



INVESTIGATION OF HYDROGEOCHEMICAL PROCESSES AND GROUNDWATER QUALITY OF THE KAKONTWE AQUIFERS IN NDOLA, ZAMBIA

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DECLARATION

I, Benard Tembo GOMO, at this moment declare that the dissertation herewith submitted

by the author to the Institute for Groundwater Studies in the Faculty of Natural and Agri-

cultural Sciences at the University of the Free State, in fulfilment of the degree of Magister

Scientiae, is independent work. I have not previously submitted it to any other institution

of higher education. Besides, I declare that all sources cited have been acknowledged using

a list of references.

I furthermore cede copyright of the dissertation and its contents in favour of the University

of the Free State.

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ABSTRACT

The study was aimed at investigating the hydrogeochemical processes of the Kakontwe aquifers in Ndola Zambia. The objective of the study was the characterisation the groundwater quality and related hydrogeochemical processes in the study area as well as to assess the quality of the groundwater to determine its suitability for industrial and agricultural uses. The researcher did not assess domestic water suitability due to limitations in analysis parameters.

The researcher collected groundwater samples for Laboratory analysis in 2017 and 2018. Sixty-Five samples were collected from the 33 locations during the two years for laboratory analysis for water quality assessment. Classification of the main water types and hydrogeochemical processes assessment and data interpretation was done using complementary tools such as stoichiometry and bivariate analysis, statistical analysis (hierarchical cluster analysis and principal component analysis), Gibbs Diagrams and Saturation indices.

The average groundwater level recorded was 7.3 mbgl (approximate 1261 masl) with a range from 2.6 mbgl to 16.99 mbgl and correlation showed that the groundwater flows towards the nearby stream. The average ion balance error shows that the samples analysis is generally accepted as was within the acceptable range of below 5%. Major ions concentration in the groundwater for both 2017and 2018 data were recorded in the following order; $HCO_{3^-} > Ca^{2+} > CO_{3^-} > Mg^{2+} > SO_{4^{2-}} > Cl^- > K^+ > Na^+$.

The main water types assessed in the study area were calcium bicarbonate. Chloride was also observed to have a significant influence in the process even though the chloride could not be associated with the predicted weathering process. The Chloride can be predicted to be from external sources causing accumulation in the system. The main hydrogeochemical processes that were inferred to be influencing the groundwater chemistry and quality are carbonate dissolution and silicate weathering.

A Langelier Saturation Index estimated indicated the saturated water with calcium carbonate and scale forming and corrosion could occur in the industrial equipment using the water in the study area. Treatment of the water before using for industrial purposes especially in boilers and heating equipment is therefore advisable. Based on the calculated Kelly's Ratio, the Kakontwe aquifer water showed lower levels of sodium ions and was classified as Good/Excellent for irrigation purposes. The Wilcox plots showed a Low-Risk classification on the Sodium (Alkali) hazard scale while the values for the salinity hazard showed a Medium Risk further confirming the suitability of the groundwater for irrigation use.

The study also demonstrated the value of utilising various assessment tools as complementary techniques to improve the understanding of hydrogeochemical processes, and its influence on progression of groundwater chemistry and quality.

Keywords: Hydrogeochemical, Groundwater chemistry, Groundwater quality, Hydrogeochemical processes, Principal component analysis, Water types.

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ABREVIATIONS AND ACRONYMS

ArcGIS ESRI Mapping software

Ca²⁺ Calcium ions

CaCO₃ Calcite

Ca-HCO₃ Calcium Bicarbonate

Cl- Chloride ions

CaMg[CO₃] Dolomite

CO₂ Carbon dioxide

CO₃²- Carbonate ions

DRC Democratic Republic of Congo

DTM Digital Terrain Model

EC Electrical Conductivity

FeCO₃ Siderite

GPS Global Positioning System

HCA Hierarchical Cluster Analysis

HCO₃- Bicarbonate ions

H₂CO₃ Carbonic Acid

H₂O Water

HPBH Boreholes Names

IDW Inverse distance weighted

KR Kelly's Ratio

LSI Langelier Saturation Index

Mg²⁺ Magnesium ions

MgCO₃ Magnesite

mm/a millimetre per annum

MnCO₃ Rhodochrosite

MSc Master of Science

PCA Principle Component Analysis

PTE Polyethylene

SAR Sodium Adsorption Ratio

SI Saturation Index

SO₄²- Sulphate ions

SPSS Soluble Sodium Percent

SSP Soluble Sodium Percentage

TDS Total Dissolved Solids

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

Groundwater worldwide is an essential source of drinking water, supports agricultural irrigation as well as supports and plays a vital part in the ecological balance (American Water Works Association, 2003; Cherry et al., 1979; Kannan and Joseph, 2009). Chapman (1992) also showed that groundwater contributes about two-thirds of the freshwater resources of the world and therefore, plays an essential role in human life, ecological life and economic activities. Groundwater has, therefore, several aspects that require detailed scientific understanding for the derivation of optimum value. The groundwater quality and related hydrogeochemical processes are one such aspect of groundwater that has been studied in detail for the Kakontwe Aquifers in Ndola, Zambia by this researcher. The chemical interactions between groundwater and the geological materials provide a wide variety of constituents into the contacting groundwater. This study attempts to develop an understanding of the hydrogeochemical and groundwater quality characteristics of the Kakontwe Limestone aquifers in Ndola.

Limestone and dolomite geology have continued to play a crucial role in the modernisation of human life through human civilisation products such as cement and lime produced and used in various construction projects. Limestone and Dolomite aquifer systems are also significant groundwater sources and examples of sensitive aquifer systems that can be prone to human disturbance of the groundwater systems. It is, therefore, imperative to understand the hydrogeochemical characteristics of such aquifers systems. The hydrogeological characterisation study of the Itawa-Mwateshi catchment was aimed at helping the understanding of the hydrogeochemical characteristics of the aquifer systems in the area.

The study area is one of the central lime/cement producing zone of the country and the region at large. The study was undertaken in line the requirements for the award of MSc Degree at the University of the Free States in South Africa. The Mwateshi Catchment is located partly in Masaiti District of Ndola, Zambia and roughly 10 km from the Ndola – Kabwe road (approximately 20 km southeast of Ndola town centre. The catchment is also home to several Lime and Cement producers such as Dangote Cement, Ndola Lime, Larfage Cement, Zambezi Cement and other small companies exploiting the limestone and dolomite that have played a significant economic role for Zambia and the region over the years. **Figure 1.1-1** shows the location of the catchment. The study area s further described in **Chapter 3** below.

This study covers the steps of materials and methods followed during the Hydrogeochemistry and water quality study. The main steps followed were hydrocensus, sampling, laboratory analysis of the samples and detailed scientific analysis of the laboratory results using various hydrogeochemical and statistics tools.

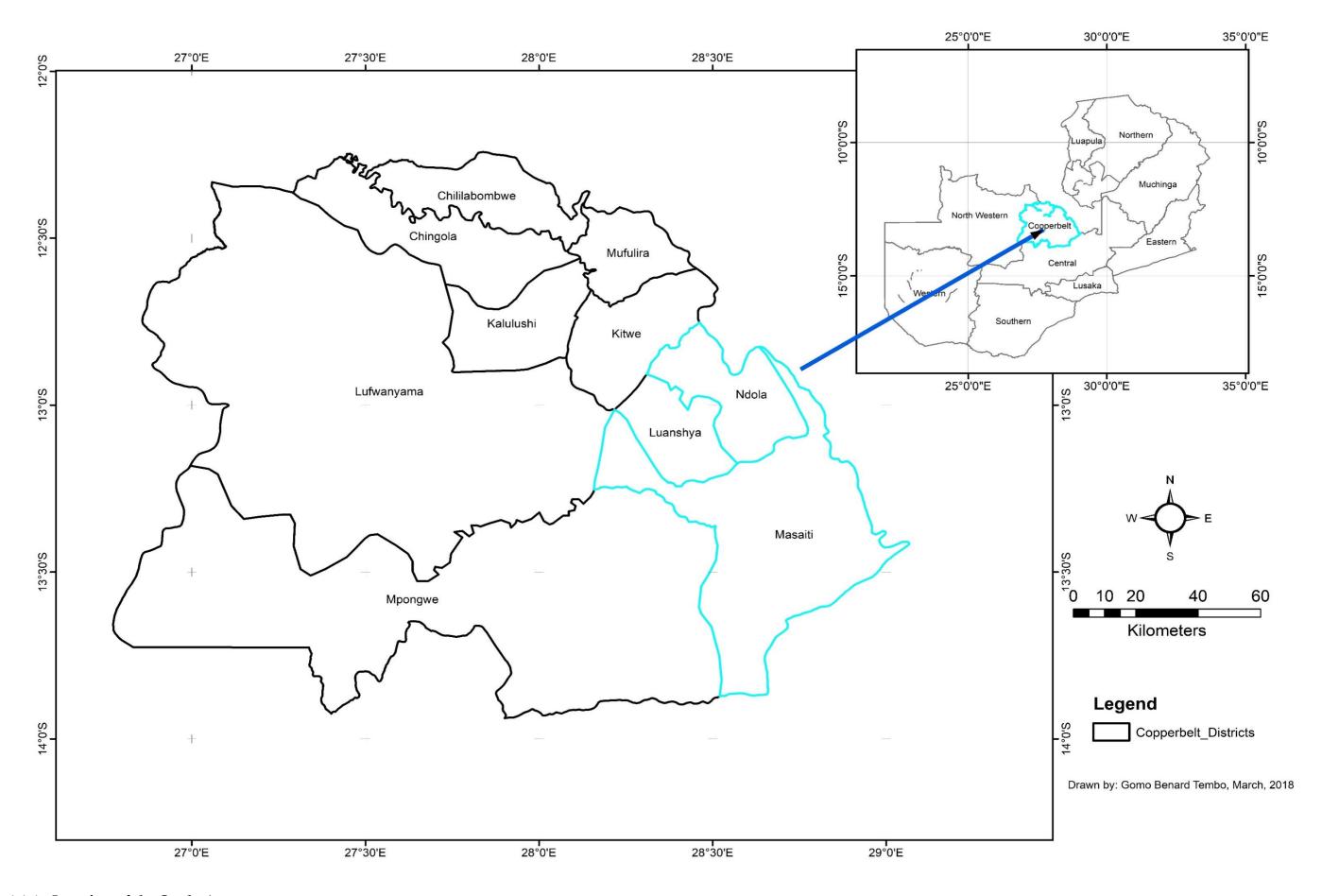


Figure 1.1-1 - Location of the Study Area

1.2 PURPOSE AND SCOPE

The purpose of the study is to undertake a hydrogeochemical characterisation of the Kakontwe aquifers in Ndola, Zambia. The research involves the collection, analysis and interpretation of groundwater samples from the study area. A variety of other existing data such as geological, hydrological and other relevant datasets such as topographic data was also used to help further the understanding of various related areas of the study. Relevant scientific and technical literature on the study areas was collected and evaluated. Local subject-matter experts, including professionals employed by state government agencies under the Department of Water Affairs both in Ndola and Lusaka, provided valuable information.

1.3 AIMS AND OBJECTIVES

The overall objective of this study is the characterisation of the hydrogeochemistry and groundwater quality in the Itawa-Mwateshi catchment in Ndola, Zambia.

The main objectives of the study are: -

- Developing an improved knowledge base relating to the hydrogeochemistry and groundwater quality characteristics of this vital limestone and cement producing area of Zambia that has significantly contributed to the economy of the country over the years;
- Understanding of the hydrogeochemical processes that can be critical for understanding behaviour and impacts on any water-related system, and;
- ❖ Assessment of the groundwater quality of the region.

1.4 STUDY APPROACH SUMMARY

This involved literature review, data collection, analysis and interpretation of hydrogeochemical and water quality data, and the application of relevant software such as AquaChem, SPSS, Excel, Geographic Information Systems (GIS) to enable data compilation, detailed assessment and analysis. The detailed study methodology is presented in **Chapter 4** below detailing the materials and methods of the study.

1.5 OUTLINE OF THE DISSERTATION

- Chapter 1 introduces the study theme, background information and the aims/objectives of the study;
- Chapter 2 reviews the literature by explaining the findings from previously conducted studies and characterising the hydrogeochemical tools;
- Chapter 3 gives an in-depth description of the study area, including hydrogeology, the geology of the study area;
- Chapter 4 outlines the study methodologies used in the study;
- Chapter 5 presents and discusses the findings of the study in line with the aims and objectives as described in the methods, and;
- **Chapter 6** describes the conclusions and recommendations of the study.

