QUALITY ASSESSMENT OF HAND DUG WELLS WATER IN OTUKPO TOWN AND ITS ENVIRONS, BENUE STATE, NIGERIA

BY

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DECLARATION

I declare that the work in this thesis titled "Quality Assessment of Hand Dug Wells Water in Otukpo Town and Its Environs, Benue State, Nigeria" was performed by me in the Department of Chemistry, under the supervision of Professor V.O. Ajibola. The information derived from literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree at any university.

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CERTIFICATION

This thesis titled ”Quality Assessment of Hand Dug Wells Water in Otukpo Town and Its Environs, Benue State, Nigeria ” meets the regulations governing the award of the degree of Masters of Science of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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Prof. A. A. Joshua Dean, School of Postgraduate Studies	_____ Signature	_____ Date

DEDICATION

This work is dedicated in loving memory of my late father, Mr. M. O. Owuna.

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I remain eternally grateful to God almighty for His love, mercies and grace bestowed upon me during the course of this work, and filling the vacuum human beings could not occupy.

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ABSTRACT

This study determined the quality of twenty five underground water samples in Otukpo town and environs using eighteen physicochemical parameters. Samples were collected between May and June 2010 when underground water flow was high. The water quality of the wells examined, especially wells in cluster 4, were in conformity with World Health Organization standard for most of the parameters measured. Multivariate statistical techniques, such as principal component analysis (PCA), cluster analysis (CA) and discriminant analysis (DA) were applied to evaluate spatial variation and identify sources of pollution. Spatial CA generated a dendrogram consisting of four statistically significant clusters while PCA of the whole data also yielded four sets explaining 60.21% of the total variance. Discriminant analysis using the standard and stepwise mode rendered the corresponding group memberships, correctly assigning 96% of the original grouped cases. Standard mode DA suggested that Cd, Pb, Mn and *Escherichia coli* were the discriminant variables while the stepwise mode had colour, K and Pb as variables that discriminated between the wells.

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ABBREVIATIONS

AAS	-	Atomic Absorption Spectrophometer
ANOVA	-	Analysis of Variance
BOD	-	Biochemical Oxygen Demand
CA	-	Cluster Analysis
COD	-	Chemical Oxygen Demand
DA	-	Discriminant Analysis
DS	-	Dissolved Solid
EC	-	Electrical Conductivity
EDTA	-	Ethylenediaminetetracetic acid
e.g.	-	For Example
e.t.c.	-	And So Forth
FTU	-	Forrnazin Turbidity Unit
i.e.	-	That Is
NPK	-	Nitrogen Phosphorus Potassium
SPSS	-	Statistical Package for the Social Science Software
US-EPA	-	United State Environmental Agency
WHO	-	World Health Organization

CHAPTER ONE

INTRODUCTION

1.1 Water

Water is essential for life. It is a universal solvent and is the most abundant substance in plants and animals tissues, as well as, the world around us (Fabio *et al.,* 2009). Metabolic functions within living cells occur in aqueous medium. Water carries waste out of the cells and finally out of the body. Water occurs in all spheres of the environment- in the oceans as a vast reservoir of salt water, on land as surface water in lakes and rivers, underground as groundwater, in the atmosphere as water vapour and in polar ice caps as solid ice (Bhatia, 2002). About 97.2% of water on earth is salty and only 2.8% is present as fresh water from which about 20% constitutes ground water (Goel, 2000).

The major sources of water include rainfall, snow, sleet, hail, fog and dew from the atmosphere. On the solid part of the earth (lithosphere), there are lakes, rivers, streams, waterfalls, glaciers, oceans and seas; there are also underground waters (Nebel and Wright, 1993). Precipitation and hence water resources are far from evenly distributed on the earth. Some regions are heavily endowed with water such as areas along the equatorial axis while others experience water shortage or scarcity. Also, the major seasons of these zones play a significant role in the distribution of water e.g. winter, summer, autumn and spring all are occasioned by different variation of rainfall, icefall, snowfall, etc (Raven and Berg, 1998).

In Nigeria, however, water is more abundant in the southern part that lies just above the tropical equatorial region while the central and northern parts have variable water supply depending on the season (Filani, 1991).

Since water is constantly recycled in the biosphere, it is theoretically a sustainable resource.

1.2 Ground Water Source

Ground water is both an important direct source of water supply, which is tapped by wells, and a significant indirect source of supply, since a large portion of the flow streams is derived from subsurface water. This is formed as a result of a portion of precipitation (rainfall and snowfall), which sink into the ground. Groundwater movement is generally slow and not as much mixing occurs in an aquifer as with the case of surface waters. Its quality changes as water percolates through natural sediments. These changes are drastic in certain sediments, while negligible in other cases (Deju *et al.,* 1990). During its movement through the surface layers of the earth, it carries some minerals as it passes through porous rocks, since the rocks are subject to mechanical and chemical weathering and leach out (Glenn and William, 1981).

Near the surface of the earth, in the zone of aeration, soil pore spaces contain both air and water. These zones, which may have a zero thickness in swamp lands and several hundred feet thick in mountainous regions, contain three types of moisture. Gravity waters are in transit after a storm through small pore space by capillary action and are available for plant up-take. Hydroscopic moisture is water held in place by molecular forces during all seasons except the driest climatic conditions. Moisture from the zone of aeration cannot be tapped as a water supply source.

The zone of saturation offers water in a quantity that is directly available. In this zone, located below the zone of aeration, the pores are filled with water, and this is considered as ground water (Vesilind and Pierce, 1983). Ground water is highly valued because of certain

properties that are not possessed by surface water. It is usually characterized by low contents of organic substances and as such usually preferred as a source of drinking water (Goel, 2000).

1.3 Justification of Study

Well water is a major source of water supply to the entire populace of Otukpo and its environ, owing to the fact that, there is inadequate supply of pipe-borne water from the water works and no boreholes because the area is underlain by the Agwu shales, a unit of cretaceous sedimentary formation of the Benue valley which is generally considered to be hydrogeologically difficult due to the poor hydraulic characteristics.

This research therefore, became necessary to ascertain the quality of the wells and invariably its suitability for various purposes, in order to ensure the protection of the health of users and determine liable sources of pollution. The information will be of great importance to relevant authorities, since such research has not been carried out in the area.

1.4 Scope and Aims of Study

a. This study covers analysis of twenty five wells in different locations of Otukpo town and four surrounding villages and seeks to determine and characterize the quality of groundwater (wells) in Otukpo town, where well water serves as a main source of water supply.
b. To determine the suitability of wells for various purposes.
c. Determine factors (or parameters) that are discriminate among them.
d. To determine the source(s) of contamination.
e. To evaluate the spatial variation of water quality parameters and their distribution geographically.

1.5 Objectives of study

a. To determine the physical characteristics (odour, colour, turbidity, total dissolved solids, suspended solids, taste) of the wells.

b. To determine the chemical characteristics (pH, conductivity, hardness, COD, DO, silicates, nitrates, phosphate, ammonia, chloride, Pb, Ca, K, Na, Mn, Cd, Cr) of the wells.

c. To determine biological characteristics (BOD, and total coliform count) of the wells.

CHAPTER TWO

LITERATURE REVIEW

2.1 Water Quality

Water is one of the most indispensable resources and is the elixir of life. It 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 media for both chemical and biochemical reactions and also serves as an internal and external medium for several organisms (Rajankar *et al.,* 2009). Additionally, basic functions of a society require water; for cleaning, for public health consumption, for industrial processes and cooling 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 it's consistent good quality, which makes it an ideal supply for drinking water (UNESCO, 2000). However, ground water resources are under a serious threat due to growing interest in mechanized agricultural practices, increasing population density and rapid urbanization as well as domestic and industrial usage. Ground water provisions are sometimes unsustainable because of poor water productivity of wells, drying of wells after prolonged drought and sometimes due to poor water quality (Kortatsi, 1994; Xu and Usher, 2006).

Contaminated water resources have important implications on health and environment (Peterson *et al.,* 1971). The importance of water quality in 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 pollution sources. For example, Hamilton and Helsel (1995) stated that a connection between agricultural and ground water pollution is well

established. According to Chandio (1999), applications of Nitrogen Phosphorus Potassium fertilizer (NPK) have been increasing in Pakistan over the last few decades. As a result, 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 analysis 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 (surface and ground water) may be considered as a naturally induced change in water quality or conditions induced directly by man's numerous activities which renders it unsuitable for food, human health, industry, agriculture or leisure per suit (Dix, 1981; Cifuentes and Rodriguez, 2005). With exploding population and increasing 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 under developed and developing countries. Thus, the quality as well as the quantity of clean water supply is of vital significance for the welfare of mankind.

2.2.1 Types of Water Pollution

Water pollution may be divided into the following five major categories on the basis of sources and storage of water:

1) Groundwater pollution 2) Surface water pollution

3) Lake water pollution 4) River water pollution

5) Sea water pollution

Groundwater pollution

Groundwater contamination is generally irreversible, i.e. it is difficult to restore the original water quality of the water of the aquifer once contaminated. Excessive mineralization of groundwater degrades water quality producing an objectionable 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, but groundwater is not completely free from the menace of chronic pollution (Bhatia, 2009). The extent of groundwater pollution depends on the following factors: (a) Depth of water table; (b) Rainfall pattern; (c) Soil properties; (d) Distance from the sources of contamination.

Pollutant of groundwater can be classified broadly into five categories as follows:

1. **Organic Pollutants**: The organic pollutants may be further categorized as follows:
   a. **Oxygen - Demanding Wastes**: These include domestic and animal's sewage, biodegradable organic compounds and industrial wastes from food processing plants, meat-packing plants, slaughter-houses, paper and pulp mills, tanneries, etc., as well as agricultural runoff. All these wastes undergo degradation and decomposition by bacterial activity in presence of dissolved oxygen (DO) and this result 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, which is essential for supporting aquatic life. Any decrease in this value is an index of pollution by the above mentioned oxygen-demanding wastes.
   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 synthetic pesticides, synthetic detergents (syndents), 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 lie, resistant to microbial degradation. Organics such as aromatic chlorinated hydrocarbons may causes offensive colours, odours and tastes in water, even when present in traces and 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:** Raw sewage dumped into shallow soak pits and seepage from polluted lake, pond or stream pollutes water. Fertilizers, pesticides, insecticides, processing wastes and animal waste etc. are added to the 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. It 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. This pollution reduces the DO in water.

2. **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 metal 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 release 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.

3. Suspended Solids and Sediments

Sediments are mostly contributed by soil erosion, natural processes, 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 thus shortens their life. 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.

4. Radioactive Materials

The radioactive water pollutants may originate from the following anthropogenic activities:

a. Mining and processing of ores, e.g. uranium tailings.

b. Increasing use of radioactive isotopes in research, agricultural, industrial and medical/diagnostic, as well as, therapeutic applications e.g. I^{131}, P^{22}, Co^{60}, Ca^{45}, S^{35}, C^{14}, Rb^{86}, Ir^{132} and Cs^{137}.

c. Radioactive materials from nuclear power plants and nuclear reactors, e.g. Sr^{90}, Cs ^{127} Pu^{248}, Am^{241}.

d. Radioactive materials from testing and use of nuclear weaponry, e.g. Sr^{90}, Cs^{137}. The radioactive isotopes found in water include Sr^{90}, I^{131}, Cs^{37}, Co^{60}, Mn^{54}, Fe^{55}, Pu^{239}, Ba^{140}, K^{40}, Ra^{226}. These radioactive isotopes are toxic to life forms.

5. Heat

Waste heat is produced in all processes in which heat 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 the 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 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 (Nsi, 2007).

2.3.1 Physico-Chemical Characteristics

Most common physical contaminants of water are suspended sediments. These are properties which are often apparent to casual observer 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 by manufactured chemicals**.**

a. **Taste and Odour**

The odour in potable water may be defined as the sensation due to the presence of substances having an appreciable vapor pressure and stimulates the human sensory organs in the nasal and sinus cavities (Nsi, 2007). Odour in water may have natural origins, such as earthly, fishy, rotten hydrogen sulphide, aromatic swampy, clayey or artificial flavors, for instance, of chlorine, camphor, pharmaceuticals, e.t.c. (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).

b. **Colour**

Colour is the sensation produced in the eyes by the rays of a decomposed light. Even pure water is not colourless: it has a pale green-blue tint in large volumes. It is necessary to differentiate between true colour due to material in solution and apparent colour due to suspended matter. Natural yellow colour in water from upland catchments is due to organic acids which are not in any way harmful, being similar to tannic acid from tea (Tebbutt, 1983). 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).

c. **Turbidity**

Turbidity may be defined as the measure of clarity of water. It 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 index of the particulates (Vesilind and Pierce, 1983; Nsi, 2007).

d. **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 settleable and non- settleable solids (Nsi, 2007).

e. **Electrical Conductivity**

Conductivity is a quantitative measure of the ability of water to pass 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. Thus, organic compounds do not ionize greatly in aqueous solutions; therefore organic pollutant would not be monitored by conductivity measurement (Nsi, 2007).

f. **pH**

The degree of acidity or alkalinity of any water is determined by its hydrogen ion concentration, pH. This is defined by

$pH = - \log_{10} [H^+]$

$[H^+]$ is the concentration of hydrogen ions in solutions moles/liter. The pH is measured using pH meter. Most natured water usually has pH between 6.0 and 9.0. However, 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.

g. **Alkalinity**

The capacity of water to accept H^+ ions 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 fertility. Generally, the basic species responsible for alkalinity in water are bicarbonate ion, carbonation, and hydroxide ion.

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \quad (2.1)$$

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \quad (2.3)$$

$$OH^- + H^+ \rightarrow H_2O \quad (2.3)$$

h. **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, 1993). An elevated hardness, however, makes water unsuitable for domestic and industrial use.

Hardness can be determined by various methods such as EDTA, tritrimetric method (Vesilind and Pierce, 1983).

2.3.2 Metallic Pollutants

Some metallic elements present in natural waters act as pollutants. Typical chemical form or oxidation state for each element is also present. In any particular situation, the element might be present in some other form, depending on the source. It should be noted that, many of the metals that can act as a pollutant are actually essential in human nutrition. For example copper has a relatively low toxicity. An absence of copper in the diet produces an anemic or iron deficient condition, because copper is used in the body along with iron in some metabolic processes. The minimum dietary requirement is in the order of 2mg of copper daily. However, a much higher intake, say about 55mg daily cause diarrhea, vomiting and other miserable symptoms.

