3	89×10^4/ 100 cm^3
T1	12×10^4/ 100 cm^3	23×10^4/ 100 cm^3
T2	13×10^4/ 100 cm^3	25×10^4/ 100 cm^3

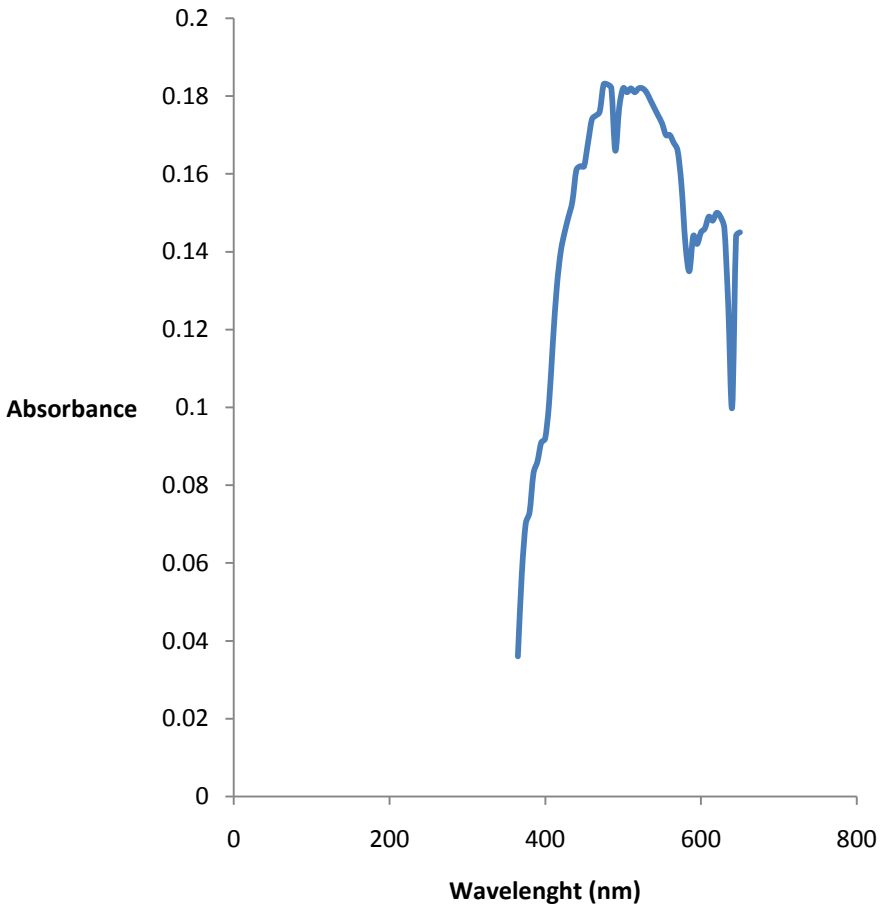

Figure 4. 3:UV and visible Absorption Spectrum of Methanol Extract

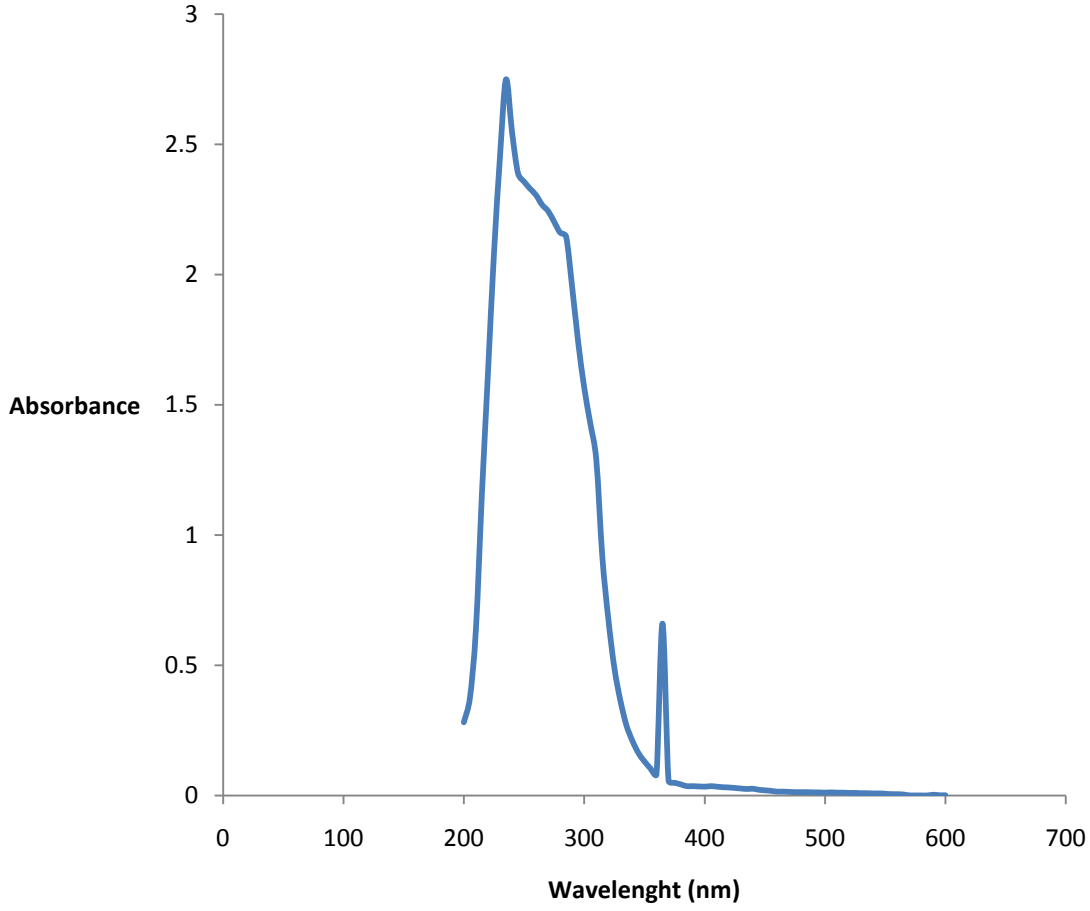

Figure 4.4: UV and Visible Absorption Spectrum of Diethyl Ether Extract

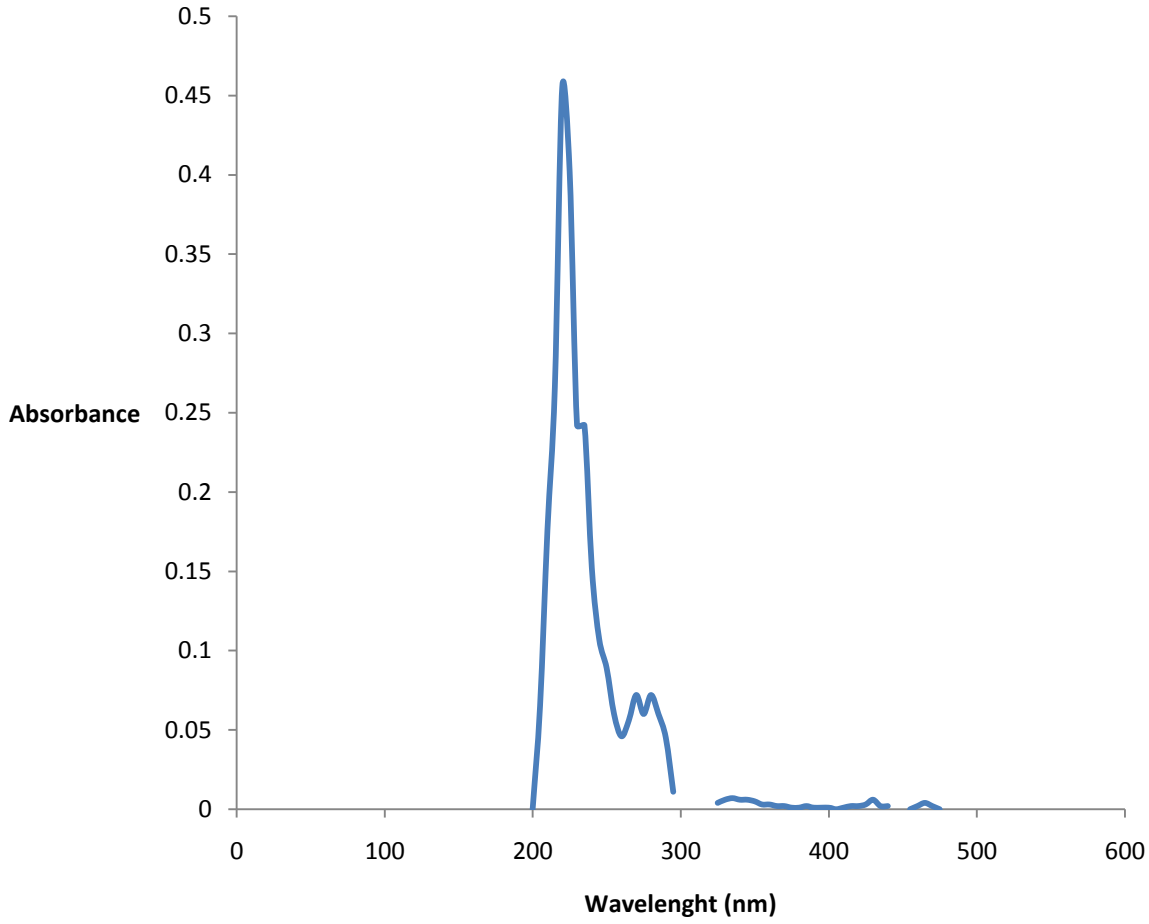

Figure 4.5:UV and visible Absorption Spectrum of n-haxane Extract

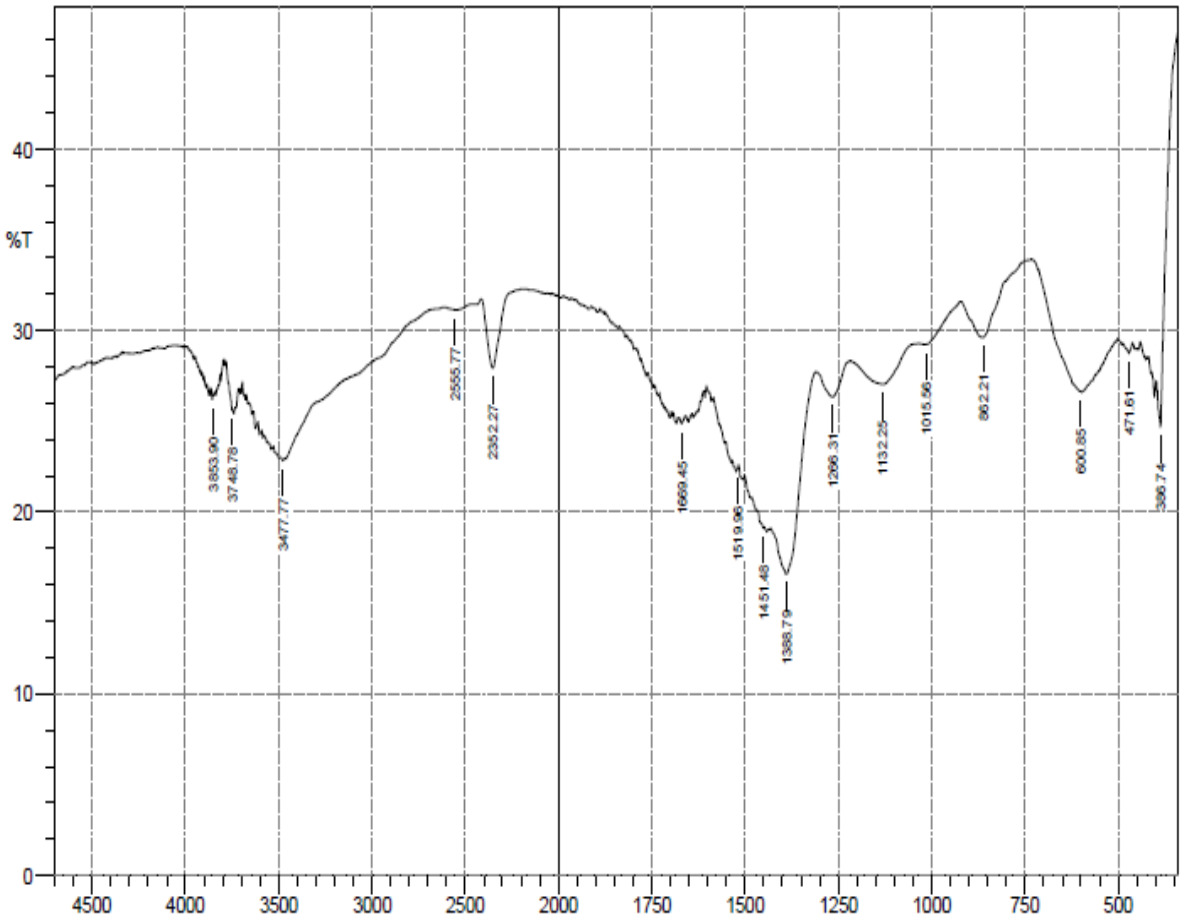

Figure 4. 6: FTIR Analysis Result for Dry Water Residue

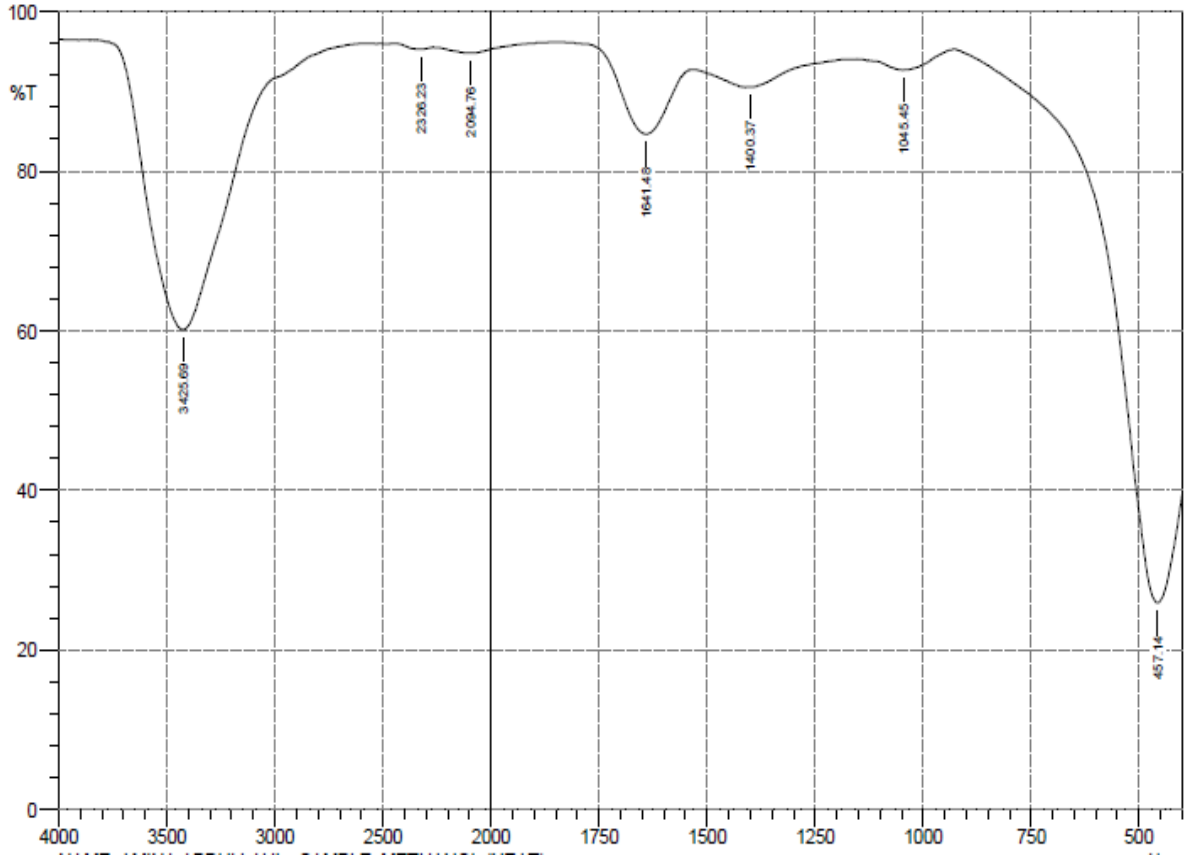

Figure 4. 7: FTIR Analysis Result for Methanol Extract

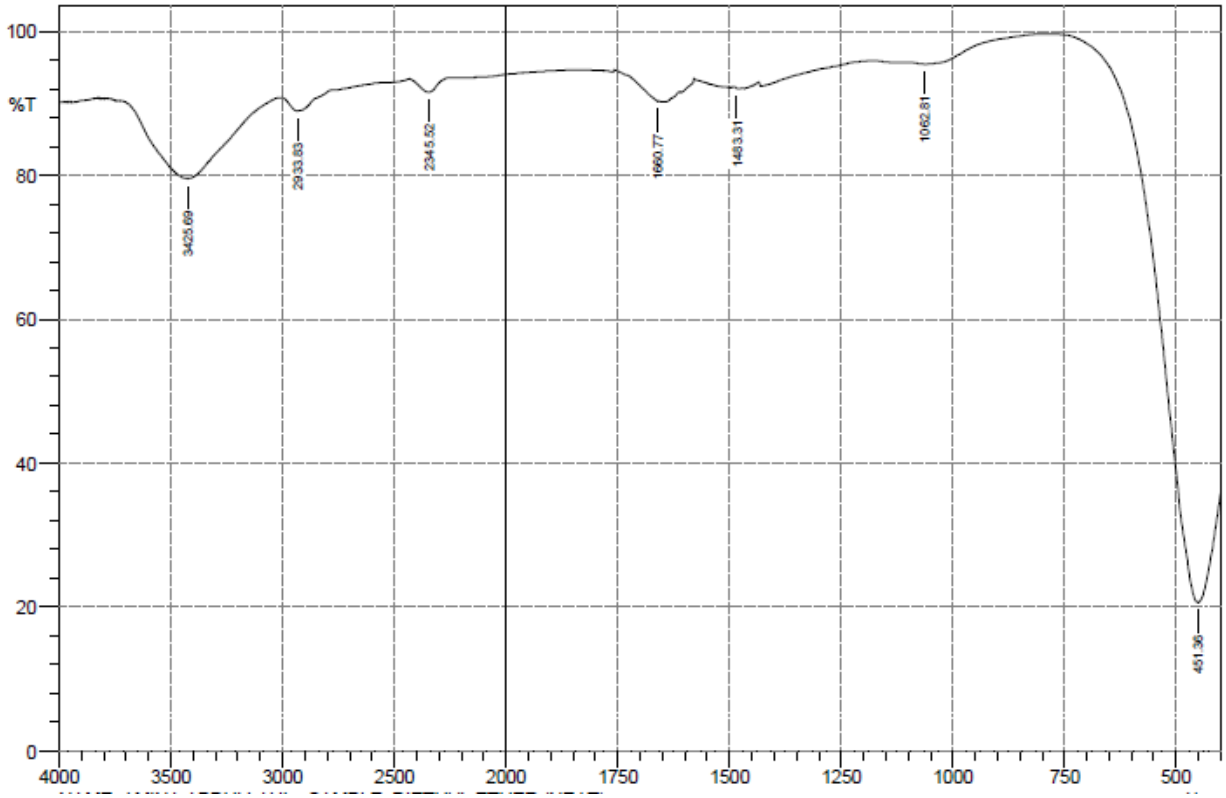

Figure 4. 8: FTIR Analysis Result for Diethyl Ether Extract

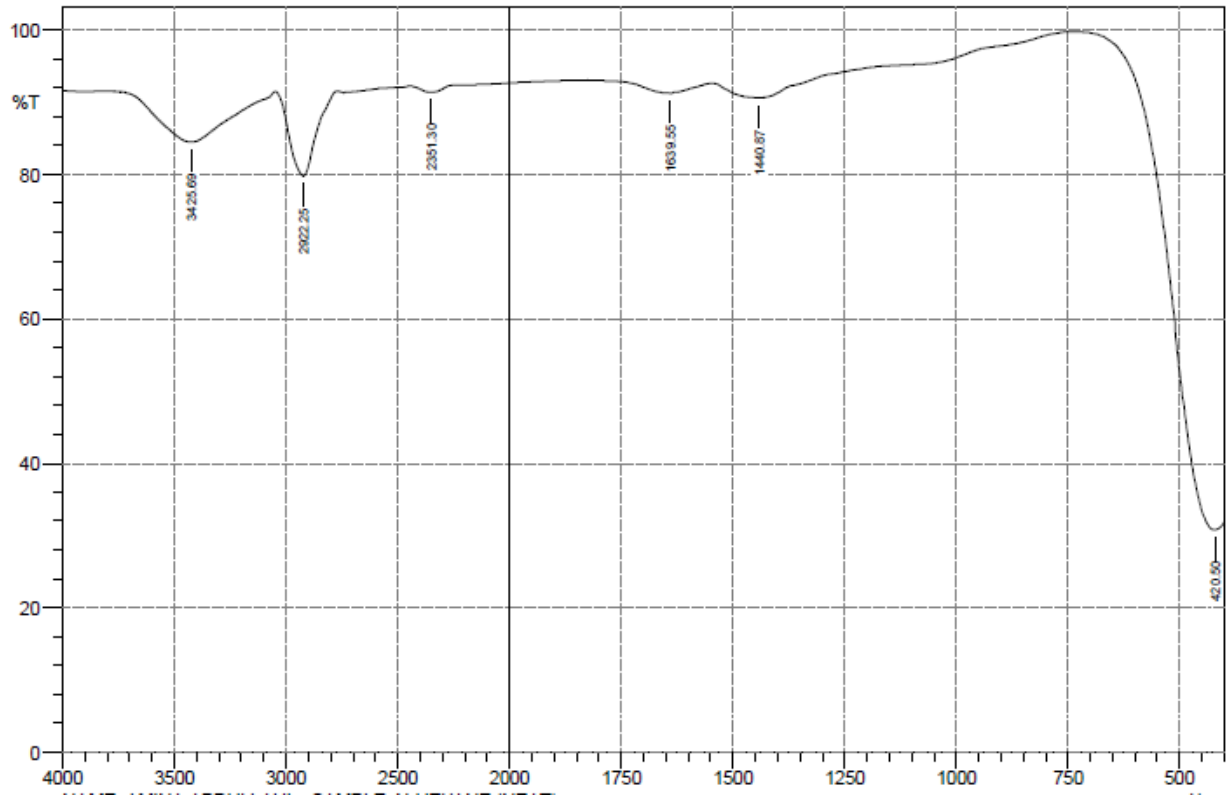

Figure 4. 9: FTIR Analysis Result for n-Hexane Extract

CHAPTER FIVE

5.0 DISCUSSION

The data of the average values for all the parameters characterising the water quality at different sites and seasons are shown in Tables 4.1-4.6. The pH was found to be slightly alkaline in site S ranging from 8.75-8.45 and 8.57-8.14 for dry and