CHAPTER 2: LITERATURE REVIEW

2.1 INTRODUCTION

This chapter presents the details of the literature as well as previous studies done in the area and region including the applicable methodologies as well as principles. This section is a result of reviews of relevant hydrogeochemical, geological and hydrogeological data. Few hydrogeochemistry studies were available in the project vicinity areas. The researcher attempted as much as possible to fill in the gaps with a literature review from other regions based on similarities of study objectives or conditions. Ndola like many other places in Zambia has not had many studies conducted in Hydrogeology as compared to geological studies. Some studies were available in specific areas. Examples of particular studies include but not limited to Applied Science and Technology Associates (2014), Dynamic Design (2014) and WSM Leshika (2015) as well as several studies that have conducted by the department of water affairs under the new Ministry of Energy and Water Affairs (now the Water Resources Management Authority or WARMA). This section, therefore, presents some information on the studies that have been conducted in the past in hydrogeology in Ndola and specifically the Kakontwe area.

2.2 WATER STATUS

The distribution use of groundwater use in Zambia is approximately 30% irrigation, 27% rural water supply, 22% livestock and 13% urban supply (SADC Groundwater Grey Literature Archive, n.d.). Although there are limited statistics, private development of groundwater has increased in many parts of the country since the 1990s. Private usage is primarily for irrigation on farms and domestic water supply. Drilling for domestic supply is widespread for residents who are trying to avoid the erratic water supplies from water utilities and in areas not serviced by piped water (Groundwater Consultants Bee Pee (Pty) Ltd and SRK Consulting (Pty) Ltd, 2002; Groundwater Grey Literature Archive, n.d.; Nyambe, 2017); Trottier and Chileshe, 2005; Shahin, 2002).

The increasing demand and exploitation of groundwater in mining/quarrying activities, agriculture, commercial and domestic needs require that the characteristics of groundwater be first understood scientifically for safe and sustainable use of the resource. The first steps are therefore assessment and characterisation of the aquifers and determination of available quantities and qualities of groundwater. Management of water resources at the operations level, therefore, require adequate knowledge for better management. Studies, such as hydrogeological and hydrogeochemical characterisation of aquifer systems, are therefore necessary to understand the groundwater resources in all scientific spheres for appropriate control and mitigation.

The groundwater resources of Zambia are not fully quantified, and the data is scanty, but rough estimates do exist (refer to **Table 2.2-1** and **Table 2.2-2** below). The total groundwater storage was estimated at 1, 740x10⁹ m³, while the groundwater recharge estimate was approximately $160x10^9$ m³/ year according to the Zambia National Water Policy (1994). The Copperbelt Province (the study area province) has an estimated 2.6 X 10^9 m³ of recharge per annum (**Table 2.2-2** below). In terms of the catchment, the study area is in the Kafue Catchment and the Kafubu as the sub-catchment. No secondary hydrogeochemistry data for the Kafubu sub-catchment was available during this study.

Table 2.2-1 - Groundwater Potential in Zambia (Zambia National Water Policy)

Table 2.2-1 - Gloundwater I otential in Zambia (Zambia National Water I oney)					
Drainage Basin	Luapula - Tanganyika	Luangwa	Kafue	Zambezi	Total
Basin Area km ²	194,000	147,000	155,000	256,000	752,000
Total Mean Annual Rainfall (mm)	214.1	122.3	149.72	228.69	714.85
Groundwater through flow (mm)	0.83	1.634	0.96	0.22	3.65
Vertical Recharge (mm)	41.5	33.02	24.45	64.03	160.08
Groundwater Storage (m³)	377.7	242.76	252.06	86.82	1,740.40

Table 2.2-2 - Groundwater Potential by Province (Zambia National Water Policy)

Tuble === Cloudia valet I otential by 110 vince (Euriteia valetial valet I oney)				
Province	Groundwater (Estimated Annual Recharge Rates) X 109m³/year			
Central	7.7			
Copperbelt	2.6			
Eastern	6.1			
Luapula	3.9			

Province	Groundwater (Estimated Annual Recharge Rates) X 109m³/year	
Lusaka	1.5	
Northern	11.5	
Northwestern	11.4	
Southern	5.7	
Western	7	
Total	57.5	

The Zambia National Water Resources report indicated that Ndola's supply of water comes from the Kafubu River, Ndola Lime Quarries, old Bwana Mkubwa Mine Pit – within the area of influence of the project study area. These sources inherently are connected to the groundwater through the surface water-groundwater interface. Hence, the connection of Ndola's water sources to the Itawa-Mwateshi catchment even though there is very little data collected and reported. The Kafubu river and dam streamflow, as well as groundwater, discharge through the Mwateshi Stream draining the basin.

2.3 HYDROGEOLOGY

Lambert (1961) showed that the rocks of the Katanga age, within Zambia, have the uppermost groundwater potential as a single geological sequence and are found mainly in the Northern and Central parts of Zambia. The Lower Katanga Dolomite is by far the most critical aquifer from which Towns such as Lusaka, Ndola, Kabwe and Mazabuka derive part of their water supply (Lambert, 1961). From a hydrogeological point of view, the geology of Zambia can be classified into simplified lithostratigraphic units indicating the main aquifer lithologies, their relative groundwater productivity and percentage occurrence in the country are shown in **Table 2.3-1** below.

Table 2.3-1 - Classification of Aquifers in Zambia (Chenov, 1978)

Lithostratigraphic Unit		Main Aquifer Li- thology	Productivity of Groundwater	Percentage of the Whole Country (%)	
Cenozoic	Alluvium	Sand, Gravel	Medium-High	11.9	
Super- group	Kalahari	Sand	Medium-High	23.8	
	Upper Karoo	Basalt	Low	0.5	

Lithostratigraphic Unit		Main Aquifer Li- thology	Productivity of Groundwater	Percentage of the Whole Country (%)
Karoo Su-		Sandstone	High	4.5
pergroup	Lower Karoo	Mudstone	Low	0.7
	Kundelungu	Carbonate Rock	High	2.0
Katanga	Undeferential Kundelungu	Shale	Low	12.9
Super- group	Upper Roan	Dolomite	High	0.4
	Lower Roan	Quartzite, Dolomite	Medium-High	0.8
	Mine Series	Quartzite, Shale	Low - Medium	3.7
Muva Supergroup		Shale	Low	9.4
Basement Complex		Gneiss, Magmatites, Schist	Low - Medium	14.2
Granite		Granite	Low - Medium	
Other Igneous Rocks		Basic – Igneous, Meta - Igneous	Low	15.2
Metamorphic Rocks		Metasediments, Metavolcanics	Low	

Source: Hydrogeological Map of Zambia (Scale 1:1,500,000); Groundwater Inventory of Zambia (Chenov, 1978)

Chenov (1978) showed that the aquifers in Zambia are classified into three main types as shown below:

- a) Aquifer where groundwater flow is mainly in fissures, channels or discontinuities: Groundwater occurs in secondary rock features and structures such as weathered zones, faults, joints, fractures and solution features that usually extend to around 30m to 40m in depth within consolidated hard rocks and often extend to more than 90m in depth. UNICEF, USAID, RWSA, GRZ, 2009 showed that such aquifers can further be sub-divided into two, namely:
 - δ Highly productive aquifers: These include Upper Roan Dolomite and Kundelungu Limestone (yielding from 1-70 L/s) but have limited and very narrow area of distribution. These aquifers distribution in Copperbelt, Lusaka, Northwestern and Central provinces and cities such as Lusaka, Ndola and Kabwe. These are the aquifers of concern in the Kakontwe limestone area (the study area).

- δ Low productive aquifers: The Lower Roan Quartzite, Muva sediments, granites and undifferentiated Kundelungu formations (0.1-10 L/s). These aquifers were mainly distributed in Northern, Luapula, Central, North-Western and Copperbelt Province.
- b) Aquifers where intergranular groundwater flow is dominant: These aquifers are found in the Alluvial formations, Kalahari Group and Karoo Supergroup. These aquifers are distributed mainly in the Western, and parts of Southern and along Luangwa River in Eastern Zambia. They were also distributed around Chambeshi River in Northern Province and Lake Bangweulu in Luapula Province (0.1 15 L/s)
- c) Low yielding aquifers with limited potential: These include the major part of Argillaceous formations, Karoo basalts and older Basement Complex. These aquifers were mainly distributed in Eastern and Southern parts of Zambia (0-2 L/s) as well as parts of Northern, Luapula, Central Copperbelt, Lusaka and North-Western provinces.

Several authors showed that the Underlying Ndola geology had three principal aquifers - the Bwana Mkubwa and Skyways aquifers have a northwesterly flow direction, while the Kakontwe aquifer flows south-west. The Kakontwe aquifer is known as an extremely high-yielding aquifer due to the carbonated nature of this area, providing a rich source of groundwater to some regions of Ndola (Adams and Kitching, 1979; Moore, 1967). The Bwana Mkubwa aquifer supplies the Itawa Springs area, while the Kakontwe supplies the main Itawa dambo area.

Within the Ndola aquifer network, the geogenic structure is of importance due to its influence on groundwater quality. The Copperbelt lies in sedimentary deposits, including shales, siltstones and sandstone mixed with carbonates such as limestone and dolomite (Pettersson et al. 2000). In Ndola specifically, the bedrock is dominated by two principal rock formations, carbonaceous rocks in the east, including dolomite-limestone, and crystalline rocks in the west, including gneiss, granite and argillitic deposits. The western side and southern half of the city sits on limestone, a significant source of calcium carbonate,

which readily dissolves in contact with naturally-acidic waters, and produces a landscape susceptible to submerged lakes, springs, and deranged river networks.

The Kafubu Stream marks the edge of the limestone section, which emerges from a spring-fed natural wetland. Adjacent to the limestone is a band of carbonaceous dolomite conglomerate, comprised of silt and sandstones, with a further outcrop in the south-west. Adjacent to the dolomite of the Central Business District (CBD) area is a tight semi-circular band of chert, sandstone, siltstone and argillite, a band of greywacke, argillaceous and felspathic quartzite, and a thin band of felspathic quartzite and arkose conglomerate. The eastern half the city is dominated by crystalline gneiss and foliated granite, which extends up into the northern area. In the southwest, there is also a pocket of quartz-mica schist. The geology, therefore, transitions from intensely metamorphosed limestone in the east, through the different levels of metamorphosed sandstone, siltstone and greywacke in the central area, and further through to the plutonic area of gneiss and granite in the west.

2.4 HYDROGEOCHEMISTRY

Groundwater lies beneath the surface in the saturated zone below the water table, and stored in geologic formations known as aquifers (Freeze and Cherry, 1979; Bird and Macklin, 2009). The understanding of hydrochemistry is critical to estimate the origin of the chemical composition of groundwater (Zaporozec, 1972). Several researchers have studied the importance of hydrochemistry of groundwater quality deterioration and geochemical evolution of groundwater in many parts of the globe (Deutsch, 1997; Kannan and Joseph, 2009; Tyagi et al., 2009; Srinivasamoorthy et al., 2010; Stevanovic, 2017; Vasanthavigar et al., 2010).

Groundwater has been widely considered as being a safe source of clean drinking, domestic and irrigation water and believed safe from contamination that affects surface waters. As a result, groundwater is extracted globally for drinking water, and in developing countries, it is widely held as the keystone for water security, particularly in water-poor countries (Morris et al. 2003). Groundwater is believed to have the advantage of being a safe source of water that if thus developed can help to sustain remote communities and forego the challenges of collecting water from distant river sources or drinking holes, that

are often contaminated by faecal matter and water-borne diseases (Cobbing et al., 2008). Poor water quality often harmfully distresses human health and plant growth (Hem, 1991). The water quality is therefore vital in determining the waters appropriateness for several purposes.

Subramani, Elango and Damodarasamy (2005) showed that groundwater quality discrepancies are a function of physical and chemical forms in an area predisposed by geological and anthropogenic activities. Groundwater quality gets transformed when it flows along its flow path from recharge to discharge areas through the processes like: evaporation, transpiration, selective uptake by vegetation, oxidation/reduction, cation exchange, dissociation of minerals, precipitation of secondary minerals, mixing of waters, leaching of fertilizers, manure and biological process (Srinivasamoorthy et al., 2014, Appelo and Postma, 2005; Morris et al. 2003).