Metals vary a great deal in their toxicity and in the toxic effects they bring about. This is so because they differ in the kind of chemical reactions they undergo with biochemical systems. Cadmium, for instance owes its high toxicity to the fact that, it is chemically similar to zinc, a metallic element that is essential in many biochemical reactions. For example, zinc is an essential part of carbonic anhydrase, the enzyme that catalyzes the reaction of carbondioxide and water. When cadmium takes the sites of zinc, it fails to perform precisely as zinc would and this brings about serious problem.

a. **Cadmium** - Cadmium is not essential in nutrition but has high toxicity.

   Its' toxicity effect are felt in the form of high blood pressure, kidney damage and red blood cells loss. The limit per liter is 0.01mg.

b. **Chromium** - This is present in aquatic system as CrO_4^{2-}. It is essential in nutrition.

   It has medium level toxicity. Chromium is expected to be carcinogenic. Its major source is electroplating. The maximum tolerable level is 0.5mg/l.

c. **Lead** - Lead is not essential in nutrition and has high toxicity level. It causes anemia, kidney failure, mental retardation (in children) and convulsions when taken above the maximum tolerable level of 0.05mg/l. Sources of lead to aquatic system include lead piping, lead paints and auto emissions from lead petrol as well as batteries.

d. **Manganese -** Manganese is essential in nutrition and low level of toxicity. Its toxicity effect is not well characterized. 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).

2.3.3 Biological Characteristics

Biological contaminants are primarily from animal and human wastes. The presence of organic matter and bacteria are measured by Biological Oxygen Demand (BOD) and 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 microorganisms 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, *Escherichia coli*, which is present in excrement. 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.

2.4 STATISTICAL TREATMENT OF DATA

Environmental data is complex and depends on unpredictable factors that are usually characterized by their high variability. The main origins of this variability are geogenic, hydrological, meteorological and also anthropogenic (such as different emitters and discharges) (Einax *et al.*, 1998). Due to the non – linear nature of environmental data, analyzing these data may be tricky. The multivariate nature of these data together with the complex interrelation requires that, multivariate data analysis techniques be employed.

Multivariate statistics can be used to evaluate large amounts of data in order to decipher patterns within the data set that otherwise might not be observed. In this study, the application of chemometric methods was used to determine the number of sampling sites which appear significantly different to each other, the variables that account for their similarities and factors that caused variations in the observed quality data.

Chemometrics can be defined as "a chemical discipline that uses mathematics, statistics and formal logic;

a. To design or select optimal experimental procedures.
b. To provide maximum relevant chemical data, and
c. To obtain knowledge about chemical systems.

Chemometric methods have been used for the classification and comparison of different samples (Massart *et al.,* 1997). Some examples of the use of chemometrics are as a multicriteria decision making (Khali *et al.*, 2003), chemometric investigation of variable and site correlations (Abollina *et al.*, 2001), determination of correlation of chemical and sensory data drinking waters by factors analysis (Meng and Suffet, 1997).

The chemometric methods used in this study were principal component analysis (PCA), cluster analysis (CA) and discriminate analysis (DA). Prior to any multivariate statistical analysis, the data were arranged in a (n x p) metric, representing the number of samples (n), that is, the well and the number of variables (p), including all parameters analyzed.

Most multivariate statistical methods required variables to conform to the normal distribution thus, normality of the distribution of each variable was checked by analyzing kurtosis and skewness statistical test. Since most of the values of kurtosis and skewness were greater than zero, the original data were transformed in the form $x = (\log Y)^2$ (Kowalkowski *et al.*, 2006; Papatheodorou *et al.,* 2006).

2.4.1 Principal Component Analysis (PCA)

PCA is simply the generation of pairs of eigen values and eigenvectors (Johnson and Wichern, 2002). Eigen values describe the amount of variation within the original data set explained by each principal component (loadings). PC scores are linear combinations of the standardized data and the loadings and therefore combine information on all the hydrochemical measurements for given samples into a single number. The total number of principal components generated indicates the total numbers of possible sources of variation in the data, components are ranked in order of merit. Often, the population variability for large data sets, such as those with large number of samples and variables can be attributed to the first one, two

or three components (Johnson and Wichern, 2002). The first component has the highest eigenvectors sum and represents the most important source of variation in the data. The last component is the least important process contributing to the chemical variation. In order to maximize the variation among the variables under each component, the component axis was subsequently varimax rotated. PCA is a data reduction technique used to simplify data sets, while capturing the underlying pattern within the data (Stetzenbach *et al.*, 1999; Farnham *et al.*, 2003). It helps extract the principal factors corresponding to the different sources of variation in the data.

2.4.2 Cluster Analysis (CA)

Cluster analysis is a statistical classification technique in which data or observations are subdivided into groups (clusters) such that the item in a cluster are similar (but not identical) to one another and very different from items of another cluster. It is a discovery tool that reveals association, relationships and structure.

In this study, hierarchical CA was performed on the standardized data using Ward's method with squared Euclidean distances as a measure of similarity. Euclidean distance usually gives similarity between two samples and a distance can be represent by the difference between transformed values of the samples (Otto, 1998). Ward's method uses analysis of variance (ANOVA) to calculate the distances between clusters, attempting to minimize the sum of square of any two possible clusters at each step (Ward, 1963). The analysis detects multivariate similarities between sampling sites (wells).

2.4.3 Discriminant Analysis (DA)

DA is a method applied on already generated groups from cluster analysis to determine the significance of different variables that allow for separation of groups. It is a method of analyzing dependence, that is, a special case of canonical correlation, and one of its objectives is to determine the significance of different variables , which can allow the separation of two or more naturally occurring groups. DA operates on original data, and the method constructs a discriminant function for each group (Johnson and Wichern, 1992; Wunderlin *et al.*, 2001) as follows;

$$f(G_i) = K_i + \sum_{j=1}^{n} W_{ij}.P_{ij}$$

where *i* the number of group (G), K_i is the constant inherent to each group, n is the number of parameters used to classify a set of data into a given group, w_j is the weight coefficient as assigned by DA to a given parameter (P_j). In this study, DA was performed on the original data using standard mode and stepwise mode. The sampling sites were the group variable and measured parameters were the independent variables which were used to build the best discriminant functions that would allow an assessment of the variation of water quality. All the statistical and mathematical calculations were performed using the Microsoft office – Excel spread sheet (2007) and "Statistical Package for the Social Sciences Software - SPSS 17.

CHAPTER THREE

EXPERIMENTAL

3.1 Description of Study Area.

The study area (Figures 3.1 and 3.2) is Otukpo town in Otukpo Local Government Area and located along latitude $7^{o}13^{o}57^{o}$N and longitude $8^{o}05^{o}26^{o}$ E of Benue State. It is bounded to the North by Apa Local Government, the East by Obi Local Government, and the South by Ohimini Local Government, all of Benue State. The town is strategically located at the intersection of the eastern railway line and the only trunks "A" road linking the Northern parts of the country to the Eastern parts.

The town has double maxima rainfall: the major one is around April – July and the minor between September – October. The dry dusty harmattan wind blow from the North between November and December. Depending upon a particular year, there are variations of rain output, thus from no rains, isolated rains or fair to heavy rains.

The area is underlain by the Agwu shales, a unit of cretaceous sedimentary formation of the Benue valley. The sedimentary rock consists of lateritic soils, clays and shales with occasional thin lenses of sand stone. Besides, the area is endowed with thick forests. The cultural life of the people in Otukpo is linked to farming, trading, small scale soap-making and palm oil industries. The choice of sampling sites and locations was due to their strategic location, bulk of human activities as well as population densities. Twenty five samplings points in thirteen zones within the town were earmarked for ground waters sampling (Fig 3.3). These points are listed in the Table 3.1:

Table 3.1: Sampling Sites and their Designated Codes

Site codes	Locations
OT-1	Igbanomaje 1
OT-2	Igbanomaje 2
OT-3	Obaganya 1
OT-4	Obaganya 2
OT-5	Depot 1
OT-6	Depot 2
OT-7	Zone HB 1
OT-8	Zone HB 2
OT-9	Eupi 1
OT-10	Eupi 2
OT-11	New Heaven 1
OT-12	New Heaven 2
OT-13	Ojira 1
OT-14	Ojira 2
OT-15	Rice Mill
OT-16	G.R.A 1
OT-17	G.R.A 2
OT-18	Asa 1
OT-19	Asa 2
OT-20	Edikwu 1
OT-21	Edikwu 2
OT-22	Upu 1
OT-23	Upu 2
OT-24	Ikobi 1
OT-25	Ikobi 2

