PHYSICO-CHEMICAL ANALYSIS OF SOME SELECTED WATER SOURCES AROUND THE WASTE TREATMENT PLANT OF AHMADU BELLO UNIVERSITY TEACHING HOSPITAL ZARIA, NIGERIA

BY

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M.Sc/SCIE/5667/2010-2011

A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIAIN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARDOFA MASTER OF SCIENCE IN ANALYTICAL CHEMISTRY

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
AHMADU BELLO UNIVERSITY, ZARIA
NIGERIA

AUGUST, 2014

DECLARATION

I declare that the work in this thesis entitled **"PHYSICO-CHEMICAL ANALYSIS OF SOME SELECTED WATER SOURCES AROUND THE WASTE TREATMENT PLANT OF AHMADU BELLO UNIVERSITY TEACHING HOSPITAL ZARIA, NIGERIA"**, has been carried out by me in the Department of Chemistry, Faculty of Science, Ahmadu Bello University, Zaria, Nigeria. The information derived from the literature has been duly acknowledged in the text and list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other institution.

ADEGBE ELIJAH ABAKPA _____ _____

CERTIFICATION

This thesis entitled "PHYSICO-CHEMICAL ANALYSIS OF SOME SELECTED WATER SOURCES AROUND THE WASTE TREATMENT PLANT OF AHMADU BELLO UNIVERSITY TEACHING HOSPITAL ZARIA, NIGERIA" by ADEGBE ELIJAH ABAKPA meets the regulations governing the award of degree of Master of Science in Analytical Chemistry of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This thesis is dedicated to the Lord Jesus Christ the source of all wisdom.

ACKNOWLEDGEMENT

My appreciation goes to God for giving me the privilege of undergoing this programme. To Him be all glory, honour and praise.

The priceless guide provided by the members of my supervisory committee comprising Professor C.E. Gimba and Professor (Mrs) E.B. Agbaji is duly acknowledged. I remain eternally grateful to you all for your guidance.

My thanks go to the lecturers and staff of the Department of Chemistrywho in one way or the other supported me during the course of this work.

I sincerely appreciate Prof A.S.Agbaji of Kaduna State University for his support and fatherly role in my life and all through the course of this work.

My sincere thanks go to Mr P.C. Alika, Mr G. Ameh and Mr. Y. Yakubuall of the Water Resources and Environmental Engineering for their assistance in the laboratory analysis.

I will also like to thank Nnenna Ukwuije, Judith Okodua, Yusuf Usman and Dr. Moses Yilleng all of the National Research Institute for Chemical Technology Zaria for their assistance in the laboratory analysis.

I will not fail to appreciate my colleague and friends – Comfort Oke, Josiah Haruna, Yabo Stephen, Mallam Ibrahim, Akinola Solomon, Arome Emmanuel, Akawu Irimiya, Justin Thomas, Ugochi Egbeagu, Matthew Habila, Naana Yeboaand Edoma Akpakpan for their support all through the research period.

I also thank members of my family – my parents and siblings for making my stay in school financially and morally worthwhile.

To members of the Postgraduate Fellowship and the Chapel of Redemption and all those who in one way or the other had played a role during the course my study, I say a big thank you.

ABSTRACT

The assessment of the surface andground water sources within the vicinity of Ahmadu Bello University Teaching Hospital liquid waste treatment plant was conducted. A total of sixty-six (66) water samples were collected from eight sites (S1, S2, S3, S4, U1, U2, U3 and U4) from the study area. These samples were examined for heavy metal contamination using Atomic Absorption Spectrophotometer (AAS), organic contamination using Gas Chromatography Mass Spectrometer (GCMS), bacteriological contamination and some physicochemical parameters. The levels of seven (7)heavy metals (chromium, lead, cadmium, iron, manganese, nickel and cobalt) in the water samples were analysed. Sites S1-S4 had the level of Cr ranging from 0.16-0.58 mg/l,Pb from 1.10-2.60 mg/l, Cd from 0.04-0.10 mg/l, Fe from 4.10-9.70 mg/l,Mn from 0.04-0.64 mg/l, Ni from 0.05-0.63 mg/l,Co from 0.50-0.90 mg/l and sites U1-U4 had the level of Cr ranging from 0.20-0.80 mg/l, Pb from 1.71-3.20 mg/l, Cd from 0.02-0.10 mg/l, Fe from 2.19-11.40 mg/l, Mn from 0.05-0.50 mg/l, Ni from 0.04-0.14 mg/l and Co from 0.22-0.40 mg/l. The levels were found to be above the World Health Organization (WHO) permissible limit for most of the sites. Xylene, ethylbenzene, butylatedhydroxytoluene and toluene were identified in the samples using GCMS. The bacteriological analysis showed that the total coliform count ranged from 2×10^4 (Cfu/ml) to 31×10^4 (Cfu/ml) which is an indication of faecal contamination. The dissolved oxygen(1.03-1.50 mg/l) of the samples was lower than the World Health Organization (WHO) standard for aquatic life, indicating poor support for aquatic life. The turbidity (3.1-9.70 NTU) exceeded the permissible levels set by World Health Organization (WHO). All other physicochemical parameters(pH ranged from 6.30 – 7.70, electrical conductivity 43 – 820µS/cm, sulphate 1.20 – 6.90 mg/l, nitrate 3.00 – 18.90 mg/l, phosphate 0.10 – 3.30 mg/l, biochemical oxygen demand 0.13 – 0.80 mg/l, chemical oxygen demand 1.10 – 6.70 mg/l and temperature 24 - 27ºC) were below the WHO permissible limits. This study shows that hospital effluent and other human activities have a negating influence on water quality. Strict compliance to government policies on waste disposal and management is therefore recommended for Ahmadu Bello University Teaching Hospital liquid wastes.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

AAS	-	Atomic Absorption Spectrophotometer
ANOVA	-	Analysis of Variance
BOD	-	Biochemical Oxygen Demand
DO	-	Dissolved Oxygen
COD	-	Chemical Oxygen Demand
EC	-	Electrical Conductivity
FTU	-	Formazin Turbidity Unit
GCMS	-	Gas Chromatography Mass Spectrometer
min	-	Minute
SPSS	-	Statistical Package for the Social Science
WHO	-	World Health Organization

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of Study

Water is vital to life. Adequate supply of fresh and clean drinking water is a basic need for all human beings on the earth. The main sources of fresh water are ground and surface water. These sources of freshwater resources are threatened by overexploitation, poor management and pollution.

Waste water from hospitals is usually referred to as hospital waste and is defined as a special category of waste which comprise of all waste, biological or non-biological that is discarded from hospital/health care centres and not intended for further use (Oyeleke*et al*., 2008). Hospital effluents consist of both organic and inorganic substances including pathogenic microorganisms, toxic chemicals, radioactive elements and heavy metals. Their presence in such effluent, especially in high quantity could sometimes pose grave problem for the populace (Omoruyi*et al*., 2011).The amount of waste water discharged from hospitals varies from hospital to hospital. Tsakona*et al* (2006) reported an estimate on per capital production of waste water in hospitals to be 1000litres/person/day.

About 85% of hospital waste is said to be non-hazardous, 10% infective/hazardous and 5% not infective in the United States of America (Oyeleke and Istifanus, 2009). Meanwhile about 15% of hospital waste is regarded infective in most developed countries. In India, it was reported that the value could increase from 15% to 35% depending on the total amount of hospital waste generated. In Pakistan, about 20% of hospital waste could be found potentially infective or hazardous (Agarwal, 1998; Ekhaise and Omavwoya, 2008). Hazardous medical wastes consist primarily of chemicals and discarded cytotoxic drugs which find their way into the environment due to improper

usage and indiscriminate disposal. Their presence in the environment have been reported to pose serious environmental health risk due to their toxic, genotoxic and/or carcinogenic effects (Akter*et al*.,1998;Shaner, 1997; Omoruyi*et al.*, 2011) and could have potential negative effects on the biological balance of the natural environment.The direct exposure of workers and members of the public, soil and water bodies to hospital wastewater increases the hazard that it pose to the environment.

The major health risk posed by hospital wastewater to the inhabitants of the terrestrial and aquatic ecosystem includes contamination of surface water and ground water,accumulation of toxic non-biodegradable hospital waste products andaccumulation of heavy metals and unprotected landfills as well as inefficient sorting of waste materials.The toxic substances discharged into water bodies are likely toaccumulatethrough the food chain (Odiete, 1999).

Different countries are however putting down systems for complete management of hospital effluents. All healthcare units in Greece for example are obliged to design and implement a comprehensive management strategy so as to safeguard the public and the environment (Tsakona*et al*., 2006). Some countries, especially developing countries are however yet to put down legislature as to reducing the environmental effects of hospital effluents. In Nigeria, many healthcare centres/hospitals lack effluent treatment plants, the untreated waste are either disposed on the ground or discharged into nearby water bodies which may pose serious health problems to host communities (Odiete, 1999; Chukwuraand Okpokwasil,1997). Such hospital waste can have effects even at low concentrations. Aquatic organisms for instance respond negatively to concentrations of formaldehyde which is a frequently found contaminant in hospital effluents (Murphy*et al*.,1989). It was reported that formaldehyde in the range of 10-100mg/l was toxic to the microorganisms used in wastewater treatment system (Lu and Hegeann, 1998). In

addition, the presence of organochlorine compounds in high concentrations in hospital effluents has also been reported as toxic to aquatic life (Gartiser*et al*., 1996).

Fish are often at the top of the aquatic food chain and may concentrate large amount of heavy metals from polluted water that build up by ingestion, ion-exchange of dissolved metals across lipophilic membranes and absorption on tissue and membrane surfaces (Mendil*et al.*, 2005; Agbozu*et al.*, 2007). Some metals areessential to human health. Heavy metalpollution is a serious and widespread environmentalproblem due to thetoxicity of the metals (Kalay and Canli, 2000).

Pollutants are responsible for many illnesses such as cancer, neurological conditions, chronic bronchitis and asthma (Kump, 1996). Pollutants therefore have been classified into two groups; primary pollutants which are those which exert harmful effects in the form in which they enter the environment and secondary pollutants which are synthesized as a result of chemical processes from less harmful precursors in the environment. Most pollutants enter the environment as emissions or discharges (to water bodies) either from discrete point such as factories, hospitals or diffuse sources such as runoff from agricultural lands. The effect of any pollutant discharged into the environment depends on its toxicity, persistence, dispersion properties, chemical reactions including the decomposition of the compound, tendency to be bioaccumulated in food chains and ease of control. Every type ofpollution has a pathway which involves the pollutant, the source, the medium of transport (air, water and land) and the target (ecosystem) (Holdgate, 1979).

1.2 Justification

Effluents discharged from liquid waste treatment plants in hospitals contain both organic and inorganic substances including heavy metals and pathogenic microorganisms.

Thepresence of these substances in effluents especially in high quantity could pose grave danger to the receiving environment (Omoruyi*et al*., 2011).

This study was undertaken to ascertain the concentrations of organic pollutants, heavy metals, faecal coliform bacteria and the physicochemical parameters of the surface water sources andground water sources in the vicinity of Ahmadu Bello University Teaching Hospital liquid waste treatment plant. This is being embarked on to investigate the quality of the water bodies in the vicinity of the liquid waste treatment plant so as to establish a correlation between the effluent, human activities and the perceived pollution of the water bodies.

1.3 Aim and Objectives of the Study

The aim of the study is to validate the correlation between poorly treated hospital effluents, human activities and the pollution of surface water and ground water sources around the immediate environment of Ahmadu Bello University Teaching Hospital liquid waste treatment plant.

To achieve this aim, the following objectives have been outlined:

i. To determine some physicochemical parameters which are temperature, conductivity, pH, sulphate, nitrate, phosphate, turbidity, dissolved oxygen (DO), biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of the surface and ground water samples collected from the study area;
ii. To identify and determine the amount of heavy metals (Pb, Cd, Fe, Ni, Mn, Co and Cr) present in the surface water andground watersourceswithin the study area and to comparethe levels of the metals with the World Health Organization (WHO) permissible levels;

iii. To identify organic pollutants (methylene chloride, xylene, butylatedhydoxyltoluene, ethyl benzene,toluene and formaldehyde) present in the surface and ground water sources and

iv. To determine the colony forming unit in the surface water and ground water sources in the study area.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 WATER

Water is one of the most indispensable natural resources and is called the elixir of life. Water constitutes about 70% of the body weight of almost all living organisms. Life is not possible on this planet without water. It acts as a medium for both chemical and biochemical reactions (Rajankar*et al.,* 2009). Several living organisms live in water. The basic functions of a society require water; for cleaning, for public consumption, for industrial processes and cooling of gas turbines for electricity generation.

Ground water constitutes 20% of water present as freshwater. The value of groundwater lies not only in its wide spread occurrence and availability but also in its consistent good quality, which makes it an ideal supply for drinking water. However, ground water resources are under serious threat due to growing interest in mechanized agricultural practices, increasing population density and rapid urbanization as well as effluent discharge from industries and healthcare centres. Ground water provisions are sometimes unsustainable because of poor water productivity of its sources, drying of hand dug wells after prolonged drought and sometimes due to poor water quality.

Contaminated water resources have grave implications on human health and the environment (Peterson *et al.,* 1971). The importance of water quality on human health has recently attracted a great deal of interest. In developing world, 80% of all diseases are directly related to poor drinking water and unsanitary conditions (Olajire and Imeokparia, 2001; Chung *et al.,* 2007). Ground water quality can be affected by varied pollutants ranging from organic and inorganic chemicals and microbes. This makes users of groundwater susceptible to diseases of different kinds. High concentration of NO_3-N has

been reported to be common in ground water sources in the world (Wassenaar, 1995; Goulding, 2000). The natural water analyses for physical, chemical, biological properties including trace elements contents are very important for public health studies. These studies are also a main part of pollution studies in the environment (Bakraji and Karajo, 1999; Zereen*et al.*, 2000).

2.2 Water Pollution

Water pollution is any chemical, physical or biological change in the quality of water bodies such as lakes, rivers, oceans, and groundwater due to the direct or indirect activities of humans. Water pollution (surface and ground) may be considered as a naturally induced change in water quality or conditions induced directly or indirectly by man's numerous activities which renders it unsuitable for food, human health, industry, agriculture or leisure pursuit (Dix, 1981; Cifuentes and Rodriguez, 2005).

With the increasing population, industrialization and urbanization, water pollution by agriculture, municipal and industrial sources has become a major concern for the welfare of mankind. The menace of water borne diseases and epidemics still threatens the well-being of population, particularly in developing countries. Thus, the quality as well as the quantity of clean water supply is of vital importance for the welfare of mankind (Owuna, 2012).

2.2.1 Groundwater and surface water pollution

Groundwater contamination is generally irreversible i.e. it is difficult to restore the original water quality of the aquifer once contaminated. Excessive mineralization of groundwater degrades water quality producing an unpleasant taste, odour and excessive hardness. Although the soil mantle through which water passes acts as an adsorbent retaining a large part of colloidal and soluble ions with its cation exchange capacity,

groundwater is not completely free from the menace of chronic pollution (Bhatia, 2009). The extent of groundwater pollution depends on the depth of water table, rainfall pattern, soil properties and the distance of the groundwater source from the perceived contamination source.

Groundwater and surface water pollutants can be classified broadly into the following:

i. Organic Pollutants

The organic pollutants may be further categorized as follows:

a. **Oxygen - demanding wastes**: These include domestic and animal sewage, bio-degradable organic compounds and industrial wastes from food processing plants, meat-packing plants, slaughter-houses, paper and pulp mills, tanneries, as well as agricultural runoff. All these wastes undergo degradation and decomposition by bacterial activity in presence of dissolved oxygen (DO). This results in rapid depletion of DO from the water, which is harmful to aquatic organisms. The optimum DO in natural waters is 4-6 mg/L and this is essential for supporting aquatic life. Any decrease in this DO value is an index of pollution by the above mentioned oxygen-demanding wastes(Owuna, 2012).

b. **Disease-causing wastes:** These include pathogenic microorganisms which may enter the water along with sewage and other wastes and may cause tremendous damage to public health. These microbes, comprising mainly of viruses and bacteria, can cause dangerous water-borne diseases such as cholera, typhoid, dysentery, polio and infectious hepatitis in humans.

c. **Synthetic Organic compounds:** These are the man-made materials such as pesticides, detergents, food additives, pharmaceuticals, insecticides, paints, synthetic fibres, elastomers, solvents, plasticizers, plastics and others industrial

chemicals. These chemicals may enter the hydrosphere either by spillage during transport and use or by intentional or accidental release of wastes from their manufacturing establishments. Most of these chemicals are potentially toxic to plants, animals and humans. Some bio-refractory organics such as aromatic chlorinated hydrocarbons may cause offensive odour and taste in water, even when present in trace amounts and it makes the water unacceptable from aesthetic point of view. Non-degradable chemicals such as alkyl benzene sulphonate from synthetic detergents often lead to persistent foams.

d. **Sewage and agricultural runoff:** The direct dumping of sewage or leakage from broken sewers into lakes, ponds or streams pollutes water. Leachate from agricultural lands containing nitrates, phosphates and potash, moves downward with percolating water and join the aquifers below posing danger to the groundwater. The leachate also supplies plant nutrients, which may stimulate the growth of algae and other aquatic weeds in the receiving water body.

e. **Oil:** Oil pollution may take place because of oil spills from cargo oil tankers on the seas, losses during off-shore exploration and production of oil, accidental fires in ship and oil tankers and leakage from oil pipe lines crossing waterways and reservoirs. Oil pollution reduces the DO in water(Owuna, 2012).

ii. **Inorganic Pollutants**

Inorganic pollutants comprise of mineral acids, inorganic salts, finely divided metals or metal compounds, trace elements, cyanides, sulphates, nitrates, organometallic compounds and complexes of metals with organics present in natural water. The metal-organic interactions involve natural organic species such as fulvic acids and synthetic organic species such as EDTA. Various metals and metallic compounds released from

anthropogenic activities add up to their natural background levels in water. Some of these trace metals play essential roles in biological processes, but at higher concentrations they may be toxic to biota. The most toxic among the trace elements are the heavy metals such as Hg, Cd and Pb and metalloids, such as As, Sb and Se. Water pollution by heavy metals occurs mostly due to street dust, domestic sewage and industrial effluent. Polyphosphates from detergents serve as algal nutrients and thus are significant as water pollutants (Owuna, 2012).

iii. Suspended Solids and Sediments

Sediments results mostly from soil erosion, agricultural development, strip mining and construction activities. Suspended solids in water mainly comprise of silt, sand and minerals eroded from the land. Soil may get removed from agricultural land to areas where it is not at all required, such as water reservoirs. This reduces the water storage capacity of the reservoirs and eventually dries them up. Suspended solids present in water bodies may also block the sunlight required for photosynthesis. The organic matter content in sediments is generally higher than that in soils. Sediments and suspended particles exchange cations with the surrounding aquatic medium and act as repositories for trace metals such as Cu, Co, Ni, Mn, Cr and Mo(Owuna, 2012).

iv.Temperature

Water bodies undergo temperature variations along with normal climatic fluctuations.