The primary determinant on groundwater quality is the lithology of any region followed by contamination from anthropogenic activities (Schwartz and Zhang, 2003). Firstly, the physical characteristic of the geology determines the rate that recharge (and by inference, potential contamination) enters an aquifer. Secondly, by naturally filtering contaminants as they pass through the permeable media via processes of adsorption, attenuation, and redox reactions. Thirdly, the rock type also affects the mobility of these contaminants if they reach the saturated zone, and lastly, the composition of the geology also contributes natural levels of contaminants via chemical and physical weathering of the aquifer rock itself. The specific lithology that contains groundwater acts as a potential source of pollutants through chemical and physical weathering as water flows within the aquifer, as well as in determining the background chemistry of the groundwater. (Bird et al., 2009; Cherry et al., 1979).

Chemical weathering takes place, whereby the minerals within the aquifer rock undergo complete dissolution or partial alteration, resulting in elements leaching into groundwater (Deutsch, 1997). Weathering, therefore, could naturally alter the quality or introduce contaminants into groundwater based on the specific lithologies are known to add certain elements (refer to **Table 2.4-1** below showing the natural sources of major cations). The

significant cations can also come from a range of different geology types, these being important in determining metal mobility.

Table 2.4-1 - Natural Sources of major cations indicating the levels of contamination expected from different geogenic areas

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Geology	gy Groundwater Composition - Cations	
Sandstone	Sodium, Calcium, and Magnesium – all in similar concentrations	
Limestone	Calcium - dominant cations	
Dolomite	Magnesium and Calcium - both in similar concentrations	
Granite	Calcium and Sodium	
Basalt	Sodium, Calcium and manganese – all in similar concentrations	
Schist	Calcium and Sodium	

Source: Mazor, 1997

The bedrock of the project region is widely believed to be dominated by two principal rock formations, carbonate (dolomite-limestone) and crystalline (granite-gneiss). Whether bedrock is carbonate or crystalline will have a significant impact on permeability and the rate that groundwater recharge occurs. Carbonates are primarily comprised of calcium carbonate, resulting in hard water that is difficult to wash with and produces scaling on heating elements. Calcium carbonate has a high solubility, particularly in the presence of dissolved carbon dioxide in water that dissociates to produce carbonic acid, which acts to dissolve the rock, increasing the pore space, thus the capacity to hold water (Mays, 2011).

In determining the impact of different metals on drinking and irrigation water, metal mobility is a significant factor. The background chemistry of water directly controls metal mobility (Fenemor and Robb, 2001). Metals are found in two fundamental forms, dissolved or particulate, which combined, form the total recoverable concentration. In the aquatic system, the term 'dissolved' refers to the concentration of a metal that is dissolved into solution, while 'particulate' refers to that which is in a solid state and can combine with other species (Drever, 2002). The state of metal is essential when assessing the respective impacts on the physical environment, whereby the state determines the bioavailability and the toxicity of the metal (Drever, 2002). These factors have positively correlated with mobility; hence bioavailability and toxicity are greater under dissolved conditions ((Mulligan, Yong and Gibbs, 2001)). pH, alkalinity, and redox (Eh) act to determine this

form, whereby the form a metal takes, depends on physical conditions: namely, advection, dilution, dispersion and sedimentation.

Moreover, chemical conditions such solution reactions, precipitation, adsorption onto the bedrock or suspended particles, and desorption back into solution have been documented to influence the process. (Bird and Macklin, 2009; Deutsch, 1997; Drever, 2002; Salomons, 1995). Of these controls, adsorption and desorption are of primary interest in terms of the role that pH, alkalinity, and Eh play. Adsorption is the removal from solution as a dissolved ion attaches to a solid species, while desorption occurs as a particulate ion precipitates off a solid species, transforming into a dissolved state (Drever, 2002; Deutsch, 1997).

Alkalinity (which is a measure of a water body's ability to neutralise an acid) is essential as a buffer against low pH levels (Ballance, 1996). The main components that contribute to alkalinity are carbonate, bicarbonate, and carbonic acid. Carbonate rocks (limestone and dolomite) act as a significant source of alkalinity due to the dissolution (or precipitation) of the rock as water flows through it. Carbonate rock is composed of CaCO₃; thus, dissolution causes the release of Ca²⁺ and CO₃²⁻ into a solution, whereby the latter increases alkalinity (Schwartz and Zhang, 2003). This increase provides a buffer against low pH values, therefore decreasing metal mobility (Edmunds and Smedley, 1996).

On the contrary, flow through crystalline rocks offers poor buffering capacities, hence may be more likely to contain acidic waters and more conducive to the mobilisation of metals (Edmunds and Smedley, 1996). Hardness is the sum of polyvalent cations (calcium and magnesium) dissolved in water and can be an alternative measure of the buffering capacity of water to alkalinity. Hardness is expressed as milligrams of calcium carbonate equivalent per litre (CaCO₃ mg/l) and takes two forms: carbonate hardness; and non-carbonate hardness (WHO, 2011; APHA, 2012). Carbonate hardness is due to the metals associated with HCO₃-, while non-carbonate hardness is due to the metals associated with SO₄-, Cl-, or NO₃- (Shaw et al. 2011). Carbonate hardness is the equivalent to total alkalinity, whereby any excess hardness above total alkalinity is taken to be non-carbonate hardness (APHA, 2012). Carbonate hardness assessed on a scale, whereby the more significant the hardness, the higher the buffering capacity.

2.4.1 Hydrogeochemical Processes

Mineral weathering is a significant controller of global atmospheric CO₂ concentrations. During silicate weathering, HCO₃- is a derivative entirely from the atmosphere and is a net long-term sink for CO₂. Carbonate weathering draws down even more enormous amounts of atmospheric CO₂, but the removal is short term because CO₂ returned to the atmosphere by carbonate precipitation.

Fetter, 2001 showed that the various dissolved carbonates species (H_2CO_3 , HCO_3^- and CO_3^2 -) as a function of the pH. At a pH of 6.3, the activities of HCO_3^- and H_2CO_3 are equal. With pH>6.3, HCO_3^- becomes the predominant species, and at pH<6.3 there is more H_2CO_3 as more predominant species. The same relation for the CO_3^2 - and HCO_3^- , the two species have similar activity at a pH of 10.3.

Bicarbonate dissolution is a modest and common weathering reaction in carbonate rocks (Drever, 2002). The Carbon dioxide (CO₂) from the organic matter in the aquifer reacts to form H_2CO_3 . Infiltrating recharge water accumulated H_2CO_3 intermingles with calcite, reacting with calcite (CaCO₃) and dolomite Ca-Mg(CO₃)₂ in the aquifer system. The reaction mainly leads to the dissolution of calcite and dolomite in the carbonate minerals causing an increase in Ca^{2+} , Mg^{2+} and HCO_{3^-} ions can be measured in the laboratory. This reaction gives carbonate and bicarbonate water type such as estimated in the Kakontwe aquifer system based on the levels in mostly equilibrium (Belkhiri and Mouni, 2013).

2.5 LIMESTONE QUARRIES AND PROCESSING

The Copperbelt Province holds 34% and 10% of global cobalt and copper reserves respectively, with many Zambia's mines located in this province, mainly along the Kafue anticline (Norrgren et al. 2000; Pettersson and Ingri, 2001). Intensive copper and cobalt mining have dominated the Copperbelt Province over the past century and presently account for 80% of foreign exchange earnings (British Geological Survey, 2001; Sracek et al. 2012; von der Heyden and New, 2003).

Limestone mining in Zambia is mainly centred around Lusaka, with various marble, aggregate and cement quarries and in Ndola with quarries for aggregate, lime and cement

production. The primary quarry in the Lusaka area is the Chilanga cement factory and several other quarries exploiting limestone to produce various grades of limestone and dolomite aggregates for the local and international market (Mills, 2000).

Mills (2000) also discussed the concept of mining limestone, particularly for the lime and cement manufacture, in Zambia and Malawi. The writer further showed that region has massive limestone deposits that have been exploited for many years and believed to still have limestone deposits to last for more than two thousand (2000) years including the study area – the Kakontwe limestone in the Itawa-Mwateshi catchment. Zambia is believed to have vast amounts of limestone and dolostones that is yet to be fully explored and exploited. Current cement production for Zambia has estimated at 2.5 million tonnes of cement per annum in 2017. More than 70% of this production comes from the study area. The major companies in the region are Lafarge Cement Zambia, Ndola Lime Limited (a subsidiary of ZCCM-IH), Zambezi Portland Cement, Handyman's Lime Limited, Neekanth Lime and Dangote Cement Zambia. There are also several smaller operations in the area all exploiting the massive limestone deposit (refer to Figure 2.5-1 below).

Some special attention is required for zones underlain by limestone and dolomite because these regions contribute about 25% of the land surface of the world and are a source of abundant water supplies, minerals and construction materials (SADC Groundwater Grey Literature Archive, n.d.). Groundwater Consultants Bee Pee (Pty) Ltd, Nyambe (2017) and SRK Consulting (Pty) Ltd (2002) also showed that groundwater has a significant role in the water sector in Zambia, both in rural and urban water supplies, irrigation and mining. Like many southern African countries, the bulk of water supply in rural villages comes from groundwater through hand pumps, open wells and pumped boreholes. However, even large urban centres, including Lusaka and Ndola, receive a large proportion of their water from groundwater and the figures are bound to increase soon as the cities develop more, hence the need to preserve groundwater.

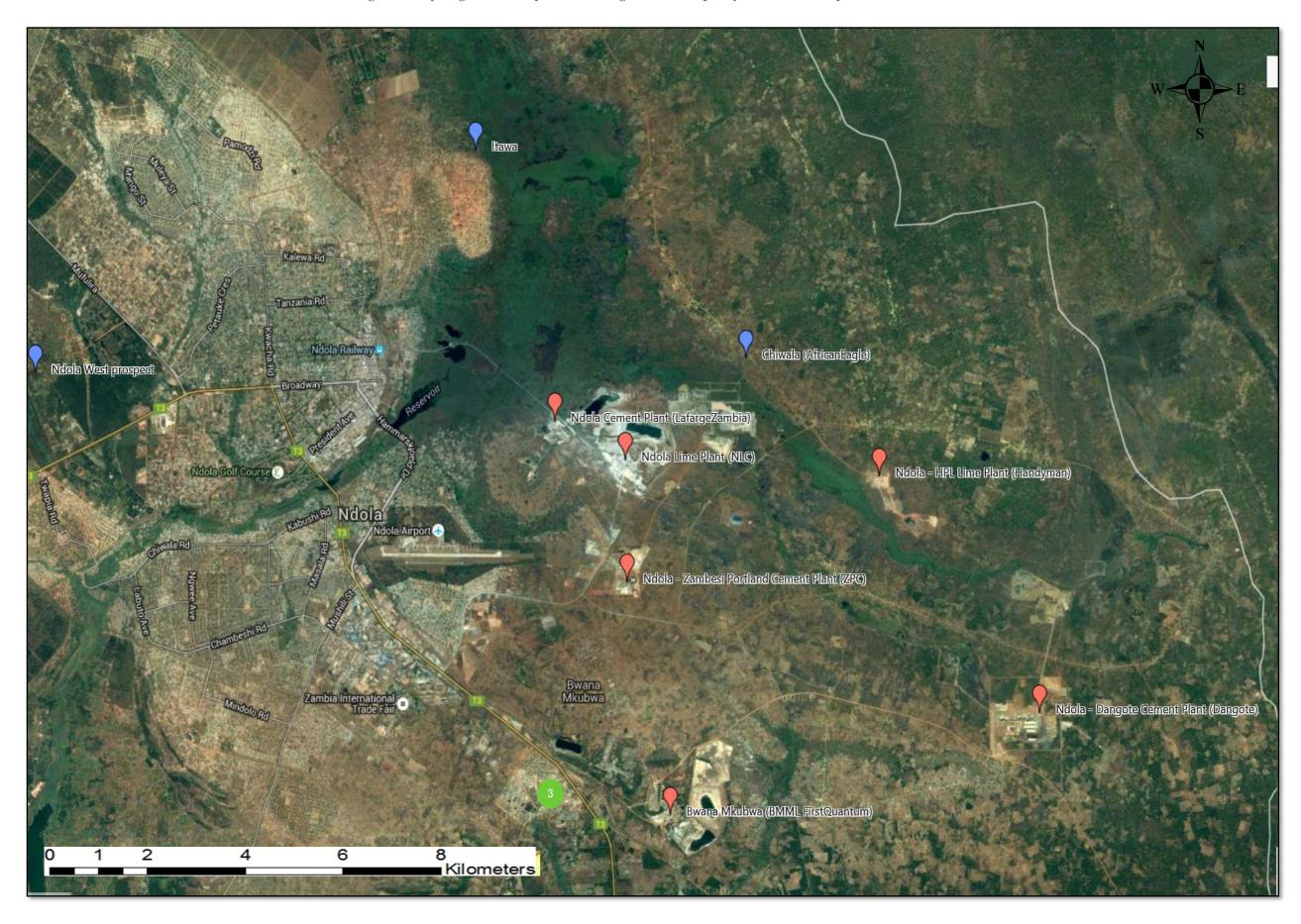


Figure 2.5-1 - Locations of Limestone Mines in the area (Source: MapPro, 2016)

2.5.1 Manufacture of Cement and Lime

Limestone is a naturally occurring and abundant sedimentary rock comprising of high levels of calcium and magnesium carbonate and dolomite (calcium and magnesium carbonate), along with minerals. The first stage for cement and lime manufacturing is the quarrying of the limestone used in the manufacturing process. The Portland Cement Association (2015) showed that quarrying of limestone and shale had been achieved by using explosives to blast the rocks from the Quarry. After blasting with explosives, huge power shovels are used to load dump trucks or small railroad cars for transportation of limestone to the cement plant, which is usually nearby, as the case for the companies operating in the study area. It is this quarrying stage that has a potential to impact on the groundwater of the quarry area, hence, is of primary interest for this study.