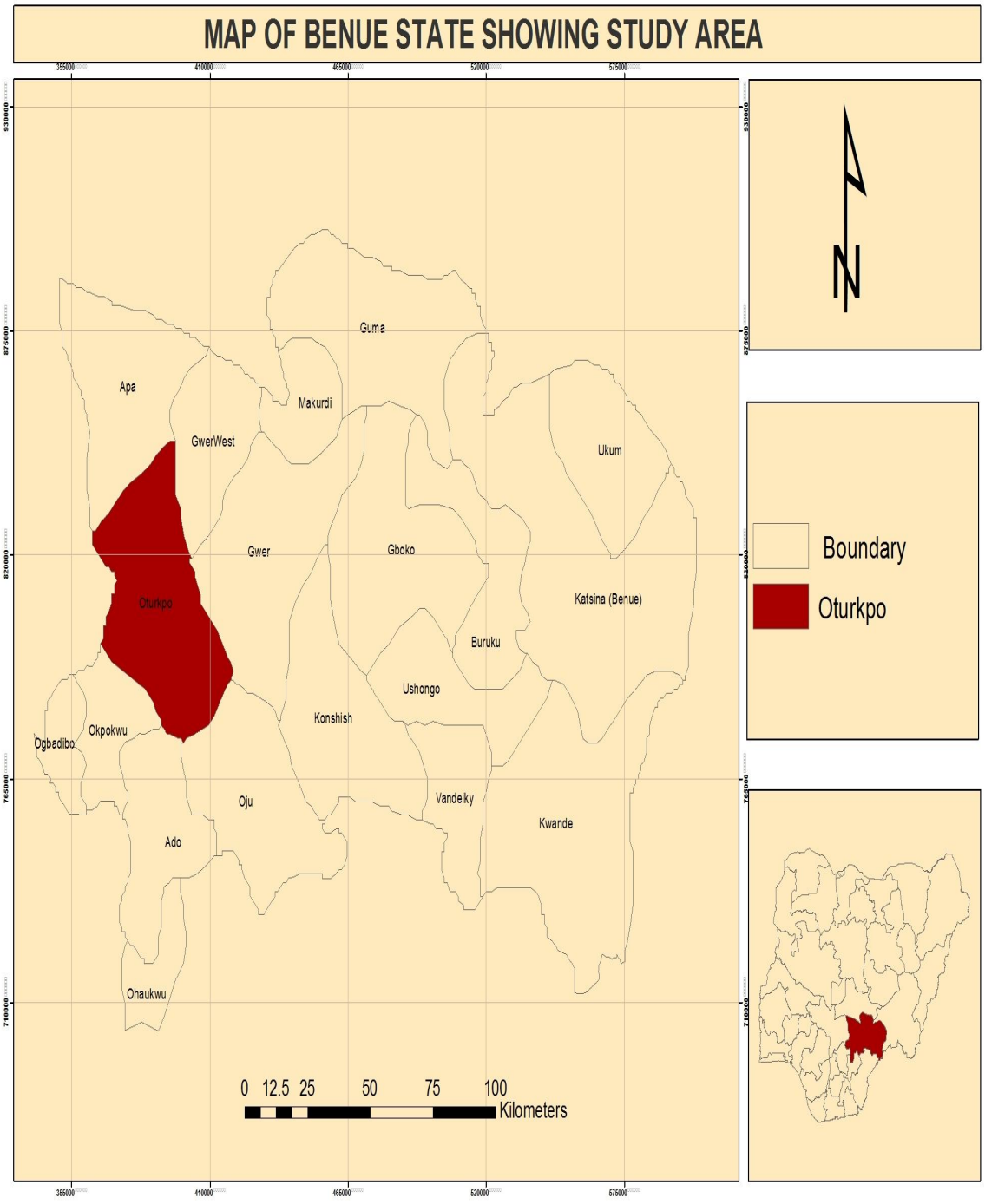


Figure 3.1: Map of Benue State showing Otukpo Local Government Area

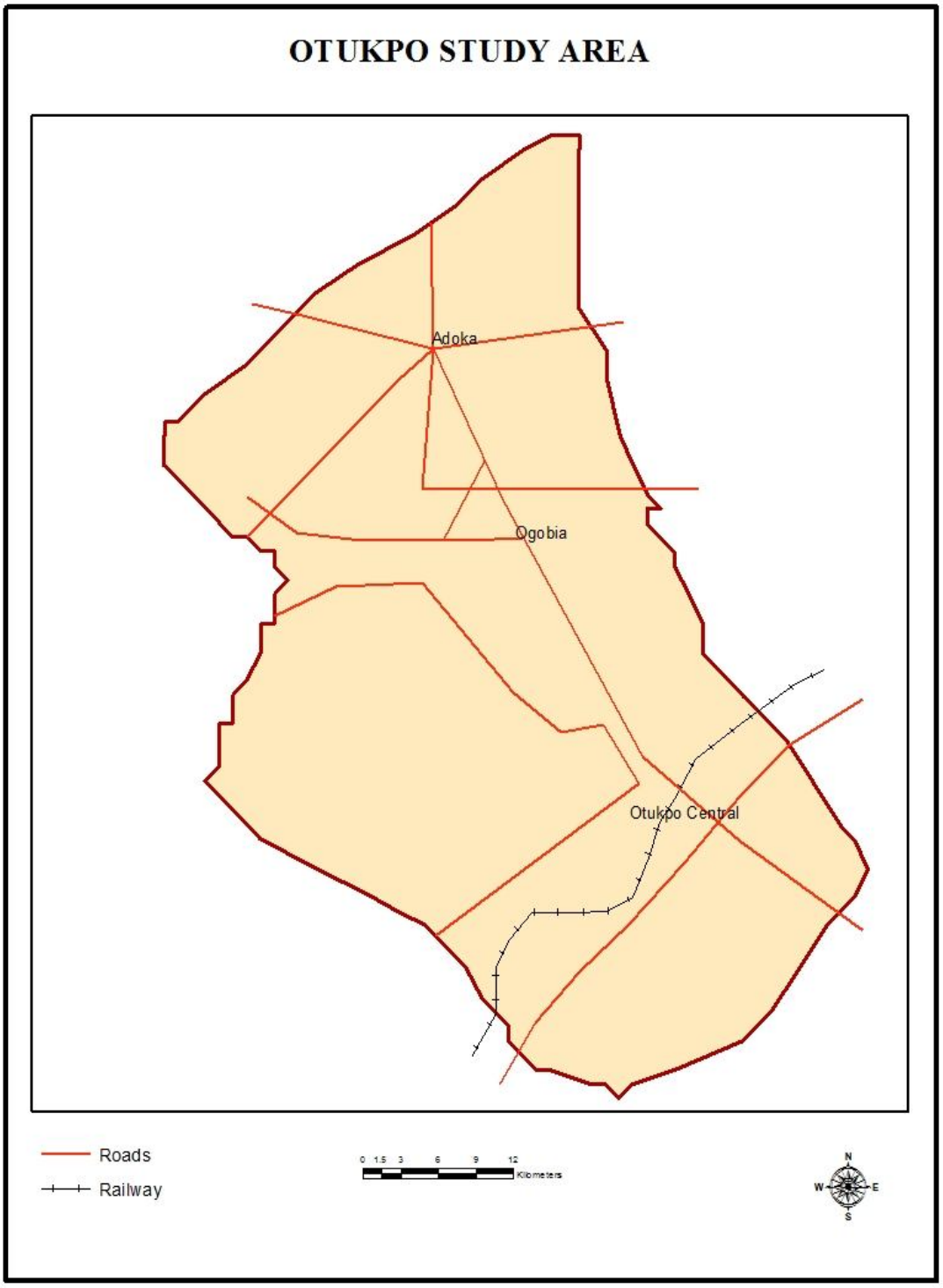


Figure 3.2: Map of Otukpo Local Government Area

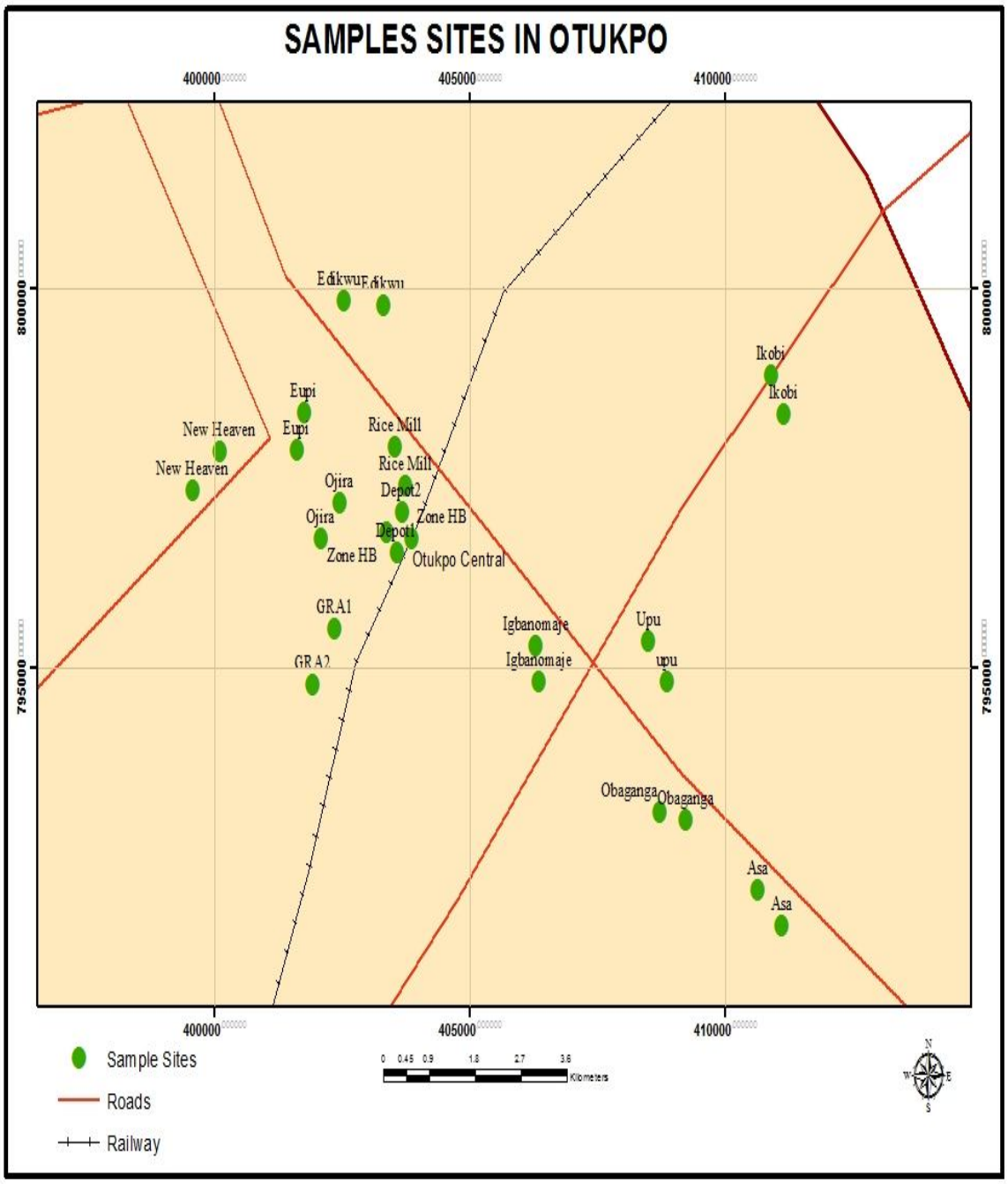


Figure 3.3: Map of Otukpo Town Showing the Sampling Sites

3.2 Sample Collection and Treatment

Water from the study area which comprised twenty five sampling wells was collected between May and June (30^{th} May, 5^{th} June and 10^{th} June) the peak of raining season. The wells earmarked for sampling were picked from each zone to give a good representation of the entire study area. Fifteen of these wells are sited in private residence, three are public wells, five of the wells are located along the flow path of pit latrines and two are sited by a market. The choice of wells sited with different activities around them is to ascertain how this contributes to variation in their quality.

Samples from the wells were collected in duplicate by lowering a clean plastic container tied to a synthetic rope down the well. Four litres of samples collected were transferred into washed and labeled containers and labeled appropriately.

Samples for heavy metals determination was preserved by adding analytical grade HNO_3 acid, causing it to attain a pH of 2. Those for bacteriological analysis were preserved in well sterilized glass bottles and stored in ice box at 4^oC to 10^oC

3.3 Determination of Physico-Chemical Parameters

Standard methods as recommended by relevant authorities such as World Health Organization (WHO), United State Environmental Protection Agency (US- EPA), etc were employed for the preparation of reagents and determination of all water quality parameters.

3.3.1 Preparation of pH 9 Buffer Solution

30g of MgCl was weighed and mixed with 5g of sodium acetate in a beaker and 1g of potassium nitrate was added, then $20cm^3$ of acetic acid was introduced and the mixture was

diluted with 500cm^3 of distilled water and was then transferred into a volumetric flask and made up to 1litre.

3.3.2 Preparation of 0.01M Ethylenediaminetetracetic Acid (EDTA)

60g of EDTA was dissolved with distilled water and mixed in 60cm^3 of NH_4OH in a beaker.

3.3.3 Preparation of 0.04M Potassium dichromate

12.259g of $K_2Cr_2O_7$ was weighed and dissolved in a litre of distilled water in a volumetric flask.

3.3.4 Preparation of 0.8M Alkali-iodide azide Reagent

100g of NaOH was dissolved in 125cm^3 of distilled water in a beaker and cooled slightly to produce Solution A. Then 225g of Sodium iodide was dissolved in solution A to produce solution B. 2g of Sodium azide was weighed and dissolved in 10cm^3 of distilled water and mixed separately, it was then added to the mixture of solution A and B and made up to mark in a 1litre volumetric flask.

3.3.5 Preparation of Starch Solution

2g of soluble starch and 0.2g of Salicylic acid was weighed and dissolved in 100cm^3 of distilled water in a conical flask.

3.3.6 Preparation of 0.21M Ammonium molybdate

25g of Ammonium molybdate crystal was dissolved in 175cm^3 of distilled water in a beaker. H_2SO_4 (with specific gravity of 1.84) was diluted with 400cm^3 of distilled water in a

beaker and allowed to cool, and then the molybdate solution was added to it and transferred into a volumetric flask and made up to 1 litre.

3.3.7 Preparation of 0.11M Stannous chloride

2.5g of $SnCl_2.2H_2O$ was weighed and added into 100cm^3 of glycerol in a beaker. It was then heated in a water bath while been stirred with a glass rod to produce stannous chloride solution.

3.3.8 Preparation of 2.13M Manganous sulphate

90g of $MnSO_4$ was weighed and dissolved in 250cm^3 of distilled water in a beaker.

3.3.9 Determination of Temperature.

The temperature was determined in situ with a Hg filled glass thermometer. The thermometer was dipped into each sample and observed to movement of the Hg thread, reading was taken at point when there no more development. It was ensured that the thermometer was brought to room temperature (30^oC) before each reading was taken and held upright to avoid parallax error (US-EPA, 1983; APHA-AWWA-WPCF, 1985; Trivedy and Goel, 1986).

3.3.10 Determination of pH

The pH meter was standardized using buffer solutions of pH 4 and 9, the response of the pH meter corresponded with the manual temperature of the buffer solution at both instances. Before each sample was measured, the electrode was placed in distilled water. In measuring the pH of sample, the meter was placed inside the sample and the electrode response taken. This was repeated thrice for accuracy for all samples measured (US-EPA, 1983; APHA-AWWA-WPCF, 1985; Trivedy and Goel, 1986).

3.3.11 Determination of Colour

Colour was determined by visual comparism using Lovibond colour disc (Pt-Co).The disc consist of different colours which is graduated. Sample was placed on disc and observed to see colour changes, and then the reading was taken for the colour which it corresponds with (US-EPA, 1983; ARHA-AWWA-WPCF, 1985; Trivedy and Goel, 1986).

3.3.12 Determination of Odour

Sample was introduced into a bottle that has been rinsed with 4M HCl and distilled water. A stopper was inserted in the bottle and shaken for 2 or 3 seconds. The stopper was removed and quickly the odour was observed by putting the nostrils near the mouth of the bottle (WHO, 1985; Nsi, 2007).

3.3.13 Determination of Conductivity

A conductivity meter was used .The conductivity cell was calibrated with the standard KCl solution. The sample was brought to room temperature. The conductivity cell was washed with portion of the sample and then filled completely with the sample ensuring there was no air bubble adhered to the electrode and reading taken. The results were expressed as micro siemens per centimeter (μS/cm) (US – EPA, 1983; APHA – AWWA – WPCF, 1985; Trivedy and Goel, 1986; NWRI, 2001).

3.3.14 Determination of Turbidity

A nephelometer was used in determining turbidity of the samples. The turbidimeter was first set to zero with distilled water. Sample was thoroughly shaken and a portion of it poured into the sample tube, making sure that no air bubbles were trapped. The sample tube was shaken

vigorously and then thoroughly wiped dry and then inserted into the instrument and the reading noted. Calibration curve was prepared from standard turbidity suspension (Formazin polymer which is a product of hydrazine sulphate and hexamethylenetetramine). Standard solutions of the suspension of concentrations of 5, 10, 15, 20, 25, and 30 were prepared and this was used to determine the turbidities of the samples and to calibrate the instrument. The unit of measurements is called Formazin Turbidity Units (FTU) (Knight, 1951; Mechan and Beattle, 1961).

3.3.15 Determination of Total Hardness

The EDTA titration method was used in determining the total hardness of the samples. The sample was shaken thoroughly. 25cm^3 of the sample was taken and diluted with 50cm^3 of distilled water and transferred quantitatively into a clean 250cm^3 Elemeyer flask. 2cm^3 of buffer solution ($NH_4CL - NH_4OH$) was added, followed by two drops of Eriochrome Black indicator and the sample titrated with standard EDTA solution that has been standardized using the standard calcium solution. The formation of blue colour indicated the end point, titre value was recorded. (US-EPA, 1983; APHA-AWWA-WPCF, 1985; Trivedy and Goel, 1986; NWRI, 2001)

Calculation

$$\text{Hardness (EDTA)} \quad \text{as mg } CaCO_3$$

$$= \frac{A \times B \times 100}{\text{ml of sample}}$$

where A = Titre for sample (ml) and B = mg $CaCO_3$ equivalent to 1.00ml EDTA titrant

3.3.16 Determination of Total Dissolved Solids

100ml of the sample was quantitatively transferred into an evaporating dish that has been previously weighed and dried in an oven for one hour and cooled in desiccators. The content of the dish was evaporated to dryness on a water-bath to a constant weight. The residue was dried in an oven between 103-105^{o}C for two hours, cooled in a desiccators and the difference in weight calculated (US-EPA, 1983; APHA-AWWA-WPCF, 1985; Trivedy and Goel, 1986; NWRI, 2001).

Calculation

$$\text{TDS (mg/l)} = \frac{\text{difference in weight x 1000}}{\text{ml of sample}}$$

.

3.3.17 Determination of Suspended Solids

A 20cm^3 of well-mixed water sample was filtered through Gooch funnel under slight suction ensuring all solids were transferred ,the residue was washed three times with about 5-10cm^3 of water allowing to drain free from water after each wash. The residue was placed on a watch glass and dried in an oven at 105^{o}C for one hour. It was then allowed to cool in a dessicator and its constant weight was taken. Weight of the filter was subtracted to obtain the weight of the suspended solids (Nsi, 2007).