wet seasons respectively, for sites M and K the pH range from slightly alkaline (8.44-8.11) and (8.46-7.92) in dry season, (8.05-7.83) and (8.31-7.40) in wet season respectively. The alkaline nature of the water may likely be as a result of the dyeing pits located around these wells, since the waste from dyeing process is strongly alkaline (Imtiazuddin *et al*., 2012). The control samples have values 7.81 and 7.55 for dry and wet season respectively which are lower in pH than the sampling wells for both seasons. All pH values obtained were within the SON (2007) permissible limits of 6.5-8.5for drinking water except for values of sampling location S during dry season.The temperature values obtained in this work are within 30°C, although the seasonal fluctuation in temperature values could be due to climate condition.

Electrical Conductivity was found to vary from 272-5840µ℧/cm and 1736.33-4783.33µ℧/cm for site S, 816.00-3826.00µ℧/cm and 933.33-3964.33µ℧/cm for site M, also 1333.67-2666.67µ℧/cm and 1497.00-2503.33µ℧/cm for site K for dry and wet seasons respectively. The values obtained are above the SON (2007) value for drinking water of 750µ℧/cm except for some wells in site S during dry season. Total dissolved solids were found to be very high with very large values and having values of 1195.67-2670 mg/dm^3 and 873.00-2486.67 mg/dm^3 for site S, 663.33 -3189.67 mg/dm^3 and 444.3 -3563.33 mg/dm^3 for site M and 617.33-1195.67mg/dm^{3}and 575.00-1274.33mg/dm^3 for site K for dry and wet seasons respectively. TDS values obtained were above SON (2007) standard for drinking water of

500mg/dm^3, this may be due to leaching of various pollutants into the wells which can decrease the palatability of the water and cause gastrointestinal irritation in human (WHO, 1997).

Turbidity was highly varied ranging from 2.33-281.33NTU and 2.33-66.33NTU for site S, 1.33-53.67NTU and 1.33-10NTU for site M and 1.67-93.33NTU and 2.00-10.67NTU for dry and wet seasons respectively. Turbidity hinders disinfection of water by shielding microbes, some of them are pathogen (Hauser, 2001). The values obtained for colour in the control sites was found to be 5 hazen lower than values found in sampling wells.