Cement is a synthetic chemical product that, when mixed with water and allowed to hydrate, forms a robust binding material, and has been extensively used in the history of construction. Often, it is used to cement aggregates together to form concrete. Cement being manufactured through a meticulously controlled chemical combination of calcium, silicon, aluminium, iron and other ingredients. Manufacture is by, intimately mixing finely ground limestone and argillaceous materials in the correct proportions and burning the mixture at a temperature of between 1,300 and 1,500 degrees centigrade at which time partial fusion occurs, and nodules of clinker produced. The clinker is then rapidly cooled, and together with a small percentage (usually about 5%) of gypsum finely ground to make cement. The gypsum is used to delay the reaction time of the cement other forms of calcium sulphate may partly replace it.

The composition of the finished cement must fall within a narrow range to give a cement of the required performance. The ratios of the active components have been defined by certain factors laid down as internationally used standards. Usually, Portland cement contains CaO 60-65%, SiO₂ 20 - 25% with 2% Fe₂O₂ and Al₂O₃. Strict limits set in most standards for the maximum content of certain harmful impurities. For example, British Standards set 4% as the maximum content of magnesia (The European Cement Association, 2015; Portland Cement Association, 2015).

The ancient Egyptians originated lime production. Their kilns were of stone construction with large stones forming an arch at the bottom (Carran et al., 2017; Graymont, n.d., 2017). The kiln charged cold, and a wood fire lit beneath the stone arch. After four or five days the fire would be extinguished, and after cooling, the carbon would get released as carbon dioxide gas (calcined), and the lime extracted for use mainly in agriculture. Calcination refers to the reaction wherein the limestone is heated to less than its melting point (approx. 1,100 degrees C), to drive off matter that evaporates quickly, in this case, carbon oxides. Traditionally in Southern Africa, lime production has been, and in some areas still is, achieved by use of an intermittent batch process, with layers of limestone being burned using wood in covered heaps (reducing environment) in a single operation. The process has been modernised and improved to use the Kilns fired by Morden fuels or even electricity instead of the traditional methods.

Further production involves completely recharging the kiln. Kilns of this type would yield about one and a half tonnes of product per burn. A burn took 48 hours and 24 hours for cooling (The European Cement Association, 2015).

2.6 IMPORTANCE OF LIMESTONE GEOLOGY

The significance of the study area has been documented in that the subsurface dolomites and limestones of the Kakontwe formations have also identified as the significant water-producing zones in the Ndola area by their high permeability (Mills, 2000). Mills (2000) further shows that surface water features such as the Mwateshi Stream has been formed where the saturated sections of these limestones and dolomites crops out.

Groundwater is also the primary source of base flow in all the perennial rivers. However, some groundwater resources, are facing increasing threats from pollution resulting from exposure to pit latrines, septic tanks and unplanned quarrying of construction material. There is also a threat to over-pumping because of unregulated exploitation. Some mining companies, such as Dangote Quarries have even diverted the stream to access the limestone materials (JA Consultancy, 2011). Groundwater often represents a substantial augmentation of natural river flows and may be beneficial in ameliorating contamination but presents long-term challenges to sustainable management of the upper areas of the Kafue River

catchment. The main water sourced of the catchment such as the Kakontwe aquifer area has not been prudently managed with limited or zero research in most cases to understand to dynamics of the system as an early warning.

The Kakontwe Limestone aquifers in the study area support directly or indirectly the water needs for the city of Ndola and Zambia/region at large, hence the need for their understanding and protection.

The Kafubu river discharges from the Kafubu Dam and drains in the southeast direction towards the Kafue River central Zambia. The study area is therefore critical for water management of this whole catchment as well as the Kafue River that also contributes to power generation downstream the Kafue River as well as on the Zambezi River. Any mismanagement of this catchment could, therefore, affect the water starting from the Kafubu Dam as well as the other sources of water for the people of Ndola. Other possible impacts of mismanagement would be reduced flow of surface water into the Kafue River from the Kafubu River affecting all life and the activities. The capability of the rock to permit for recharge and embrace water depends on the state of weathering and tectonic structures such as folds, faults, and shear zones.

CHAPTER 3: STUDY AREA DESCRIPTION

3.1 LOCATION

The Mwateshi Catchment is located partly in Ndola and Masaiti Districts of Ndola, Zambia and is approximately 10 km from the Ndola – Kabwe road (T3), about 20 km southeast of Ndola town centre. The catchment is also home to several Lime and Cement producers such as Dangote Cement, Ndola Lime, Larfage Cement, Zambezi Cement and other small companies exploiting the limestone and dolomite. **Figure 1.1-1** in **Chapter 1** above shows the location map of the study area. The study area is a significant lime and cement production area of Zambia that has contributed significantly to the development of the country as well as the region for many years.

3.1.1 Regional Setting

The study area has significant economic, social and ecological importance as a water resource for domestic and industrial purposes to the city of Ndola (Karen, El-Fahem and Kolala, 2015). The author further showed that the environment around the spring had been altered by industrial development and by people settling close to the spring; the development has created issues due to the changes in land use and related issues such as sanitation and water quality.

The regional gradient is controlled by the Itawa River draining the catchment in the northwest direction. The quarries lie on relatively flat land between 1257-1267 mamsl, with a slope of 1.5% to the Southwestern of the study area. The topography and landscape of the project site are generally flat and undulating. The terrain within the project area lies between 900m and 1000m above sea level (Global Environmanagement Consult Ltd, 2013; JA Consultancy, 2011).

3.2 CLIMATE

The rainfall is distributed over a rainy season (October – April) lasting around six months, with very little precipitation occurring outside this period. Peak rainfall is in January. Over

80% of the total annual rainfall occurs during the four months from November to February. Generally, the annual rainfall is consistent with low drought risk. The average annual rainfall over the catchment is approximately 1221 mm/a (Adams and Kitching, 1979). Potential Evapotranspiration is estimated 1,681 mm/a. A surplus of 285 mm/a of rainfall exists during the rainy season, and since no surface drainage features exist indicative of surface runoff, a substantial proportion of this rainfall surplus contribute to recharge (WSM Leshika Consulting (Pty) Ltd, 2015).

3.3 LANDUSE AND SOILS

Soils are sandy loams to sandy, clayey Loam in the topsoil, grading to sandy clay in the subsoil. Soils are well drained, and few surface drainage channels were observed. The few channels emerging from the hills to the Northeast disappear as they appear onto the limestones, suggesting runoff infiltrates into the ground and that soils are well drained. The exception is in the valley bottom dambo, where saturated conditions exist (WSM Leshika Consulting (Pty) Ltd, 2015; Global Environmanagement Consult Ltd, 2013; JA Consultancy, 2011).

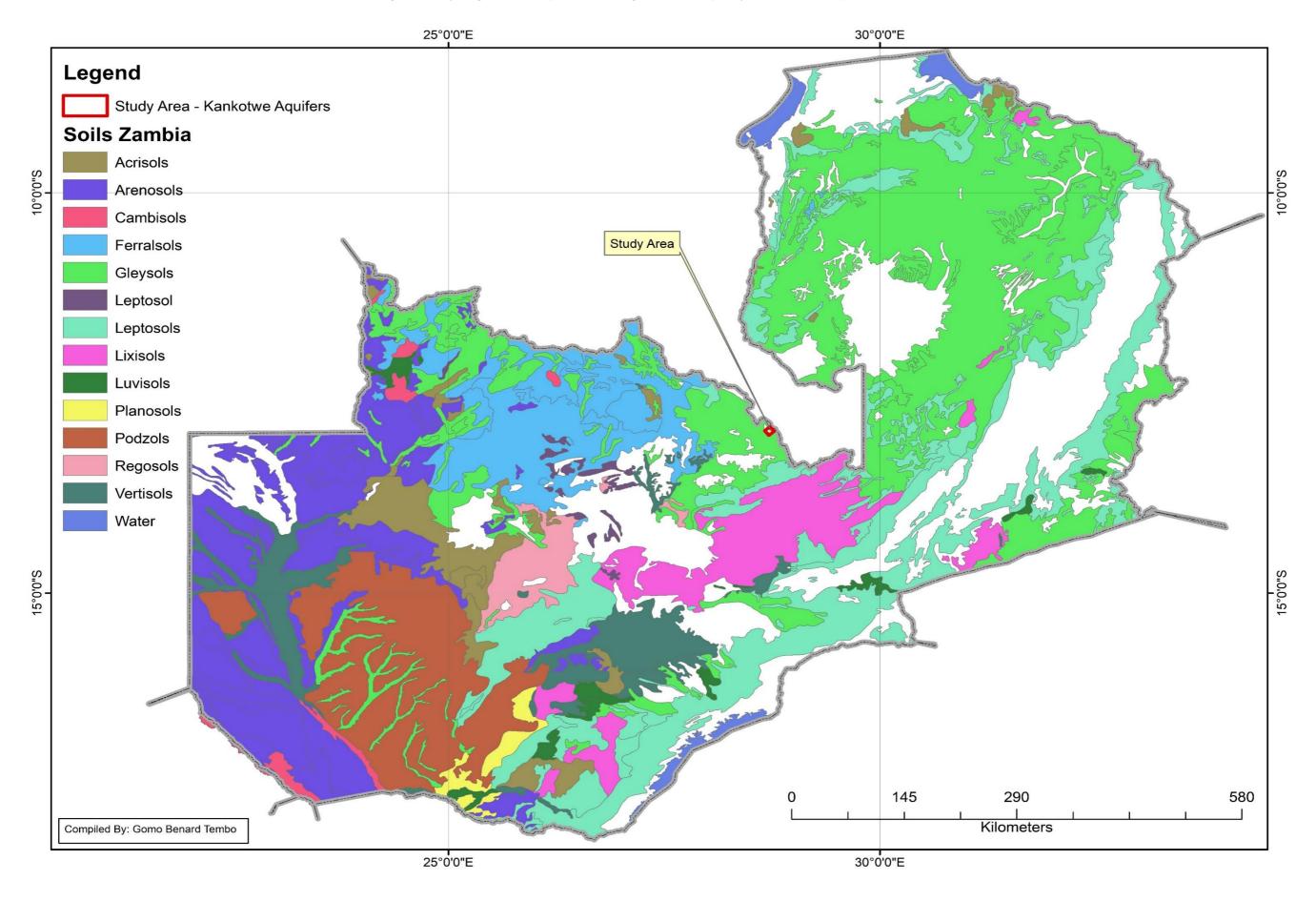


Figure 3.3-1 - Soils of Zambia

3.4 ENVIRONMENTAL ASSETS

3.4.1 Vegetation

The vegetation in the license area consists mainly of regenerating chipwa scrub and other disturbed species that have arisen because of locally extensive historical impacts associated with previous unauthorised/unlicensed limestone mining and agriculture activities. This vegetation type occurs in areas that had been historically broad scale cleared. Vegetation in these disturbed areas consisted of a tall regrowth of mostly herbaceous and weakly perennial species with scattered emergent low trees (both regrowth and remnant individuals; the latter occasionally associated with scattered termitaria). The common dominant species include the chipya indicators *Wild Ginger Aframonum alboviolaceum, Bracken Ptendium aquilinum,* along with Elephant Grass *Pennisetum polystachion* ssp. *atrichum, Sesamum angolense, Clematis wefwitschii, Bauhinia petersiana, Tephrosia sp., Cenchrus ciliaris* and *Digitana scalarum.* Tree species commonly present include *Cassia singueana, Albizia gummifera, Baphia bequaertii* and *Peltophorum africanum* (Global Environmanagement Consult Ltd, 2013; JA Consultancy, 2011).