These variations occur seasonally and, in some water bodies, over periods of 24 hours.

The temperature of surface waters is influenced by latitude, altitude, season, time of day, air circulation, cloud cover and the flow and depth of the water body. In turn, temperature affects physical, chemical and biological processes in water bodies and, as a result, the concentration of many variables. As water temperature increases, the rate of

chemical reactions generally increases together with the evaporation and volatilisation of substances from the water. Increased temperature also decreases the solubility of gases such as O_2, CO_2, N_2, and CH_4 in water.

The metabolic rate of aquatic organisms is also related to temperature. In warm waters respiration rates increase leading to increased oxygen consumption and increased decomposition of organic matter. Growth rates also increase (this is most noticeable for bacteria and phytoplankton which double their populations in very short time periods) leading to increased water turbidity, macrophyte growth and algal blooms, when nutrient conditions are suitable(Chapman and Kimstach, 1996).

Surface waters are usually within the temperature range 0°C to 30°C. These temperatures fluctuate seasonally with minima occurring during rainy or wet periods, and maxima in the summer or dry seasons, particularly in shallow waters. Abnormally high temperatures in surface water can arise from thermal discharges, usually from power plants, metal foundries and sewage treatment plants. Groundwater usually maintains a fairly constant temperature which, for superficial aquifers, is normally close to the mean annual air temperature. However, deep aquifers have higher temperatures due to the earth's thermal gradient.

Heat is produced as waste in all processes in which it is converted into mechanical work. Thus, considerable thermal pollution results from thermal power plants, particularly the nuclear-power-based electricity generating plants. In such industries, where water is used as a coolant, the waste hot water is returned to the original water bodies. Hence, the temperature of the water body increases. This rise in temperature decreases the DO content of waters (Dara, 2009).

2.3 Hospital Waste

Hospital waste refers to waste generated, discarded and not intended for further use in the hospital (Heen, 1999). Hospital waste is made up of both liquid and dissolved substances generated within the hospital environment.It is classified as follows:

2.3.1 General waste: This consists largely of non-hazardous particles such as kitchen waste, paper and plastic.

2.3.2 Infectious waste: This include waste which contains pathogens (bacteria, viruses, parasites, or fungi) in sufficient concentration or quantity to cause disease in susceptible hosts, e.g cultures and stocks of infectious agents from laboratory work, waste from surgery and autopsies on patients with infectious diseases (e.g. tissues, and materials or equipment that have been in contact with blood or other body fluids) waste from infected patients in isolation wards (e.g. excreta, dressings from infected or surgical wounds, clothes heavily soiled with human blood or other body fluids), waste that has been in contact with infected patients undergoing haemodialysis (e.g. dialysis equipment such as tubing and filters, disposable towels, gowns, aprons, gloves, and laboratory coats), infected animals from laboratories and any other instruments or materials that have been in contact with infected persons or animal

2.3.3 Pathologicalwaste: Pathological waste consists of tissues, organs, body parts, human foetuses and animal carcasses, blood, and body fluids. Thisincludes recognizable human or animal body parts and can also be called anatomical waste.

2.3.4 Sharps: Sharps are items that could cause cuts or puncture wounds, including needles, hypodermic needles, scalpel and other blades, knives, infusion sets, saws, broken glass, and nails. Whether or not they are infected, such items are usually considered as highly hazardous hospital waste.

2.3.5 Pharmaceutical waste: Pharmaceutical waste includes expired, unused, spilt, and contaminated pharmaceutical products, drugs, vaccines, and sera that are no longer required and need to be disposed of appropriately. It also includes discarded items used in the handling of pharmaceuticals, such as bottles or boxes with residues, gloves, masks, connecting tubing, and drug vials.

2.3.6 Genotoxicwaste: Genotoxic waste is highly hazardous and may have mutagenic, teratogenic, or carcinogenic properties. It raises serious safety problems, both inside hospitals and after disposal. Genotoxic waste may include certain cytostatic drugs, vomit, urine, or faeces from patients treated with cytostatic drugs, chemicals, and radioactive material.

2.3.7 Chemical waste: Chemical waste consists of discarded solid, liquid, and gaseous chemicals, for example from diagnostic and experimental work and from cleaning, housekeeping, and disinfecting procedures.

2.3.8 Radioactive waste: Radioactive wastes are wastes that contain radioactive material. Radioactive wastes are usually by-products of nuclear power generation and other applications of nuclear fission or nuclear technology, such as research and medicine. Radioactive waste is hazardous to most forms of life and the environment, and is regulated.It includes solid, liquid and gaseous wastes contaminated with radionuclides from *in-vitro* analysis of body tissues and fluid. Radionuclides continuously undergo spontaneous disintegration (known as "radioactive decay") in which energy is liberated, generally resulting in the formation of new nuclides. The process is accompanied by the emission of one or more types of radiation, such as α- and β -particles and γ-rays. These cause ionization of intracellular material; radioactive substances are therefore genotoxic.

2.4 Water Quality Assessment

Water quality is the physical, chemical and biological characteristics of water. It is the measure of the condition of water relative to the requirements of one or more biotic species and to any human need or purpose. Water quality is determined by the concentration of physical, chemical and biological contaminants. If fresh and pure, water has no taste, odour, colour or turbidity. But water is never 100% pure as it carries traces of other substances, which bestow physical, chemical and biological characteristics on it (Nsi, 2007).

2.4.1 Physico-chemical characteristics

The most common physical contaminants of water are suspended sediments. These are properties which are often apparent to the eyes such as colour, odour, taste and turbidity. Chemicals are the major sources of water contamination. Some chemicals are introduced during movement through geological materials or when disposed directly into water bodies.

2.4.1.1*Nitratesand nitrites*

Nitrate ion (NO_3^-) is the common form of combined nitrogen found in natural waters. It may be biochemically reduced to nitrite(NO_2^-) by denitrification processes, usually under anaerobic conditions. Nitrite ion is rapidly oxidised to nitrate. Natural sources of nitrate in surface waters include igneous rocks, land drainage and plant and animal debris. Nitrate is an essential nutrient for aquatic plants and seasonal fluctuations can be caused by plant growth and decay. Natural concentrations, which seldom exceed 0.1 mg/l, may be enhanced by municipal and industrial waste-waters, including leachates from waste disposal sites and sanitary landfills. In rural and suburban areas, the use of

inorganic nitrate fertilizers can be a significant source. Nitrate (NO_3^-) is found naturally in the environment and is an important plant nutrient (Chapman and Kimstach, 1996).

Concentrationsof nitrate in surface water can change rapidly owing to surface runoff of fertilizer, uptake by phytoplankton and denitrification by bacteria, but groundwater concentrations generally show relatively slow changes. Some ground water may also have nitrate contamination as a consequence of leaching from natural vegetation.

In general, the most important source of human exposure to nitrate and nitrite is through vegetables (nitrite and nitrate) and through meat in the diet (nitrite is used as a preservative in many cured meats). In some circumstances, however, drinking-water can make a significant contribution to nitrate and, occasionally, nitrite intake. In the case of bottle-fed infants, drinking water can be a major external source of exposure to nitrate and nitrite (WHO, 2011).

2.4.1.2 *Sulphates*

Sulphates occur naturally in numerous minerals and are used principally in the chemical industry. They are discharged into water in industrial wastes and through atmospheric deposition; however, the highest levels usually occur in groundwater and are from natural sources. In general, the average daily intake of sulphate from drinking-water, air and food is approximately 500 mg, food being the major source. However, in areas with drinking-water supplies containing high levels of sulphate, drinking-water may constitute the principal source of intake.

2.4.1.3 *Taste and Odour*

Water odour is usually the result of labile, volatile organic compounds and may be produced by phytoplankton and aquatic plants or decaying organic matter. Industrial and human wastes can also create odours, either directly or as a result of the biological

activity they initiate. Organic compounds, inorganic chemicals, oil and gas can all impart odour to water although an odour does not automatically indicate the presence of harmful substances. Usually, the presence of an odour suggests higher than normal biological activity and is a simple test for the suitability of drinking water, since the human sense of smell is far more sensitive to low concentrations of substances than human taste. Warm temperatures increase the rate and production of odour-causing metabolic and decay products. Different levels of pH may also affect the rate of chemical reactions leading to the production of odour.

The odour in potable water may be defined as the sensation due to the presence of substances having an appreciable vapour pressure and stimulates the human sensory organs in the nasal and sinus cavities (Nsi, 2007). Odour in water may have natural origins, such as earth, rotten fish, hydrogen sulphide, clayey or artificial flavours; of chlorine, camphor, pharmaceuticals, etc. (Nikoladze and Mints, 1989). Water may have a salty, bitter, sweet or acidic taste. This may be due to dissolved inorganic and organic substances in nature, e.g. Phenols and chlorophenols. Both taste and odour are subjective properties, which are difficult to measure (Nsi, 2007; Tebbutt, 1983).

2.4.1.4 *Colour*

The colour and the turbidity of water determine the depth to whichlight is transmitted. This, in turn, controls the amount of primary productivity that ispossible by controlling the rate of photosynthesis of the algae present. The visible colourof water is the result of the different wavelengths not absorbed by the water itself or theresult of dissolved and particulate substances present. It is possible to measure bothtrue and apparent colour in water. Natural minerals such as ferric hydroxide and organicsubstances such as humic acids give true colour to water. True colour can only bemeasured in a sample after filtration or centrifugation. Apparent colour is caused bycoloured particulates and the

refraction and reflection of light on suspended particulates.Polluted water may, therefore, have quite a strong apparent colour.Different species of phyto- and zooplankton can also give water an apparent colour. Adark or blue-green colour can be caused by blue-green algae, a yellow-brown colour bydiatoms or dinoflagellates and reds and purples by the presence of zooplankton such as*Daphnia* sp. or copepods.Colour in water may be due to the presence of colouring matter such as humic and tanning substances leached into water and suspended in it. Colour of water aesthetically affects its potability and may not be necessarily harmful (Nikoladze and Mints, 1989; Nsi, 2007)

2.4.1.5 *Turbidity*

Turbidity may be defined as the measure of clarity of water. Turbidity is caused by the presence of suspended insoluble materials such as clay and silt particles, discharges of sewage or industrial wastes, or the presence of large numbers of micro-organisms mainly occurring in surface water, which makes them objectionable for almost all uses (Tebbutt, 1983).

Excessive turbidity protects microorganisms from effects of disinfectants, stimulates the growth of bacteria in water. There is no constant linear relationship between turbidity and concentration of suspended matters, since the former is affected by shapes, sizes and refractive indices of the particulates (Vesilind and Pierce, 1983; Nsi, 2007).

2.4.1.6 *Total Dissolved Solids*

This is given as a number expressing the concentration of filterable solids present in water. Water with high concentration of dissolved solid present has poor taste and may induce unfavorable psychological reaction in the consumer. For this reason, a limit of 500mg/l of dissolved solids is desirable for potable waters. This includes settleableand non-settleable solids (Nsi, 2007).

2.4.1.7 *Electrical Conductivity*

Conductivity is a quantitative measure of the ability of water to conduct electric current. This ability depends largely on the quantity of dissolved salts present in any water sample. In dilute form conductivity is approximately proportional to dissolved solids (DS) content. Monitoring of conductivity can thus usefully indicate variations in salt concentration in water, but for water quality control, various limitations abound. For instance organic compounds do not ionize greatly in aqueous solutions; therefore organic pollutant would not be monitored by conductivity measurement (Nsi, 2007).

2.4.1.8 *pH*

Most natured water usually has pH between 6.0 and 9.0. pH can be said to have indirect effect on health since it affects the removal of viruses, bacteria and other harmful organisms. For potable water, the recommended value of the pH is 6.5 to 8.5.

2.4.1.9 *Alkalinity*

The capacity of water to accept H^+ ions (protons) is called alkalinity. Alkalinity is important in water treatment and in the chemistry and biology of natural water. Frequently, the alkalinity of water must be known to calculate the quantities of the chemicals added in treating water. Highly alkaline water often has a high pH and generally contains elevated levels of dissolved solids. These characteristics may be detrimental for water to be used in boilers, food processing and municipal water systems. Alkalinity serves as a pH buffer and reservoir for inorganic carbon, thus helping to determine the ability of water to support algae growth and other aquatic life, so it can be used as a measure of water quality. Generally, the basic species responsible for alkalinity in water are bicarbonate ion, carbonation, and hydroxide ion.

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$

$$OH^- + H^+ \rightarrow H_2O$$

2.4.1.10 ***Hardness of water***

Hardness may be defined as the concentration of all multivalent metallic cations in solution. The principal ions causing hardness in natural water are calcium and magnesium. Others, which may be present though in much smaller quantities, are iron, manganese, strontium and aluminum. Ground water is much prone to hardness due to high concentration of calcium and magnesium ions (Nsi, 2007). Hardness of natural water is not harmful to the health of man; on the contrary, calcium promotes removal of cadmium; an element that can adversely affect the cardiovascular system (Nikoladze and Mints, 1989). An elevated hardness, however, makes water unsuitable for domestic and industrial use. Hardness can be determined by methods such as EDTA and tritrimetric method (Vesilind and Pierce, 1983).

2.4.2: Metallicpollutants

The ability of a water body to support aquatic life, as well as its suitability for other uses, depends on many trace elements. Some metals, such as Mn, Zn and Cu, when present in trace concentrations are important for the physiological functions of living tissue and regulate many biochemical processes. The same metals, however, discharged into natural waters at increased concentrations in sewage, hospital effluents, industrial effluents or from mining operations can have severe toxicological effect on humans and the aquatic ecosystem. Water pollution by heavy metals as a result of human activities is causing serious ecological problems in many parts of the world. This situation is aggravated by the lack of natural elimination processes for metals. As a result, metals shift from one compartment within the aquatic environment to another, including the biota, often with

detrimental effects. Where sufficient accumulation of the metals in biota occurs through food chain transfer, there is also an increasing toxicological risk for humans. As a result of adsorption and accumulation, the concentration of metals in bottom sediments is much higher than in the water above and this sometimes causes secondary pollution problems.

The toxicity of metals in water depends on the degree of oxidation of a given metal ion together with the forms in which it occurs. As a rule, the ionic form of a metal is the most toxic form. However, the toxicity is reduced if the ions are bound into complexes with natural organic matter such as fulvic and humic acids. Under certain conditions, metallo-organic, low-molecular compounds formed in natural waters exhibit toxicities greater than the uncombined forms. An example is the highly toxic alkyl derivatives of mercury (e.g. methyl mercury) formed from elemental mercury by aquatic micro-organisms.

Metals in natural waters can exist in truly dissolved, colloidal and suspended forms. The proportion of these forms varies for different metals and for different water bodies. Consequently, the toxicity and sedimentation potential of metals change, depending on their forms. The assessment of metal pollution is an important aspect of most water quality assessment programmes (Chapman and Kimstach, 1996).

2.4.2.1 *Cadmium*

Cadmium is produced as a by-product of zinc. Since it occurs naturally within the ore, the most significant use is in nickel/cadmium batteries. Other uses of cadmium are as pigments, stabilizers for polyvinyl chloride, in alloys and electronic compounds. Cadmium is not essential in nutrition but has high toxicity. Its toxicity effects are felt in the form of high blood pressure, kidney damage and red blood cells loss. The limit per litre is 0.05mg (WHO, 2011).

2.4.2.2 *Chromium*

Chromium is widely distributed in the Earth's crust. It can exist in valences of +2 to +6.This is present in aquatic system as CrO^{2-}_4. It is essential in nutrition. It is necessary for the proper utilization of sugars and other carbohydrates by optimizing the production and effects of insulin. It is widely distributed in the body. It has medium level toxicity. Chromium deficiency causes impaired insulin function, hence increased insulin secretion and the risk of diabetes mellitus (Csuros and Crusos, 2002). Its major source is electroplating. The maximum tolerable level is 0.05mg/l (WHO, 2011).

2.4.2.3 *Lead*

Lead is used principally in the production of lead-acid batteries, solder and alloys. The organolead compounds tetraethyl and tetra methyl lead have also been used extensively as antiknock and lubricating agents in petrol, although their use for these purposes in many countries is being phased out. Owing to the decreasing use of lead containing additives in petrol and of lead-containing solder in the food processing industry, concentrations in air and food are declining, and intake from drinking-water constitutes a greater proportion of total intake. Lead is rarely present in tap water as a result of its dissolution from natural sources; rather, its presence is primarily from household plumbing systems containing lead in pipes, solder, fittings or the service connections to homes. The amount of lead dissolved from the plumbing system depends on several factors, including pH, temperature, water hardness, and standing time of the water, with soft, acidic water being the most plumbosolvent.

Lead is not essential in nutrition and has high toxicity level.Placental transfer of lead occurs in humans as early as the 12th week of gestation and continues throughout development. Young children absorb 4–5 times as much lead as adults, and the biological half-life may be considerably longer in children than in adults. Lead is a general toxicant that accumulates in the skeleton. Infants, children up to 6 years of age and pregnant

women are most susceptible to its adverse health effects. Inhibition of the activity of d-aminolaevulinicdehydratase (porphobilinogen synthase; one of the major enzymes involved in the biosynthesis of haem) in children has been observed at blood lead levels as low as 5mg/dl, although adverse effects are not associated with its inhibition at this level. Lead also interferes with calcium metabolism, both directly and by interfering with vitamin D metabolism. These effects have been observed in children at blood lead levels ranging from 12 to 120mg/dl, with no evidence of a threshold. Lead is toxic both to central and peripheral nervous systems, inducing subencephalopathic neurological and behavioural effects. There is electrophysiological evidence of effects on the nervous system in children with blood lead levels well below 30mg/dl. It has a maximum tolerable level of 0.01mg/l in surface and underground water (WHO, 2011).