Alkalinity values are from 603.33-1663.33 mg/dm^3 and 376.67-1160 mg/dm^3 for Site S, from 313.33-953.33mg/dm^3 and 153.33-813.33mg/dm^3 for site M and from 316.6-710 mg/dm^{3}and186-543.33 mg/dm^3 for Site K during dry and wet seasons respectively. The values obtained for alkalinity are greater than the 150 mg/dm^3 recommended units by SON (2007) for both seasons. The values obtained for total hardness ranging from 1014.45-1967.51mg/dm^3 and 538.93-3046.80mg/dm^{3}for Site S, from 1266.03-2898.98mg/dm^3 and 740.89-2036.88mg/dm^3 for site M and from 276.36-2114.68 mg/dm^3 and 925.74 -2155.11 mg/dm^3 for site K for dry and wet seasons respectively are greater than the values obtained for alkalinity. Since the values obtained for hardness are larger than that of alkalinity, this implies that the well water contains carbonate and non-carbonate salt which causes permanent hardness of water. The concentrations of chloride were observed to be higher during dry season than wet season this might be due to dilution by percolating rain and surface ran off of water during wet season, i.e. 14538.13-44613 mg/L and 2409.67-7277.03mg/L for site S, 16042.42-41620.00mg/L and 1798.67-5522.96 mg/L for site M and 2017.33-15526.40mg/L and 2215.49 -4367.06mg/L for site K for dry and wet season respectively. This implies that the water is more saline during dry season.

Sulphates were found to vary from 95.00-438.33 mg/dm^3 and 42.67- 351.67 mg/dm^3 for site S, 77.33-356.67 mg/dm^3 and 52.00 -241.00 mg/dm^3 for site M and 73.33-246.67 mg/dm^3 and 47.33-208 mg/dm^3. Control site has value (96.00 mg/dm^3) lower in some cases compared to sampling sites. With this, the source of sulphates may not only be from underlying bedrock but also from dying pits. Ingestion of high level of sulphate has been linked to catharsis, dehydration and gastrointestinal irritation (Bertem and Balance, 1996) and elevated concentrations were observed for nitrates (30.90-119.20mg/dm^{3}and 4.43-105.13mg/dm^3 for site S, 36.63-46.20 mg/dm^3 and 18.00-55.33mg/dm^3 for site M, 10.83-34.63 mg/dm^3 and 3.20 -33.03 mg/dm^3 for sites K for dry and wet seasons respectively) and phosphates (0.9-12.67mg/dm^3 and 0.43-17.37 mg/dm^3 for site S, 0.70-6.30 mg/dm^3 and 0.47-5.60 mg/dm^3 for site M, 1.73 -8.47 mg/dm^3 and 1.83-7.83.00mg/dm^3 for site K for dry and wet seasons respectively), these concentrations would support growth of planktons which may deplete dissolved oxygen concentration. Dissolved oxygen concentrations were found to be low.

Biological oxygen demand concentrations depends on sanitary condition of well, is mainly as a result of seepage from pits toilets. BOD concentrations of wet season (0.13-0.63 mg/dm^3, 0.13 -0.93 mg/dm^3 and 0.10 -0.90 mg/dm^3) are higher than that of dry season (0.13-0.30 mg/dm^3, 0.13-0.63 mg/dm^3 and 0.13-0.43 mg/dm^3) for sites S, M and K respectively, due to increased underground water flow during this period. The presence of dye residues which increases COD level could be the reason of elevated concentrations of chemical oxygen demand for dry season (13.33-56.67mg/dm^3, 12.67-35.67mg/dm^3 and 8-34.33mg/dm^3) over that of wet season (3.67-35.00mg/dm^3, 2.03-9.90mg/dm^3 and 2.33-11.33mg/dm^3) for sites S, M and K respectively.

Lead concentrations obtained are above the SON (2007) recommended value of 0.01mg/dm^3 for all the seasons except for some wells in site S during the dry season. The wet season (0.12-0.19mg/dm^3, 0.13 -0.16mg/dm^3 and 0.11 -0.14mg/dm^3) had higher values than that of dry season (BDL-0.06mg/dm^3, 0.01-0.05mg/dm^3 and BDL-0.09mg/dm^3) for sites S, M and K respectively. The high concentration of lead here can be attributed to waste such as lead batteries used in filling the abandoned dyeing pits. The wells analysed showed high concentrations of cadmium for both seasons and concentrations were higher for the dry season than wet season. According to limits prescribed by SON (2007), it was found that all the samples collected from the sources were free from copper. The average value of copper in all water samples are below the permissible limits for all the seasons, except a well in site S in wet season which had a value of 2.26mg/dm^3, this might due to the proximity of the well to the dyeing pits. The obtained data shows that chromium concentrations of site S (0.06-0.21mg/dm^3 and 0.06-0.18mg/dm^3) and K (0.01-0.11mg/dm^3 and 0.07-0.16mg/dm^3) were above the SON (2007) permissible limits of 0.05mg/dm^3 for dry and wet seasons respectively. While the concentrations for site M (0.0-0.05mg/dm^3) for dry season are within the limits. The SON (2007) standard for nickel concentration is 0.02mg/dm^3 all the samples studied showed nickel concentrations of site S (BDL-0.04mg/dm^{3}and 0.01-0.04), M (0.02-0.04mg/dm^3 and0.03-0.04mg/dm^3) and K (0.01-0.04mg/dm^3 and 0.02-0.03mg/dm^3).

5.1 Statistical Treatment of Data

5.1.1 Principal component analysis

This was employed to investigate the sources of pollution and the cause of variation in the observed quality data at threesampling sites for two seasons. Tables 4.13-4.18 showed

principal component with eigenvalues greater than 1 explaining the total cumulative percentage in the water-quality data.

The accumulated percentage of the total variances of the four extracted components with eigenvalues greater than one for site S during dry season explains 91.69% of total variance and communalities show that variance of all the variable have been described well by the four components (Table 4.13). Component loading PC1 explained 53.61% of the total variance while PC2 explained 16.366%, PC3 explained 11.688% and PC4 explained 10.018%. First component gives information about the variation in sulphate, hardness, alkalinity and TDS these quality parameters indicate that the well water contain substantial amount of carbonate and non-carbonate salts which causes permanent hardness of water. This shows that there are non-anthropogenic sources contributing to the water quality that is not from the dyeing activity. Phosphate contributes to algal growth hereby depleting dissolved oxygen. The loading nickel, copper and chromium also indicate that seepage of leachate from the indigo dyeing pits to the wells. In the second Component PC2, pH, chloride copper and cadmium, the relationship of these water parameter results from inorganic waste which are related to dyeing activities seeping into the wells. The combination of turbidity, BOD, DO and nitrate in PC3 is an indication of seepage from pits toilets located close to the wells. This is possible because well linings are not adequately sealed and no provision of concrete floor apron. PC4 shows degradation of dye residue thus increasing COD level.

PCA rendered three significant components (eigenvalue >1) for site S during wet season, explaining 81.94% of the total variance of parameters analysedand communalities showed that variance of all the variable were described well by the three components (Table 4.14). This was slightly different from what was observed in SD with percolating rain water as an important

contributor to well water quality. The first component loading (PC1) accounts for as much as 43.76% of the total variance and was strongly correlated with TDS, conductivity, chloride, alkalinity, sulphate, nickel and colour. This is due to dissolution of soil mineral resulting from pH changes and permeability of the soil allowing the passage of leachates from the dyeing pits to the wells and also pollution from non-point sourcesby percolating rain water. It was noted that PC2 is associated with decomposition process of organic waste. The second component which account for 21.37% of the total variance strongly correlated with nitrate, temperature, colour, turbidity, COD, cadmium, nickel and lead. This shows that there is seepage of organic waste which contains substantial amount of Cr, Pb and Ni from the dyeing pits to the wells. The decomposed organic wastes act as chemical oxidant, thereby increasing the level of COD in water.PC3 explains the 16.81% of the total variance. In this component copper strongly correlated with pH and hardness might not have a major controlling effect on the water quality in this component due to increased dilution during this period.

The PCA of site M during dry season yielded four components with eigenvalue > 1 explaining 91.05% of total variance. Communalities showed that variance of all the variables have been described well by the four components (Table 4.15).PC1 was responsible for 28.33% of the total variance representing high input of organic pollution in colloidal form in water. This gave rise tohigh turbidity of the water during sampling period. PC2 explained 26.844% of the total variance which contains correlated variable showing (TDS, hardness, nickel, conductivity, chloride and cadmium) mineral characteristic of the well water. COD, pH, temperature and alkalinity, copper, phosphate and colour make the components in PC3,which explains 21.33% of the total variance. Theseare important variables that can be attributed toinorganic materials and dye residual wastes leached into the wells. The fourth component explains 14.55% of the total

variance,colour, lead, chromium, phosphate and sulphate as variables. The extracted lead and chromium can be linked to dyeing wastes pits.