3.4.2 Animal Life

The project area is substantially cleared of fauna habitat and has minimal value in this respect. As there is no habitat in the project area, the ground fauna is likely limited to small mammals (primarily rodents) and herpetofauna species that commonly persist in urban and near-urban contexts, such as the Striped Skink Mabuya striata wahlbergii, House Gecko Hemidactylus mabouia and the Square-marked Toad Bufo gutturafis. Several insects and birds have been recorded in the area. These include the Red-coloured Widow Euplectes, white-necked cormorant, red-faced mousebird, honey bees (Apis mellifera) termites (Microtermes goliath) various species of grasshoppers (Global Environmanagement Consult Ltd, 2013; JA Consultancy, 2011)

3.5 SURFACE WATER SYSTEMS

Zambia has six main catchment areas (Zambezi, Kafue, Luangwa, Chambeshi, Luapula and Lake Tanganyika), and four major rivers (the Zambezi, Kafue, Luangwa and Luapula. It also has four main natural lakes (Bangweulu, Mweru, Tanganyika and Mweru-wa-ntipa), extensive swamps around Lake Bangweulu, Lake Mweru-wa-ntipa and the Lukanga swamps (Nyambe, 2017).

Zambia is endowed with relatively abundant water resources predominantly from a distinct rainy season, which starts in October and ends in April. The total renewable water resources from both surface and groundwater are calculated at 144 cubic kilometres per annum and give potential per capita water of 19500 cubic metres per annum. Groundwater recharge was estimated at 57.5 billion cubic meters per year equivalent to 78 mm per year (Nyambe, 2017; Yachiyo Engineering Co., Ltd, n.d.).

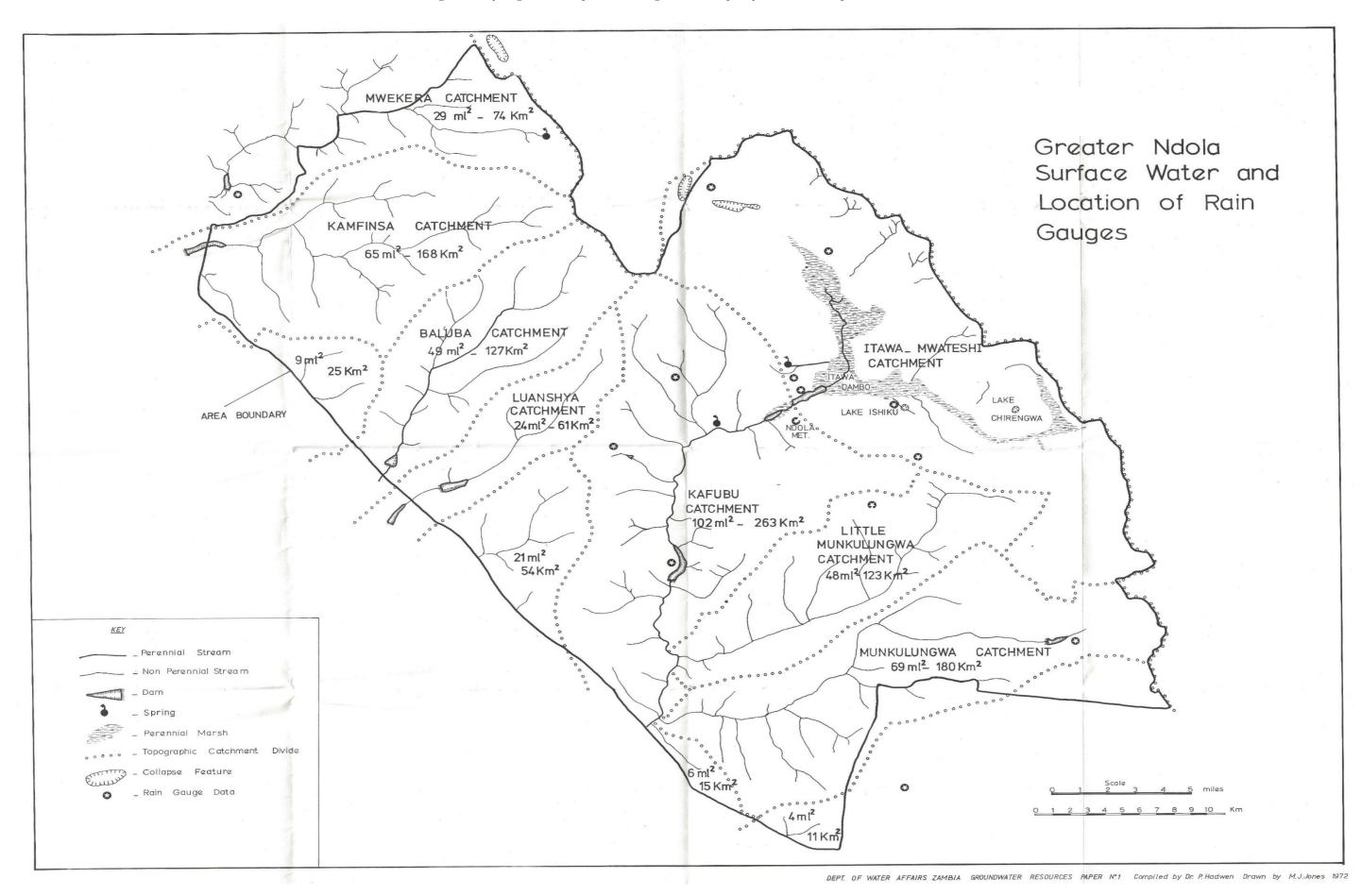


Figure 3.5-1 - Surface Water Catchment (Source: Dept. of Water Affairs, 1972)

3.5.1 Rivers and Streams

3.5.1.1 Drainage

The Zambia-Congo border coincides with a significant watershed between the Zambezi and Congo drainage basins. East of the border the land drained by tributaries of the Luapula, which is a tributary of the Congo River, and west of the watershed drainage is mainly via the Kafulafuta River and its tributaries to the Kafue and thence to the Zambezi. The most important tributary of the Kafulafuta is the Kafubu, which, together with its main tributaries, the Munkulungwe, Little Munkulungwe and Katuba, drains the northern half of the area.

The catchment area of the Itawa-Mwateshi catchment has derived from a Digital Terrain Model (DTM). The catchment has an area of 312.08 km² (**Figure 3.5-1**) and drains into the Kafubu River system. The catchment forms the headwater region of the Itawa River, which emerges from a dambo. The dambo fed by the Mwateshi system from the south-west and the northwest.

Runoff was measured by Adams (1977) in 1973 - 74, and he found discharge to be 380 Mm³/a, in a period when rainfall was 1,218 mm/a. Runoff is therefore 312 mm/a, or 26% of rainfall. Except for the portion of rainfall falling directly on the saturated dambo and running off over the surface, the bulk of this discharge originates from groundwater.

Adams (1977) recorded abstractions at the time as being 4.9 Mm³/a. Figure 3.5-2 shows that the onset of the rainy season does not result in storm runoff from the surface flow. There is a long lag before there is a runoff response. The response can be attributed to the delay before recharge replenishes aquifer storage and results in baseflow, followed by attenuation of runoff by the dambo.

The discharge was measured at one moment in time in May 2014 near the outlet of the Mwateshi. The measurement was taken in May, near the end of the rainy season when the discharge is above the average. The discharge was estimated at $8806 \text{ m}^3/\text{d}$ or $0.27 \text{ Mm}^3/\text{month}$.

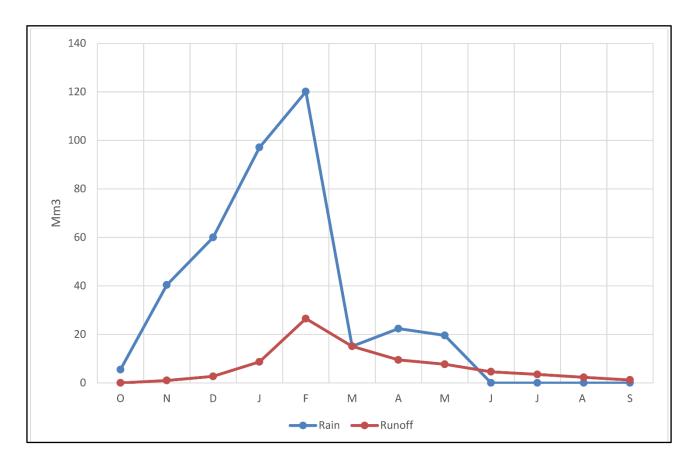


Figure 3.5-2 - Rainfall and Runoff, Mm³ (Source: Adams, 1977)

3.6 GEOLOGY

3.6.1 Regional Geology

Kakontwe Formation in the Itawa-Mwateshi catchment was described by Drysdall (1964) as predominantly Limestone and Dolomite of the Lower Katanga System (age 840-465 million years) falling within the Lufilian arc of the Copperbelt region and are one of the significant groundwater aquifers in the Republic of Zambia.

The Itawa-Mwateshi catchment predominantly overlaid with dolomite and limestone and according to Adams (1977) forms the upper unit of the Kafubu catchment, above the Itawa dambo and is situated to the Northeast of Ndola. Its long north-eastern boundary coinciding with the international border between and Democratic Republic of Congo (DRC) to the east

The geology of Zambia is dominated by crystalline rocks and several sedimentary sequences also occurring in different parts of the country. The rock types have been divided into four

main units (UN, 1989). The bulk of Zambia is underlain by Archean to Recent sedimentary units, with more limited areas of igneous and metamorphic basement present in the southeast (Nyambe, 2017). Generally, the Precambrian continental basement in Zambia comprises of granites, meta-igneous and meta-volcanic units. Nyambe (2017) further showed that relatively minor amounts of intruded dolerite dykes and sills have also been occasionally recorded in the bedrock formations. Sedimentary bedrock units include the Precambrian Muva and Katanga Supergroups and the Palaeozoic/Mesozoic Karoo Supergroup (refer to Figure 3.6-1 below). The Katanga Supergroup overlies the Basement and Muva sequences with marked angular unconformity and spans an approximate time interval of 1000 Ma - 500 Ma. The rocks are exposed throughout the Copperbelt and north-western Zambia, partially overlie the southern edge of the Bangweulu Block, and occur within the Zambezi Belt south and east of Lusaka ("Zambia Mining," n.d.).

All these formations include elastics and carbonates, while the Karoo Supergroup also consists of the basalt. Rocks of the Karoo Supergroup (late Carboniferous to Jurassic) occupy the rift troughs of the Mid-Zambezi, Luangwa, Luano-Lukusashi and Kafue valleys and outcrop in western Zambia ("Zambia Mining," n.d.). The Lower Karoo Group comprises a basal conglomerate, tillite and sandstone overlain unconformably by a conglomerate, coal, sandstone and carbonaceous siltstones and mudstones (the Gwembe Formation), and finally fine-grained lacustrine sediments - the Madumabisa Formation. The unconformably overlying Upper Karoo essentially comprises a series of arenaceous continental sediments and overlying mudstones capped by basalts of the Batoka Formation ("Zambia Mining," n.d.). The sedimentary bedrock units are found throughout the north and central regions of the country and are interpreted to underlie unconsolidated cover in the west of the country. The overlying meta-sedimentary Muva Supergroup generally exhibits a tectonized contact with the Basement sequences.

The Cretaceous to Recent Kalahari Beds as well as locally extensive areas of alluvium forms a largely unconsolidated sedimentary cover over western Zambia, because of the Zambezi River system, as well as localised areas of alluvium in the other regions of the country. The thickness of the Kalahari Beds generally increases to the west and southwest where it can

exceed 100 meters. The lithologies for the Kalahari beds are generally fine sands and friable sandstones, clays and duricrust horizons (silcrete and calcrete) whereas alluvial sediments are similar but lack duricrusts and can have coarser sand units (Nyambe, 2017).