2.4.2.4 *Manganese*

Manganese is one of the most abundant metals in the Earth's crust, usually occurring with iron. It is used principally in the manufacture of iron and steel alloys, as an oxidant for cleaning, bleaching and disinfection as potassium permanganate and as an ingredient in various products. Manganese greensands are used in some locations for potable water treatment. Manganese is an essential element for humans and other animals and occurs naturally in many food sources. The most important oxidative states for the environment and biology are Mn^{2+}, Mn^{4+} and Mn^{7+}. Manganese is naturally occurring in many surface water and groundwater sources, particularly in anaerobic or low oxidation conditions, and this is the most important source of drinking-water.

The greatest exposure to manganese is usually from food. Manganese is an essential element for humans and other animals. Adverse effects can result from both deficiency and overexposure. Manganese is known to cause neurological effects following inhalation exposure, particularly in occupational settings, and there have been

epidemiological studies that report adverse neurological effects following extended exposure to very high levels in drinking-water. However, there are a number of significant potential confounding factors in these studies, and a number of other studies have failed to observe adverse effects following exposure through drinking-water. Maximum tolerable limit is 0.05mg/l. However, this limit is not determined by its toxicity, but because they stain clothing and ceramic plumbing fixtures (Nsi, 2007)

2.4.2.5 *Iron*

Iron is one of the most abundant metals in the Earth's crust. It is found in natural fresh waters at levels ranging from 0.5 to 50 mg/litre. Iron may also be present in drinking-water as a result of the use of iron coagulants or the corrosion of steel and cast iron pipes during water distribution. Iron is an essential element in human nutrition. Estimates of the minimum daily requirement for iron depend on age, sex, physiological status and iron bioavailability and range from about 10 to 50mg/day (WHO, 2011).

2.4.2.6 *Nickel*

Nickel is used mainly in the production of stainless steel and nickel alloys. Food is the dominant source of nickel exposure in the non-smoking, non-occupationally exposed population; water is generally a minor contributor to the total daily oral intake.

However, where there is heavy pollution, there are areas in which nickel that naturally occurs in groundwater is mobilized or where there is use of certain types of kettles, of non-resistant material in wells or of water that has come into contact with nickel- or chromium-plated taps, the nickel contribution from water may be significant.

Nickel and its compounds have little known toxicity. Chronic exposure to nickel causes cancer in the respiratory tract and the lungs (Csuros and Csuros, 2002).

2.4.2.7 *Cobalt*

Cobalt is a transition metal that exists in oxidation states +2 and +3. Cobalt is widely distributed in the environment, accounting for 0.001% of the earth's crust. It forms bivalent and trivalent compounds, those of biological interest being bivalent.Small amounts of cobalt are naturally found in most rocks, soil, water, plants, and animals, typically in small amounts. Cobalt is also found in meteorites. Elemental cobalt is a hard, silvery grey metal. However, cobalt is usually found in the environment combined with other elements such as oxygen, sulphur, and arsenic. Small amounts of these chemical compounds can be found in rocks, soil, plants, and animals. Cobalt is even found in water in dissolved or ionic form, typically in small amounts. (Ions are atoms, collections of atoms, or molecules containing a positive or negative electric charge.) A biochemically important cobalt compound is vitamin B_{12} or cyanocobalamin. Vitamin B_{12} is essential for good health in animals and humans. Cobalt (0.16–1.0 mg cobalt/kg of body weight) has also been used as a treatment for anaemia (less than normal number of red blood cells), including in pregnant women, because it causes red blood cells to be produced. Cobalt also increases red blood cell production in healthy people, but only at very high exposure levels. Cobalt is also essential for the health of various animals, such as cattle and sheep.

Cobalt metal is usually mixed with other metals to form alloys, which are harder or more resistant to wear and corrosion. These alloys are used in a number of military and industrial applications such as aircraft engines, magnets, and grinding and cutting tools. They are also used in artificial hip and knee joints. Cobalt compounds are used as colorants in glass, ceramics, and paints, as catalysts, and as paint driers. Cobalt colorants have a characteristic blue colour; however, not all cobalt compounds are blue. Cobalt compounds are also used as trace element additives in agriculture and medicine.Cobalt

may enter the environment from both natural sources and human activities. Cobalt occurs naturally in soil, rock, air, water, plants, and animals. It may enter air and water, and settle on land from windblown dust, seawater spray, volcanic eruptions, and forest fires and may additionally get into surface water from runoff and leaching when rainwater washes through soil and rock containing cobalt. Soils near ore deposits, phosphate rocks, or ore smelting facilities, and soils contaminated by airport traffic, highway traffic, or other industrial pollution may contain high concentrations of cobalt. Small amounts of cobalt may be released into the atmosphere from coal-fired power plants and incinerators, vehicular exhaust, industrial activities relating to the mining and processing of cobalt-containing ores, and the production and use of cobalt alloys and chemicals. ^{58}Co and ^{60}Co may be released to the environment as a result of nuclear accidents, radioactive waste dumping in the sea or from radioactive waste landfills, and nuclear power plant operations.Cobalt cannot be destroyed in the environment. It can only change its form or become attached or separated from particles. Cobalt released from power plants and other combustion processes is usually attached to very small particles. Cobalt contained in windborne soil is generally found in larger particles than those released from power plants. These large particles settle to the ground or are washed out of the air by rain. Cobalt that is attached to very small particles may stay in the air for many days. Cobalt released into water may stick to particles in the water column or to the sediment at the bottom of the body of water into which it was released, or remain in the water column in ionic form. The specific fate of cobalt will depend on many factors such as the chemistry of the water and sediment at a site as well as the cobalt concentration and water flow. Cobalt deposited on soil is often strongly attached to soil particles and therefore would not travel very far into the ground. However, the form of the cobalt and the nature of the soil at a particular site will affect how far cobalt will penetrate into the soil. Both in soil

and sediment, the amount of cobalt that is mobile will increase under more acidic conditions. Ultimately, most cobalt ends up in the soil or sediment.

Exposure of humans and animals to levels of cobalt normally found in the environment is not harmful. When too much cobalt is taken into the human body, however, harmful health effects can occur. Workers who breathed air containing 0.038 mg cobalt/m^3 (about 100,000 times the concentration normally found in ambient air) for 6 hours had trouble breathing. Serious effects on the lungs, including asthma, pneumonia, and wheezing, have been found in people exposed to 0.005 mg cobalt/m^3 while working with hard metal, a cobalt-tungsten carbide alloy. People exposed to 0.007 mg cobalt/m^3 at work have also developed allergies to cobalt that resulted in asthma and skin rashes. The general public, however, is not likely to be exposed to the same type or amount of cobalt dust that caused these effects in workers (ATSDR, 2004)

2.4.3:Organic Contaminants

The primary sources of ethylbenzene in the environment are the petroleum industry and the use of petroleum products. Because of its physicochemical properties, more than 96% of ethylbenzene in the environment can be expected to be present in air. Values of up to 26μg/m^3 in air have been reported. Ethyl benzene is found in trace amounts in surface water, groundwater, drinking-water and food.The health based guideline value for ethylbenzene is 0.3 mg/l (300 μg/l). Concentrations in drinking-water are generally below 1 μg/l; levels up to 300 μg/l have been reported in groundwater contaminated by point emissions. Ethylbenzene is readily absorbed by the oral, inhalation or dermal route. In humans, storage in fat has been reported. Ethylbenzene is almost completely converted to soluble metabolites, which are excreted rapidly in urine. The acute oral toxicity is low. No definite conclusions can be drawn from limited teratogenicity data. No data on

reproduction, long-term toxicity or carcinogenicity are available. Ethylbenzene has shown no evidence of genotoxicity in in- vitro or in- vivo systems (WHO, 2011).

Toluene (in the form of benzene–toluene–ethyl benzene–xylene mixtures) is used in the blending of petrol. It is also used as a solvent and as a raw material in chemical production. The main exposure is via air. Exposure is increased by smoking and in traffic. The health based guideline value for toluene in surface and underground water is 0.7 mg/l. Concentrations of a few micrograms per litre have been found in surface water, groundwater and drinking-water but point emissions can lead to higher concentrations in groundwater (up to 1 mg/l); it may also penetrate plastic pipes from contaminated soil. Toluene is absorbed completely from the gastrointestinal tract and rapidly distributed in the body, with a preference for adipose tissue. Toluene is rapidly metabolized and, following conjugation, excreted predominantly in urine. With occupational exposure to toluene by inhalation, impairment of the central nervous system and irritation of mucous membranes are observed. The acute oral toxicity is low (WHO, 2011).

Xylenes (o and p-xylene) are used in blending petrol, as a solvent and as a chemical intermediate. They are released to the environment largely via air. Exposure to xylenes is mainly from air, and exposure is increased by smoking. Concentrations of up to 8 µg/l have been reported in surface water, groundwater and drinking-water; levels of a few milligrams per litre were found in groundwater polluted by point emissions; xylenes can also penetrate plastic pipe from contaminated soil. Xylenes are rapidly absorbed by inhalation. Data on oral exposure are lacking. They are rapidly distributed in the body, predominantly in adipose tissue. They are almost completely metabolized and excreted in urine. The acute oral toxicity of xylenes is low (WHO, 2011).

ButylatedHydroxyltoluene (BHT) or 2, 6 – bis (1, 1-Dimethyl) – 4 – phenol is an organic compound that is primarily used as an antioxidant food additive as well as an antioxidant additives in pharmaceuticals.

2.4.4: Biological contaminants

Biological contaminants are primarily from animal and human wastes. The presence of organic matter and bacteria are measured by Biochemical Oxygen Demand (BOD) and the coliform count. BOD is a measure of oxygen required to oxidize the organic matter present in a sample, through the action of microorganisms contained in a sample of wastewater. It is the most widely used parameter of organic pollution applied to wastewater as well as surface and groundwater (Bhatia, 2009). To evaluate BOD, the total volume of oxygen gas taken up by microorganisms in a given quantity of water in a period of 5 days at $20^{o}C$ is measured. Microorganisms use the oxygen to decompose complex organic molecules present in the water in their aerobic metabolic processes. The BOD test thus provides a measure of the total quantity of microorganism in the sample, and of the nutrient available to them. The determination of DO is the basis of BOD test, which is commonly used to evaluate the pollution strength of waste waters. BOD represents the quantity of oxygen required by bacteria and other microorganisms during the biochemical degradation and transformation of organic matter present in water under aerobic conditions.

The coliform count is used to determine the presence of harmful bacteria in the water. This is done by looking for the presence of a common bacterium E. coli, which is present in faeces. The idea is that if the water is contaminated with this common bacterium, there is a possibility of contamination by pathogenic or harmful bacteria as well.

Chemical oxygen demand is the amount of oxygen required for complete oxidation of carbon (IV) oxide and water of organic matter present in a sample of water, wastewater or effluents.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Description of Study Area

Zaria is located on latitude 11°30' and longitude 7°50' and is about 686m above sea level. It falls within the tropical savannah (AW) climate, according to Koppen's world climate classification. It lies in the natural vegetation of the Northern Guinea Savannah, some 80 km North of Kaduna town, along the major high way from Kaduna to Kano State.Zaria is blessed with abundant water resource both ground and surface and the distribution of this resource have very little variation in both time and space amongst the sub-settlements (Yusuf *et al*., 2007). There are two major river systems; the Kubanni and Saye, joined at a confluence to form river Galma. These rivers together with their tributaries (Kamacha and Shika) drain the land area of Zaria (Lukman*et al*., 2009).

This studywas carried out at Ahmadu Bello University Teaching Hospital located in Shika as shown in Fig. 3.1. The surrounding area of the University Teaching Hospital liquid waste treatment plant was studied as shown in Fig. 3.2. The treated wastewater from the plant is normally discharged into the surrounding area, this forms a small stream which is the surface water source used in the study. Four sampling points separated from one another by a distance of about 10 m were selected on the surface water.These were designated points S1, S2, S3 and S4 respectively.

The underground water around the treatment plant was also studied. Four hand dug wells were used as the underground water source. These are used by the local farmers for irrigation purposes and drinking. The wells were designated U1, U2, U3 and U4 respectively.

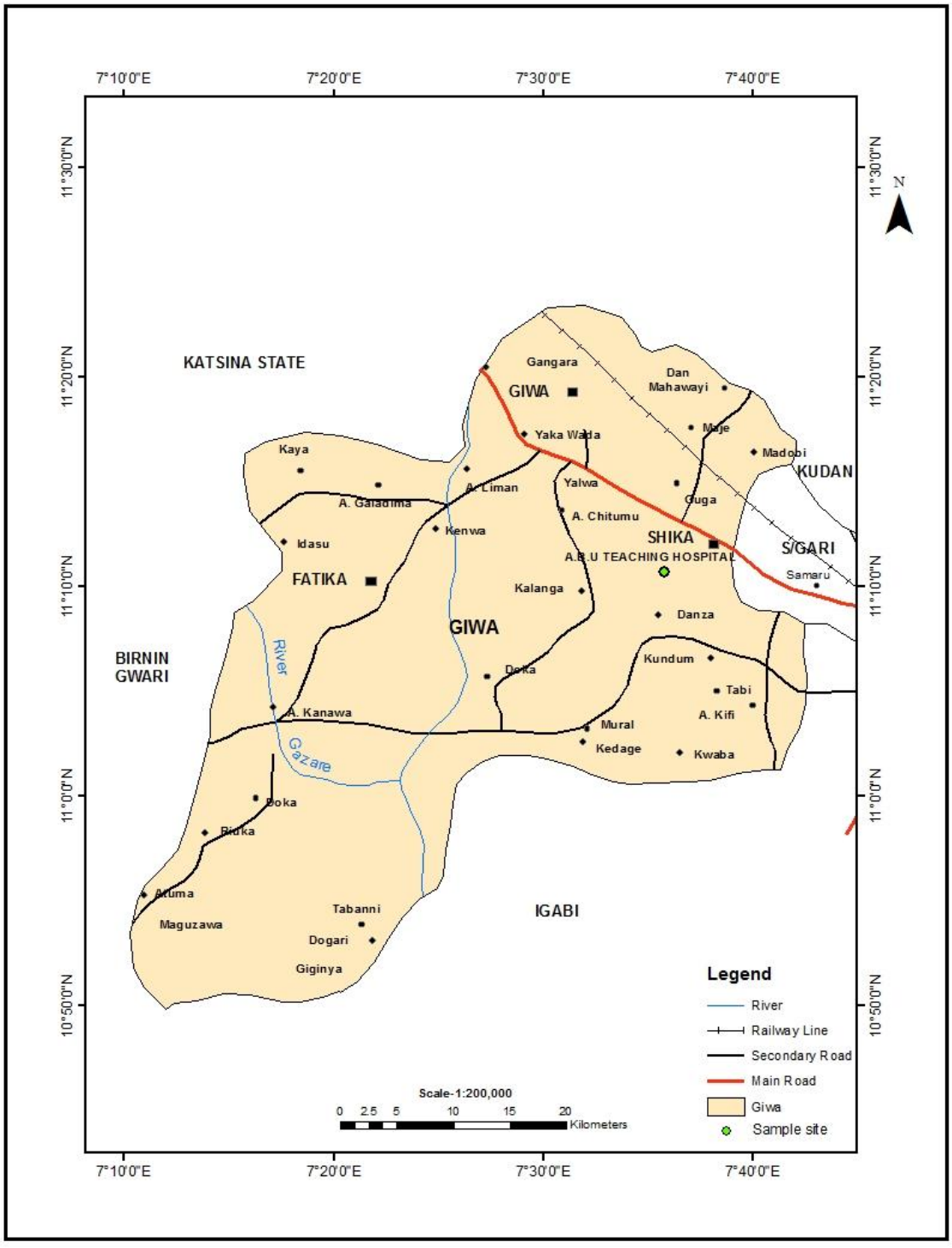

Figure 3.1:Map of Giwa Local Government Area of Kaduna State

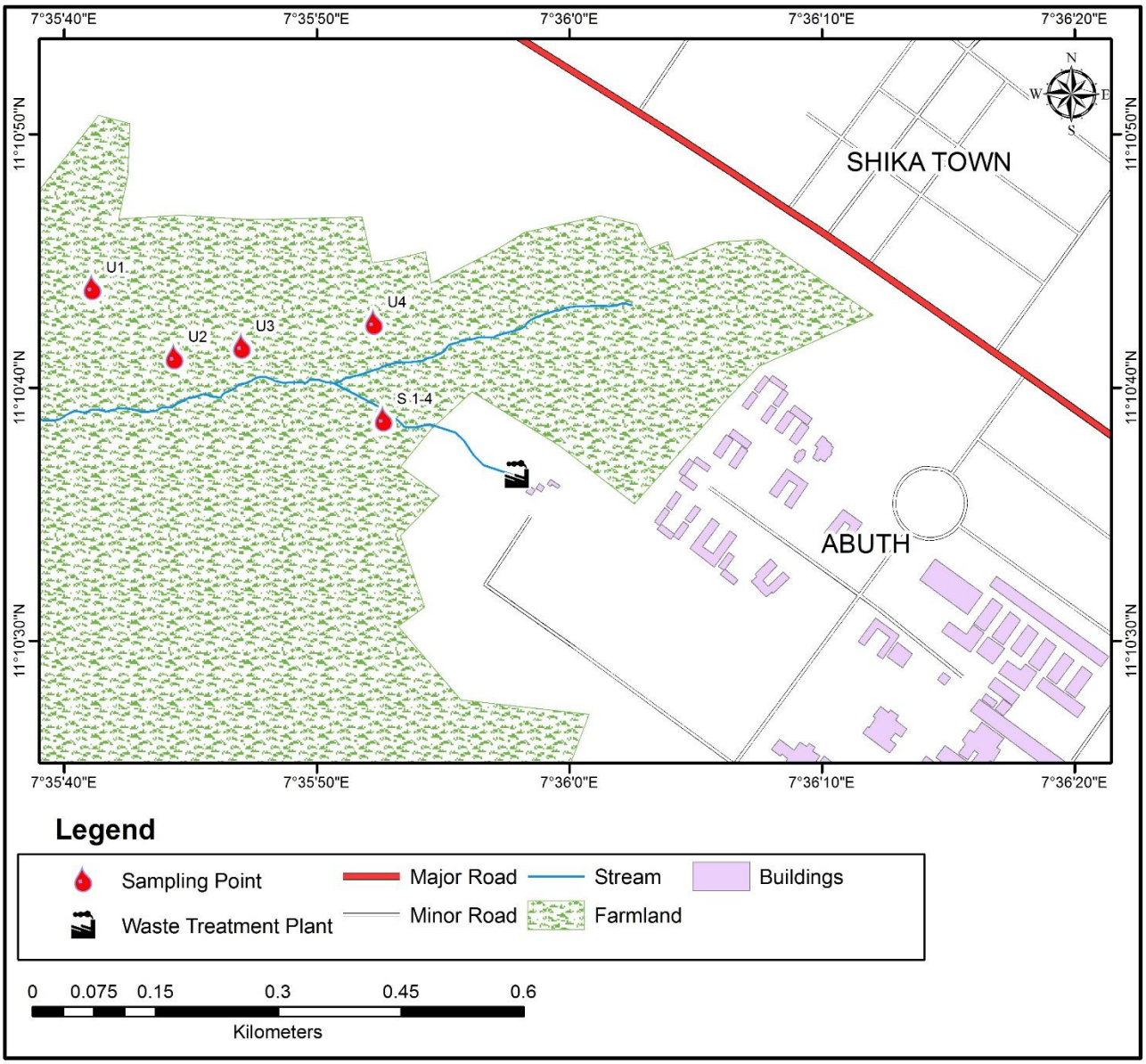

Figure 3.2:Map of the Study Area
NOTE: U – Ground water site (U1, U2, U3, and U4 are the various ground water sites).