Calculation

$$\text{SS (mg/l)} = \frac{\text{mgSS x 100}}{\text{ml sample}}$$

3.3.18 Determination of Chemical Oxygen Demand (COD)

20cm^3 of sample was placed in a 500cm^3 refluxing flask. 10cm^3 of standard $K_2Cr_2O_7$ with several glass beads already heated for 1 hour was added and 30cm^3 of sulphuric acid containing 0.4g of Ag_2SO_4 was added slowly and mixed to dissolve Ag_2SO_4. It was then refluxed for 1hour.It was cooled and diluted with 150cm^3 of distilled water, the mixture was titrated against standard ferrous ammonium sulphate (FAS) using 0.15cm^3 ferrion indicator. Reflux of blank containing the reagents was also titrated as above (Nsi, 2007).

Calculation

$$\text{COD as } O_2/l = \frac{(A-B) \times M \times 8000}{\text{ml of sample}}$$

where A = ml FAS used for blank, B = ml FAS used for sample and M = Molarity of FAS

3.3.19 Determination of Dissolved Oxygen and Biochemical Oxygen Demand

The Azide modification of the Winkler's method was used to determine DO and BOD. 250cm^3 of the sample was introduced into a stopped dark bottle and 2cm^3 of manganese sulphate solution and 2cm^3 alkali-iodide-azide reagent was added and mixed by inverting the bottle several times. Then 5cm^3 of H_2SO_4 was added immediately precipitate settled. The bottle was then shaken to ensure distribution of iodine. 25cm^3 of the mixture was taken into a conical flask and titrated against 0.01M sodium thiosulphate, until titrand changed to pale-straw colour. 5cm^3 of starch indicator was then added to it and the titration continued until first disappearance of the blue colour. The titration was carried out three times and average titre value was noted as dissolved oxygen (DO).

A fresh sample was incubated at 20°C for 5 days and the above procedure repeated with it. The difference between DO for incubated sample and DO not incubated was determined (US-EPA, 1983; APHA – AWWA – WPCF, 1985).

Calculation

$$\underset{\text{mg/l}}{BOD_5} = \frac{DO0 - DO5}{\text{dilution factor}}$$

where dilution factor = $\frac{\text{No of days}}{\text{ml of sample}}$

3.3.20. Determination of Nitrate.

100cm^3 of the sample was evaporated to dryness on a boiling water bath. The residue left in the dish was treated with phenoldisulphonic acid until it was completely dissolved. The dissolved residue was diluted slightly with distilled water and quantitatively filtered into a 50cm^3 volumetric flask. Concentrated ammonia solution (6-7cm^3) was added to the solution to produce a permanent yellow phenoldisulphonic acids reagent nitrate colour. The flask was made to mark with distilled water, allowed to cool and measurement made at 500nm.

Blank: Blanks was used to calibrate the instrument. Nitrate standard of 0.5mg/l, 1.0mg/l, 2.0mg/l, 3.0mg/l, 4.0mg/l and 5.0mg/l was prepared from anhydrous KNO_3. Nitrate congregation in the sample was determined from the calibration curve (Tewas, 1950; US-EPA, 1983; APHA – AWWA-WPCF, 1985; Trivedy and Goel, 1986; NWRI, 2001).

Calculation

$$\text{mg/l } NO_3^- = \frac{mgNO_3^-}{mlofsample}$$

$mgNO_3^-$ = mg/l NO_3^- x ml of sample

.

3.3.21 Determination of Phosphate.

Reagents 'A': This was prepared by dissolving 12g of ammonia molybdate in 250cm^3 of distilled water and 0.2908g potassium antimony tartate in one liter of distilled water. Both solutions was added to a standard solution of H_2SO_4 (2.5M), mixed thoroughly and made up to two liters.

Reagent 'B': This reagent was prepared by dissolving. 1.05g of ascorbic acid in 200cm^3 of reagent A and mixed thoroughly.

10cm^3 of the sample was transferred into 50cm^3 volumetric flask, 2cm^3 of reagent B was then added and the solution made to mark with distilled water. Measurement was made at 912nm wavelength after fifteen minutes. Sample blanks and phosphate standard solutions prepared from KH_2PO_4 was also determined. Concentration of phosphorus in sample was estimated from calibration curve. (Murphy and Riley, 1952; US-EPA, 1983; APHA-AWWA-WPCF, 1985; Trivedy and Goel, 1986).

3.3.22 Determination of Silicate

0.5cm^3 of molybdate reagent was added to the sample in a sample cell bottle and swirled for proper mixing and was allowed to stand for 4 minutes for reactions to take place. Then citric acid was added and allowed to stand for 1 minute to destroy any form of phosphate interference. Amino acid reagent was added, after which it was placed on the cell holder of a direct reading spectrophometer, then reading corresponding to the concentration of silicates was recorded. (US-EPA, 1983; APHA-AWWA-WPCF, 1985; Trivedy and Goel, 1986).

3.3.23 Determination of Chloride

Highly colored samples was treated with $Al(OH)_3$ suspension, allowed to settle and then filtered. 50ml of the sample was placed in 250cm^3 flask. 1.0cm^3 of K_2CrO_4 indicator solution was added and sample titrated with standard $AgNO_3$ (0.14M) to a reddish brown color. Blank and standard titrations were carried out. (US-EPA, 1983; APHA-AWWA-WPCF, 1985; Trivedy and Goel, 1986; NWRI, 2001; Nsi, 2007)

3.3.24 Determination of Total Alkalinity

100cm^3 of the sample was transferred into a conical flask, two drops of phenolphthalein indicator was added and the solution titrated with standard H_2SO_4 to the end point. Again, two drops of methyl orange was added to the titrated mixture and titration continued to methyl orange end point (US-EPA, 1983; APHA-AWWA-WPCF, 1985; Trivedy and Goel, 1986; NWRI, 2001).

Calculation

Total Alkalinity, mg $CaCO_3$

$$= \frac{A \times B \times 1000}{\text{ml of sample}}$$

where A = Vol. of standard H_2SO_4 and B = Titre of standard acid

3.3.25 Determination of Heavy/Trace Metals

Heavy/trace metals were determined using Atomic Absorption Spectrophotometer.

a. Sample preparation: 50cm^3 of the sample was transferred quantitatively into a beaker, 5cm^3 conc. HCl and 3cm^3 conc. HNO_3 acid was added and heated in a boiling water bath until the volume was reduced to about 15cm^3. The sample was then allowed to cool,

filtered and transferred into a 50cm^3 standard flask and made to mark with distilled water.

b. Measurement: The atomic absorption spectrophotometer was operated in the air-acetylene flame mode and lamps operated at the following wavelengths according to the manufacturer's instruction (Cd, 228.2nm; Pb, 283nm; Cr, 302.2nm; Mn, 205.1nm; Ca, 435; Na, 589nm.

Blanks readings were obtained from those of standards and samples before calibration curves were prepared from where each metal concentration was determined. (US-EPA, 1983; APHA-AWWA-WPCF, 1985; Trivedy and Goel, 1986; Alloway, 1992).

3.3.26 Determination of Coliform organism

a. **Presumption Phase Fermentation**

A single strength broth (McKonkey Broth Purple) was prepared by dissolving 40g of the Broth in 500cm^3 distilled water in a beaker. 10cm^3 of the solution was transferred into five specimen bottles, filled with Durham tubes. These were sterilized by autoclaving at 120^{o}C for fifteen minutes. The medium (Broth) was then inoculated with 10cm^3 of the various water samples, mixed thoroughly and incubated at 35^{o}C for 48 hours. After wards, the tubes were shaken gently and then examined for gas production. The result was recorded.

b. **Confirmed Phase**

The tube showing positive test (gas production) was shaken gently and a sterile metal loop (3mm in diameter) was used to transfer one loop-full of culture to the fermentation tubes containing brilliant lactose bile broth. The metal loop was removed and discarded. The inoculated green brilliant green lactose bile broth tube was inoculated for 48 hours at

35^{o}C. The tube was then examined for gas production after this period. The result was then recorded. (Trivedy and Goel, 1986; Nsi, 2007).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

Results of the physicochemical and bacteriological analysis of the well water samples from Otukpo are presented in Tables 4.1 to 4.4. Each table was generated based on the classification of the wells by cluster analysis representing cluster 1 to 4 respectively.

4.2 Results and Discussion

4. 2.1. Taste and Odour:

Results for taste/odour are given in Tables 4.1 - 4.4. Generally, all the water samples showed unobjectionable taste/odour with exception of OT-1 and OT-2 in Table 4.1, OT-5, OT-24 and OT-25 in Table 4.2 and OT-6 in Table 4.3 showing objectionable taste. Since taste and odour are strictly of chemical and microbial origin (Schneider, 1975), this suggest that levels of materials causing taste/odour are minimal in the water samples. According to WHO, odour should totally be absent or very faint for water to be acceptable for drinking. Therefore, from the results, majority of the wells can be used for the purpose of drinking.

4.2.2 Temperature and pH

Temperature is basically important for its effects on other properties e.g. speeding up of chemical reactions, reduction in solubility of gases, amplification of taste and odour. The measured temperature values of the well water samples were between 29 and 31°C. The small variation in temperatures in the well water shows some uniformity of the groundwater

Table 4.1: Results of Physicochemical Analysis of Wells Classified together by CA

SAMPLING			SITES		
PARAMETER	OT-18	OT-19	OT-1	OT-2	WHO(2004)
Taste	Obj	Un-Obj	Obj	Obj	
Odour	Un-Obj	Un-Obj	Un-Obj	Un-Obj	
Temperature(^{o}C)	29	30	29	29	-
Turbidity(F.T.U)	260	122	80	101	5-25
Colour(Pt-Co)	550	550	377	451	5-50
Conductivity(µS/cm)	94	86	98.6	96	500-1500
Total Dissolved Solids(mg/l)	150	190	370	950	500-1500
Suspended Solids(mg/l)	368	121	36	39	-
Total Solids(mg/l)	518	311	406	989	-
Ph	6.1	6.1	6	6	6.5-8.5
Total Hardness(mg/l)	200	180	180	160	100-500
Total Alkalinity(mg/l)	182	96	150	16	100-400
Phosphate(mg/l)	1.42	1.38	0.64	0.56	
Silicates(mg/l)	32	20	32	36	
Nitrate(mg/l)	0.5	2.4	1.4	0.2	45
Chloride(mg/l)	68.2	64	46.4	52	250
Dissolved Oxygen, DO(mg/l)	4.9	4.8	4.7	4.9	
Biochemical Oxygen Demand, BOD(mg/l)	62	52	60	54	6
Chemical Oxygen Demand, COD(mg/l)	140	140	380	450	10
Ca(mg/l)	140	140	120	120	
K(mg/l)	1.4	2.2	2.2	3.1	30
Na(mg/l)	4.5	2	4.2	12	20-200
Cr(mg/l)	0.07	0.10	0.09	0.04	0.05
Cd(mg/l)	0.02	0.01	0.02	0.012	0.01
Pb(mg/l)	0.12	0.18	0.45	0.27	0.05
Mn(mg/l)	0.11	0.11	0.06	0.10	0.5
Coliform Count	220	170	110	79	-

Obj → Objectionable

Un-Obj→Unobjectionable

- → Value not available

Table 4.2: Results of Physicochemical Analysis of Wells Classified together by CA

SAMPLING	SITES										
PARAMETER	OT-3	OT-4	OT-5	OT-17	OT-20	OT-21	OT-22	OT-23	OT-24	OT-25	WHO (2004)
Taste	Un-Obj	Un-Obj	Obj	Un-Obj	Un-Obj	Un-Obj	Un-Obj	Un-Obj	Obj	Obj	
Odour	Un-Obj	Un-Obj	Obj	Un-Obj	Un-Obj	Un-Obj	Un-Obj	Un-Obj	Un-Obj	Un-Obj	
Temperature(^{o}C)	30	29	31	29	29	30	30	31	29	30	-
Turbidity(F.T.U)	281	117	26	55	73	95	47	187	34	236	5-25
Colour(Pt-Co)	550	550	136	317	365	492	216	550	189	550	5-50
Conductivity(µS/cm)	72	71.2	78	78	78.4	72	76	70	78.2	79	500-1500
Total Dissolved Solids(mg/l)	300	200	210	120	50	100	100	160	20	400	500-1500
Suspended Solids(mg/l)	179	105	19	53	32	46	97	28	30	148	-
Total Solids(mg/l)	479	305	229	173	82	146	197	188	50	548	-
pH	6	6.2	6	6	6	6	6	6.05	6.15	6.1	6.5-8.5
Total Hardness(mg/l)	140	120	180	140	140	100	120	80	160	180	100-500
Total Alkalinity(mg/l)	48	36	78	44	110	84	100	130	118	56	100-400
Phosphate(mg/l)	0.58	0.52	1.22	0.62	0.44	0.4	0.52	0.46	0.68	0.72	
Silicate(mg/l)	52	46	16	22	28	31	20	38	16	48	
Nitrate(mg/l)	0.3	3.8	0.1	2.2	2.2	0.1	0.5	0.8	1	2.6	45
Chloride(mg/l)	60.8	54.2	66.2	58	64.2	58	46	44	54	56.8	250
Dissolved Oxygen, DO(mg/l)	4.8	5	5.1	5.2	5.2	5.1	5.4	5.6	5.1	5.3	
Biochemical Oxygen Demand, BOD(mg/l)	36	38	28	36	42	40	36	32	41	42	6
Chemical Oxygen Demand, COD(mg/l)	160	210	390	220	330	390	350	240	60	210	10
Ca(mg/l)	100	80	120	100	100	80	80	60	120	120	
K(mg/l)	3.3	1.2	1.8	3.3	0.9	0.8	0.9	6.7	1.5	0.7	30
Na(mg/l)	13	3.7	6.2	5.6	3.2	3.3	6.1	6.8	4.6	1.5	20-200
Cr(mg/l)	0.06	0.03	0.07	0.10	0.08	0.05	0.03	0.03	0.04	0.06	0.05
Cd(mg/l)	0.02	0.02	0.01	0.01	0.01	0.01	0.00	0.01	0.02	0.03	0.01
Pb(mg/l)	0.34	0.39	0.10	0.50	0.27	0.13	0.86	0.18	0.31	0.19	0.05
Mn(mg/l)	0.15	0.05	0.09	0.07	0.02	0.06	0.01	0.03	0.03	0.05	0.5
Coliform Count	22	26	33	21	33	31	27	23	33	34	-