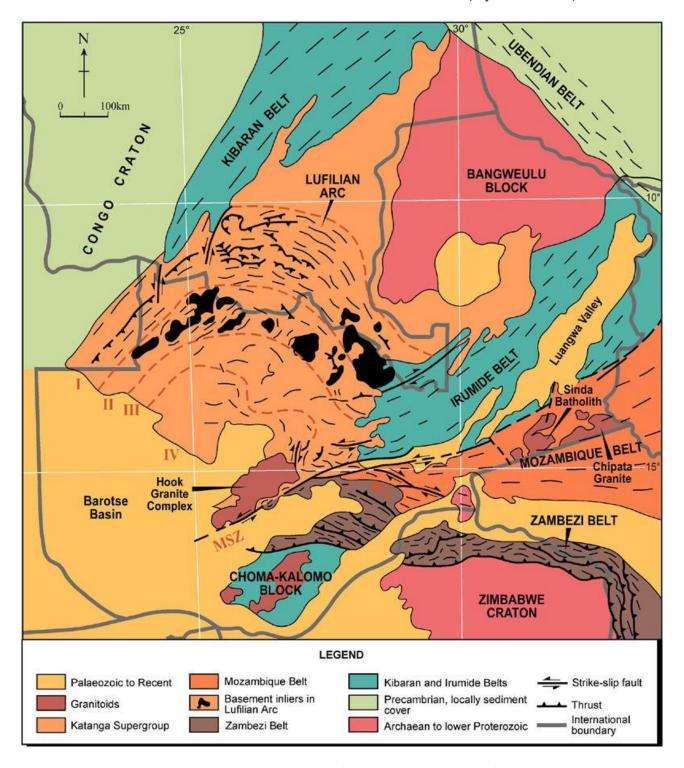


Figure 3.6-1 - Geological Terrain of Zambia (Zambia Mining, n.d.)

The Copperbelt has two main lithologic units, the Basement Complex and the Katanga System rocks according to Geospectrum Engineering, 2006 and Porter GeoConsultancy Pty Ltd, n.d. The regional geology of the area was also described by Mills (2000) to comprise the northeast limb of the Kafue anticline that is east of the Ndola Dome and the Mufulira syncline to the north. The basement rocks consist of gneiss, foliated granite and minor quartzmica schist, and they form the core of the anticline and the dome. Unconformably overlying the basement is the Proterozoic Katanga system as stated by Mills, 2000 and is divided into two series namely the mine series and above that is the Kundelungu series.

The mine series represents a marine transgression and consists of the Lower Roan, Upper Roan and Mwashia group. The Lower Roan is predominantly argillites and arenites. The Upper Roan is dolomites and argillites. The Mwashia group is carbonaceous shales. The Kundelungu series is represented by lower, middle and upper series. The middle and upper series do not outcrop in the Ndola area and are therefore not relevant to this study. The lower Kundelungu series has a base of marine deposited mudflows or tillites; this is known as the Great Conglomerate. The upper part of the lower Kundelungu series is known as the Kakontwe limestone, a dolomitic base overlain by limestone according to Mills (2000).

The minerals of economic importance, as reported by Moore (1965), include copper orebody around the Bwana Mkubwa, limestone and dolomite in the Itawa-Mwateshi Catchment. The insignificance occurrences of zinc, iron, gold, graphite, talc and fluorspar have also been reported in the area.

Moore (1965) indicated that the geological sequence of Ndola areas comprises several units, distinguished on lithological and stratigraphical grounds, ranging from Basement Complex to Lower Kundelungu in age. The Basement Complex consists mainly of gneisses, but there are also schists, quartzites, amphibolites and metadolerites. Schists and quartzites belonging to the younger Musofu Formation crop out in the south-east, where they are faulted against the still younger Kalonga Formation consisting of the metamudstones, phyllites, motasiltstones, slates and quartzites, which overlie the Basement Complex unconformably, although the boundary is obscured by later remobilisation of the basement gneisses. **Figure 3.6-2** below summarises the different geological structures of the Copperbelt.

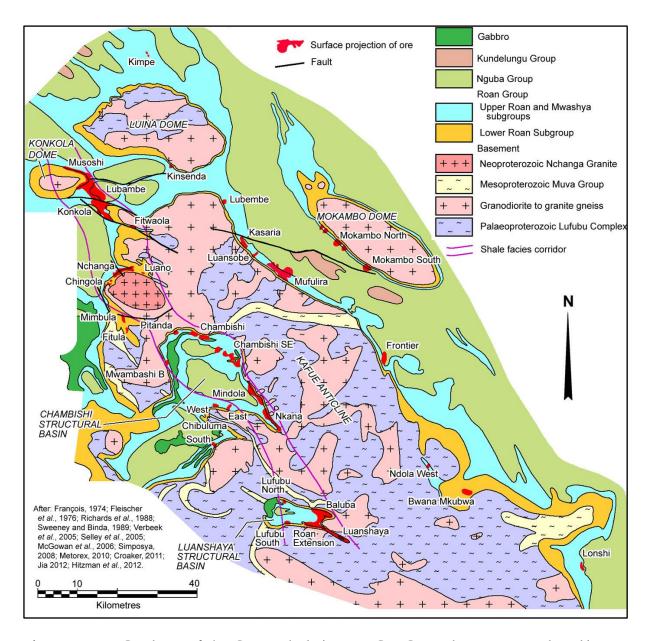


Figure 3.6-2 - Geology of the Copperbelt (Porter GeoConsultancy Pty Ltd, n.d.)

3.6.2 Local Geology

The geology of the Ndola area is complex, consisting of superimposed structural deformations. It is typified by normal and reverse faulting within synclinal and anticlinal features. The Grand Conglomérat is overlain by a 400 to 500 m thick, upward-deepening sequence of carbonates, dolomitic sandstones and siltstones and siltstones-mudstones, becoming progressively carbonate-poor and coarser to the north (Batumike, Kampunzu and Cailteux, 2006; El Desouky et al., 2010; Porter GeoConsultancy Pty Ltd, n.d., Portergeo, 2017). The lowest of geology the massive carbonate part is rocks of the Kakontwe Limestone represented by 350 to 500 m of immense dolostones and limestones in Zambia, and by a thinner sequence of carbonate-bearing to carbonate-poor siltstones and sandstones northward into the DRC and appear to represent shallow marine to fluvial sediments. The Kakontwe Limestone is better developed on the northern margin and over the domes of the Domes Region.

The geology of the study area is predominantly limestone of the Kakontwe formation of the lower series of the Kundelungu system of the Pre-Cambrian age occurring as a significant synclinal ford structure of dolomite and limestone, with beds plunging northwest across the border into the Democratic Republic of Congo (DRC). The limestone is believed to be karstic in development as evidenced from the Lake Chilengwa – a sinkhole where the overlying shales have collapsed into an underlying dolomite sinkhole. The Kakontwe formation is overlaid by the border formation comprising of shales and mudstones (Adams and Kitching, 1977) – see **Figure 3.6-3** below. The Hydrogeology is of the study area is therefore believed to be partly Karstic (see **Section 3.7** for a detailed analysis and description of the hydrogeology of the area) (Williams and Ford, 2007). Recharge of the Kakontwe aquifer appears to be under the control of infiltration in areas of bare rock and shallow soils, and by lateral groundwater movement where the overburden is thicker.

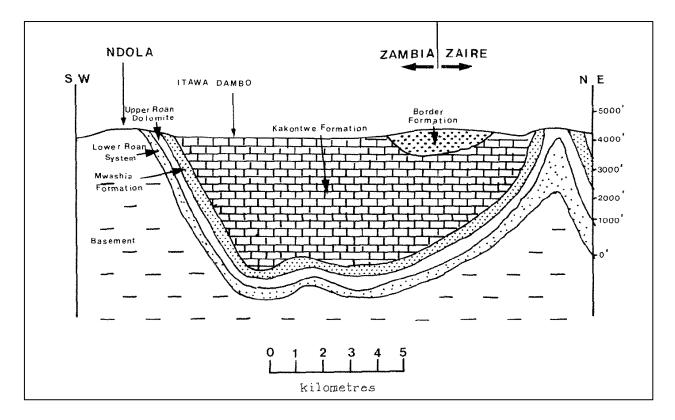


Figure 3.6-3 - Study Area Cross Section Geology (Adams and Kitching, 1977)

The Ndola Lime Company and Larfage, Ndola mines are located on an outcrop of the Kakontwe limestone with dolomite forming the footwall. A transition zone of high magnesian limestone occurs below the footwall. The dolomite is typically fine-grained, white to light grey with little banding or laminations. The hanging wall outcrops along the length of the deposit where it displays as calcareous shale with changes to limonitic and pyritic shale. The general strike of the area is north-west to south-east. The Ndola dome together with the Chiwala anticline and syncline have modified the local strike to east-west. The deposit dips about 30 degrees to the north (Mills, 2000).

3.6.3 Sedimentology

Lithologies and chemical compositions of the Kakontwe Limestone were related in line with what Moore (1967) deduced, suggesting that the composition is an original feature. However, no attempt has ever been made to place the deposits in a sedimentary environment. Binda and Van Eden (1971) concluded that the underlying Great Conglomerate is a claciomarine deposit, deposited mainly by mudflows and turbidites. They infer that the deposits

of finely bedded argillites, are of lacustrine origin and above the conglomerate, they identified layered argillitic dolomite that they also suggest is lacustrine in origin. Katonto, (1991) considered the Ndola limestone to have been deposited by turbidite flows, these probably off a limestone reef in the early history.

The suggested sedimentary framework for the Kakontwe limestones is;

- Dolomite;
- massive limestone;
- breccia;
- laminated limestone.

No evidence has been found of evaporites within the Kakontwe limestone, and the conclusion is that the dolomite was formed from limestones deposited in a nearshore environment. The carbonaceous, pyritic, massive limestone indicates deposition in a reducing environment and its texture suggests deposition as a lime mud. The origin of the organic matter is probably algae. Van Eden and Binda (1972) stated that the black carbonates contained an abundance of micro-fossils and it is speculated that the pyrite could have replaced the algae. A shelf margin is a possible origin for the limestone with deposition of algal mud in an environment shallow enough to be slightly affected by wave motion (Mills, 2000).

Limestone and dolomite breccias occur commonly, and the large size of the clasts suggest the source to be near, with the limestone breccias grading into micrites, suggesting deposition by turbides. The calcareous shales are rich in organic matter and pyrite and show no internal structure apart from layering. The origin is probably a low energy reducing environment such as deep water, and the source is probably wind-blown material.

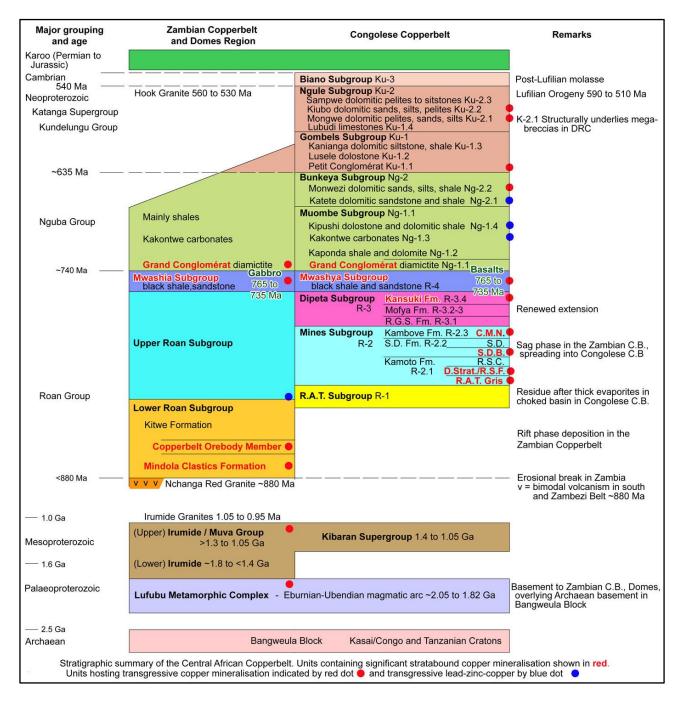


Figure 3.6-4 - Stratigraphic Units of Copperbelt (Porter GeoConsultancy Pty Ltd, n.d.)

3.6.4 Stratigraphy

The oldest succession of rocks in the country, the Basement Supergroup, consists mostly of granitic gneisses and migmatites which are evident throughout eastern, central and southern Zambia, in places in-folded with meta-carbonate, meta-quartzite, and meta-pelite units.