S – Surface water site (S1, S2, S3 and S4 are the different points on the surface water).

3.2 Sample Collection

A total of 66 samples werecollected within a period of four months for analysis fromAugust to December 2012 from eight different sites in the study area. The treated water from the liquid waste treatment plant was discharged via a pipe into the environment.

3.2.1 Collection of Surface Water Sample.

The surface water samples were collected from four sampling points designated S1, S2, S3 and S4. The samples were collected after shaking the water body within aerated vessels with a water sampler before fetching 500cm^3 of surface water for analysis from each sampling point (Wyasu, 2011).

Surface water samples for bacteriological and physicochemical analyses were collected in clean sterile containers. Samples for dissolvedoxygen (DO), chemical oxygen demand (COD) and biochemical oxygen (BOD) were collected in 250cm^3bottles with stoppers. One millimetre each of Winkler's solutions A and B were added to the samples on site to fix the oxygen (Anonymous, 1989).The samples were collected and transported to the laboratory for analysis within twenty four hours of collection.Surface water samples for determination of organic pollutants were collected in clean containers within a depth of 500cm for analysis.

3.2.2 Collection of ground Water Samples.

The ground water samples were collected from four sampling points U1, U2, U3 and U4.The sampling points werehand dug wells sited in the small farming community within the study area. Ground water sample (500cm^3) was fetched from each of the sampling point and transported to the laboratory within two hours of collection.The ground water samples for bacteriological, physiochemical analysis and organic pollutants

determination were collected in clean sterile containers. Samples for dissolved oxygen (DO), chemical oxygen demand (COD) and biochemical oxygen demand(BOD) were collected in 250cm^{3}bottles sealed withstoppers. One millimetre each of Winkler's solutions A and B were added to the samples on site to fix the oxygen (Anonymous, 1989).

3.3 Sample Preparation

Samples were prepared using the standard methods stated below.

3.3.1 Wet digestion of surface water and ground water samples

The surface water and ground water samples for Atomic Absorption Spectroscopy (AAS) analysis were each collected within a depth of 500cm from the surface of the water. The water samples were filtered using Whatman 0.45µm filter paper into a clean plastic container and acidified with 3cm^3 of Concentrated HNO_3 per litre of water(Ramos *et al*., 1999) and frozen before analysis to prevent loss of metals by surface adsorption (Kahraman*et al*., 1976).

Furthermore,25 cm^3 of concentrated HNO_3 and 20cm^3 concentrated $HClO_4$ were added to 50cm^3 of each sample in a 250cm^3 beaker. Themixture was heated gently on a hot plate until it was clear and white fumes of $HClO_4$ appeared. This was cooled and 20cm^3 of distilled water added. This was then be filtered and made up to 50cm^3 in a volumetric flask (Greenberg *et al*., 1992).

3.3.2 Preparation ofsurface water samples andground water samples for GC-MS analysis using solvent extraction (Greenberg *et al*., 1992)

Liquid-liquid solvent extraction was used to extract the organic compounds present in the surface and underground water samples.A portion (10 cm^3) of surface water and underground water samples wereeach treated with 20cm^3 of chloroform first and 20cm^{3}of

diethyl ether in a separatory funnel to extract the organic compounds present in each by shaking the funnel vigorously until the aqueous and organic layer is clearly separated. The organic layer was carefully drained into clean glassware and subsequentlytaken for GCMS analysis.

3.4 Preparation of Standard Solution for AAS

Standard stock solution was prepared from metal compounds of high purity and appropriate volumes were diluted to obtain working standard solutions for plotting the calibration curves. The various preparations were as follows;

i. Lead stock solution

A portion (1.599g) of lead nitrate $Pb(NO_3)_2$ was dissolved in $20cm^3$ of 1% v/v HNO_3 and made up to $1000cm^3$ with distilled water to obtain concentration of 0.004M. Working solutions of 2.0, 4.0, 6.0, and 8.0mg/l were prepared by diluting 2.0, 4.0, 6.0 and $8.0cm^3$ of the stock solution respectively to $1000cm^3$ mark in a onelitre volumetric flask which was used to plot a standard calibration curve.

ii.Chromium Stock Solution

A portion (2.828g) of potassium heptaoxodichromate(VI) $K_2Cr_2O_7$ was dissolved in distilled deionised water and made up to $1000cm^3$to obtain a concentration of 0.01M. Working solutions of 1.0, 2.0, 3.0, 4.0 and 5.0mg/l were prepared by diluting 1.0, 2.0, 3.0, 4.0 and 5.0 $cm^3$of stock solution respectively to $1000cm^3$ mark in a onelitre volumetric flask.

iii. Cadmium Stock Solution

A portion (2.059g) of anhydrous cadmium sulphate $CdSO_4.8H_2O$ was dissolved in water and made up to $1000cm^3$to obtain a concentration of 0.006M. Working solutions of 0.25,

0.5, 1.0, and 2.0mg/l were prepared by diluting 0.25, 0.50, 1.0 and 2.0cm^3 of the stock respectively to a 1000cm^3 mark in a onelitre volumetric flask.

iv. Iron Stock Solution

A portion (1.404g) of ammonium iron (II) sulphate$Fe(NH_4)_2SO_4.6H_2O$ was dissolved in distilled water and made up to 1000$cm^3$to obtain a concentration of 0.004M. Working solutions of 1.0, 1.5, 2.0, 2.5 and 3.0mg/lwereprepared by diluting 5.0, 7.5, 10, 12.5, and 15cm^3 of stock respectively to 1000cm^3 in a volumetric flask.

v. Cobalt Stock Solution

A portion (0.4770g) of dry cobalt sulphate $CoSO_4$.$7H_2O$ was dissolved in distilled water and made up to 1000cm^3 to obtain a concentration of 0.001M. Working solutions 1, 2, 3,4 and 5mg/lwere prepared by diluting 10, 20, 30, 40 and 50cm^3respectively to 1000m^3 in a volumetric flask

vi. Nickel Stock Solution

A portion (4.648g) of nickel sulphate $NiSO_4.6H_2O$ was dissolved in distilled water and made up to 1000cm^3 to obtain a concentration of 0.02M. Working solutions of 0.5, 1.0, 2.0, and 4.0 mg/lwere prepared by diluting 0.5, 1.0, 2.0, and 4.0cm^3 of the stock to a 1000cm^3 mark in a volumetric flask.

vii. Manganese Stock Solution

A portion (4.144g) of potassium tetraoxomanganate (VII) $KMnO_4$ was dissolved in water and made up to 1000$cm^3$to obtain a concentration of 0.03M. Working solutions of 0.25, 0.50, 1.0 and 2.0cm^3 respectively to a 1000cm^3 mark in a volumetric flask.

3.5 Microbial Analysis(Nester *et al*, 2004)

Sterile distilled water (9ml each) was transferred into four test tubes using a pipette. A sterile 10ml pipette was used to transfer 1ml of the thoroughly mixed water sample to the first test tube and the pipette was discarded. A new 10ml pipette was used to mix the sample and the distilled water by drawing it in and out ten times. One millilitre of the resulting mixture was then transferred to the second tube. This method continued until the fourth test tube. A portion (1 ml) of the sample was discarded from the last test tube such that each all contained 9ml of the solution. A sterile 1ml pipette was used to transfer 0.1ml of the mixture from the fourth test tube onto the surface of Eosine methylene blue agar. The innoculum was spread evenly over the surface of the agar with a sterile glass rod. The plates were incubated at 37˚C for 24 hours and the various colonies present were counted and recorded.

3.6 Analysis of Physicochemical Parameters

All field meters and equipment were checked and calibrated according to the manufacturer's specifications. The pH meter was calibrated using HACH (1997) buffers of pH 4.0, 7.0 and 10.0 Dissolved oxygen (DO) meter was calibrated prior to measurement with the appropriate traceable calibration solution (5% HCl) in accordance with the manufacturer's instruction. The spectrophotometer (HANNA multi parameter HI83200) for anions determination was checked for malfunctioning by passing standard solutions of all the parameters to be measured; blank samples (deionised water) was passed between every three measurements of surface water and underground water samples to check for any eventual contamination or abnormal response of equipment.

The parameters analysed were pH, temperature, dissolved oxygen, nitrate, sulphate, phosphate, chemical oxygen demand, biochemical oxygen demand,electrical conductivity and turbidity.

Standard methods were followed in determining the above parameters (APHA, 1998)**3.6.1 Determination of Conductivity (AOAC, 1998)**

Conductivity of the surface water and the ground water samples were determined using the standard procedure approved by AOAC (1998). The conductivity meter (Hach model CO150) was used. The power key and the conductivity key of the conductivity meter were switched on, and the temperature of the meter adjusted; the instrument was calibrated with 0.001 MKCl to give a value of 14.7ms/m at 25^0C. The probe was dipped below the surface of both samples. Time was allowed forthe reading to be stabilised and the reading was recorded.

3.6.2 Determination of Nitrate, Phosphate and Sulphate (Greenberg *et al*., 1992)

The HANNA multi parameter logging spectrophotometer (HI83200) was used to digitally determine the nitrate, phosphate and sulphate in the surface water and underground water samples. The concentrations of nitrate, sulphate and phosphate were determined using standard procedures.

Nitrate as nitrogen was determined by the cadmium reduction metal method 8036. The cadmium metal in the added reagent reduced the entire nitrite in the samples to nitrate;Sulphatewas determined using Sulfa Ver methods 8051. Phosphate was determined using direct reading from HI 83200 HANNA multi parameter.

3.6.3 Determination of Temperature (APHA, 1998)

The temperature was measured using mercury- filled Celsius thermometer Hanna Digital Compo metre (HI991405, Hanna, UK). The thermometer was immersed in the sample long enough to permit accurate and stable reading and the result was recorded.

3.6.4 Determination of pH(APHA, 1998)

The pH was measured using a pH metre Hanna Digital Compo Metre (HI991405 Hannan, UK). The electrode was washed thoroughly first with distilled water and then with the sample. The pH metre was standardized using buffer solution. The pH of the samples was measured and the readings recorded.

3.6.5 Determination of dissolved oxygen (DO) (APHA, 1998)

The dissolved oxygen (DO) content of the surface water and underground water samples was measured using the Jenway Model 9070 waterproof meter according to the standard method described by APHA (1998).

3.6.6 Determination of biochemical oxygen demand (BOD) (Ademoroti, 1996)

The BOD determination of the surface water and underground water samples was carried out using standard methods described by Ademoroti (1996). Samples were incubated for five days at 20^{o}C in BOD bottles. The dissolved oxygen (DO) content of the samples was determined before and after the incubation. BOD was calculated after the incubation period.

BOD_5= Dissolved oxygen after incubation period (5 days) - Dissolved oxygen of the first day.

3.6.7 Determination of chemical oxygen demand (COD) (Ademoroti, 1996)

The COD of the surface water and the underground water samples was determined using the standard method described by Ademoroti (1996).

A portion (0.4ml) of H_2SO_4 was placed in a refluxing flask. About 20ml of the samples was diluted with 20ml of diluted water. A standard solution (10ml) of $K_2Cr_2O_7$ was then added to glass beads already heated to 600^oC for 1 hour. The flask was then attached to the reflux condenser and about 30ml of concentrated H_2SO_4 containing Ag_2SO_4 was added through theopen end of the condenser. The resulting solution was thoroughly mixed by switching.

The mixture was refluxed for 1hour, cooled and the condenser was washed with about 25 ml of distilled water. The mixture was diluted with 150ml of distilled water and cooled to room temperature. About 3 drops of (0.10-0.15ml) ferroin indicator was added.

The mixture wasthen titrated with 0.25M $Fe(NH_4)_2(SO_4)_2$ taking as the end point the sharp colour change from blue-green to reddish brown.In the same manner a blank containing 20ml distilled water was refluxed together with the reagent.

Calculation

$$\text{mg/l COD} = \frac{(a-b)xMx16000}{\text{ml of sample}}$$

Where

COD=Chemical oxygen demand

a =Vol of $Fe(NH_4)_2(SO_4)_2$ used as blank

b =Vol of $Fe(NH_4)_2(SO_4)_2$ used for sample.

M= molarity of $Fe(NH_4)_2 (SO_4)_2$

3.7 Statistical Analysis

Two types of statistical analyses were used:

a. Analysis of variance was used to conduct a test of significance at $p<0.05$, in order to assess the difference between the parameters at each sampling point.

b. Correlation matrix was obtained for all metals determined in each sampling point so as to establish the relationship between them.

CHAPTER FOUR

4.0 RESULTS

4.1 Physicochemical Parameters

The meanconcentrations of the physicochemical parameters of the surface water arepresented in Table 4.1. The pHvaried between 6.90 and 7.70 across the sites. Generally the pH of the samples tended to be slightly alkaline among the sites except for samples S2 where the pH was slightly acidic.Analysis of variance (ANOVA) showed that pH varied significantly(at $p<0.05$) across the sampling sites.Electrical conductivity varied between 74.00µS/cm (S2) and 820.00µS/cm (S3) as shown in Table 4.1.The dissolved oxygen(DO)values varied between 1.03mg/l(S1) and 1.40mg/l (S2).The DO values showed no significant difference across the sampling points. The biochemical oxygen demand (BOD) fluctuated between 0.20mg/l at S2 and 0.80mg/l at S3. There was no significant difference in the mean B.O.D values ofthe surface water samples. The chemical oxygen demand (COD) values for the surface water samples S1, S2, S3 and S4 were found to be 1.10mg/l, 3.10mg/l, 3.71mg/l and 1.72mg/l. The difference in the mean COD values of the surface water samples were not significant using analysis of variance.The turbidity of the samples varied between 3.10NTU (S1) and 9.70NTU (S3).The difference in the mean turbidity values was not significant at a confidence limit of$p<0.05$. The mean nitrate concentration was found to vary between3.00mg/l (S1) to 9.00mg/l (S2). The difference in the mean nitrate values was not significant. Sulphate was found to vary between 2.30mg/l and 6.50mg/l across the surface water sites. There was no significant difference in the mean of the sulphate concentration. The phosphate concentrations in the surface water sites were found to vary between 0.90mg/l and 3.30mg/l. The mean phosphate values were not significant.

Table 4.1: Physicochemical Parameters of Surface Water

PARAMETER	Site S1	Site S2	Site S3	Site S4
pH	7.25±0.01	6.90±0.01	7.70±0.01	7.35±0.02
E.C (µS/cm)	75.00±1.00	74.00±1.00	820.00±1.00	701.00±1.00
DO (mg/l)	1.03±0.10	1.40±0.10	1.10±0.10	1.10±0.01
BOD (mg/l)	0.23±0.10	0.20±0.10	0.80±0.10	0.40±0.12
COD (mg/l)	1.10±1.53	3.10±1.00	3.71±1.00	1.72±1.53
Turbidity (NTU)	3.10±0.12	3.90±0.02	9.70±0.01	7.00±0.01
Nitrate (mg/l)	3.00±0.20	9.10±0.02	3.50±0.10	5.90±0.10
Sulphate(mg/l)	3.90±0.10	6.50±0.10	2.30±0.20	2.50±0.20
Phosphate (mg/l)	1.00±0.10	0.90±0.10	3.30±0.10	3.10±0.10
Temperature (ºC)	24	22	24	26

Values are mean± SD of the physico-chemical parameters of the surface water samples.ºC- degree centigrade, µohms/cm-micro-ohms per centimeter, NTU-Nephelometric turbidity units, mg/l- milligramme per litre.

Table 4.2 Correlation Matrix among Surface Water Samples

Parameter	pH	EC	DO	BOD	COD	Turbidity	Nitrate	Sulphate	Phosphate	Temperature
pH	1.000									
EC	0.831	1.000								
DO	-0.670	-0.331	1.000							
BOD	0.896	0.881	-0.272	1.000						
COD	0.234	0.373	0.543	0.628	1.000					
Turbidity	0.844	0.949	-0.199	0.976*	0.615	1.000				
Nitrate	-0.764	-0.321	0.936	-0.431	0.289	-0.300	1.000			
Sulphate	-0.910	-0.834	0.795	-0.706	0.099	-0.714	0.738	1.000		
Phosphate	0.821	0.998**	-0.362	0.851	0.313	0.926	-0.329	-0.853	1.000	
Temperature	0.558	0.641	-0.741	0.296	-0.467	0.418	-0.469	-0.762	0.690	1.000

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

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

The temperature of the surface water sites was observed to vary between 22˚C and 26˚C.Table 4.2 presents the correlation matrix between the various parameters in the surface water sites. Some of the parameters were found to bear statistically high correlation with each other indicating close association of these parameters with each other. The electrical conductivity(EC) and the levels phosphate in the water samples showed high positive correlation (0.998). Further positive correlations were observed between BOD and Turbidity; pH, BOD and turbidity; E.C, turbidity and BOD; DO and turbidity; BOD and phosphate; Turbidity and phosphate, an indication of influence of one parameter on the other.

Sulphate showed negative correlation with all parameters except DO, COD and nitrate. Nitrate also showed negative correlation with all parameters except DO and COD. Hence, sulphate and nitrate may serve as useful indices of water quality of the surface water because with increase or decrease in the value of these parameters, nitrate and sulphate falls or rises.