Table 4.3: **Results of Physicochemical Analysis of Wells Classified together by CA**

SAMPLING	SITES				
PARAMETER	OT-6	OT-7	OT-8	OT-16	WHO(2004)
Taste	Obj	Un-Obj	Un-Obj	Un-Obj	
Odour	Un-Obj	Un-Obj	Un-Obj	Un-Obj	
Temperature(^{o}C)	31	30	31	29	-
Turbidity(F.T.U)	28	9	9	6	5-25
Colour(Pt-Co)	148	45	57	47	5-50
Conductivity(µS/cm)	80	77.4	74.8	80.6	500-1500
Total Dissolved Solids(mg/l)	390	300	440	24	500-1500
Suspended Solids(mg/l)	17	12	17	20	-
Total Solids(mg/l)	407	312	457	260	-
pH	6	6	6	6	6.5-8.5
Total Hardness(mg/l)	180	160	100	160	100-500
Total Alkalinity(mg/l)	270	100	240	53	100-400
Phosphate(mg/l)	1.36	0.72	0.68	0.84	
Silicates(mg/l)	18	7	8	8	
Nitrate(mg/l)	0.6	7.1	0.9	4.9	45
Chloride(mg/l)	68	60.4	52.4	64.2	250
Dissolved Oxygen, DO(mg/l)	5.4	5.3	5.2	5.4	
Biochemical Oxygen Demand, BOD(mg/l)	30	22	24	32	6
Chemical Oxygen Demand, COD(mg/l)	210	110	150	190	10
Ca(mg/l)	120	120	80	120	
K(mg/l)	5.2	9.6	24	7.3	30
Na(mg/l)	33	32	75	21	20-200
Cr(mg/l)	0.02	0.09	0.05	0.06	0.05
Cd(mg/l)	0.01	0.02	0.02	0.02	0.01
Pb(mg/l)	0.19	0.43	0.55	0.13	0.05
Mn(mg/l)	0.80	0.15	0.04	0.15	0.5
Coliform Count	31	26	22	17	-

Table 4.4: **Results of Physicochemical Analysis of Wells Classified together by CA**

SAMPLING SITES								
PARAMETER	OT-9	OT-10	OT-11	OT-12	OT-13	OT-14	OT-15	WHO (2004)
Taste	Un-Obj	Un-Obj	Un-Obj	Un-Obj	Un-Obj	Un-Obj	Un-Obj	
Odour	Un-Obj	Un-Obj	Un-Obj	Un-Obj	Un-Obj	Un-Obj	Un-Obj	
Temperature(^{o}C)	31	29	31	30	31	31	30	-
Turbidity(F.T.U)	4	14	11	9	31	37	27	5-25
Colour(Pt-Co)	43	74	65	179	171	202	169	5-50
Conductivity(µS/cm)	67.4	69	78.4	70	71.2	74	70.4	500-1500
Total Dissolved Solids(mg/l)	800	460	230	370	220	530	450	500-1500
Suspended Solids(mg/l)	12	16	16	17	33	38	41	-
Total Solids(mg/l)	812	476	246	387	25.3	568	491	-
pH	6.05	6	6.1	6.1	6.1	6	6	6.5-8.5
Total Hardness(mg/l)	80	80	120	100	60	80	80	100-500
Total Alkalinity(mg/l)	56	24	75	290	10	35	110	100-400
Phosphate(mg/l)	0.42	0.38	0.72	0.6	0.32	0.48	0.72	
Silicates(mg/l)	16	20	12	8	22	28	36.2	
Nitrate(mg/l)	2.3	0.8	2.6	3.9	0.5	0.4	0.1	45
Chloride(mg/l)	54.8	52	50	48.2	46	50.1	52.4	250
Dissolved Oxygen, DO(mg/l)	5	4.8	4.7	4.6	4.8	4.6	4.8	
Biochemical Oxygen Demand, BOD(mg/l)	42	48	51	52	53	54	52	6
Chemical Oxygen Demand, COD(mg/l)	260	360	370	160	210	110	360	10
Ca(mg/l)	60	60	80	60	40	60	60	
K(mg/l)	27	18	3.1	15	5	16	20	30
Na(mg/l)	67	53	4.5	32	19	40	34	20-200
Cr(mg/l)	0.07	0.04	0.12	0.06	0.08	0.03	0.09	0.05
Cd(mg/l)	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01
Pb(mg/l)	0.42	0.12	0.10	0.30	0.18	0.27	0.37	0.05
Mn(mg/l)	0.38	0.20	0.09	0.20	0.05	0.08	0.28	0.5
Coliform Count	21	26	46	49	63	70	27	-

temperature in the study area. The temperature of the water source does not have a direct health implication (Willis, 1989).

The pH values for the well water samples ranged between 6.0 and 6.5 indicating all the well waters are slightly acidic. Chemically, pH has synergistic effects on water as they react with other substances. For example, when acid waters (waters with low pH values) come into contact with certain chemicals and metals, they often make them more toxic than normal. The values obtained from the wells were below the WHO recommended range of 6.5 – 8.5.

4.2.3 Colour

The colour values of water samples from the sampling sites are given in Tables 4.1- 4.4. The sampling sites that recorded the highest value for colour are OT-18, OT-19, OT-3, OT-4, OT-23 and OT-25 with 550 Pt – Co. Only 3 water samples, OT-16, OT-7 and OT-9 had colour value below WHO standard of 5 – 50 Pt –Co. Generally, the presence of colour in water is usually due to colouring matter (organic and inorganic) and also the underlying soil characteristics. Biotic activities and biodegradation of organic substances usually impact colour to water (Miller, 1988; Willis, 1989). The primary importance of colour in drinking water is aesthetic, but the sensory effects may be regarded as a health effect. Colour in domestic water may stain fixtures and clothes. From colour value obtained from the samples examined, there is need for water to be treated before use.

4.2.4 Turbidity

Turbidity values for the study area are given in Tables 4.1- 4.4. The samples OT-10, OT-9, OT-11, OT-12, OT-7, OT-8 and OT-16 had turbidity values within WHO standard range of 5 – 25 F.T.U, while samples from OT-1, OT-2, OT-3, OT-4, OT-5, OT-6, OT-13, OT-14, OT-15, OT-17, OT-18, OT-19, OT-20, OT-21, OT-22, OT-23, OT-24, OT-25 were outside this

range. The clarity of water, which is measured in terms of turbidity, is an expression of its optical property which causes light to be scattered and absorbed rather than transmitted in straight lines (Willis, 1989). Since turbidity may be caused when light is blocked by large amounts of silt, microorganisms, plant fibers, sawdust, wood ashes, and certain chemicals (Duncan, 1996), the high values recorded at some of the wells may be explained by these factors. High turbidity is often associated with high levels of disease – causing microorganisms such as viruses, parasites and some bacteria. These organisms cause symptoms such as nausea, cramps, diarrhea and headaches. The variation in turbidity of the well waters may be due to some of the factors mentioned above, as well as depth, soil characteristics and high movement of underground water during the period of sampling.

4.2.5 Conductivity

The lowest electrical conductivity (EC) value measured for the sampling sites was 67.4 µS /cm and the highest value was 98.6 µS /cm as shown in Tables 4.1- 4.4. The highest EC value was recorded in OT-1 and OT-9 registering the lowest. Conductivity is the numerical expression of the ability of water to carry an electric current at 25^{o}C and a measure of free ion (charged particles) content in the water. These ions can come from natural sources such as bedrock, or human sources such as storm water runoff. The values indicate the extent to which chlorides, nitrates, sulphates, phosphates, sodium, magnesium, calcium, iron and aluminium ions are present in the water samples (Thriodore, 2004). The measured EC values indicate that all the 25 wells examined had values which were within the WHO maximum permissible EC level of between 500-1500µs/cm for drinking water. This also shows that contaminations due to dissolve ions are relatively low. Conductivity of a body of water has no health implications, but

it is an important criterion in determining the suitability of water and waste water for irrigation and other uses (WHO, 1992; Thriodore, 2004).

4.2.6 Total Dissolved Solids (TDS)

Tables 4.1- 4.4 gives TDS values for the water samples of the wells. The amount of TDS in a given source of water depends on the nature of the geological materials found in the area where the source is located. It also depends on the quantum of foreign materials that find their way into the source, as well as the chemistry of the source. The chemistry of a water source to a large extent determines the degree to which such materials or substances dissolves in it (Lindorff, 1979). TDS relates with electrical conductivity (EC) in dilute solutions. The values of TDS obtained in the wells did not exceed the maximum contaminant levels as recommended by WHO. According, to WHO (2004), the palatability of water with a TDS level less than 600mg/L is generally considered to be good and becomes significantly and increasingly unpalatable at TDS level greater than 1000 mg/L.

4.2.7 Total Alkalinity

Alkalinity values for the wells are shown in Tables 4.1- 4.4. Alkalinity is not a pollutant but is a total measure of the substances in water that have acid-neutralizing ability or quantitative capacity to react with hydrogen ions. Alkalinity of natural or treated waters is usually due to the presence of bicarbonates, carbonates and hydroxyl ions that may have been leached into ground water sources (Thriodore, 2004). Borates, silicates, and phosphates may also contribute to alkalinity.

The measured alkalinity values for the water samples show that they are below WHO stipulated range of 100 – 500mg/L $CaCO_3$.

4.2.8 Total Hardness

Hardness is mostly due to the presence of carbonates and bicarbonates, chlorides, nitrates and sulphates of Ca and Mg. Tables 4.1-4.4 give total hardness values for the well water samples from the study area. According to WHO (2004) water hardness classification, water can be classified as; soft (0 – 50mg/L $CaCO_3$.), moderately soft (50 – 100 mg/L $CaCO_3$), slightly hard (100 – 150 mg/L $CaCO_3$), moderately hard (150– 200mg/L $CaCO_3$), hard (200 – 300mg/L $CaCO_3$) and very hard (over 300mg/L $CaCO_3$). Using the above water hardness classification by WHO, wells in Table 4.1(OT-18 > OT-19 > OT-1 > OT-2) according to their measured values can be said to be moderately hard, three wells in Table 4.2 (OT-5 > OT-25 > OT-24) are moderately hard and OT-3 > OT-17 > OT-20 > OT-4 > OT-22 > 0T-21 > OT-23 are slightly hard, wells in Table 4.3 (OT-6 > OT-7 > OT-16 > OT-8) are moderately hard, wells in Table 4.4 (OT-9 > OT-10 > OT-14 > OT-15 > OT-13) are moderately soft with only two (OT-11 > OT-12) slightly hard. Hard water has a number of advantages; it tastes better than soft water because of the dissolved minerals salts in it, helps animals to build strong teeth and bones and can be supplied in pipes made of Pb as it does not dissolve Pb, which is the case with soft water (Thriodore, 2004). Hard water, if not in excess of 500mg/L does not constitute a health problem. It only leads to chronic diseases, especially cardiovascular diseases at levels higher than WHO maximum permissible limit of 500mg/L. From the measured values for the study area with respect to total hardness, only some wells in Table 4.4 are moderately soft, the rest are considered to be moderately hard.

4.2.9 Dissolved Oxygen, Biochemical Oxygen Demand and Chemical Oxygen Demand

DO values obtained from the wells as shown in Tables 4.1 - 4.4 are relatively low, indicating a high demand of oxygen in the wells. DO determination is vital for maintaining aerobic condition in natural water and it is the basis of BOD, which is commonly used to evaluate the pollution strength of water (Bhatia, 2009).

BOD test which measures the quantity of microorganisms in a water sample and of the nutrients available to them produced values as shown in Tables 4.1 – 4.4. The wells in Table 4.1; OT-18, OT-19, OT-1, OT-2 with values between the range of 52- 62mg/L were higher when compared to wells in Tables 4.2, 4.3, and 4.4. OT-6, OT-7, OT-8, OT-16 had the lowest values ranging between 22-32mg/L.

COD like BOD, is also used to determine the amount of organic pollutants found in water. However, COD results are generally higher than BOD value since the test will oxidize materials such as fats and lignin's which are only slowly biodegradable. The increase of COD values is due to oxidizable organic matter (Bhatia, 2009). COD values obtained from samples (Tables 4.1 – 4.4) also reveals high amount of microorganisms in the wells. OT-2 had the highest COD value of 450mg/L. The high BOD and COD values recorded, accounts for the high oxygen demand, hence, low DO values. This is due to the fact that, microorganisms use oxygen to decompose complex organic molecules present in water in their aerobic metabolic processes (Nsi, 2007). The BOD and COD values obtained from the sampling sites, exceeds the WHO standard of 6mg/L and 10mg/L respectively. Run-off from farm fields containing phosphate and nitrate fertilizers and refuse dumps around the wells may account for the results obtained.

4.2.10 Chloride, Phosphate, Nitrate and Elemental analysis

The concentrations of chloride ions found in the samples of the well water were between 46 mg/L and 68.2 mg/L as shown in Tables 4.1- 4.4. The chloride ion (Cl^-) found naturally in some surface and groundwater is usually as a result of saltwater intrusion which elevates its concentration in drinking water wells especially those situated near coastlines. These amounts of chloride ions found in all the wells are within the WHO allowable levels for ground water 10 – 250 mg /L. However, because the natural background level of chloride in drinking water is 10 mg/L, the values obtained for all the wells is an indication of human influence which may have been introduced through agricultural and/or domestic activities.

Although chloride is not harmful to human at threshold levels (250 mg/L), the water source may not be palatable (De Zuane, 1990). Adverse effects of high chloride concentration in drinking water would be a build–up of potentially carcinogenic chloro–organic compounds, which are dangerous to health (De Zuane, 1990; WHO, 1992).

The concentration of phosphate in the water samples of the wells are shown in Tables 4.1- 4.4. The highest phosphate value was recorded in OT-18 as 1.42 mg/L. Phosphate constitute a very important pollution problem whenever it is found in significant amount. It promotes algae growth and / or microphytes, leading to the cyclic problem of eutrophication (Thriodore, 2004). It is established that high phosphorus concentration has no health implication (WHO, 2004) except for its role in causing eutrophication of water bodies.