The Supergroup rocks are mostly younger than 2050Ma (Zambia Mining Geology, n.d.). The chart (**Figure 3.6-4**) shows the stratigraphic units of the Copperbelt.

3.6.5 Structural Geology

According to Moore (1965), the main areas of Kalonga outcrop are south of the Kafulafuta River, and between the Kafubu River and the DRC border. The Katanga System, which rests unconformably on all the older formations, comprises feldspathic quartzites, conglomerates, argillites, carbonate rocks, shales and sandstones. The formations appear correlated with those of the Copperbelt and south of the Congo Pedicle. The pre-Katanga rocks were deformed by the lrumide orogeny and were refolded and refoliated at the time of the later Lufilian orogeny, during which the rocks of the Katanga cover were folded. 'The structural pattern is complicated by the crossing of the Lufilian Arc and lrumide belt, and some late folding on the north-east to east-north-east lrumide trend. The southern part of the area probably represents the unfolded foreland to the Lufilian orogeny, while the northern part constituted the basement to the folded Irumide cover. Except for the basement, the grade of metamorphism is generally low. Geospectrum Engineering, 2006 showed that the ENE-WSW elongated Irumide belt stretches over approximately 900 km from central Zambia to the Zambia-Tanzania border and northern Malawi, bounded to the NW by the Archaean to Palaeoproterozoic basement lithologies of the Bangweulu block and truncated to the NE by Mesoproterozoic and Neoproterozoic transcurrent shear zones within reactivated parts of the Palaeoproterozoic Ubendian belt. To the SE and south, Irumide rocks were reworked within the Neoproterozoic Lufilian and Zambezi belts, and to the east by the Mozambique Belt.

3.6.5.1 Folding and Faulting

The Kakontwe Formation which is part of the Lower Series of the Kundelungu System of the Pre-Cambrian Era and occurs in this area as a major synclinal fold structure of dolomite and limestone beds plunging north-west across the border with DRC (Adams, 1977).

Moore (1967) recognised two generations of folding events, with each generation having two-fold styles affecting the Katangan in the Ndola area. The first was generation associated

with the Lufilian Orogeny and the second being post-Lufilian. The first generation of folds is more critical to the area west of the quarry site and may be seen at the Bwana Mkubwa mine where the folds are recumbent and overturned, generally plunging to the WNW with occasional folds plunging to the NNE. The second style of the first generation folds, that Moore identified at the quarry are symmetrical, plunging WNW at a shallow angle, with occasional plunge reversals. The decrease in intensity to the east. The first style of second-generation folds plunge at approximately 30° to the NW and have axial planes dipping steeply to the NE. This folding is associated with the formation of the Kafue Anticline, the Ndola Dome and the Mufulira Syncline. The second generation of folds are gentle broad domes.

3.6.6 Limestone and Dolomite

Mills, 2000 showed that Limestones and dolomites are collectively referred to as carbonates because they consist predominantly of the carbonate minerals calcite (CaCO₃) and dolomite (CaMg[CO₃]). Limestones occur throughout the world in every geological period, from the Cambrian onwards and make up approximately 15 per cent of the Earth's sediments and sedimentary rocks and about 2 per cent of the terrestrial crust. The limestones and dolomites are composed of calcite and dolomite, respectively, other calcite group minerals such as magnesite (MgCO₃), rhodochrosite (MnCO₃), and siderite (FeCO₃) occur in limited amounts in restricted environments. Modern carbonate sediments are composed almost entirely of metastable aragonite (CaCO₃) and magnesium-rich calcite, both of which readily recrystallise during diagenesis to form calcite (Encyclopedia Britannica, 2017).

The Kakontwe area is predominately limestone and dolomite that the companies exploit for cement and lime manufacturing. Using compositional classification, the first half of the name will describe the dominant visible chemical content. The name will end in micrite if it has a fine matrix and sparite if it has a crystalline cement. Micrite can also be found in Ndola. Microcrystalline carbonate mud (micrite) and sparry carbonate cement (sparite) can be collectively referred to as ortho-chemical carbonate.

3.7 HYDROGEOLOGY

The Kakontwe aquifers consist of the Kakontwe Formation which is part of the Lower Series of the Kundelungu System of the Pre-Cambrian Era and occurs in this area as a major synclinal fold structure of dolomite and limestone beds plunging north-west across the border with DRC. There is evidence of large transverse fissure systems, and the limestone is in the process of karsts as has been confirmed by drilling as well as surface evidence has shown the presence of sub-surface caverns, and sinkholes (Adams, 1977). Perched water table conditions have been shown to exist at a few locations in the overburden which varies significantly in permeability over the area. Adams (1977) further indicated that the recharge of the Kakontwe aquifer appears to be controlled by direct infiltration in areas of bare rock and shallow soils as well as by lateral groundwater movement where the overburden is thicker and in the sunken caverns.

The occurrence and movement of groundwater have a direct bearing on the geohydrological characteristics of the geological formations such as the limestone formation of the Nguba group in Ndola. Such formations vary significantly in their lithology, texture and structure which influence their hydrological characteristics (Singhal and Gupta, 2010). A regional assessment of the hydrogeology of Zambia was done as part of the National Water Master Plan completed in 1995. In this study, groundwater occurrence can be divided into three major categories: aquifers with the intergranular flow, aquifers with the flow in fissures and discontinuities and basement aquifers (Nyambe, 2017).

Aquifers with primarily intergranular flow include the Kalahari Beds and alluvium as well as limited zones within some Karoo sandstone units. Over much of western Zambia's Kalahari sands, groundwater occurs in shallow perched aquifers and deeper semi-confined aquifers. Aquifers are best developed near present drainage systems where recharge occurs from both rainfall and surface flow (Nyambe, 2017).

DWA Dolomite Guidelines (2009) shows that "karst" is a common word in geology and hydrogeology that refers to the typical landforms and processes in areas that are underlain by dolomite (calcium/magnesium carbonate) rock. Dolomite and Limestone rocks can

dissolve in contact with water combined with carbon dioxide. The reaction is a slow process that happens naturally as part of the weathering process. If the solution process has been carrying on for many millions of years, landforms, erosion features and subsurface solution cavities and cave systems form a unique environment that has been referred to as karst. In some places, large openings can form underground as dolomite rock weathers and dissolves. If the ground collapses down into the opening, a sinkhole is formed. Sinkholes vary in size from a few centimetres deep to many metres (Botha, 1998; Department of Water Affairs - South Africa, n.d.). The sinkholes have been reported and recorded in the Itawa-Mwateshi catchment in Ndola.

Laterally extensive alluvial deposits are associated with the major river drainages, particularly along the upper Zambezi near Mongu, and around lakes such as Lake Bangweulu. In areas along the Luangwa River, Karoo sandstones are characterised by an intergranular flow. Yields within this aquifer type are variable and reflect grain size, sorting, clay content as well as secondary fracturing in consolidated sandstones and range from 1 to 20 l/s (Nyambe, 2017).

Aquifers with the flow in fissures and discontinuities include the sedimentary bedrock as well as Karoo basalt units within the country. The aquifer types include both fractured sedimentary and basalt units as well as fractured and karstic dolomite limestone units. The highest yielding aquifers in the country fall into the second group (dolomites and limestones) where yields range from 20 to more than I 00 l/s. Due to the yield characteristics as well as the proximity of the aquifers to urban areas, this unit is a significant source of supply for Lusaka, Kabwe and Ndola. Yield from fractured elastic and basalt lithologies of the Muva and Karoo Supergroups aquifer is more variable, but productive aquifers are locally developed (1 to 10 l/s) (Nyambe, 2017).

Basement aquifers are present in the south-eastern portion of the country and are primarily formed in fractured or weathered zones in the shallow weathered mantle of bedrock. Borehole yields are low but are generally sufficient for hand pump installation, which forms the prime water supply method in these areas. As already indicated, groundwater will continue

to play a major role in the water sector in Zambia, particularly in irrigation agriculture and water supply for domestic use. The completion of privatisation of the water supply subsector will see much of the population receiving water from various utilities with the most important aquifers in Zambia such as the Karstic Aquifers of Lusaka and Kabwe providing most of the supplies (Nyambe, 2017).

3.7.1 Karsts Formation

Rainwater (H₂O) takes up carbon dioxide (CO₂) in the atmosphere and soil to form a weak carbonic acid (H₂CO₃). The weakly acidic groundwater circulating along tension fractures, faults and joints in the dolomitic succession causes leaching of the carbonate minerals. The carbonates are removed in the form of bicarbonates by groundwater. This leaching is most pronounced in the first few tens of metres within bedrock or below the water table and has resulted in a vertically zoned succession of residual products, which in turn are generally overlain by geologically younger formations and soils. This vertical succession and particularly the lateral variation thereof is the key to understanding the general stability, or instability, of sites in dolomitic areas. (Department of Water Affairs - South Africa, n.d.; Kresic and Goldscheider, 2007,)

Hard, competent dolomitic bedrock is succeeded vertically by slightly leached jointed bedrock and after that, through a sudden, dramatic transition, to leached, and incompetent, insoluble residual material consisting of mainly manganese oxides, chert and iron oxides that reflect the original insoluble matrix structure.

Depending upon the local subsurface structure, this very incompetent, porous and permeable horizon might be up to several tens of metres thick but is generally less than ten metres thick in some locations (Department of Water Affairs - South Africa, n.d.). With the passage of geological time, concurrently with the downward progression of the intense leaching of the dolomitic bedrock, compaction by the mass of the overlying materials has resulted in progressive densification of these incompetent materials. Ultimately, subsurface fluids may have cemented these older materials to form densely compacted horizons.

Consequently, the vertical succession of the residual products of leaching reflects upward increase incompetency and a decrease in Given sufficient time and the correct triggering mechanisms, instability may occur naturally, but human activities can significantly increase it. The primary triggering mechanisms in these instances include but not limited to the ingress of water from leaking water-bearing services, poorly managed surface water drainage and groundwater level drawdown. Topography and drainage, the natural thickness and origin of the transported soils and residuum, the nature and topography of the underlying strata, the depth and expected fluctuations of the water table, and the presence of structural features such as faults, fractures and dykes are all factors which influence the risk of subsidence taking place (Department of Water Affairs - South Africa, n.d.; Oosthuizen and Richardson, 2017).

3.8 HYDROCHEMISTRY

The groundwater quality in Zambia is generally acceptable for most uses. The major quality problem in the country is contamination of both surface and groundwater from anthropogenic sources, especially in Urban and Peri-Urban areas. Due to urbanisation of much of the population and industrial growth, as well as uncontrolled growth in the cities, local aquifers are at high risk from such contamination. Major dolomitic aquifers, which generally have shallow water tables and high rates of local recharge, are particularly vulnerable in such situation. There are some reported cases of groundwater pollution in the Lusaka area with contamination sources including uncontrolled dumping in low-lying (i.e. recharge) areas, uncontrolled industrial waste discharges, cemeteries and non-point sources such as runoff in the urban environment (Nyambe, 2017).

The groundwaters in Zambia are either bicarbonate type (in Muva Sediments, dolomites, Kundelungu and Karoo Groups) or sulphate type (in Basement rocks, granites, Mine Series and Kalahari). Sodium chloride waters are known to occur in the Muva sediments of the Lunsemfwa Valley. The groundwater in the project area is expected to be a bicarbonate type based on this classification (Nyambe, 2017).

CHAPTER 4: STUDY METHODS AND MATERIALS

4.1 INTRODUCTION

This section covers the steps materials and methods followed during the Hydrogeochemistry and water quality study. The main steps followed were hydrocensus, sampling, laboratory analysis of the samples and detailed scientific analysis of the laboratory results using various hydrogeochemical and statistics tools. These steps taken during the study were discussed in detail in the subsections below.

4.1.1 Study Limitations

The Laboratory analysis was only done for the major cations and anions listed in Section 4.4 below. The laboratory analysis aspect was recorded as study limitation in the sense that analysed water be declared fit for uses such as agriculture or industry but can still have a high concentration of trace elements that were not analysed in this study such as Fe, F, nitrate, Mn, Cr, As. These elements were not analysed due to limitation at the available Laboratory and cost implications. The study was therefore only based on the significant cations and anion required for the various tools used for hydrogeochemical and statistical assessment using the various tools used in **Chapter 5** below.

4.2 HYDROCENSUS

A Hydrocensus was carried out to establish background hydrogeological conditions and water use status around the project area. The hydrocensus focussed on confirming any of the site relevant data identified during the desk study. All locations of interest were marked using the geographic coordinates. Data for each marked site was then analysed against the project objectives and compared with the literature review.