Table 4.3 presents the mean concentration of the physico-chemical parameters of the ground water samples. The pH varied between 6.30 and 7.23 across the sites. Generally the pH of the samples tended to be slightlyacidic among the sites except for samples U2 where the pH was slightly alkaline and U3 where it was neutral. Analysis of variance (ANOVA) showed that pHdid not vary significantly(i.e. at $p<0.05$) across the sampling sites. Electrical conductivity varied between 43.00µS/cm (U4) and 62.00µS/cm (U1). The EC values were not significant across the ground water sites. The DO value varied between 1.13mg/l (U2) and 1.50mg/l (U4).The DO values showed no significant difference statisticallyacross the sampling points. The BOD fluctuated between 0.130mg/l at U2 and 0.50mg/l at U1. There was no significant difference in the mean BOD values oftheground water samples. The COD values for the ground water samples

U1was 1.80mg/l; U2 had 3.50mg/l; U3 had2.31mg/l and U4was6.70mg/l. Analysis of variance (ANOVA) showed that COD varied significantly($p < 0.05$) across the sampling sites. The turbidity of the samples varied between 5.70NTU (U4) and 7.40NTU (U2). The difference in the mean turbidity values was not statistically significant at a confidence limit of$p<0.05$. The meanconcentration of nitrate was found to vary between 3.40mg/l (U1) to 18.90mg/l (U3). The difference in the average mean was not statistically significant. Sulphate was found to vary between 1.20mg/l and 6.90mg/l across the ground water sites. There was no significant difference statistically in the mean of the sulphate concentration. The phosphate concentration in the surface water sites were found to vary between 0.10mg/l and 0.60 mg/l. The mean phosphate concentrations were not significant statistically.

The temperature of the ground water samples variedbetween 25˚C and 27˚C.

Table 4.4 presents the correlation matrix between the various parameters in the ground water samples.COD and temperature showed high positive correlation(0.976). COD and pH showed high negative correlation (-0.990). Turbidity and DO also showed high negative correlation (-0.998).This implies that an increase in one leads to a decrease in the other.

4.2 Heavy Metal Concentration in Water

The mean levels of the heavy metal concentration in the surface water samples are presented in Table 4.5. Cr varied between 0.16mg/l and 0.58mg/l, Pb ranged from 1.10mg/l to 2.60mg/l, Cd from 0.04mg/l to 0.10mg/l, Fe ranged from 4.10mg/l to 9.70mg/l, Mn from 0.04mg/l to 0.64mg/l, Ni from 0.05mg/l to 0.63mg/l and Co ranged from 0.50mg/l to 0.90mg/l.

Table 4.3: Physicochemical Parameters of ground Water

Parameter	Site U1	Site U2	Site U3	Site U4
pH	6.80±0.02	7.23±0.01	7.00±0.01	6.30±0.01
E.C (µS/cm)	62.00±1.00	44.00±1.00	49.00±1.00	43.00±1.00
D.O (mg/l)	1.40±0.10	1.13±0.10	1.20±0.10	1.50±0.10
B.O.D (mg/l)	0.50±0.20	0.13±0.10	0.13±0.10	0.30±.10
C.O.D (mg/l)	1.80±1.00	3.50±2.00	2.31±1.20	6.70±2.00
Turbidity (NTU)	6.00±0.01	7.40±0.01	7.20±0.01	5.70±0.01
Nitrate (mg/l)	3.40±0.20	13.70±0.10	18.90±0.10	16.40±0.10
Sulphate (mg/l)	1.90±0.10	6.90±0.10	1.20±0.10	1.50±0.20
Phosphate (mg/l)	0.10±0.00	1.40±0.20	0.60±0.12	0.40±0.10
Temperature (ºC)	25	26	25	27

Values are mean± SD of the physico-chemical parameters of the ground water samples.ºC- degree centigrade, µohms/cm-micro-ohms per centimeter, NTU-Nephelometric turbidity units, mg/l- milligramme per litre

Table 4.4: Correlation Matrix within the Ground Water Samples

Parameter	pH	EC	DO	BOD	COD	Turbidity	Nitrate	Sulphate	Phosphate	Temperature
pH	1.000									
EC	0.652	1.000								
DO	-0.581	0.232	1.000							
BOD	0.000	0.740	0.763	1.000						
COD	-0.990**	-0.716	0.489	-0.068	1.000					
Turbidity	0.538	-0.288	-0.988*	-0.829	-0.457	1.000				
Nitrate	-0.440	-0.837	-0.271	-0.824	0.448	0.392	1.000			
Sulphate	0.182	-0.346	-0.683	-0.429	-0.042	0.587	-0.043	1.000		
Phosphate	0.073	-0.642	-0.821	-0.798	0.055	0.792	0.411	0.885	1.000	
Temperature	-0.938	-0.734	0.381	-0.091	0.976*	-0.379	0.368	0.164	0.203	1.000

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

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

Table 4.5: Heavy Metal Concentration in Surface Water (mg/l)

Metal	Site S1	Site S2	Site S3	Site S4
Cr	0.58 ± 0.11^{b}	0.51 ± 0.06^{b}	0.29 ± 0.12^{a}	0.16 ± 0.14^{a}
Pb	1.14 ± 0.73^{a}	1.10 ± 0.87^{a}	1.25 ± 0.93^{a}	2.60 ± 0.80^{a}
Cd	0.04 ± 0.01^{a}	0.10 ± 0.01^{b}	0.10 ± 0.01^{a}	0.10 ± 0.00^{a}
Fe	9.60 ± 0.60^{b}	9.70 ± 1.33^{b}	4.30 ± 0.45^{a}	4.10 ± 0.10^{a}
Mn	0.04 ± 0.04^{a}	0.43 ± 0.04^{b}	0.31 ± 0.16^{b}	0.64 ± 0.10^{c}
Ni	0.05 ± 0.06^{a}	0.60 ± 0.03^{a}	0.63 ± 0.05^{c}	0.20 ± 0.03^{b}
Co	0.90 ± 0.50^{a}	0.60 ± 0.07^{a}	0.50 ± 0.30^{a}	0.80 ± 0.40^{a}

Values are mean± SD of the heavy metal concentration of the surface water samples. Mean value in the same row followed by the same superscript letters are not significantly different ($P < 0.05$).

Analysis of variance (ANOVA) showed that Pb and Co did not vary significantly in the surface water samples ($P < 0.05$) whereas the levels of Cr, Cd, Fe, Mn, and Ni varied significantly in the samples collected from the surface water.

The correlation matrix between the heavy metals present in surface water is presented in Table 4.6. There was no positive correlation between most of the metals except for Cr and Fe which showed high positive correlation which implies they are inter-related and are from the same source. A negative correlation was observed between Ni and all the metals except for Mn where a weak positive correlation exists. Thus, as the concentration of the other metals increases the concentration of Ni decreases and vice-versa. .

The mean concentration of heavy metals present in the ground water samples are shown in Table 4.7. Cr varied between 0.20 mg/l and 0.80 mg/l, Pb ranged from 1.71 mg/l to 3.20 mg/l, Cd from 0.02 mg/l to 0.10 mg/l, Fe ranged from 2.19 mg/l to 11.40mg/l, Mn from 0.05 mg/l to 0.50 mg/l, Ni from 0.04 mg/l to 0.14 mg/l and Co ranged from 0.22 mg/l to 0.40 mg/l. Analysis of variance showed that Pb, Co and Ni did not vary significantly ($P < 0.05$) whereas Cr, Cd, Fe, and Mn varied significantly ($P < 0.05$) at the various sites where ground water samples wereanalysed.

The correlation matrix between the heavy metals present in the underground water is presented in Table 4.8. High correlation was observed between some of the metals implying a close association between them. Fe and Cr showed a high positive correlation (0.996) which indicates that they are from the same source. A positive correlation was also observed between Ni and Pb (0.985) and this also points to the similarity in the source from which they emanate. Co showed negative correlation with all the metals.

Table 4.6:Correlation Matrix for Heavy Metals in Surface Water

Parameter	Chromium	Lead	Cadmium	Iron	Manganese	Nickel	Cobalt
Chromium	1.000						
Lead	-0.825	1.000					
Cadmium	0.234	-0.318	1.000				
Iron	0.957*	-0.685	0.396	1.000			
Manganese	-0.728	0.698	0.420	-0.515	1.000		
Nickel	-0.523	-0.008	-0.277	-0.722	0.017	1.000	
Cobalt	0.151	0.406	-0.465	0.248	-0.153	-0.704	1.000

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

Table 4.7: Heavy Metal Concentration in Ground Water (mg/l)

Metal	Site U1	Site U2	Site U3	Site U4
Cr	0.20±0.10[a]	0.80±0.11[a]	0.22±0.14[c]	0.44±0.04[b]
Pb	1.71±1.20[a]	3.01±0.83[a]	3.20±1.51[a]	1.90±0.71[a]
Cd	0.03±0.00[ab]	0.06±0.01[c]	0.02±0.11[a]	0.10±0.01[bc]
Fe	2.19±1.32[a]	11.40±0.30[c]	2.50±0.65[a]	5.20±0.44[b]
Mn	0.10±0.01[a]	0.20±0.05[a]	0.50±0.10[b]	0.05±0.10[a]
Ni	0.04±0.10[a]	0.11±0.05[a]	0.14±0.10[a]	0.06±0.05[a]
Co	0.40±0.33[a]	0.22±0.14[a]	0.35±0.04[a]	0.40±0.20[a]

Values are mean± SD of the heavy metal concentration of the underground water samples. Mean value in the same row followed by the same superscript letters are not significantly different (P>0.05).

Figure 4.1 shows the variation of heavy metal concentration in the surface and ground water samples.The highest level of Cr was found at U2 with a value of 0.80 mg/l and the lowest concentration of 0.16mg/l at S4. The variation of Cr across the sampling sites is in the order: U2>S1>S2>U4>S4>U3>U1>S4.

The highest concentration of Pb was observed at U3 (3.20mg/l) and the lowest concentration of 1.10mg/l was observed at S2. Pb varies across the sites in the ascending order: S2<S1<S3<U1<U4<S4<U2<U3.

The concentration of Cd ranged from 0.10mg/l at S2 to 0.02mg/l at U3. The variation across the sites is in the order: S2>U2> S3 >S4>U4>S1>U1>U3.

U2 has the highest concentration of 11.40mg/l and U1 has the lowest concentration of 2.19mg/l. Fe varies across the sampling site in the order: U2> S1 >S2>U4>S3>S4>U3>U1.

Mn was observed to be highest at S4 with a concentration of 0.64mg/l and lowest at U1 with a concentration of 0.10mg/l. The variation observed across the sites is in the order: U1<S1<U4<U2<S3<S2<U3<S4.

The highest concentration of Ni was found to be 0.63mg/l at S3 and lowest at U4 with a concentration of 0.06mg/l. The variation of Ni across the sampling sites is in the order: S3>S4>U3>U2>S2>S1>U1>U4.

The concentration of Co varied from 0.90mg/l at S1 to 0.22 mg/l at U2. The variation observed is in the order: S1>S4>S2>S3>U4>U1>U3>U2.

Table 4.8 Correlation Matrix for Heavy Metals in Underground Water

Metal	Cr	Pb	Cd	Fe	Mn	Ni	Co
Cr	1.000						
Pb	0.341	1.000					
Cd	0.891	-0.124	1.000				
Fe	0.996**	0.392	0.861	1.000			
Mn	-0.197	0.836	-0.611	-0.155	1.000		
Ni	0.179	0.985*	-0.287	0.238	0.897	1.000	
Co	-0.870	-0.600	-0.625	-0.910	-0.065	-0.494	1.000

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

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

4.3: Organic Contaminants in the Water Samples

The chromatogram of the organic contaminants in the water samples from the underground and surface water sites are shown in Figures 4.2-4.12. Butylated hydroxyltoluene, toluene and O-xylene were identified in the samples from ground water site U1; toluene, butylated hydroxyltolune and P-xylene were identified in site U2; butylated hydroxyltoluene, toluene and ethyl benzene were identified in site U3 and toluene and ethyl benzene were detected in site U4. In the surface water site, butylated hydroxyltoluene was detected in site S1; toluene, ethyl benzene and O-xylene were identified in site S2; butylated hydroxyltoluene was identified in site S3 and P-xylene was identified in site S4.Formaldehyde and Methylene Chloride were not detected in both surface and underground water sites. The retention time(in minutes) of the observed organic contaminants is shown in Table 4.9.

4.4: Microbial Analysis of the Water Samples.

The results of the bacteriological analysis of the surface and underground water are shown in Table 4.10. The colony forming unit was observed to fluctuate between the surface water and underground water. The highest colony forming unit of 31×10^4 was observed at U1 and the lowest colony forming unit of 2×10^4 was observed at U3.

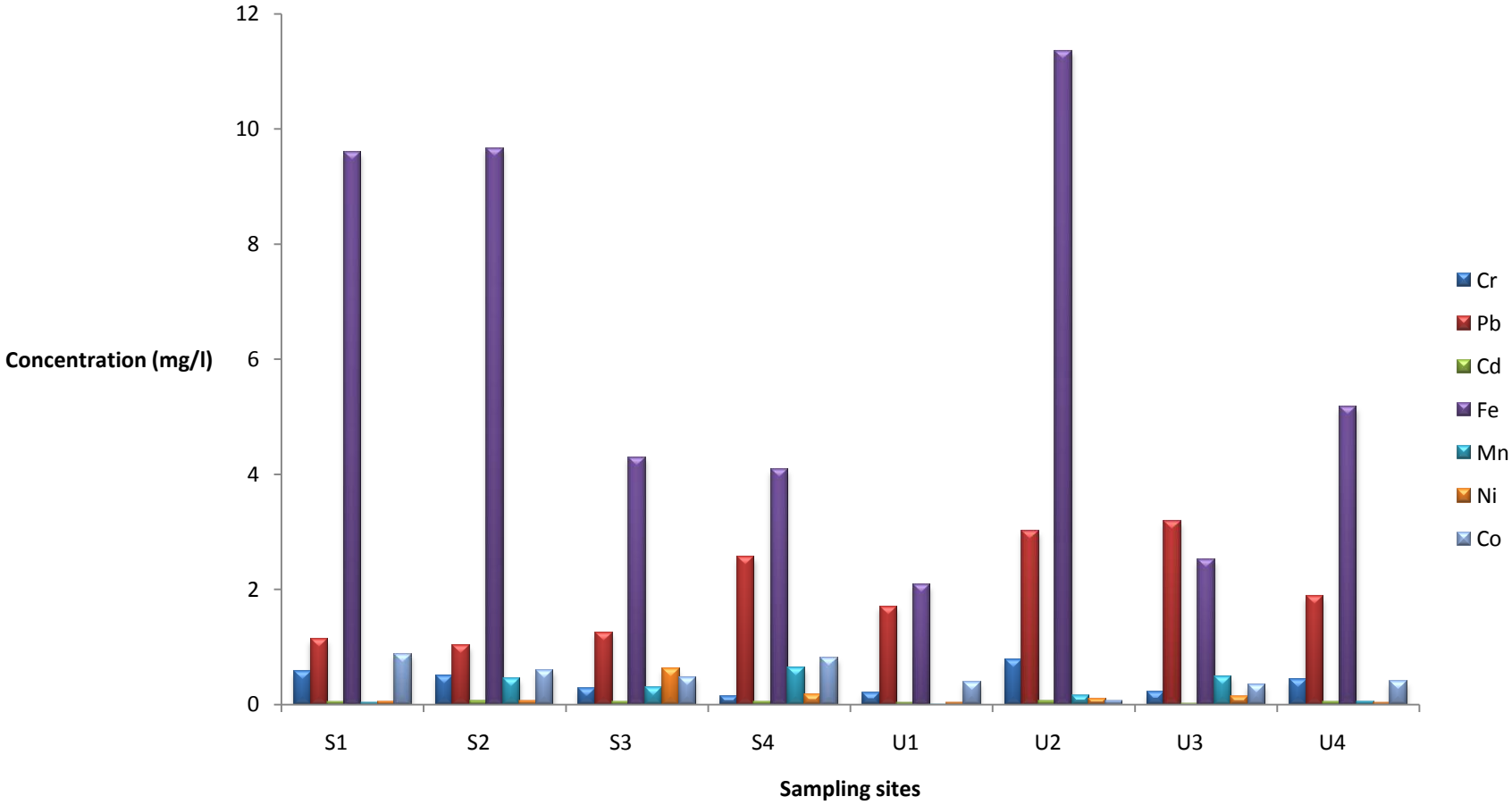

Figure 4.1: Levels of Heavy metals in surface and underground water across the study area (ABUTH, Zaria)

Table 4.9: Results of Organic Contaminants present in Surface and Underground Water

SITE	ORGANIC CONTAMINANTS	RETENTION TIME(mins)
UI	Butylated Hydroxyltoluene	18.51
	Toluene	3.61
	O-Xylene	5.59
U2	Toluene	3.61
	Butylated Hydroxyltoluene	18.53
	P-Xylene	5.60
U3	Butylated Hydroxyltoluene	18.53
	Toluene	3.61
	Ethyl Benzene	5.43
U4	Toluene	3.64
	Ethyl Benzene	5.44
S1	Butylated Hydroxyltoluene	18.53
S2	Toluene	3.61
	Ethyl Benzene	5.43
	O-Xylene	5.61
S3	Butylated Hydroxyltoluene	18.53
S4	P-Xylene	5.63

TABLE 4.10 Bacteriological Analysis Results

Site	Coliform Count (Cfu/ml)
S1	25×10^4
S2	28×10^4
S3	11×10^4
S4	10×10^4
U1	2×10^4
U2	7×10^4
U3	31×10^4
U4	4×10^4