The nitrate concentrations obtained in the wells of the sampling area are between 0.1 and 7.1mg/L. Major sources of nitrate in water are from fertilizer use, leaking of septic tanks, sewage and erosion of natural deposits. High nitrate concentration in drinking water in excess of 45mg/L has health implications, for example, it combines with the hemoglobin in the red blood cells and

impairs circulation of oxygen throughout the body. It also causes a disease condition referred to as blue – baby syndrome in children. It can also react with dietary component in the stomach to form group of compounds called N–nitroso compounds. These N-nitroso compounds have serious health implications; they cause cancer of the stomach, esophagus, oral cavity and urinary bladder (Giddings, 1993; Thriodore, 2004). The nitrate levels for well water of the sampling area are below WHO maximum allowable level of 45mg/L for portable water.

The concentration of the sodium ions in the well water samples varied between 2 mg|L and 75mg|L (Tables 4.1- 4.4).The sampling site OT-8 recorded the highest Na value of 75 mg|L. The maximum permissible level of sodium ion in drinking water is 200mg|L and therefore all the wells were within the permissible level.

Tables 4.1 – 4.4 shows the concentration of potassium for the wells analyzed. OT-18, OT-19, OT-1, OT-2 had values between the range of 1.4 to 3.1mg/L (Table 4.1). Potassium concentration for OT-22, OT-23, OT-5, OT-21, OT-3, OT-25, OT-4, OT-17, OT-20 and OT-24 were between 0.7-6.7mg/L (Table 4.2). OT-7, OT-16, OT-6, OT-8 had values between 5.2 - 24 (Table 4.3). Wells in Table 4.4, that is, OT-12, OT-15, OT-11, OT-9, OT-10, OT-13, OT-14, had values between the range of 3.1-27mg/L, recording the highest potassium concentration when compared to other wells. The concentrations of potassium ion in the wells are within the WHO standard of 30mg/L.

The results of the AAS measurements of Cr, Cd, Pb and Mn in well water samples from study area are presented in Tables 4.1- 4.4. The concentrations of chromium in the samples collected from OT-18, OT-19, OT-1, OT-3, OT-5, OT-17, OT-20, OT-25, OT-7, OT-16, OT-9, OT-11, OT-12, OT-13 and OT-15 where above the WHO maximum permissible limit of 0.05mg/L. The source of chromium in water could be as result of discharge from wood

processing industry and erosion of natural deposits. The presence of chromium can cause adverse health effects such as: Allergic dermatitis and cancer.

The concentrations of cadmium in the water samples of OT-6, OT-10, OT-20 and OT-22 wells were below the WHO detection limit of 0.01mg/L, the rest were above the WHO detection limit. The source of cadmium might have been from erosion of natural deposits, run off from economic activities involving disposal of waste batteries. The presence of high amount of Cd can cause damage to the kidney.

The concentration of lead for all sampling points exceeded the WHO detection limit of 0.05mg\L. The high level of lead may have been as a result of activities of battery chargers, vehicular emissions and erosion of natural deposits. Several health conditions result from lead poisoning. In children, it delays physical and mental development, they show slight deficits in attention span and learning abilities. In adults it causes kidney problems and High blood pressure (Giddings, 1993).

The concentrations of Mn in the samples were less than the WHO detection limit of 0.5mg\L except OT-6 in Table 4.3 which had Mn value of 0.80mg\L. Generally, ground water often contains elevated levels of dissolved Mn which originates from soils around the wells (Alloway, 1992). Mn sources are widespread, and its distribution over long distances is favoured by the fact that, it is predominantly associated with dust particles (Udo, 1990). When Mn is present in potable water, it can cause neurological disorders. It imparts an undesirable taste to beverages and stain plumbing fixtures.

4.2.11 Bacteriological Test (Total Coliform Count)

The results of the bacteriological analysis of the study area are shown in Tables 4.1- 4.4. There are primarily 18 bacteria which make up the group known as coliforms, one of which is

Escherichia coli. This bacterium is a normal component in the large intestines of humans and other warm blooded animals, and can be excreted in their fecal material. Organisms causing infections or diseases (pathogens) are also often excreted in the fecal material of humans and other warm-blooded animals. If these bacteria are found in water, it indicates other disease causing bacteria may enter through the same pathway and be present in drinking water. Runoff is most commonly implicated as source of coliform during storms (Bohn and Buckhouse, 1981). The bacteriological results showed that, almost all the sampling points are contaminated with coliform organisms. OT-18 in Table 4.1 recorded the highest level of contamination is with 220 MPN /ml followed by OT-2 with coliform value 110 MPN/ml. This high level of contamination may be attributed to the high level of biological activities resulting from animal wastes and improper waste disposal management.

4.3 MULTIVARIATE STATISTICAL ANALYSIS OF RESULTS

4.3.1 Principal Component Analysis (PCA)

PCA was performed on the standardized log transformed normalized hydrochemical data set using the equation $x = [\log Y]^2$ (Table 4.5). Where Y is the original values given in Tables 4.1 to 4.4 and x are the transformed values given in Table 4.5. The Kaiser criterion (Kaiser, 1960) was applied to determine the total number of factors (or PCs) for each dataset in this analysis. Under this criterion only the PCs with eigen values greater than 1 were considered as possible sources of variance in the data, with the highest priority ascribed to the PC that has the highest eigen value (i.e. points on the steep portion of the scree plot shown in Fig.4.1)

The results of the principal component analysis of the whole data yielded seven data sets which are presented in Table 4.6, the data set of 24 variables reduced to seven principal components (PCs). The scree plot of the eigen values as shown in Fig.4.1 reveals that the first

seven principal components extracted had eigen values greater than 1 and the rest with eigen values less than 1 were eliminated, hence, the reason for the data reduction (Chatfield and Collins, 1980).

The first four principal components with the highest eigen values were then rotated according to varimax rotation (Kaiser, 1960) in order to make interpretation easier (Table 4.7), since the 5^{th}, 6^{th} and 7^{th} components would not constitute a unique source of variance in the hydrochemistry because they all have about three loadings greater than 0.50. They were therefore dropped and the four factors were chosen for varimax rotation. The result show that the percentage of the cumulated variance of the first four components accounts for 60.21% of the total variance of the original data which is quite good and can be relied upon to identify the main sources of variation in the hydrochemistry. This also means that majority of the variance of the original data has been accounted for by these extracted components. Communalities in Table 4.7 show that variance of all the variables (parameters) have been described well by these four components.

Table 4.7 summarizes the PCA results comprising of the loadings, eigen values, percentage of variance and communalities. PC scores ≥ 0.67 were adjudged to be significant and taken as important factors. The first component which explained (or accounted for) 18.25% of the total variance was associated with Ca, hardness, phosphates, EC and chloride. Thus PC1 represented hardness resulting mainly from Ca salts and high concentration of dissolved salts. This property may have been imparted on the water by the underlying Agwu shales which is dark grey in colour and well bedded with limestone interbeds. The Agwu shales have been reported to contain a reasonable concentration of Ca and Na (Onyeku *et al*., 2010). The Cl and EC loadings also depict salinity of the water since they are usually directly correlated. The second

component which explains 18.18% of the total variance has turbidity, silicates, colour, suspended solids (SS) as the important variables. This component explains the aesthetic parameters or the physical characteristics of water. Turbidity may have resulted from colloidal materials, presence of algae and the amount of leachates contaminating underground water in these areas. These materials may have been introduced into the water from agricultural activities going on in the area. Turbidity of the water gives reasons for its coloration. The third component which explains 12.21% of the total variance show coliform and BOD as important variables. This reveals the presence of microorganisms which are indications of biological activities due to indiscriminate dumping of refuse and other domestic discharges around wells which are subsequently leached into the wells. This is also an indication that the level of dissolved oxygen is mainly a function of the amount of microorganisms present in the water. The fourth component has high loading of TDS which may be due to dissolved minerals which may include Na and K generated by use of fertilizers and other inorganic pollution from human activities. Na and K which belong to the alkali earth metals are good conductors of electricity; this also explains the high electrical conductance of the water whose source may primarily be from the bed rock materials.

Table 4.5: Log Transformed Normalized Data

PARAMETERS	SAMPLING SITES												
	OT-1	OT-2	OT-3	OT-4	OT-5	OT-6	OT-7	OT-8	OT-9	OT-10	OT-11	OT-12	OT-13
Temp.(^{o}c)	2.14	2.14	2.18	2.14	2.22	2.22	2.18	2.22	2.22	2.14	2.22	2.18	2.22
Turbidity (FTU)	3.62	4.02	5.99	4.28	2	2.09	0.91	0.91	0.36	1.31	1.08	0.91	2.22
Colour (Pt-Co)	6.64	7.04	7.51	7.51	4.55	4.71	2.73	3.08	2.67	3.49	3.29	5.08	4.99
Total Alkalinity $CaCO_3$ (mg/l)	4.74	1.45	2.83	2.42	3.58	5.91	4	5.67	3.06	1.9	3.52	6.06	1
E.C (µS/cm)	3.98	3.93	3.45	3.43	3.58	3.62	3.57	3.51	3.34	3.38	3.59	3.4	3.43
TDS (mg/l)	6.6	8.87	6.14	5.29	5.39	6.71	6.14	6.99	8.43	7.09	5.58	6.6	5.49
SS (mg/l)	2.42	2.53	5.08	4.09	1.64	1.51	1.16	1.51	1.16	1.45	1.45	1.51	2.31
TS (mg/l)	6.8	8.97	7.18	6.17	5.57	6.81	6.22	7.08	8.47	7.17	5.72	6.7	1.97
pH	0.61	0.61	0.61	0.63	0.61	0.61	0.61	0.61	0.61	0.61	0.62	0.62	0.62
Total Hardness(mg/l)	5.09	4.86	4.61	4.32	5.09	5.09	4.86	4	3.62	3.62	4.32	4	3.16
Phosphate(mg/l)	0.04	0.06	0.06	0.08	0.01	0.02	0.02	0.03	0.14	0.18	0.02	0.05	0.24
Silicates (mg/l)	2.27	2.42	2.94	2.76	1.45	1.58	0.71	0.82	1.45	1.69	1.16	0.82	1.8
Nitrate (mg/l)	0.02	0.49	0.27	0.34	1	0.05	0.72	0	0.13	0.01	0.17	0.35	0.09
Chloride (mg/l)	2.78	2.94	3.18	3.01	3.32	3.36	3.17	2.96	3.02	2.94	2.89	2.83	2.76
DO (mg/l)	0.45	0.48	0.46	0.49	0.5	0.54	0.52	0.51	0.49	0.46	0.45	0.44	0.46
BOD (mg/l)	3.16	3	2.42	2.5	2.09	2.18	1.8	1.9	2.63	2.83	2.92	2.94	2.97
COD (mg/l)	6.66	7.04	4.86	5.39	6.71	5.39	4.17	4.74	5.83	6.53	6.6	4.86	5.39
Ca (mg/l)	4.32	4.32	4	3.62	4.32	4.32	4.32	3.62	3.16	3.16	3.62	3.16	2.57
K (mg/l)	0.11	0.24	0.27	0.01	0.07	0.51	0.96	1.9	2.05	1.58	0.24	1.38	0.49
Na (mg/l)	0.39	1.16	1.24	0.32	0.63	2.31	2.27	3.52	3.33	2.97	0.43	2.27	1.64
Cr (mg/l)	1.1	1.87	1.59	2.57	1.29	3.04	1.11	1.74	1.33	1.95	0.84	1.49	1.23
Cd (mg/l)	3.33	3.13	2.89	3.33	3.44	4.94	3.13	3.13	4	4.4	3.44	3.56	2.96
Pb (mg/l)	0.12	0.33	0.22	0.17	0.97	0.51	0.13	0.07	0.15	0.85	0.97	0.28	0.56
Mn (mg/l)	1.57	1.02	0.7	1.72	1.14	0.01	0.67	1.98	0.17	0.48	1.08	0.48	1.76
Total Coliform	4.17	3.6	1.8	2	2.31	2.22	2	1.8	1.75	2	2.76	2.86	3.23

Continuation of Table 4.5

PARAMETERS	SAMPLING SITES											
	OT-14	OT-15	OT-16	OT-17	OT-18	OT-19	OT-20	OT-21	OT-22	OT-23	OT-24	OT-25
Temp(^{o}c)	2.22	2.18	2.14	2.14	2.14	2.18	2.14	2.18	2.18	2.22	2.14	2.18
Turbidity (FTU)	2.46	2.05	0.61	3.03	5.83	4.35	3.47	3.91	2.8	5.16	2.35	5.63
Color (Pt-Co)	5.31	4.96	2.8	6.25	7.51	7.51	6.57	7.25	5.45	7.51	5.18	7.51
Total Alkalinity $CaCO_3$(mg/l)	2.38	4.17	2.97	2.7	5.11	3.93	4.17	3.70	4	4.47	4.29	3.06
E.C (µS/cm)	3.49	3.41	3.63	3.58	3.89	3.74	3.59	3.45	3.54	3.40	3.58	3.60
TDS (mg/l)	7.42	7.04	1.9	4.32	4.74	5.19	2.89	4.00	4.00	4.86	1.69	6.77
SS (mg/l)	2.5	2.6	1.69	2.97	6.58	4.34	2.27	2.76	3.95	2.09	2.18	4.71
TS (mg/l)	7.59	7.24	5.83	5.01	7.37	6.21	3.66	4.68	5.26	5.17	2.89	7.50
pH	0.61	0.61	0.61	0.61	0.62	0.62	0.61	0.61	0.61	0.61	0.62	0.62
Total Hardness(mg/l)	3.62	3.62	4.86	4.61	5.29	5.09	4.61	4.00	4.32	3.62	4.86	5.09
Phosphate(mg/l)	0.1	0.02	0.01	0.04	0.02	0.02	0.13	0.16	0.08	0.11	0.03	0.02
Silicates (mg/l)	2.09	2.43	0.82	1.8	2.27	1.69	2.09	2.22	1.69	2.50	1.45	2.83
Nitrate (mg/l)	0.16	1	0.48	0.12	0.09	0.14	0.12	1.00	0.09	0.01	0.00	0.17
Chloride (mg/l)	2.89	2.96	3.27	3.11	3.36	3.26	3.27	3.11	2.76	2.70	3.00	3.08
DO (mg/l)	0.44	0.46	0.54	0.51	0.48	0.46	0.51	0.50	0.54	0.56	0.50	0.52
BOD (mg/l)	3	2.94	2.27	2.42	3.21	2.94	2.63	2.57	2.42	2.27	2.60	2.63
COD (mg/l)	4.17	6.53	5.19	5.49	4.61	4.61	6.34	6.71	6.47	5.67	3.16	5.39
Ca (mg/l)	3.16	3.16	4.32	4	4.61	4.61	4.00	3.62	3.62	3.16	4.32	4.32
K (mg/l)	1.45	1.69	0.75	0.27	0.02	0.12	0.00	0.01	0.00	0.68	0.03	0.02
Na (mg/l)	2.57	2.35	1.75	0.56	0.43	0.09	0.26	0.27	0.62	0.69	0.44	0.03
Cr (mg/l)	2.32	1.11	1.49	0.99	1.36	1.04	1.25	1.69	2.41	2.41	2.12	1.44
Cd (mg/l)	3.13	4	3.13	3.69	3.23	3.56	4.94	3.84	7.28	3.56	2.75	2.32
Pb (mg/l)	0.33	0.19	0.76	0.09	0.85	0.56	0.33	0.76	0.00	0.56	0.26	0.51
Mn (mg/l)	1.19	0.31	0.67	1.31	0.91	0.89	2.68	1.53	4.40	2.36	2.41	1.69
Total Coliform	3.4	2.05	1.51	1.75	5.49	4.97	2.31	2.22	2.05	1.85	2.31	2.35