Site M during wet season yielded three components accounting for 70.87% of the total variance and communalities show that variance of all the variable have been described well by the three components (Table 4.16).The PC1 explains 34.75% of total variance and is associated with the more mineralized water (TDS and conductivity) due to dissolution of soil mineral by percolating rain water thereby increasing the level of TDS and conductivity. PC2 explains 19.71% of the total variance, the significance of dissolved oxygen, nitrate and pH in PC2 can be attributed to organic waste discharged and nitrification process had taken place. PC3 explains 16.41% the total variance, Cr, colour, BOD and temperature in PC3 represent discharge from dyeing waste pit.

PCA rendered four significant components for site K during dry season explaining 78.50% of the total variable and communalities show that variance of all the variables have been described well by the four components (Table 4.17) PC1 gives information about the variation of nickel, lead conductivity, TDS and BOD explaining 33.90% of the total variance. This represents contamination from domestic and the dyeing pits waste. PC2 explains about 18.11% of the total variance, it is associated with loading of turbidity, colour, pH, and dissolved oxygen and phosphate. Phosphate contributes to algal growth and hereby depletes the level of dissolved oxygen. The PC3 explains 14.33% of the total variance which consists mainly of Cr, Cd, Cu and temperature, characterised by the leachate from dyeing waste. PC4 explains 12.16 of the total variance have factor illustrating contamination from waste discharge with variables such as Cr, Cl, sulphate and alkalinity.

PCA for site K during wet season resulted in three components explaining 74.16% of the total variance and Communalities show that variance of all the variables have been described well by the threecomponents (Table 4.18).PC1 explains 35.38% of the variance with loadings on phosphate, chloride, nickel, BOD, conductivity, temperature and TDS. This indicatesmineralization of soil material and contamination of from waste pits. TDS and conductivity imply more ions in solution as result of dissolution of mineral ions from underlying rock by percolating rain water. The increase in underground water flow during wet season increases the movement of the wastes into the wells. PC2 explains about 20.52% of the total variance and consists of nitrate, pH, turbidity and COD. This component explains the influence of waste involving colloidal materials from pit toilets. PC3 which explained 18.26% of the total variance can be attributed to waste discharged from dyeing pits with lead, nickel cadmium and alkalinity as factor.

5.1.2 Cluster analysis

The dendrogram obtained for dry season sampling period (Fig. 4.1) detected the similarity between groups consisting of three clusters at Euclidean distance 10. Cluster I consists of location MD5, MD7, MD4, KD2, KD3, MD6,KD6, KD7, SD3, KD9, KD8, MD9 KD5, SD9, MD1, SD5, SD1, SD2, KD4, and KD1. Cluster II consisted of only TD1 and TD2 from control site while Cluster III consisted of SD8, MD2, S6D, SD7 and SD4.The first level of aggregation starts with cluster I at a distance of about 10.0. Cluster II shows similarity with Cluster I at distance 14.0. Cluster III is associated with other clusters at 25.0. This implies that Sampling wells show that there is a high level of variation in the quality of water during dry season as result of reduction in ground water flow. Cluster II which consisted of mainly the control site

showed very small similarity of other groups could be due to the sanitary conditions of the wells and similar chemical characteristics of the wells bedrock.

The dendrogram obtained for the wet season (Fig 4.2) also detected similarity groups yielding three significant Clusters at distance 5.0. Cluster I includes KW5, KW8, KW4, KW2, KW3, KW1 SW3 KW9, SW4, KW6, KW7, TW1 and TW2, Cluster II includes SW5, SW9, SW6, SW1, SW7, SW8 and SW2 While Cluster III includes MW3, MW4, MW6, MW5, MW7, MW8, MW1, MW2 and MW9. The first level aggregation is established in Cluster I consisting mainly of wells from sites K and T (control) except for wells S3 and S4 which show similar chemical characteristics. Cluster II which consisted mainly of Site S associated with cluster I at distance 7.0. Cluster III presents very small similarity with any other cluster at a distance 25.0 consisting mainly of Site M. Grouping of locations during this period shows the sampling wells are distinctly grouped according to their sites. This shows that the variation in the quality of water in the different areas is not much during the wet season. This could be attributed to dilution of well water during this period; i.e increase in ground water flow.

5.2 Coliform Bacterial Density

This finding reveals that, none of the sampled wells gave a result that fell within the permissible level for drinking water quality given by the SON (2007) for both seasons. It was observed that large numbers of the bacteria were found in wet season. This may be as a result of favourable condition during this period that encourages bacteria growth. The wells are exposed to high sanitary risk-factors, arising from close proximity to pit latrine. Since the well linings are not adequately sealed and no provision of concrete floor apron. From the health point of view, the most important characteristic of good quality water is obviously an absence of pathogenic organisms (Richard *et al*., 1977).

5.3 Spectroscopic Studies of Dye Residues for Water

The FTIR Spectra (Figure 4.6-4.9) show the functional groups found in each of the extract and dry water residue. The FTIR spectral for dry water residue show bands (Figure 4.6) for secondary amine at N-H stretching 3477.77cm^{-1} and bending at 1519.95cm^{-1}, carbonyl bond due to ketone at 1669.45cm^{-1} , C-C=C asymmetric stretching at 1451.48cm^{-1} these are the functional groups which are characteristics of indigo dye. This show that indigo dye residue might be present in water though other bands C=C-H asymmetric stretch at 3100-3000cm^{-1} and C-C=C symmetric stretch at 1600-1580cm^{-1} for aromatic rings were absent in the spectra. Figure 4.7-4.9 show functional group bonds of each of the extract having carbonyl bond due to ketones and C-H bonds which are characteristic of indigo dye. The residualchromophores in water might settles on the skin and absorb Sunlight at a particular wavelength causing itching which leads to rashes (Ajibola and Rilwanu, 1998).

UV Visible spectral of Fig 4.3 shows maximum absorption at 465nm for methanol extracts which is at the visible regions, this is as result of the presence of conjugated bonds in methanol extract which show FTIR band at 2094cm^{-1} for –C=C-C=C- bond (Fig. 4.7). Fig 4.4 shows maximum absorption at 235nm for diethyl ether extracts and Fig. 4.5 shows maximum absorption at 220nm for n-hexane. These show there are heterogeneous compounds in each of the extract because of the multiple peaks shown in each of the spectrum and also the more polar the solvent is the more the peaks move towards visible region.

CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECOMMENDATION

6.1 Summary

This study assessed the well water quality near abandoned indigo dyeing pits in Zaria city, Nigeria. The data obtained for the physiochemical analysis falls above the SON (2007) threshold value except for temperature and Cu for both seasons. The result showed physical parameters (pH, temperature, turbidity, colour, and TDS) ranged from 7.92-8.75,24.01-24.45°C, 1.33-281.33NTU, 5-30 hazen and 617.33-3186.37 mg/dm^{3}for dry season and 7.40-8.57, 28.05-29 °C, 1.33-66.33NTU, 5-20hazen and 444.33-3563.33mg/dm^3 for wet season respectively. The result for chemical parameters (conductivity, DO, BOD, Cl, hardness, alkalinity, SO_4^{2-} , PO_4^{3-}, NO_3^-, COD) ranged from 272.00-5840.00µ℧/cm, 0.30-0.77mg/dm^{3}0.13-0.63mg/dm^3, 2017.33-44613.46mg/dm^3, 276.36-2898.91mg/dm^3, 313.33-1663.33mg/dm^3, 73.3-438.33mg/dm^3, 0.70-12.67mg/dm^3, 10.83-119.20mg/dm^{3}and 8.00-56.67mg/dm^{3}for dry season and 933.99-4783.33µ℧/cm, 0.30-2.13mg/dm^3, 0.1-0.93mg/dm^3,1798.67-7277.03mg/dm^3, 538.95-3046.80mg/dm^3, 153.33-1160.00mg/dm^3, 42.67-351.67mg/dm^3, 0.43-17.37mg/dm^3,3.20-105.13mg/dm^{3}and 2.03-35.00mg/dm^3 for wet season respectively. Values obtained for metal analysis (Pb, Cd, Cu, Cr and Ni) ranged from 0.00-0.09mg/dm^3, 0.01-0.02mg/dm^3, 0.04-0.11mg/dm^3, 0.00-0.21mg/dm^3 and 0.00-0.05mg/dm^3 for dry season and 0.11-0.19mg/dm^3, 0.00-0.02mg/dm^3, 0.00-2.26mg/dm^3,0.00-0.18 mg/dm^{3}and0.01-0.04 for wet season.