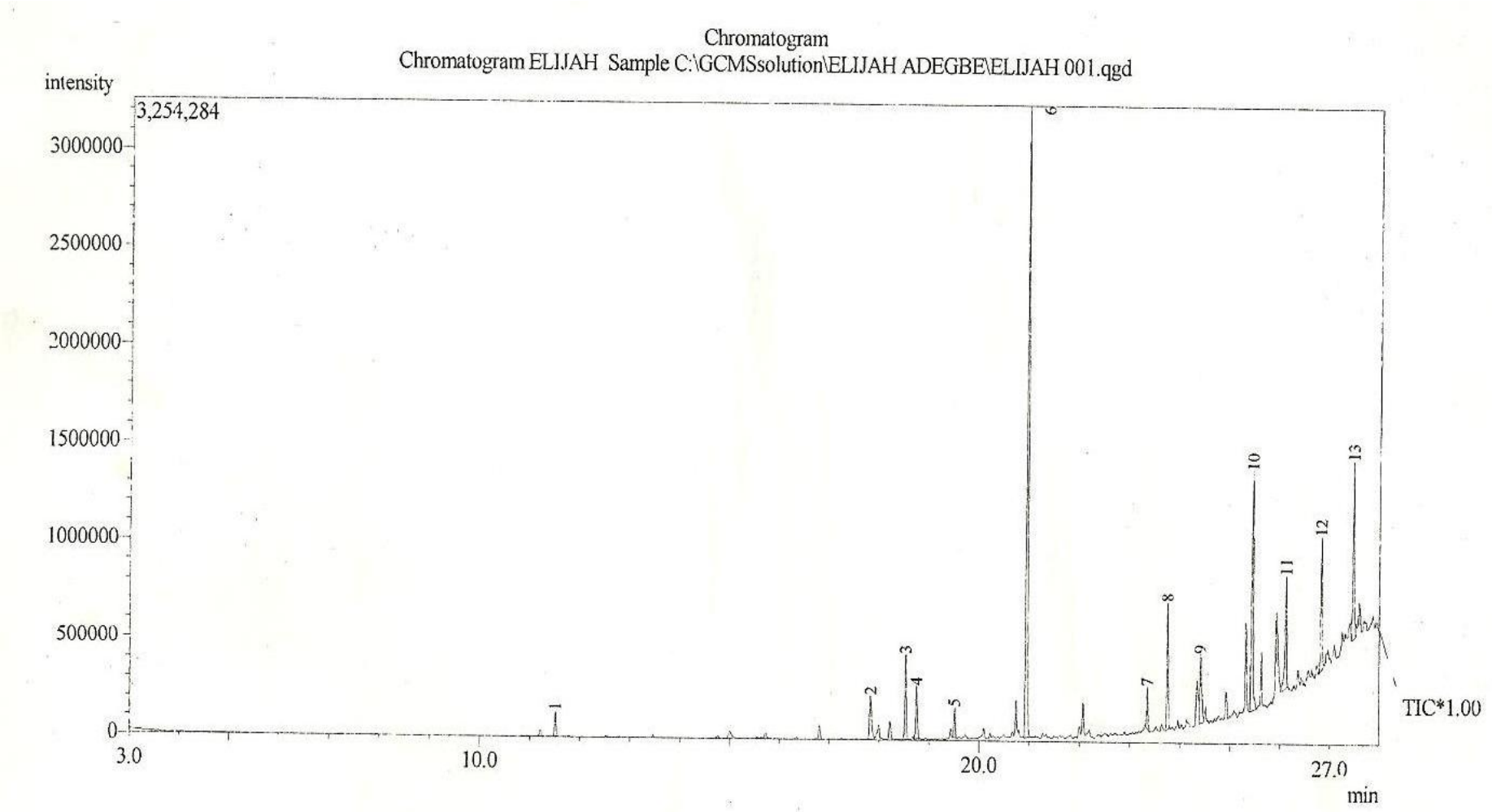

Fig 4.2: GCMS Spectra of underground water sample (U1)

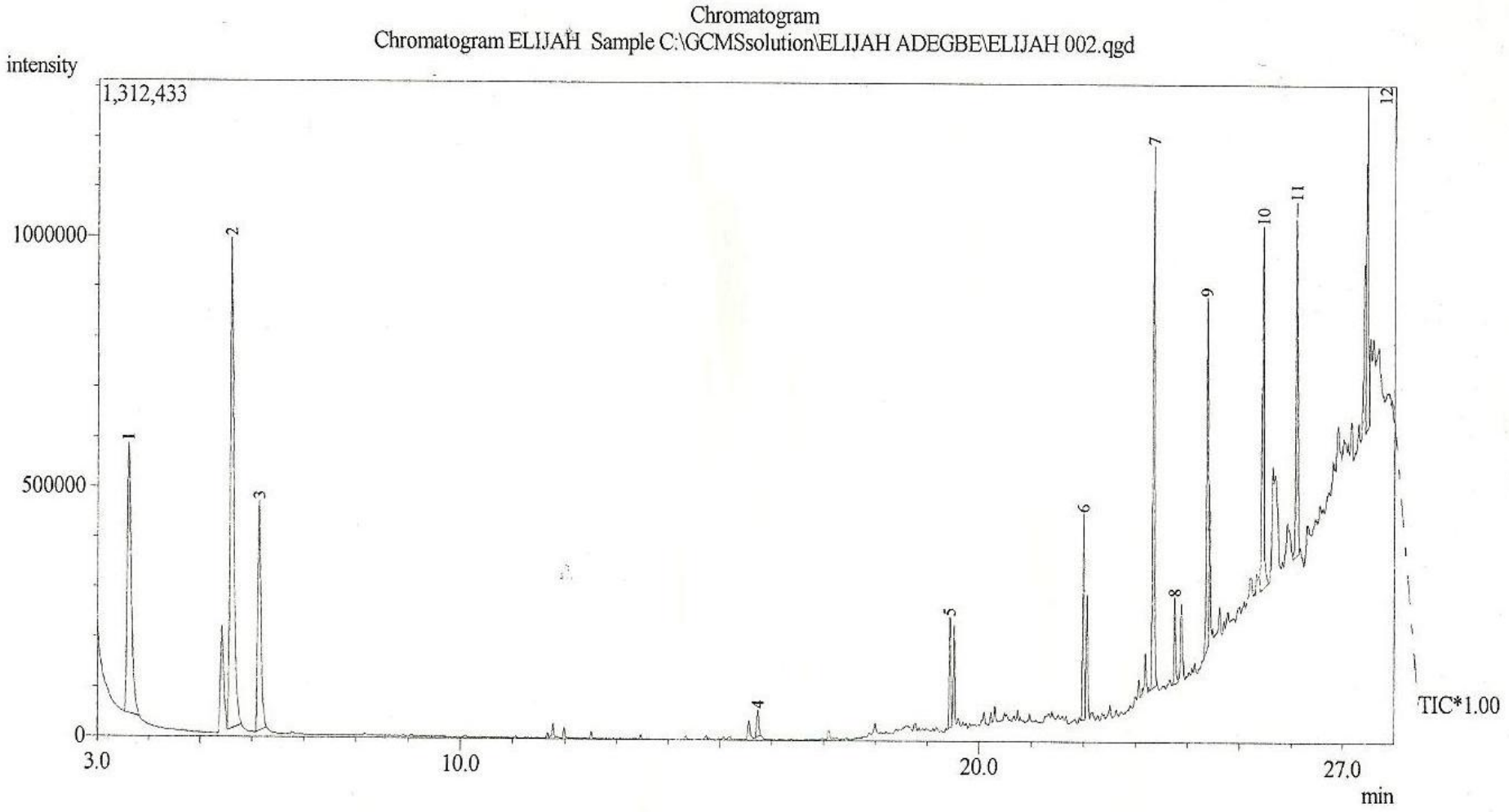

Fig 4.3: GCMS Spectra of Underground water sample (U1)

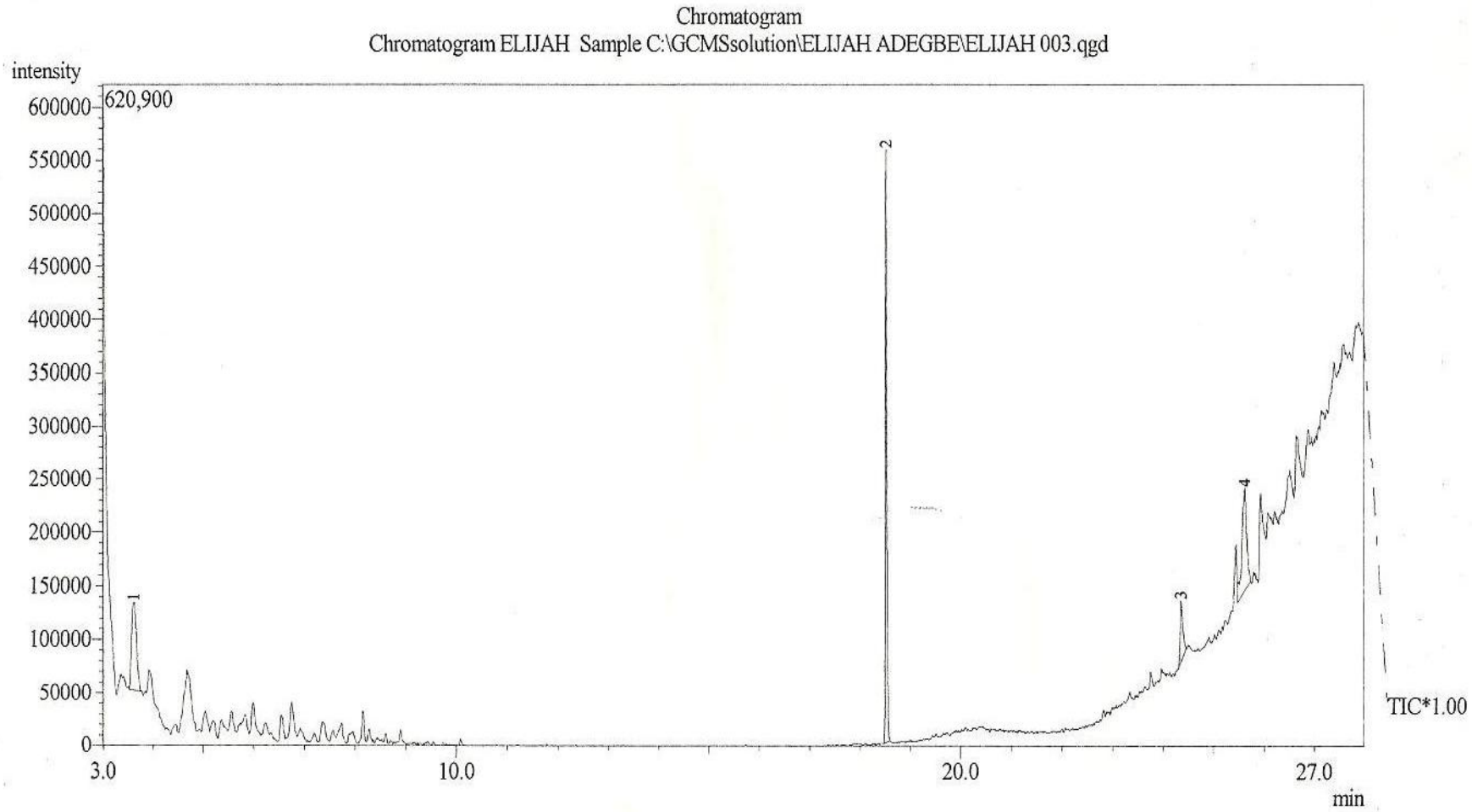

Fig 4.4: GCMS Spectra of Underground water sample (U2)

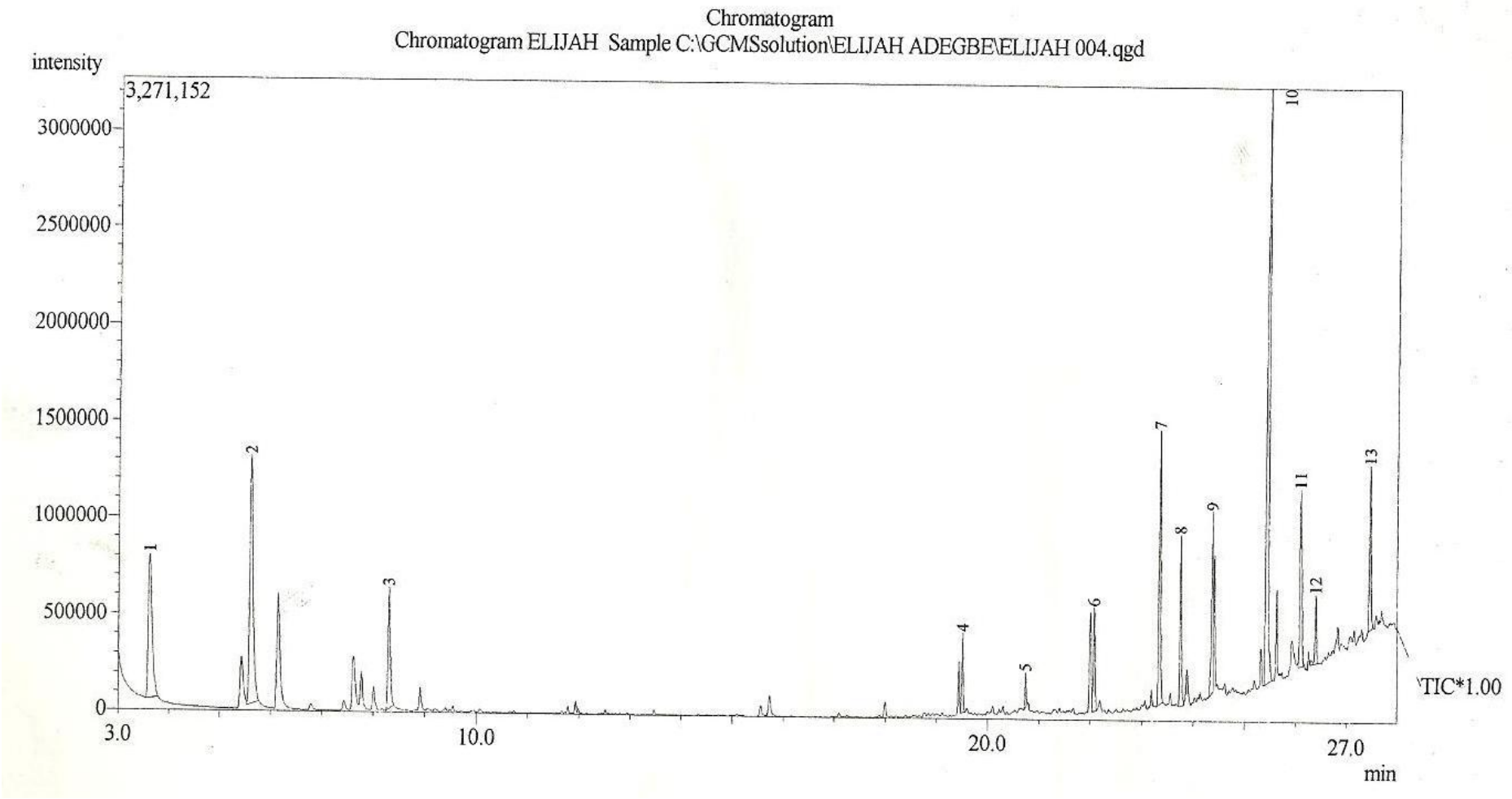

Fig 4.5: GCMS Spectra of Underground water sample (U2)

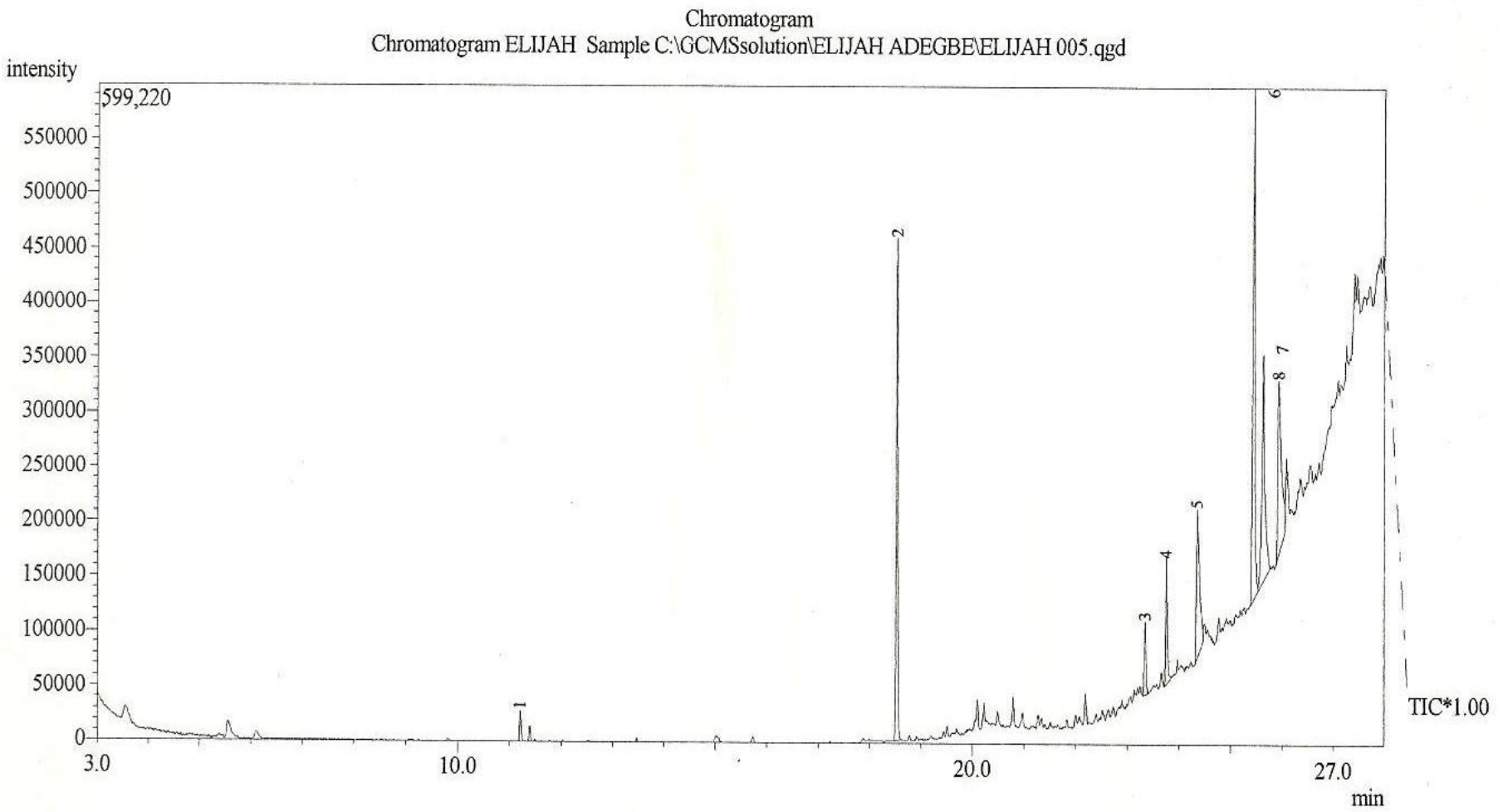

Fig 4.6: GCMS Spectra of Underground water sample (U3)