Table 4.6: Principal Component from Correlation Matrix

Parameters	PC1	PC2	PC3	PC4	PC5	PC6	PC7
K	-0.846	.014	-.284	-.73	.170	.196	-.067
Na	-.845	-.102	-.251	-.154	.213	.234	-.031
Tur	.797	.376	.175	.006	.022	.375	.082
Colour	.774	.450	.180	.006	.061	.261	.046
SS	.763	.289	.034	-.137	.011	.260	.012
Hard	.744	-.600	-.131	.012	.131	.013	-.015
Ca	.724	-.628	-.133	.027	.117	0.53	-.058
EC	.694	-.221	-.340	.041	.397	-.237	-.017
Coli	.554	.246	-.553	-.191	.201	-.251	.280
PO_4	-.357	.685	.238	.158	-.176	-.133	.029
BOD	.275	.660	-.508	-.034	.146	-.319	.032
SiO_4	.520	.620	.160	.190	.081	.462	-.043
Cl	.379	-.613	-.183	.193	-.202	.278	.108
Alk	.047	-.495	.050	-.366	.330	-.054	.365
Mn	.223	.175	.721	.075	-.045	.156	0.66
Cr	-.084	.068	.541	-.258	.184	.314	.310
Cd	-.158	-.023	.533	.232	.493	-.302	.217
TDS	-.350	.300	-.482	.062	.450	.428	.410
COD	.053	.845	0.79	.080	.099	.404	.410
NO_3	-.069	-.209	-.170	.634	-.230	.230	-.101
pH	.284	.272	-.049	-.558	-.491	-.127	.072
Temp	-.534	.021	.004	-.055	-.078	.201	.608
Pb	1.51	-.047	-.265	.371	-.505	-.187	.582
Eigen value	6.327	3.769	3.057	2.020	1.646	1.625	1.142
Variance (%)	26.364	15.703	12.737	8.415	6.859	6.769	4.760
Cumulative variance (%)	26.364	42.067	54.804	63.219	70.078	76.847	81.607

Table 4.7: Varimax Rotated Components

Parameters	PC1	PC2	PC3	PC4	Communalities
Ca	**.939**	.182	-.016	-.198	.958
Hard	**.927**	.192	.027	-.222	.948
PO_4	**-.826**	.087	.066	-.080	.727
EC	**.713**	.193	**.**500	-159	.862
Cl	**.698**	.068	-.256	.040	.721
Tur	.149	**.953**	.061	-.124	.955
SiO_4	-.163	**.935**	.053	.068	.939
Colour	0.79	**.918**	.149	-.182	.908
SS	.222	**.785**	.176	-.131	.754
BOD	-.195	.257	**.886**	.019	.894
Coli	.301	.272	**.812**	.005	892
DO	.199	.011	**-.776**	-.311	.808
TDS	-.149	.055	.246	**.848**	.844
Mn	-.224	.199	-.146	**-.693**	.835
Na	-.256	**-**.564	-.139	**.690**	.912
K	-.346	**-.**539	-.58	**.669**	.898
COD	-.187	.093	.123	-.035	.875
pH	-.151	.192	.237	-.300	.730
Cd	-.132	-.104	-.150	-.227	.746
AIK	.453	-.220	-.077	.053	.629
NO_3	.131	-.036	-.238	.162	.595
Cr	-.178	.249	-.420	.080	.599
Pb	.063	-.018	.157	-.139	.861
Temp	-.310	-.210	-.203	.410	.696
Eigen value	4.380	4.363	2.930	2.778	
Variance (%)	18.250	18.181	12.208	11.573	
Cumulative variance (%)	18.250	36.431	48.639	60.212	

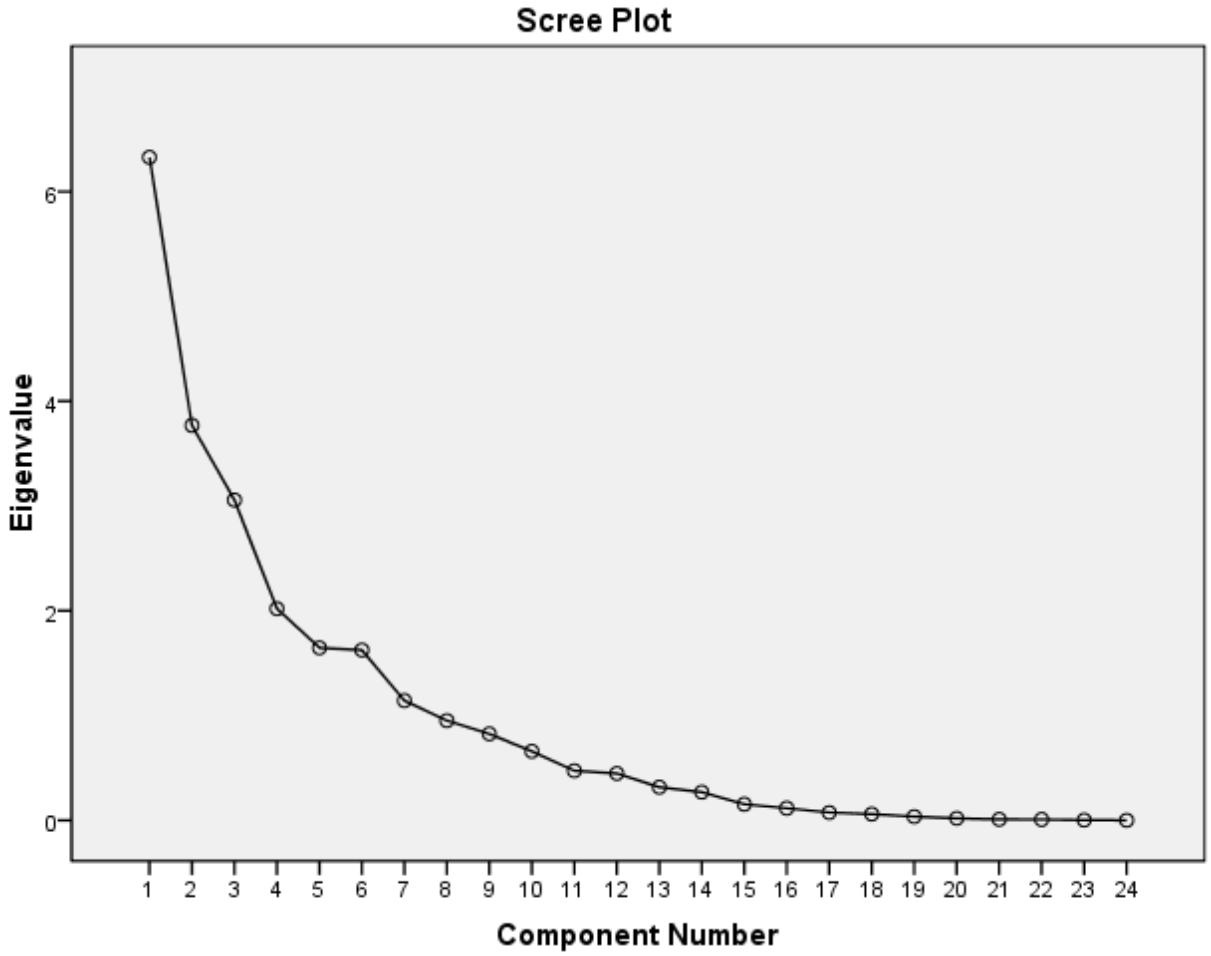


Figure 4.1: Scree Plot of the Eigen Values

4.3.2 Cluster Analysis (CA)

The Ward's method was used to determine the spatial similarities in physicochemical properties of the water samples. All log-transformed variables were z–scale standardized, that is, the mean and variance were set to zero and one, respectively to minimize the effects of different units and variance of variables and render the data dimensionless (Singh *et al.*, 2004). CA generated dendrograms showing spatial clustering of the water samples for the period under investigation (Fig. 4.2). The dendrogram shows the clusters being combined and the values of the coefficients at each step. The dendrogram plots do not show the actual Euclidean distances but rescales them to numbers between 0 and 25. The sample locations are grouped on the horizontal axis, and the lineage distances representing the relative differences between clusters, are show on the vertical axis.

Cluster analysis yields a dendrogram (Fig. 4.2) grouping 25 sampling sites into four statistically significant clusters when the tree is cut at a distance of approximately 10. The datasets cluster 1, 2, 3 and 4 fairly well separated in the PCA space and consistent with the CA derived groupings. Compact PCA distribution for majority of the water samples within the groups suggests that all the water samples in their respective groups have similar chemistries hence their flow paths or sources. The changes in the water chemistry may be as a result of source or non-source contamination.

Cluster 1 encompasses sampling sites OT-18, OT-19, OT-1 and OT-2 which are Asa 1, Asa 2, Igbanomaje 1 and Igbanomaje 2 respectively. The cluster is dominated by colour as shown in Table 4.8; this may have resulted from dissolved materials generated form parent rock, since it also shows high content for Ca and hardness. The cluster is affected by organic pollution since coliform organisms are present.

Cluster 2 comprise of OT-22, OT-23, OT-5, OT-21, OT-3, OT-25, OT-4, OT-17, OT-20 and OT-24 which are Upu 1 and 2, Depot 1, Edikwu 2, Obaganya 1, Ikobi 2, Obaganya 2, G. R.A 2, Edikwu 1 and Ikobi 1 respectively. Colour, COD and Hardness makes sampling sites in this cluster similar. Inorganic pollution resulting from indiscriminate disposal of sawdust from wood industries located in the area, agricultural practices and anthropogenic factors accounts for the variation of the group.

Cluster 3 encompasses OT-7, OT-16, OT-6 and OT-8 which represents Zone H.B 1, G.R.A. 1, Depot 2 and Zone H.B.2. Total dissolved solid, COD, Alkalinity and Hardness are the parameters that make for the similarity of the wells in this group. This cluster consisted of sites located at low lands. Typical sources of these parameters are from seasonal surface runoff of soil.

Cluster 4 has OT-12, OT-15, OT-11, OT-9, OT-10, OT-13, OT-14, which are New Heaven 2, Rice Mill, New Heaven 1, Eupi 1 and 2, Ojira 1 and 2 sampling sites. The cluster has sites with high population density and commercial activities taking place, the common features of these sites was TDS, COD, Alkalinity, Hardness and conductivity and constituents of the underlying rocks are the likely sources for the parameters.