The principal component analysis extracted important parameters which indicated the abandoned dyeing pits, pits toilet in close proximity to the well water, seasonal effects and domestic waste to be the sources of pollution. Cluster analysis was used to determine the

similarity between the dyeing sites for both seasons, during dry season wells had more of individual interaction whereas behaved much similar during wet season. Large numbers of bacteria were found in wet season than in dry, none of the sampled wells gave a result that fell within the permissible level for drinking water quality given by the SON (2007) for both seasons.

Seasonal changes could have played an important role in varying the concentration since certain parameters tend to vary with change in weather. Temperature has a negative effect on oxygen, some organic component of the dye waste have been decomposed as result of increase in temperature. Dissolution of soil minerals by rain water might increase the level of conductivity of the water.

The UV-Visible spectral of the extracts show that there are heterogeneous compounds in the each of the extract because of the multiple peaks in each of the spectrum. The spectrum of methanol extract shows absorption of maximum wavelength in the visible region. The functional groups found in the FTIR spectral of the extract are common to indigo dye are C=O, C-H, -C=C-C=C and N-H.

6.2 Conclusion

The water in wells located near abandoned indigo dyeing pit have been analysed for heavy metal (Pb, Cd, Cu, Cr and Ni) levels, physiochemical properties (pH, temperature, conductivity, turbidity, TDS, alkalinity, hardness, DO, BOD, COD, chloride, nitrate, phosphate, and sulphate), coliform levels and presence of dye residues in water.

Based on the results obtained in this study it can be concluded that leachates from indigo dyeing pits still has an effect on the quality of wells in the vicinity of the dyeing centers.

6.2 Recommendations

i. The dye residues should be quantified and identified to ascertain the pollution levels of the water from the various sites.

ii. Effective and affordable remediation processes should be developed for the water from affected wells in the study sites.

iii. Soil properties should be further evaluated to establish the reasons for similarity in site during wet season.

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Appendix I: Physiochemical Data for Site S during Dry Season

	pH	TEMP ^0C	EC µƧ/cm	COLHAZEN	TDS mg/dm^3	TURNTU	DO mg/dm^3	BOD mg/dm^3	Cl mg/dm^3	TH mg/dm^3	ALK mg/dm^3	PO_4^{3} mg/dm^3	SO_4^{2-} mg/dm^3	NO_3^{-} mg/dm^3	COD mg/dm^3	Pb mg/dm^3	Cd mg/dm^3	Cu mg/dm^3	Cr mg/dm^3	Ni mg/dm^3
SD1	8.69±0.04	24.33±0.15	5803.33±5.77	20±0	2670.00±0.00	281.33±0.6	0.43±0.0	0.13±0.06	19544.00±4.4	1808.96±1.30	1563.33±5.7	5.17±0.06	398.33±10.4	81.27±1.7	36.60±5.77	0±0	0.02±0	0.10±0.0	0.16±0	0.05±0.0
SD2	8.9±0.01	24.33±0.15	5840.0±10	30±0	2453.33±5.77	118.33±1.2	0.40±0.1	0.23±0.06	35589.78±1.9	1967.51±6.80	1663.33±5.7	12.67±0.06	438.33±10.4	119.2±1.7	56.67±5.77	0.04±0	0.01±0	0.11±0.0	0.21±0	5.06±0.0
SD3	8.81±0.02	24.31±0.06	2866.65±5.77	5±0	1358.33±0.58	41.67±2.08	0.67±0.06	0.23±0.06	19048.69±0.6	1262.82±9.99	603.33±5.77	5.23±0.06	171.67±3.79	42.67±2.5	13.33±5.77	0.02±0	0.01±0	0.09±0.0	0.01±0	0.00±
SD4	8.82±0.05	24.31±0.15	454.67±5.68	5±0	2216.67±15.28	12.33±1.16	0.47±0.	0.30±0.10	19546.00±4.6	1663.03±5.70	1283.33±5.7	3.37±0.06	95.00±3.61	38.87±0.6	23.33±5.77	0.00±0.0	0.01±0	0.07±0.0	0.09±0.0	0±0.0
SD5	8.53±0.04	24.1±0.1	3660.00±.10	15±0	1772.00±1.00	14.67±0.58	0.60±0.17	0.13±0.06	19532.67±28	1404.82±8.85	696.67±5.7	5.20±0.20	294.33±4.04	30.90±1.7	19.33±1.16	0.06±0.0	0.01±0.0	0.10±0.0	0.17±0.0	0.03±0
SD6	8.48±0.03	24.15±0.25	581.33±1.53	5±0	1195.67±5.77	41.00±1	0.43±0.06	0.23±0.06	15540.51±2.7	1350.16±5.08	740.00±10.00	4.70±0.17	237.00±3.00	34.13±2.6	23.33±5.51	0.02±0.0	0.01±0.0	0.06±0.0	0.10±0	0.04±00
SD7	8.7±0.07	24.3±0.15	272.00±3.5	5±0	1313.00±1.	2.33±0.58	0.77±0.12	0.23±0.06	44613.46±1	1014.45±9.93	803.33±5.77	0.90±0.20	215.33±5.03	37.70±1.2	25.67±3.51	0.03±0.0	0.01±0.00	0.06±0.0	0.08±0	0.00±0
SD8	8.75±0.01	24.±0.06	511.67±1.53	5±0	2456.67±5.79	21.00±1	0.53±0.15	0.23±0.06	22037.19±27	1282.63±20.25	850.00±10.0	6.00±0.17	240.33±6.51	67.37±2.1	26.33±3.78	0.06±0.0	0.01±0.0	0.07±0	0.11±0.	0.03±0
SD9	8.62±0.03	24.33±0.15	3223.33±5.77	10±0	1552.00±1.00	37.67±1.16	0.43±0.06	0.13±0.06	14538.13±2.5	1023.77±6.18	810.00±10.0	3.70±0.20	353.33±11.	35.30±270	33.00±2.00	0.04±0.0	0.01±0.00	0.06±0	0.06±0	0.02±0

Appendix II: Physiochemical Data for Site S during Wet Season

	pH	TEMP ^0C	EC µƧ/cm	COLHAZEN	TDS mg/dm^3	TURNTU	DO mg/dm^3	BOD mg/dm^3	Cl mg/dm^3	TH mg/dm^3	ALK mg/dm^3	PO_4^{3} mg/dm^3	SO_4^{2-} mg/dm^3	NO_3^{-} mg/dm^3	COD mg/dm^3	Pb mg/dm^3	Cd mg/dm^3	Cu mg/dm^3	Cr mg/dm^3	Ni mg/dm^3
S1	8.24±0.01	28.8±0.1	4783.33±5.77	10±0	2486.67±5.78	11.33±0.58	0.67±0.12	0.43±0.06	6727.41±18	1427.44±23.09	893.33±5.78	3.27±0.12	255.00±5.00	53.20±2.0	24.33±0.57	0.129±0.0	0.01±0.00	0.01±0.0	0.08±0.0	0.03±0.0
S2	8.44±0.01	28.87±0.06	4533.33±5.74	15±0	2376.67±5.77	66.33±0.58	0.87±0.06	0.63±0.06	7277.03±7.8	1632.96±29.16	1160±10.0	17.37±0.1	351.67±33.2	105.13±2	35.00±2.00	0.19±0.0	0.00±0	0.01±0.0	0.18±0.0	0.04±0
S3	8.14±0.02	28.87±0.21	2843.33±5.08	5±0	1486.00±1.00	3.67±1.16	1.13±0.00	0.43±0.06	5013.19±0.9	3046.79±29.06	463.33±5.78	4.63±0.15	55.67±3.51	33.77±1.5	8.33±0.58	0.13±0.0	0.00±0	2.26±0.0	0.076±0.0	0.02±0
S4	8.35±0.03	28.57±0.15	2880.33±0.58	5±0	1488.33±1.16	2.33±0.56	1.20±0.00	0.43±0.06	3662.81±6.2	1734.41±28.98	723.33±5.78	7.40±0.10	42.67±2.08	67.03±0.7	4.90±0.10	0.12±0.	0.00±0	0.01±0.	0.06±0	0.01±0
S5	8.31±0.02	29±0.1	3026.67±5.77	10±0	1553.33±11.55	11.67±0.58	2.13±0.06	0.63±0.06	5515.82±4.7	1043.84±28.92	583.33±5.78	1.73±0.21	247.33±3.79	14.50±0.7	9.10±0.10	0.12±0	0.01±0.0	0.02±0.	0.102±0	0.01±0 0
S6	8.22±0.01	28.93±0.06	1736.33±0.58	5±0	873.00±4.36	7.33±0.58	1.40±0.00	0.53±0.06	2409.67±3.5	639.67±29.40	376.67±11.5	0.43±0.15	138.00±4.58	4.43±0.61	5.17±1.26	0.13±0.	0.01±0.	0.05±0.	0.12±0.	0.02±0 0
S7	8.14±0.02	28.83±0.16	2590±0	5±0	1327.67±0.58	6.33±0.58	2.03±0.06	0.37±0.06	5434.43±20	723.40±28.30	456.67±5.77	6.27±0.21	225.00±5.00	80.63±1.3	7.00±1.00	0.13±0	0.01±0	0.03±0	0.14±0	0.02±0
S8	8.57±0.02	28.73±0.15	2880±0	5±0	1486.33±0.58	3.67±1.16	1.53±0.06	0.13±0.06	6549.38±43.	538.95±28.75	466.67±577	10.57±0.0	169.33±2.52	71.63±1.3	3.67±1.16	0.12±0	0.01±0	0.01±0	0.09±0	0.02±0
S9	8.15±0.02	28.83±0.12	2920±0	10±0	1614.67±3.51	2.33±0.56	0.63±0.06	0.13±0.06	5153.33±16	942.83±29.00	463.33±5.8	1.83±0.06	245.00±5.00	18.27±0.6	7.90±0.95	0.14±0	0.01±0	0.01±0	0.13±0.	0.02±0