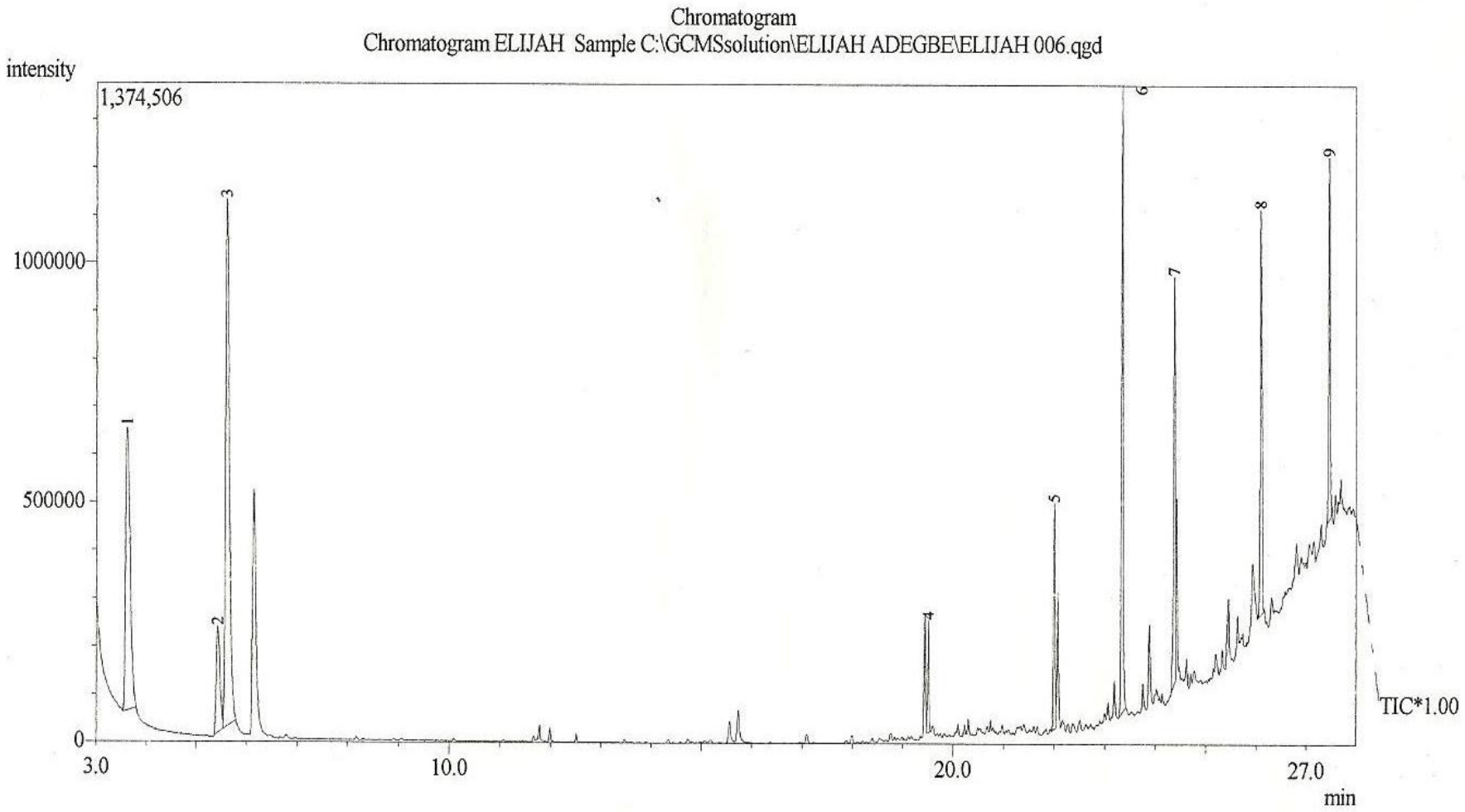

Fig 4.7: GCMS Spectra of Underground water sample (U3)

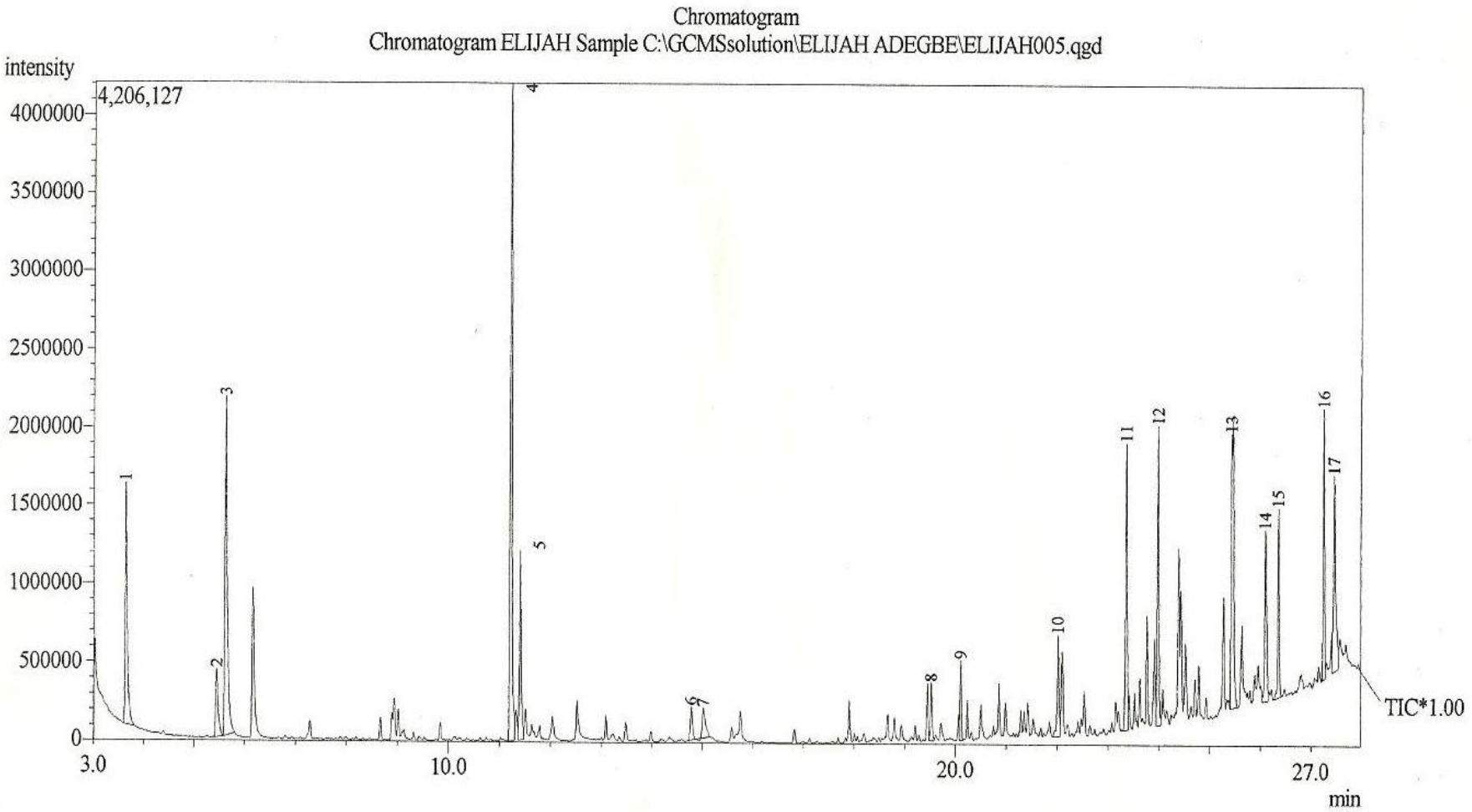

Fig 4.8: GCMS Spectra of Underground water sample (U4)

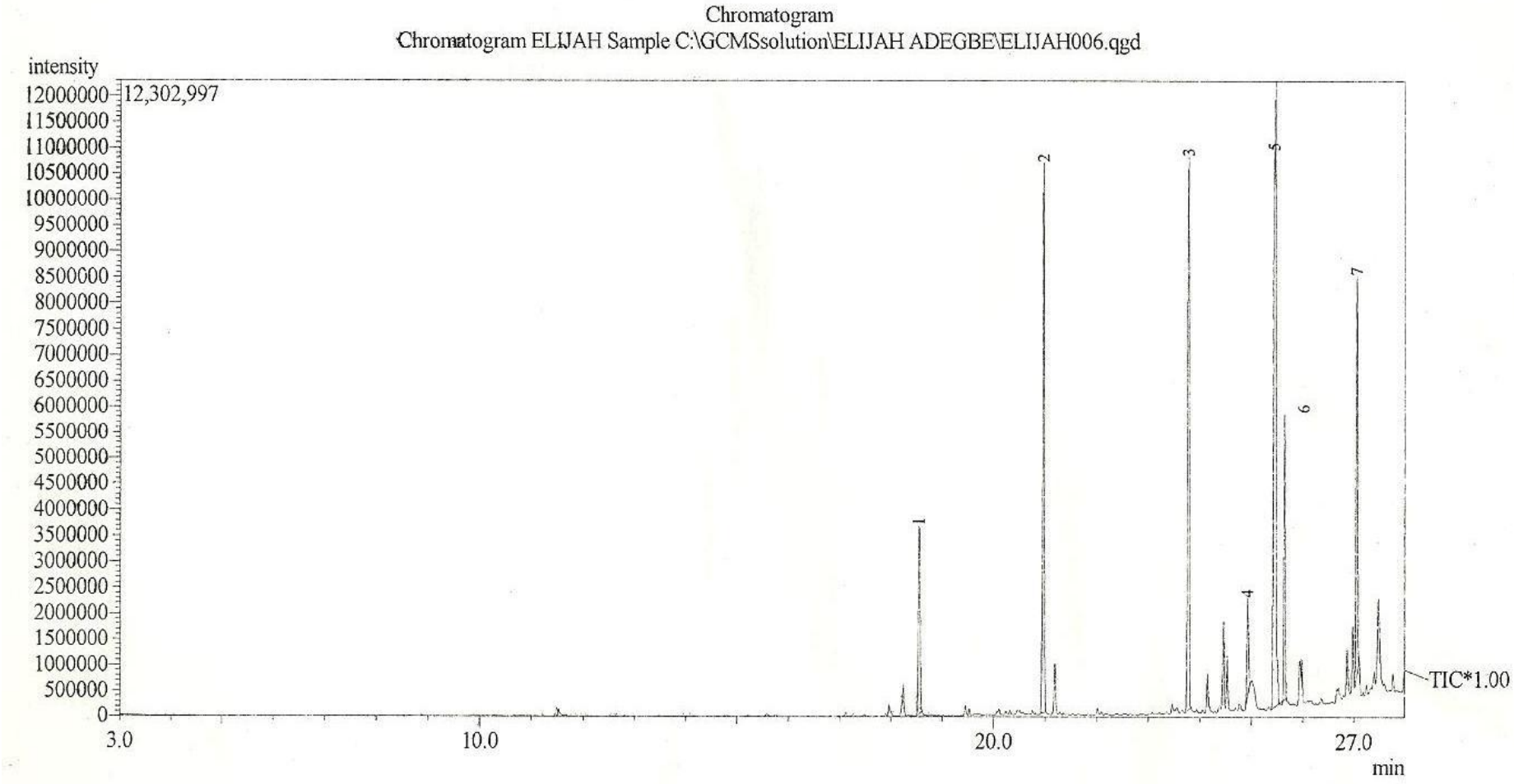

Fig 4.9: GCMS Spectra of Surface water sample (S1)

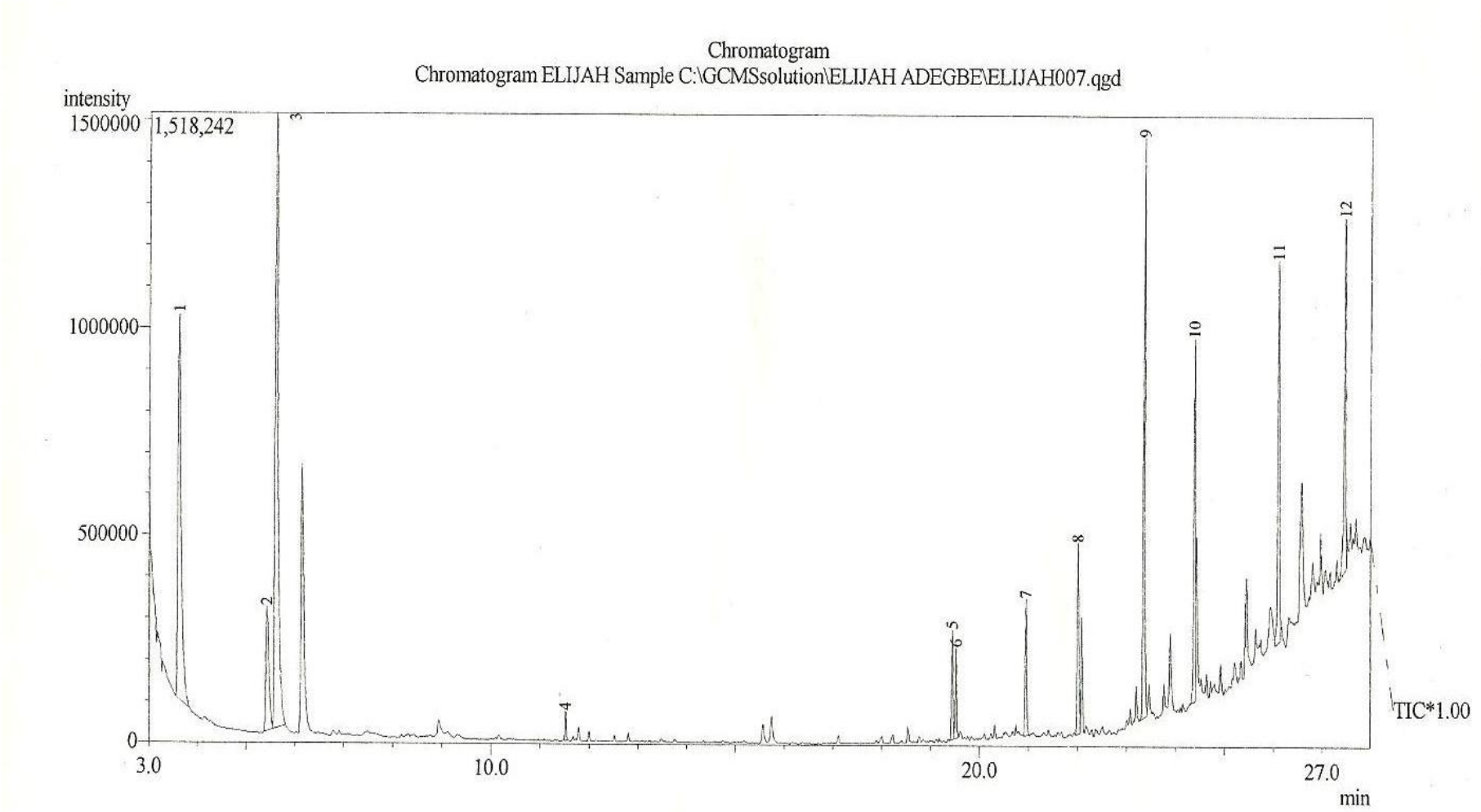

Fig 4.10GCMS Spectra of Surface water sample (S2)

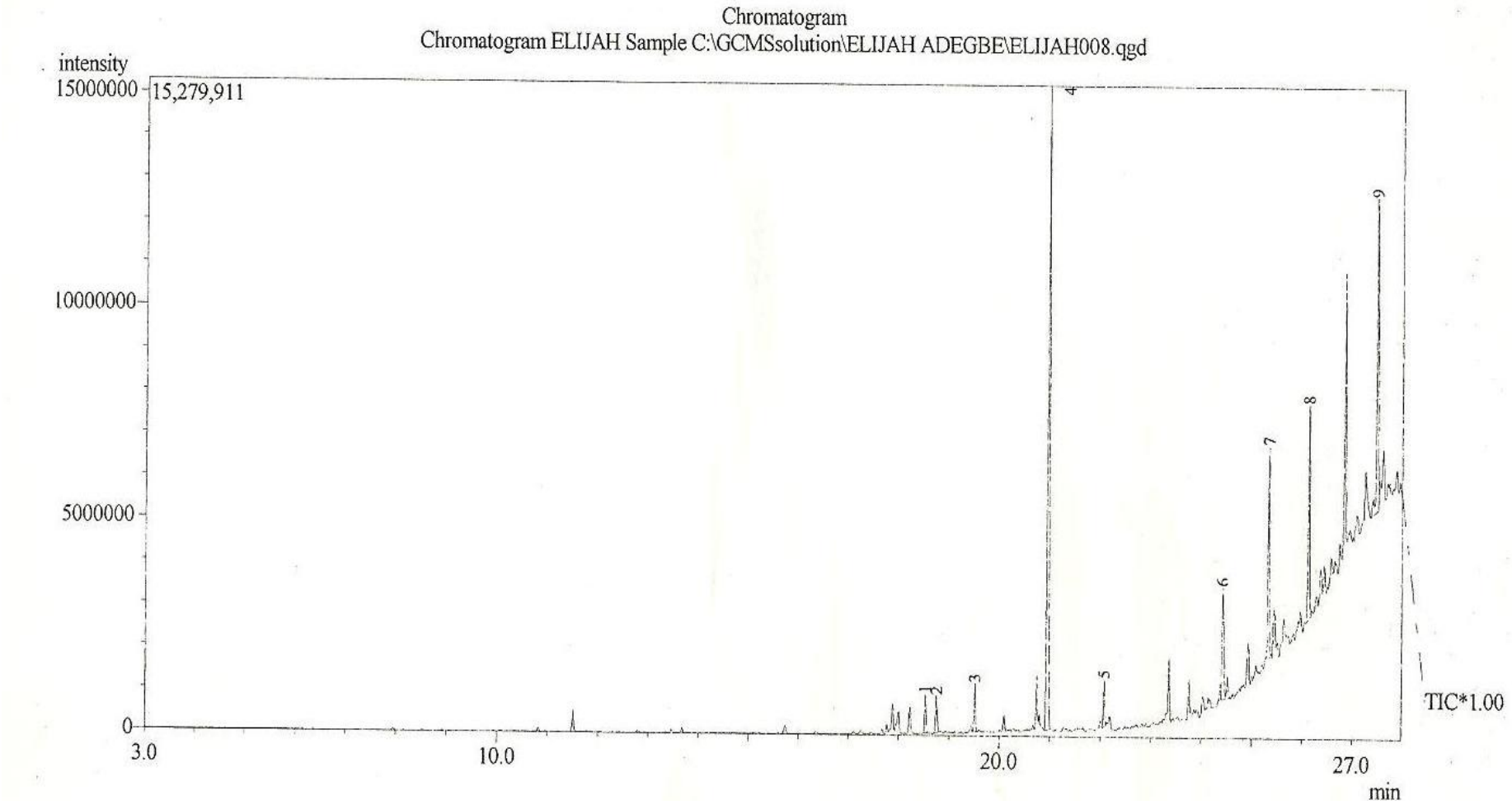

Fig 4.11: GCMS Spectra of Surface water sample (S3)