Table 4.8: Mean Parameter Values of the Four Groups Resulting from Cluster Analysis

Parameters	Cluster 1	Cluster 2	Cluster 3	Cluster 4
Tur	563	1151	36	133
Colour	1928	3915	297	903
EC	374.6	752.8	279.2	500.4
Hard	720	1360	600	600
AIK	444	804	663	600
PO_4	4	6.16	3.6	3.64
SiO_3	120	317	41	126.2
NO_3	4.5	13.6	16.6	10.6
Cl	230.6	562.2	245	353.3
DO	19.3	51.8	21.3	33.3
BOD	228	371	81	352
COD	1110	2560	660	1830
Ca	520	960	440	420
K	8.9	21.1	64.9	104.1
Na	22.7	54	161	249.5
Cr	0.296	1.029	0.214	0.399
Cd	0.061	0.145	0.057	0.081
Pb	1.009	3.278	1.306	1.38
Mn	0.379	0.547	1.14	1.008
Coli	579	283	96	302
Cluster 1: Sampling Points OT-18, OT-19, OT-1, OT-2 Cluster 2: Sampling Points OT-22, OT-23, OT-5, OT-21, OT-3, OT-25, OT-4, OT-17, OT-20 and OT-24 Cluster 3: Sampling Points OT-7, OT-16, OT-6, OT-8 Cluster 4: Sampling Points OT-12, OT-15, OT-11, OT-9, OT-10, OT-13, OT-14				

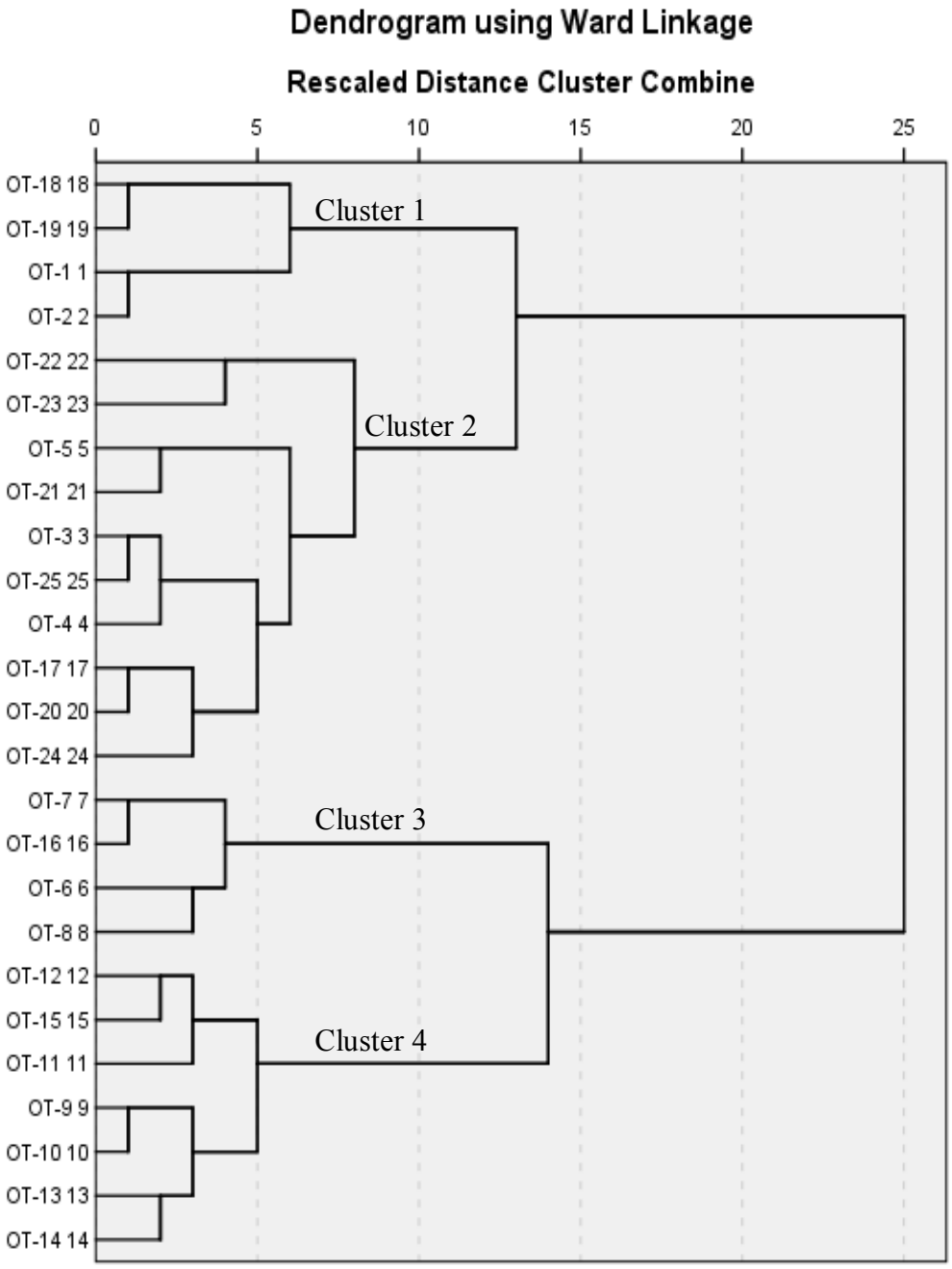


Figure 4.2: Dendrogram Showing Clustering of Sampling Sites.

4.3.3 Discriminant Analysis (DA)

The objectives of the DA were to test the significance of discriminant functions and determine the most significant variables associated with the differences among clusters. DA was performed on the original data set after classification into four major groups obtained through CA using the standard and stepwise modes. The Wilk's lambda and Chi square for each discriminant function ranged between 0.209 to 0.377 and 25.29 and 36.36 respectively at $p < 0.001$, showing that the temporal DA was effective and meaningful (Table 4.9). The discriminant functions obtained from the stepwise and standard modes of DA are shown in Tables 4.11 and 4.12. The standard DA mode constructs DFs containing all parameters except Cd, Pb, Mn and *Coli* (Table 4.11). It showed that 96% of the original grouped cases were correctly assigned as shown in Fig 4.3 all the groups located within the centroids except group 2. As revealed in Table 4.11, in the analysis, all parameters were utilized except Cd, Pb, Mn and *Coli*, suggesting that these parameters according to standard mode discriminate among the water samples. These parameters failed the tolerance test (Table 4.13). In the stepwise mode, variables are included step by step beginning with the most significant, until no significant changes are obtained. The stepwise mode suggests that colour, K and Pb (Table 4.10) are significant parameters for discriminating among the water samples for the variation of water quality.

Table 4.9: Results of Wilk's Lambda for Stepwise DA

Step	Wilk's lambda	Chi-square	Df	significance
1	0.377	36.36	22	0.000
2	0.262	29.60	21	0.000
3	0.209	25.29	20	0.000

Table 4.10: Standardized Canonical Discriminant Function Coefficients for Stepwise Mode

	Function
	1
Color	.853
K	-.751
Pb	.572

Table 4.11: Standardized Canonical Discriminate Function Coefficients for Standard Mode

	Function		
	1	2	3
Temp	.045	.560	1.318
Tur	8.262	-.860	-.141
Color	-4.640	4.816	-1.148
Alk	-7.343	-2.059	1.027
EC	-7.092	-.357	.761
TDS	6.782	.139	-.394
SS	-4.275	.729	.213
pH	3.272	.215	-.253
Hard	23.751	4.295	-3.930
PO4	9.029	-.181	-.681
SiO4	-7.997	-2.480	1.280
NO3	-.606	-1.006	1.762
Cl	-2.401	-3.148	.599
DO	-6.098	.781	.563
BOD	5.687	1.847	.981
COD	2.724	1.369	.106
Ca	-19.215	.622	3.092
K	6.174	1.279	-1.445
Na	-5.089	1.872	2.142
Cr	.865	.954	-.152

Table 4.12: Structure Matrix for DA

	Function		
	1	2	3
Cd[a]	.265*	-.083	-.029
BOD	.049	.212*	.077
Mn[a]	.103	.191*	-.134
Hard	-.031	.090*	.075
Coli[a]	.002	-.079*	.046
DO	-.035	-.078*	-.071
SS	-.005	.072*	-.046
Na	.012	-.079	.286*
Color	-.013	.124	-.274*
Pb[a]	-.150	.027	.256*
EC	-.025	.214	.232*
K	.019	-.065	.225*
SiO4	.000	.055	-.208*
TDS	.013	.025	.170*
Tur	-.010	.077	-.156*
NO3	-.006	-.033	.121*
Alk	-.007	-.008	.116*
Ca	-.037	.102	.103*
COD	.005	.025	-.074*
pH	.006	.019	-.062*
PO4	.008	-.005	-.060*
Temp	.008	-.053	.059*
Cr	.007	.026	.054*
Cl	-.016	.004	.048*

Pooled within-groups correlations between discriminating variables and standardized canonical discriminant functions

Variables ordered by absolute size of correlation within function.

a. This variable not used in the analysis.

*. Largest absolute correlation between each variable and any discriminant function

Table 4.13: Variables Failing Tolerance Test [a] for Standard Mode

	Within-Groups Variance	Tolerance	Minimum Tolerance
Cd	2.525E-5	.000	.000
Pb	.035	.000	.000
Mn	.023	.000	.000
Coli	716.880	.000	.000

All variables passing the tolerance criteria are entered simultaneously.

a. Minimum tolerance level is .001.

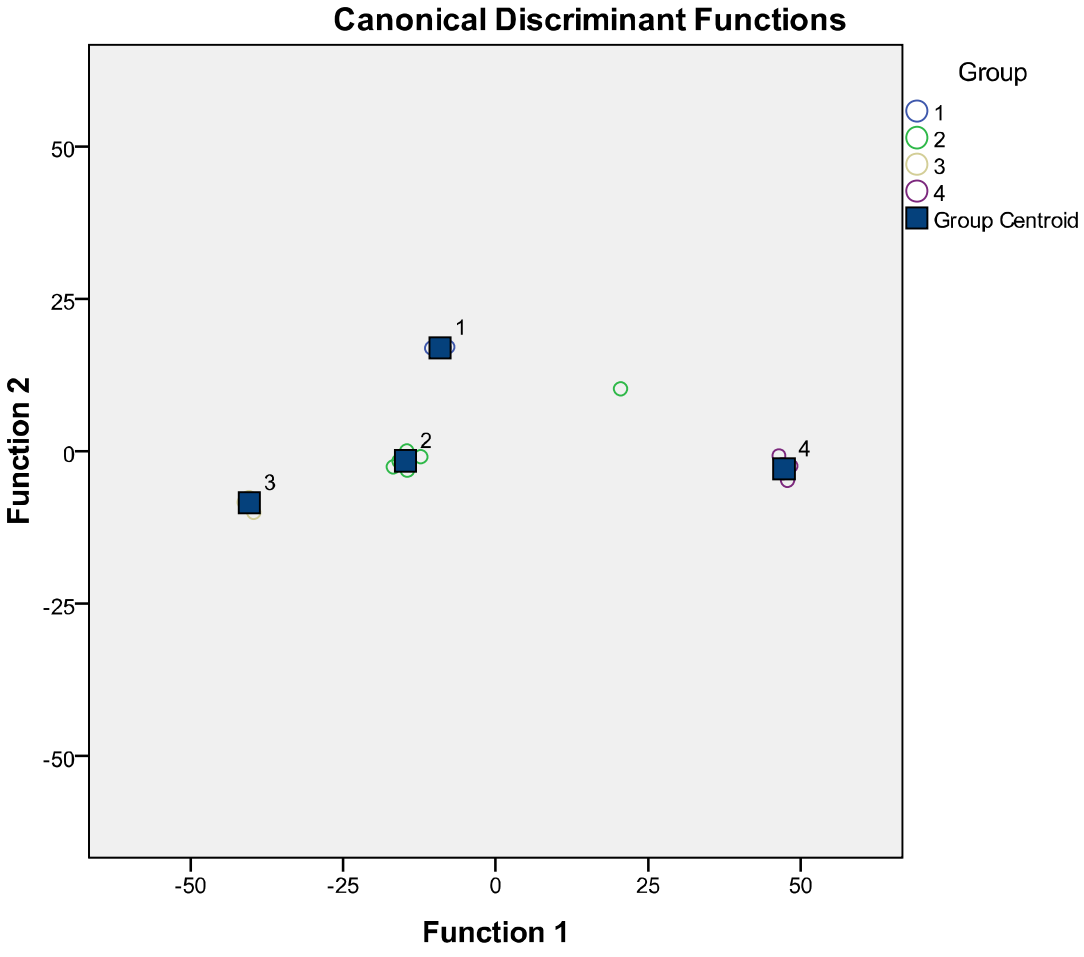


Figure 4.3: Canonical Discriminant Functions

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary

The well water samples from Otukpo town and surrounding villages were obtained to investigate their quality in terms of their physiochemical properties and heavy /trace metals.

The results obtained, revealed that well water samples from the study area were acidic during the period of investigation. Generally, the values of conductivity, total hardness, total alkalinity, total dissolved solids, chloride, phosphate, nitrate, potassium and sodium in the well water sources investigated were low when compared with WHO standards for potable water. The measured values for colour for the well samples exceed the WHO limit with exception of only three wells below the WHO standard for potable water.

The concentrations of the metals (Cd, Cr and Pb) for some of the wells were slightly above the WHO limit. Mn concentrations for all the wells were below the maximum permissible level. The bacteriological test of the water samples indicated that all the wells are contaminated with coliform organisms.

In the principal component analysis, the first 4 components explain 60.21% of the total variance in the data set. Based on the PCA results, the hydrochemical aspects of the area and land use pattern, it was concluded that the major water pollution sources are sewage, domestic and agricultural discharges, inorganic pollution due to urbanization and the constituents of underlying rocks of the area, and this implies that, these factors are the reasons for the variations in the water quality.

Hierarchical CA, classified the 25 sampling sites into four groups (1, 2, 3, and 4) based on the similarity of water quality characteristic. Cluster 1 mainly comprised of sampling sites

characterized with parent rock, cluster 2 had sampling sites similar due to high anthropogenic and agriculture activities. Cluster 3 consists of sites affected by seasonal surface run-off of soil. Cluster 4 comprised of areas densely populated which resulted into high level of inorganic pollution.

DA rendered an important reduction in the required data for the four clusters of the sampling sites, because it only used four parameters (Cd, Pb, Mn and *Coli*) in the standard mode and colour, K, and Pb in stepwise mode for the analysis and produced 96% correct assignation. These parameters are significant and responsible for the variations in the water quality.

5.2 Conclusion

Water is very vital for nature and can be a limiting resource to man and other living things. Without a well-functioning water supply, it is difficult to imagine productive human, livestock and agricultural activities. The quality of water is of utmost importance to quantity in any water supply planning. Due to the excellent solvent properties of water, it is rarely in pure nature. Water contamination has over the years been a major threat to man's health and that of animals, as well as, vegetation. It is a medium through which disease such as dysentery, cholera, typhoid, fever, skin infections and haemosidorosis among others are contracted. This has also caused death especially in Nigeria and other developing countries. By the results of the physical, chemical and bacteriological analysis of the water samples from the area under investigation, wells in cluster 4 are of better quality than wells in other clusters, since they did not exceed the limit stipulated by WHO for most of the parameters measured.

This study shows that, multivariate statistical methods are useful and excellent exploratory tool for understanding and interpreting complex water quality data sets, which generates information that are useful and effective for water quality management. The

variations and source of contamination were able to be discovered from the results obtained from PCA, CA and DA.

5.3 Recommendations

From the findings obtained from this research work, the following recommendations will help improve the water quality of Otukpo town and environ.

1. A comprehensive long term monitoring of the study area should be carried out to ascertain the effects of seasonal changes, varying depths and increase in population growth on groundwater quality.
2. Proper sanitary practices should be established and enforced to reduce level of contamination from various pollutants.
3. Proper disposal of urban and industrial waste should be carried out to avoid further degradation of groundwater.
4. The populace should be educated on the siting of wells away from liable sources of contamination.
5. The government should make available aquifer remediation techniques to clean up groundwater from heavy metals and make readily available temporal treatment kits.

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