Appendix III: Physiochemical Data for Site M during Dry Season

	pH	TEMP ^0C	EC µƧ/cm	COLHAZEN	TDS mg/dm^3	TURNTU	DO mg/dm^3	BOD mg/dm^3	Cl mg/dm^3	TH mg/dm^3	ALK mg/dm^3	PO_4^{3} mg/dm^3	SO_4^{2-} mg/dm^3	NO_3^{-} mg/dm^3	COD mg/dm^3	Pb mg/dm^3	Cd mg/dm^3	Cu mg/dm^3	Cr mg/dm^3	Ni mg/dm^3
M1	8.44±0.0	24.45±0.05	3186.67±5.7	10±0	1462.67±0.58	31.33±1.16	0.47±0.15	0.13±0.06	24073.05±21	1592.22±11.07	870.00±10.0	3.37±0.15	356.67±11.0	46.20±2.8	35.67±5.77	0.03±0	0.01±0	0.08±0.0	0.05±0.0	0.04±0.
M2	8.28±0.11	24.2±0.15	816.±3.6	10±0	3186.67±11.55	22.67±0.58	0.60±0.10	0.13±0.06	26567.44±0.5	2562.50±15.19	953.33±11.6	6.30±0.10	139.33±5.51	36.63±0.3	22.00±1.00	0.04±0	0.01±0	0.07±0	0±00	0.04±0.0
M3	8.15±0.04	24.13±0.15	2853.67±3.7	5±0	1283.33±5.78	1.33±0.58	0.30±0.00	0.13±0.06	16042.42±1.7	2228.85±11.55	313.33±11.5	1.77±0.15	216.33±9.45	37.77±1.9	23.67±2.89	0.02±0	0.01±0	0.04±0	0.01±0	0.04±0
M4	8.11±0.04	24.24±0.2	2786.00±3.61	5±0	1237.33±4.62	12.67±0.58	0.43±0.06	0.33±0.06	18045.47±0.00	2114.67±5.69	463.33±5.77	2.97±0.12	319.67±8.62	45.20±1.1	23.00±1.73	0.05±0	0.01±0	0.05±0	0.05±0	0.04±0
M5	8.28±0.02	24.13±0.15	3363.67±3.06	10±0	1342.67±2.08	8.00±1.0	0.73±0.12	0.13±0.06	18045.47±0	2232.46±10.08	416.67±5.77	3.57±0.21	146.00±2.65	39.03±0.2	27.67±1.16	0.03±0	0.01±0	0.08±0	0±0	0.02±0
M6	8.15±0.03	24.3±0.06	2577.33±2.08	5±0	1468.67±0.58	4.33±0.58	0.40±0.00	0.13±0.06	17042.94±0.	1266.03±11.55	753.33±11.5	0.73±0.15	254.33±5.69	37.77±0.7	24.00±2.00	0.01±0	0.01±0	0.08±0	0.00±0	0.03±0
M7	8.16±0.02	24.45±0.06	3826.00±4.36	5±0	1628.00±1.00	18.33±1.16	0.53±0.06	0.23±0.06	20649.67±49	2148.18±25.31	463.33±5.77	1.80±0.10	139.33±5.51	46.03±3.6	23.00±2.00	0.03±0	0.02±0	0.05±0	0.01±0	0.03±0
M8	8.28±0.03	24.23±0.12	1418.00±1..00	5±0	1626.00±1.00	53.67±0.58	0.67±0.06	0.13±0.06	17529.47±25	2898.91±0.00	536.67±5.77	0.70±0.17	77.33±5.03	45.33±0.6	33.67±0.58	0.02±0	0.01±0	0.05±0	0.2±0	0.02±0
M9	8.28±0.02	24.07±0.06	1420.67±1.53	5±0	663.33±1.53	53.67±0.58	0.63±0.06	0.63±0.06	17533.47±1	1555.86±9.83	403.33±5.77	2.67±0.25	92.33±4.93	45.73±0.4	12.67±1.16	0.01±.0	0.01±0	0.04±0	0.03±0	0.04±0

Appendix IV: Physiochemical Data for Site M during Wet Season

	pH	TEMP ^0C	EC µƧ/cm	COLHAZEN	TDS mg/dm^3	TURNTU	DO mg/dm^3	BOD mg/dm^3	Cl mg/dm^3	TH mg/dm^3	ALK mg/dm^3	PO_4^{3} mg/dm^3	SO_4^{2-} mg/dm^3	NO_3^{-} mg/dm^3	COD mg/dm^3	Pb mg/dm^3	Cd mg/dm^3	Cu mg/dm^3	Cr mg/dm^3	Ni mg/dm^3
M1	8.03±0.01	28.7±0.27	2866.67±5.78	10±0	1507.33±2.08	10.00±1	0.47±0.15	0.27±0.06	4015.00±7.0	1228.85±29.01	693.33±5.77	2.93±0.25	220.00±5.00	38.10±0.8	6.83±0.12	0.131±0.0	0.018±0	0±0	0.116±0.0	0.04±0
M2	8.05±0.01	28.80±0.1	3964.33±5.13	10±0	2070.00±2.00	8.33±0.58	0.60±0.10	0.93±0.06	5522.96±10	1548.95±87.0	813.33±5.77	5.53±0.35	107.00±4.36	17.99±0.7	9.90±0.10	0.152±0	0.012±0	0±0	0.06±0	0.04±0.0
M3	7.49±0.01	28.73±0.15	2546.67±1.55	5±0	1266.67±5.78	2.00±1.00	0.30±0.00	0.13±0.06	3508.95±3.0	1650.04±28.79	446.67±5.77	5.43±0.32	183.67±3.51	55.33±1.5	4.00±1.00	0.141±0	0.009±0	0±0	0.08±0	0.04±0
M4	7.48±0.01	28.93±0.06	2576.67±5.77	10±0	1323.33±2.08	2.33±0.58	0.43±0.06	0.53±0.06	3913.79±4.9	1951.55±31.36	436.67±5.77	2.50±0.26	241.00±5.29	42.33±1.8	3.50±0.50	0.136±0	0.009±0	0±0	0.06±0	0.04±0
M5	7.93±0.01	28.80±0.1	3720.0±0	5±0	444.33±1.16	4.00±1.00	0.73±0.12	0.63±0.06	5062.82±8.6	2036.88±28.96	546.67±11.5	4.63±0.31	93.33±4.51	50.80±1.3	2.03±0.06	0.154±0	0.01±0	0±0	0.00±0	0.04±0
M6	7.64±0.01	28.67±0.12	933.33±0.58	5±0	2633.33±5.78	2.67±0.58	0.40±0.00	0.43±0.06	1798.67±5.7	740.89±28.87	153.33±5.77	1.57±0.15	236.00±5.00	41.60±1.4	4.90±0.10	0.164±0	0.01±0	0±0	0.09±0	0.04±0
M7	7.85±0.01	28.90±0.1	2646.67±5.77	5±0	1551.67±1.16	2.33±1.16	0.53±0.58	0.13±0.06	3955.03±4.3	1245.77±29.17	680.00±10.0	5.60±0.30	76.67±3.22	52.87±1.8	7.27±1.14	0.16±0.0	0.009±0	0±0	0.06±0	0.03±0
M8	8.04±0.01	28.12±0.12	1551.67±1.16	5±0	3563.33±5.78	1.33±0.78	0.67±0.06	0.13±0.06	3308.01±1.5	822.06±24.25	403.33±5.77	0.47±0.12	52.00±2.00	35.20±1.3	4.82±0.24	0.15±0.01	0.01±0	0±0	0.07±0	0.03±0
M9	7.97±0.01	28.08±0.1	3563.33±5.77	5±0	1507.33±2.08	3.00±1.00	0.63±0.06	0.13±0.06	2153.07±4.8	1831.71±23.06	583.33±5.77	2.67±0.25	96.00±6.25	43.20±2.3	3.13±1.37	0.15±0.0	0.009±0	0±0	0.11±0	0.03±0