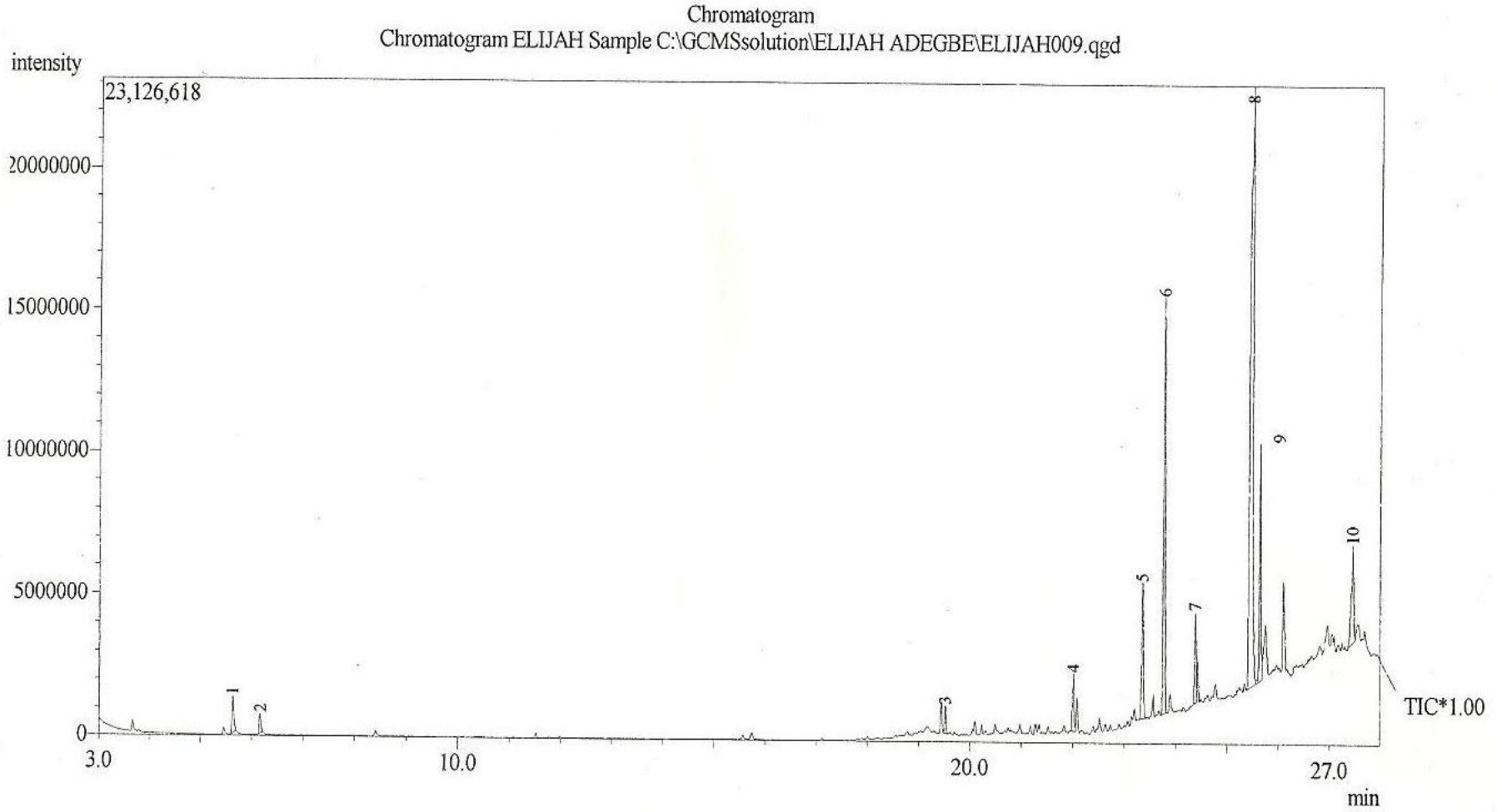

Fig 4.12: GCMS Spectra of Surface water sample (S4)

CHAPTER FIVE

5.0 DISCUSSION

5.1 Physicochemical Parameters of the Surface and Underground Water

In this study, 66 samples of surface water andground waterwere collected. The samples were collected from eight sites (S1, S2, S3, S4, U1, U2, U3 and U4) all found in the immediate environment of the liquid waste treatment plant of the Ahmadu Bello University Teaching Hospital.

The highest pH recorded in the surface water sites was 7.70. This is higher than the range of 6.20-6.88 reported by Ibeh and Omoruyi (2011) in the physicochemical parameters of a hospital effluent from a university teaching hospital based in southern Nigeria.All sites in the study area were within the WHO (2011) permissible guideline value of 6.5-8.5.

Conductivity values obtained in this study showed that the surface water sites contained appreciable amount of dissolved ions (75.00- 820.00 µS/cm) more than ground water sites (43.00-62.00 µS/cm). This high EC values observed in some sites may be as a result of the chemicals present in ionic form in the effluent discharged into the surface water from the hospital's liquid waste treatment plant. The EC of all sites fall within the WHO (1999) recommended limit of 500-1500µS/cm.

The turbidity values obtained from the ground water sites (5.70-7.40 NTU) was lower than the value of 9.7NTU recorded for surface water site S3. Thus the surface water sites were found to be more turbid than the ground water sites. This may be as a result of the open nature of the surface water making it easy for impurities that could block light reception to flow into it. All sites in the study area except for sites S1 and S2 were above the WHO (2011) permissible levels of 5NTU.

The dissolved oxygen (DO) values observed in the surface water sites (1.03-1.40 mg/l) and ground water sites (1.13-1.50 mg/l) were lower than the range of 6.21-19.78 mg/l reported by Ibeh and Omoruyi (2011) in the physicochemical parameters of a hospital effluent from a university teaching hospital based in southern Nigeria. All values obtained were lower than the WHO(2011) permissible levels of 5 mg/l. This indicates that both surface and ground water sources were polluted.Tropical aquatic ecosystem should have a DO concentration of at least 5mg/l in order to support diversified biota including fish (Jha*et al.,* 2008).

The biochemical oxygen demand (BOD) values obtained from the study were in the range of 0.13-0.50mg/l. This is lower than the range of 43.77-235.64 mg/l reported by Ibeh and Omoruyi (2011) in the physicochemical parameters of a hospital effluent from a university teaching hospital based in southern Nigeria. All the BOD values obtained in this study are below the WHO (2011) permissible guideline of 6mg/l.

The chemical oxygen demand (COD) values obtained from this study ranged from 1.10-6.70mg/l. The highest value of 6.70 mg/l was obtained at site U4 and the least value of 1.10 mg/l at site S1. This is lower than the range of 181-290.33 mg/l observed by Wyasu (2011) for effluents discharged fromthe liquid waste treatment plant of the Ahmadu Bello University Teaching Hospital in Zaria, Nigeria. Allvalues obtained in the study were below the value of 10mg/l set by WHO (2011)as the permissible limit.However, the COD values were generally higher than BOD values since the test will oxidize materials such as fats and lignins which are slowly biodegradable. The increase of COD value is due to oxidizable organic matter (Bhatia, 2009).

High nitrate level (>1mg/l) is not beneficial to aquatic life. The nitrate levels obtained in the study ranged from 3.00-9.10mg/l for the surface water sites and 3.40-18.90mg/l for ground water sites. The highest value of 18.90mg/l was observed at site U3. This islower

than the value of 30.00 mg/l reported bybyWyasu (2011) for effluents discharged fromthe liquid waste treatment plant of the Ahmadu Bello University Teaching Hospital in Zaria, Nigeria. All the nitrate values obtained in the study are lower than the WHO (2011) recommended guideline value of 50mg/l.

Phosphate concentration in the surface water sites ranged from 0.90-3.30mg/l and 0.10-1.40 mg/l for the ground water sites. Phosphate constitutes an important pollution problem when it is present in significant amounts. It promotes algae growth leading to the cyclic problem of eutrophication (Thriodore, 2004).It is established that high phosphate concentration has no health implication (WHO, 2011) except for its role in causing eutrophication of water bodies.

The sulphate concentration of the samples collected from the surface water sites of the study area ranged from 2.2-6.5mg/l and 1.2-6.9 mg/l for the ground water sites. No health-based guideline is proposed for sulfate. However, because of the gastrointestinal effects resulting from ingestion of drinking-water containing high sulphate levels, it is recommended that health authorities be notified of sources of drinking water that contain sulfate concentrations in excess of 500 mg/l. The presence of sulphate in drinking-water may also cause noticeable taste and may contribute to the corrosion of distribution systems (WHO, 2011).

The temperature of the surface water sites was observed to vary between 22-26˚C and the temperature of the ground water sites ranged from 25-27˚C. The temperature of a water source does not have direct health implication (Willis, 1989).

5.2 Heavy Metals in the Surface andGround Water

The concentration of Cr observed in the surface water sites ranged from 0.16-0.58 mg/l as shown inTable4.5. The highest concentration (0.58 mg/l) observed was lower than the highest value 0.6093mg/l reported by Wyasu (2011) for the liquid waste treatment plant of the Ahmadu Bello University Teaching Hospital in Zaria, Nigeria.The concentration of Cr in the ground water sites ranged from0.20-0.80 mg/l as presented in Table 4.7. The highest concentration (0.80 mg/l) obtained in the study was higher than the value 0.40 mg/l reported by Adefemi and Awokunmi (2010) for water samples from River Ona and selected hand dug wells in Itaogbolu area of Ondo State, Nigeria. All the values of Cr obtained from the study site exceeded the WHO (2011) permissible limit of 0.05mg/l. High concentration of Cr in the ground water is dangerous to the rural dwellers because Cr and its compounds can cause cancers of the lung, nasal cavity and para-nasal sinus and also Cr is a suspected cause of cancer of the stomach and larynx (ATSDR, 2008).

Pb in the surface water within the study area ranged from 1.10-2.60 mg/l as indicated in Table 4.5.The mean concentration of Pb in the ground water ranged from 1.71-3.20 mg/l as shown in Table 4.7. This was higher than the highest value of 0.55mg/l reported by Owuna (2012) for groundwater in Otukpo area of Benue State, Nigeria. Lead is a cumulative general poison and associated with health hazards like anaemia and reproductive defects (Moore. 1988;Wildt*et al*. 1983).All the values of Pb in both the surface and ground water sites exceeded the WHO (2011) recommended levels of 0.01mg/l.

A concentration range of 0.04-0.10 mg/l was obtained for Cd in the surface water site as shown in Table 4.5.All the values obtained from the surface water sites except for site S1are higher thanWHO (2011) permissible levels of 0.05mg/l.The mean concentration of Cd in the ground water sites ranged from 0.02-0.06 mg/l as shown in Table 4.7. This was

lower than the range of 0.07 -0.108mg/l reported by Fagbote and Olanipekun (2013)in the evaluation of the status of heavy metal pollution of water (surface and ground) and aquatic macrophyte (*Ceratophyllumdemersum*) of Agbabu Bitumen Deposit Area. All values obtained at the ground water sites except U2 and U4 are below the WHO (2011) permissible levels of 0.05mg/l.

The mean concentration of Fe ranged from 4.10-9.70 mg/l in the surface water sites as shown in Table 4.5. This was higher than the highest value of 5.30 mg/l reported by Adefemi and Awokunmi (2010)for water from River Ona and selected hand dug wells in Itaogbolu area of Ondo State, Nigeria. A concentration range of 2.19-11.40 mg/l was observed in the ground water sites as observed in Table 4.7. These high values of Fe may be connected with the use of Iron coagulants or the corrosion of steel and cast iron pipes during the discharge of the liquid effluent. Ingesting too much of iron through drinking water is not associated with adverse health. However, consuming large amounts of iron can lead to hemochromatosis, a severe disease that can damage the body's organs (Sinclair, 2011)

The mean concentration of Mn ranged from 0.04 - 0.64 mg/l in the surface water sites as shown in table 4.5. The highest value of 0.64 mg/l was lower than the highest value of 1.373mg/l reported by Fagbote and Olanipekun (2013) in theevaluation of the status of heavy metal pollution of water (surface and ground) and aquatic macrophyte(*Ceratophyllumdemersum*) of Agbabu Bitumen Deposit Area. All the values obtained from the surface water sites except for site S1 are higher thanWHO (2011) permissible levels of 0.05mg/l. The mean concentration of Mn ranged from 0.05 – 0.50 mg/l in the ground water sites as reported in Table 4.7. All the values obtained from the ground water sites except for site U4 are higher thanWHO (2011) permissible levels of 0.05mg/l.Mn is an essential element for humans and animals. However exposure to very

high levels in drinking water can affect the respiratory tract and the brain. Symptoms of Mn poisoning are hallucination, forgetfulness and nerve damage. Mn can also cause Parkinson disease, lung embolism and bronchitis (Fagboteand Olanipekun, 2013).

The concentration of Ni in the surface water sites ranged from 0.05 - 0.63 mg/l as shown in Table 4.5. The highest value of 0.63 mg/l is higher than the value of 0.1mg/l reported by Adefemi and Awokunmi (2010)for water samples from River Ona and selected hand dug wells in Itaogbolu area of Ondo State, Nigeria.All the values obtained from the surface water sites except for site S1are higher thanWHO (2011) permissible levels of 0.07mg/l.The mean value of Ni in the ground water sites ranged from 0.03 - 0.14 mg/l as indicated in Table 4.7. All the values obtained from the ground sites except sites U1 and U4 exceeded the WHO (2011) permissible levels of 0.07mg/l.

The mean concentration obtained for Co ranged from 0.50 - 0.90 mg/l. The highest value of 0.90 mg/l was higher than the highest value of 0.2093 mg/l reported by Wyasu (2011) for the liquid waste treatment plant of the Ahmadu Bello University Teaching Hospital in Zaria, Nigeria. This increase may be as a result of the accumulation of Co in the water body over time. It ranged from 0.06 - 0.40 mg/l in the ground water sites as shown in Table 4.7. Exposure to high levels of Co can cause severe effects on the lungs including asthma, pneumonia and wheezing (ATSDR, 2008).

5.3 Organic Contaminants

The chromatograms of the organic contaminants identified in the surface water and ground water sites are shown in Figures 4.2 – 4.12. Ethylbenzene was identified in surface water site S2 and ground water sites U3 and U4.Toluene was detected in ground water sites U1, U2, U3 and U4.It was also present in surface water site S2.

Xylene was identified in ground water sites U1and U2. It was also present in surface water sites S2 and S4.Butylatedhydroxyltoluene was identified in sites UI, U2, U3, S1 and S3. The identification of ethylbenzene, xylene and butylatedhydroxyltoluene in the surface water and ground water is in agreement with the findings of Wyasu (2011)for the liquid waste treatment plant of the Ahmadu Bello University Teaching Hospital in Zaria, Nigeria.

5.4 Microbial Analysis

There was reduction in the bacterialcount from S1 to S4 ($25 \times 10^4 - 10 \times 10^4$Cfu/ml) except in S2($25 \times 10^4$ Cfu/ml) where an increase was observed. The lower bacterial count observed at sites S1, S2 and S4 may be due to the ability of water to purify itself naturally. The increase in S2 could be as a result of discharge of animal waste from animals grazing in the open fields or those used for farming by the community around the study area.

The colony forming unit in ground water sites U1, U2 and U4 ($25 \times 10^4 - 10 \times 10^4$Cfu/ml) were less than U3 (31×10^4Cfu/ml). The hand dug well (U3) had openings around it through which water and other impurities seep into it and this could have informed the increase in the colony forming unit. The higher coliform values recorded from the study sites may be as a result of humanfaeces, animal feaces and other wastes from anthropogenic activities in the bushy locations close to the wells. Eventually they could be washed by rain water as run-off into the wells and thus contaminate it.

CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

The present study analysedpH,turbidity, electrical conductivity, dissolved oxygen, biochemical oxygen demand, chemical oxygen demand, nitrate, sulphate, phosphate and temperature of the water samples from the surface and ground water sites. The dissolved oxygen was lower than the WHO standard for aquatic life. This can pose risk to the aquatic life present within the study area.Turbidity exceeded the permissible limit set by WHO(2011). All other parameters were below the WHO permissible limits. From the correlation studies, nitrate and sulphate may serve as useful indices for water quality in the surface water.

Some of the metals analysed in the surface and underground water sites were below the WHO standard limits in some sites except for Cr and Pb which exceeded the standard limits in all the sites studied. This can pose harm to the rural dwellers that use this water sources for drinking and other uses.Fe was high in all the sites studied.This could be attributed to its bioavailability in the environment and its essential role in haemoglobin.

Organic pollutants were identified in the ground and surface water samples in the study area. ButylatedHydroxyltoluene, Toluene, Xylene and Ethylbenzenewere identified.

The values obtained from the microbial analysis indicate high densities of coliform count in the surface and ground water sites. This is an indication of faecal contamination of the water bodies. It may be due to the discharge of hospital wastewater and other impurities from non-point sources.

6.2 Recommendations

It is recommended that:

i. Governmental policies on waste disposal and management should be enacted and strictly enforced.
ii. Further studies should be carried out to on how to degrade organic pollutants into harmless compounds.
iii. Further studies should be carried out to identify active pharmaceutical ingredients present in the hospital liquid waste and its impact on the water bodies in the vicinity of the wastewater plant.
iv. Ahmadu Bello University Teaching Hospital Management should upgrade their treatment processes.

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