Appendix V: Physiochemical Data for Site K during Dry Season

	pH	TEMP ^0C	EC µƧ/cm	COLHAZEN	TDS mg/dm^3	TURNTU	DO mg/dm^3	BOD mg/dm^3	Cl mg/dm^3	TH mg/dm^3	ALK mg/dm^3	PO_4^{3} mg/dm^3	SO_4^{2-} mg/dm^3	NO_3^{-} mg/dm^3	COD mg/dm^3	Pb mg/dm^3	Cd mg/dm^3	Cu mg/dm^3	Cr mg/dm^3	Ni mg/dm^3
K1	8.12±0.02	24.12±0.15	2160.00±0.00	5±0	1016.33±5.86	31.33±0.58	0.83±0.06	0.43±0.06	2017.33±28	2114.68±11.24	536.67±5.7	8.47±0.04	242.67±7.0	26.10±0.3	13.00±.1.00	0.033±0.0	0.01±0.00	0.07±0.0	0.08±0.0	0.04±0.00
K2	8.04±0.01	24.09±0.17	1441.33±0.58	5±0	657.67±1.16	14.67±0.58	0.50±0.00	0.13±0.06	8024.14±6.9	1319.12±10.43	563.33±5.7	4.93±0.15	177.33±1	18.57±0.6	17.67±1.53	0.013±0	0.09±0	0.06±0.0	0.1±0. 0	0.00±0
K3	7.92±0.01	24.07±0.02	2390±0.00	5±0	1138.00±1.00	`1.67±0.58	0.37±0.06	0.23±0.06	9035.40±21	1996.36±6.17	556.67±5.7	1.73±0.15	145.00±1	17.43±0.7	22.67±1.53	0.02±0.0	0.01±0	0.06±0.0	0.06±0.0	0.025±0
K4	8.15±0.01	24.12±0.02	1490.33±0.58	5±0	685.00±2.00	13±0	0.43±0.06	0.13±0.06	10033.58±14	276.36±11.18	653.33±11	6.430±45	94.33±4.0	27.60±8.1	8.00±1.00	0.014±0	0.01±0	0.06±0.0	0.02±0.00	0.014±0
K5	8.27±0.03	24.1±0.06	1336.67±0.58	10±0	617.33±0.58	71.33±0.58	0.80±0.10	0.13±0.06	10033.58±14	1329.60±11.09	710.00±10	5.77±0.15	73.33±5.1	34.63±2.7	13.00±1.00	0.004±0	0.01±0	0.06±0.0	0.08±0.0	0.018±0
K6	8.04±0.02	24.01±0.1	2607.33±1.16	5±0	1175.00±1.0	41.33±0.58	0.53±0.06	0.13±0.06	15526.39±22	1754.11±11.55	316.67±5.7	7.50±0.36	136.33±3	10.83±0.4	17.67±0.58	0.033±0	0.09±0	0.07±0	0.02±0.0	0.038±0
K7	8.46±0.02	24.03±0.06	2666.67±0.58	10±0	1195.67±2.51	85.67±0.58	0.43±0.1	0.13±0.06	12037.17±11	1862.02±11.49	426.67±15.0	8.17±0.15	142.67±3	18.80±0.8	22.67±1.53	0.089±0	0.09±0	0.10±0.0	0.11±0.0	0.038±0
K8	8.39±0.01	24.12±0.06	2018±1.73	10±0	874.00±1.00	93.33±0.58	0.70±0.0	0.13±0.06	15148.18±17	1356.88±11.66	360.00±10	7.67±0.32	186.00±3	14.97±1.6	13.00±1.00	0.012±0	0.01±0	0.06±0.	0.01±0.0	0.017±0
K9	8.41±0	24.12±0.06	1489.67±0.58	5±0	631.67±0.58	41.67±0.58	0.70±0.2	0.13±0.06	8528.49±6.0	1026.91±11.66	423.33±5.7	3.60±0.20	158.00±3	16.67±1.3	34.33±2.50	0.019±0	0.011±0	0.04±0.0	0.09±0.0	0.033±0

Appendix VI: Physiochemical Data for Site S during Wet Season

	pH	TEMP ^0C	EC µƧ/cm	COLHAZEN	TDS mg/dm^3	TURNTU	DO mg/dm^3	BOD mg/dm^3	Cl mg/dm^3	TH mg/dm^3	ALK mg/dm^3	PO_4^{3} mg/dm^3	SO_4^{2-} mg/dm^3	NO_3^{-} mg/dm^3	COD mg/dm^3	Pb mg/dm^3	Cd mg/dm^3	Cu mg/dm^3	Cr mg/dm^3	Ni mg/dm^3
K1	7.40±0.01	28.14±0.1	2080±0.00	5±0	1054.33±4.62	2.33±0.58	1.00±0.00	0.33±0.06	4367.06±8	1481.11±28.59	543.33±5.7	3.37±0.1	208.00±8.8	14.57±1	2.77±0.40	0.11±0	0.02±0	0.±0	0.08±0.0	0.02±0
K2	8.04±0.12	28.14±0.2	2170±0.00	5±0	1087.33±3.33	2.00±1.00	1.17±0.06	0.10±0.00	3246.58±1	925.74±28.87	543.33±5.7	7.83±0.0	156.33±12	13.50±0	4.33±0.58	0.12±0	0.01±0.0	0.47±0	0.12±0	0.03±0
K3	8.03±0.01	28.12±0.15	2386.6±5.77	5±0	1225.67±3.06	3.67±1.53	1.87±0.06	0.10±0.00	4364.03±7	1347.03±28.72	390.00±10.	2.83±0.1	124.00±12	33.03±17	5.47±0.45	0.12±0.0007	0.01±0	0.0±0	0.07±0	0.02±0.0
K4	8.00±0.01	28.19±0.15	1692.33±1.53	5±0	856.67±0.58	3.00±0.00	0.83±0.06	0.43±0.06	3060.16±6	1430.85±29.00	360.00±10	4.33±0.2	76.67±3.22	12.63±1	8.67±0.58	0.13±0	0.01±0	0.0±0	0.07±0.0	0.034±
K5	7.64±0.04	28.28±0.15	1613.33±1.53	5±0	812.00±1.7	3.33±0.58	1.70±0.17	0.20±0.00	2907.22±4	925.90±28.73	286.67±15	2.50±0.2	47.33±4.04	11.63±1	11.33±0.58	0.14±0	0.01±0	0.0±0	0.14±0.0	0.03±0
K6	7.45±0.02	28.11±0.23	2503.33±5.77	5±0	1197.33±0.58	10.67±1.53	1.13±0.06	0.20±0.00	3105.88±3.	2155.11±28.69	186.67±5.7	6.63±0.2	94.33±3.22	3.20±0.2	2.33±0.58	0.13±0	0.01±0	0.0±0	0.15±0.0	0.03±0.0
K7	7.91±0.01	28.05±0.15	2486.67±5.77	5±0	1274.67±2.89	2.67±0.58	1.10±0.00	0.10±0.00	4017.01±6	1531.81±28.91	203.33±5.7	6.53±0.3	150.33±6.5	3.33±0.2	5.67±0.58	0.13±0	0.01±0.0	0±0	0.16±0.0	0.03±0.0
K8	7.81±0.02	28.12±0.17	2133.33±5.77	5±0	1068.67±1.53	3.33±0.56	0.90±0.00	0.90±0.00	3112.25±7	1245.93±28.87	330.00±5.7	2.70±0.1	72.67±2.52	4.63±0.2	11.00±1.73	0.143±0.0	0.09±0.0	0±0	0.099±0.0	0.03±0.0
K9	8.31±0.01	28.4±0.12	1497±1 .00	5±0	750.00±0.00	8.00±1.00	1.90±0.87	0.90±0.00	2215.49±1	1158.17±5.93	503.33±5.7	1.83±0.1	68.33±9.07	5.47±0.3	4.00±1.00	0.14±0.0	0.01±0.0	0±0	0.12±0.0	0.033±0.0