The objectives of the hydrocensus were to:

- δ Conduct an overall reconnaissance survey of the study area understanding the surface water, geological and groundwater features;
- δ Identify the locations of the existing boreholes; and,
- δ Measure groundwater levels in readily accessible boreholes to develop an up-todate water level map that could be used to determine groundwater flow directions.

Data collected during the hydrocensus included the following:

- δ GPS coordinates of the borehole;
- δ Boreholes owners information and current use;
- δ The static water level; and
- δ Water quality sampling and testing.

The hydrocensus also served as a reconnaissance tool for the planning of the study. **Table 4.2-1** presents some of the data collected during the hydrocensus exercise.

Table 4.2-1 - Hydrocensus Data from the Study Area (Handyman's Lime, 2014)

S/N	Location Description	Coordinates (Arc 1950)		Static Water	Elevation	Remarks
		Northing	Easting	Level	(m)	Remarks
1	Kabundi village well 1	689723	8565117	4.61	1259	In working condition
2	Kabundi village well 2	689749	8564991	8.83	1268	In working condition
3	Kabundi village well 3	689785	8564875	9.57	1264	In working condition
4	Chimbalanga village Bh 1	691437	8564924	16.99	1295	In working condition
5	Chimbalanga village Bh 2	691449	8564988	12.15	1293	In working condition
6	Chimbalanga village Bh 3	691629	8564848	15.87	1294	In working condition
7	Shimilimo farm well	691537	8565120	4.45	1300	In working condition
8	Pinta village Bh 1	690705	8565141	7	1278	In working condition
9	Pinta village Bh 2	690504	8565108	4.7	1273	In working condition
10	Pinta Village well	690294	8565152	3.92	1271	In working condition
11	Laurent village well	690242	8565230	3.52	1271	In working condition
12	Yusuf well	690084	8565195	3.7	1270	In working condition
13	Salim Village Bh	689579	8565242	10.26	1259	In working condition
14	Salim Village well 1	689264	8565218	7.6	1256	In working condition

S/N	Location Description	Coordinates (Arc 1950)		Static Water	Elevation	Remarks
		Northing	Easting	Level	(m)	Remarks
15	Salim Village well 2	689170	8565218	6.97	1253	In working condition
16	Mutuka Village well	689098	8565276	6.9	1254	In working condition
17	Kabulu Village well 1	688845	8565229	4.83	1252	In working condition
18	Kabulu Village well 2	688561	8565222	2.6	1245	In working condition
19	Kabulu Village well 3	688693	8565111	2.65	1246	In working condition

Source: Author

The hydrocensus boreholes data (boreholes location coordinates, elevation and groundwater static level) collected during the study were presented in ArcGIS for groundwater flow direction contouring using the IDW Interpolation and contouring method. The general elevation shows that the height of the area gently drops towards the Mwateshi Stream. The samples were collected for analysis, and the detailed sampling methodology is discussed below.

4.3 SAMPLING

A total of 65 groundwater samples were collected from 33 wells during the years 2017 and 2018 (see Figure 4.3-1 below). The samples were collected for chemical analysis only. One water sample was collected (after purging the wells) at each borehole using a labelled 500ml polyethylene (PTE) plastic bottle suitable for physical and chemical analysis that was planned. No Samples for biological or hydrocarbons analysis were taken that normally require special glass bottles. Some samples were filtered using 0.5 µm membrane filters that removes suspended solids from the water. The bottles were rinsed using the groundwater to be sampled. After sampling, the bottles were tightly closed to protect from atmospheric gases, labelled using an indelible marker, kept in the cooler box at 5°C and delivered to the laboratory within 8 hours after field sampling. The sampling bottles were thoroughly rinsed many times with sample solution at each site before sampling to prevent crosscontamination of the collected samples. Samples were not preserved after sampling in the field. The water samples were analysed for the parameters shown in Table 5.3-1 at the Copperbelt University Laboratory in Kitwe, Zambia.

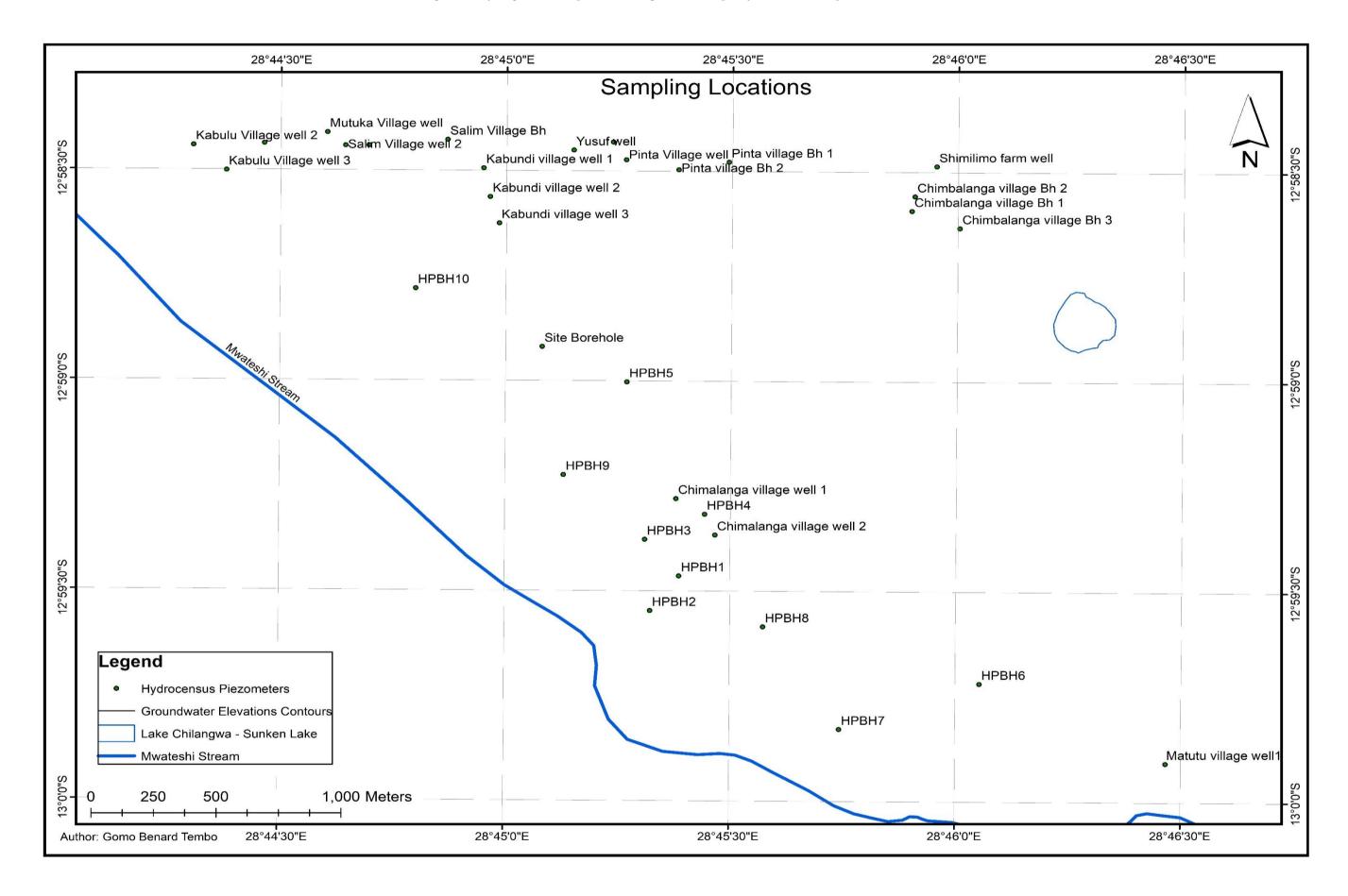


Figure 4.3-1 - Sampling Locations

4.4 LABORATORY ANALYSIS

The analysed parameters at the Laboratory included the activity of hydrogen ion concentration (pH), electrical conductivity (EC), Total Dissolved Solids (TDS) and cation groups like Calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}) and anion groups like bicarbonate (HCO_3^{-}) and Chloride (Cl^{-}).

The samples laboratory analysis for sodium, potassium, calcium, magnesium, chloride, sulphate, bicarbonate, and carbonate was done based on the standard procedures in the laboratory (American Public Health Association, 2005). The Ca²⁺ and Mg²⁺ analysis was determined via titration using the standard EDTA method, and sodium and potassium by flame photometry. The pH and electrical conductivity (EC) were measured with the aid pH and EC meters respectively (Hwang et al., 2017). The anions and bicarbonate were determined by acid titration, while the chloride concentration was determined by AgNO₃ titration and the sulphate and phosphate values by spectrophotometer (Anwar and Aggarwal, 2017).

The quality of the analyses of the parameters to obtain a reliable dataset was controlled by sending the duplicates of selected samples to the laboratory. Twenty per cent (20%) of the samples were sent as duplicates to the lab. The accuracy of the results was checked by calculating the ion balance errors as described below.

4.4.1 Ionic Balance Error

Ion balance error assessment is a quick way used to examine the accuracy of chemical analysis data of groundwater samples. Ion balance Error or Electroneutrality (E.N.) was calculated using **equation (4-1)** below (Agion, 2017).

E. N. [%] =
$$\frac{\sum cations \left[\frac{meq}{L}\right] + \sum anaions \left[\frac{meq}{L}\right]}{\sum cations \left[\frac{meq}{L}\right] - \sum anaions \left[\frac{meq}{L}\right]} \times 100$$
(4-1)

The acceptable ion balance error should be below 5% in many cases (Aqion, 2017). In

4.5 DATA INTERPRETATION

4.5.1 Specialised Plots

Chemical variables for the sampling data were plotted and interpreted using dedicated tools such as the Piper, Schoeller, Ludwig-Langelier and Wilcox to demonstrate the groundwater facies for the study area using the software AquaChem 2014.2 and Microsoft Excel. AquaChem is a software package developed specifically for graphical and numerical analysis and modelling of water quality data and has an inbuilt built-in link to the popular hydrogeochemical modelling program PHREEQC for calculating equilibrium concentrations (or activities) of chemical species in solution and saturation indices of solid phases in equilibrium with a solution.

4.5.2 Saturation Indices

The interaction of the rocks and groundwater has a strong influence on the geochemistry of the groundwater. The mineral equilibrium calculation can forecast the thermodynamic control on the composition of the groundwater that has equilibrated with various minerals (Deutsch, 1997). The author further showed that the saturation index could be applied to predict the reactive mineralogy of the subsurface from the groundwater sample data without collecting the samples of the solid phase and analysing the mineralogy. Appelo and Postma, 1996 indicated that the saturation index (SI) of a mineral in solution is obtained from **equation (4-1)** below:

$$SI = \log \frac{IAP}{K_t} \tag{4-1}$$

where IAP is the ion activity product of the dissociated chemical species in the solution, and K_t is the equilibrium solubility product for the chemical involved at the sample temperature.

Equilibrium is indicated when SI = 0; the groundwater is supersaturated when SI > 0, which shows that precipitation is needed to achieve equilibrium. If SI < 0, the groundwater is undersaturated; this indicates that dissolution is required to reach equilibrium.

The SI of minerals is important for evaluating the extent to which groundwater chemistry is controlled by equilibrium with solid phases as shown by Appelo and Postma (1996).

Langelier combined the first four terms in the Saturation Index (SI) equation into the parameter pHs (Langelier, 1936). Therefore, SI for calcium carbonate is often called the Langelier Index (LI) or the Langelier Saturation Index (LSI). The LSI was also consequently used in this assessment because of its simplicity.

4.5.3 Gibbs Diagram

Gibbs diagram is used to construe the effect of hydrogeochemical processes such as precipitation, rock-water interaction mechanism and evaporation on groundwater geochemistry. The reaction between groundwater and aquifer minerals has an essential role in groundwater quality which is useful to assume the genesis of water (Hwang et al., 2017; Nazzal et al., 2014; Gibbs, 1970; Senthilkumar et al., 2014;).

Gibbs ratio is calculated using the following equation (Hwang et al., 2017).

Gibbs ratio I (for anions) =
$$\frac{Cl^{-}}{(Cl^{-} + HCO_{3}^{-})}$$
 (4-2)

Gibbs ratio II (for cations) =
$$\frac{(Na^+ + K^+)}{(Na^+ + K^+ + Ca^{2+})}$$
 (4-3)

The Ratios were then plotted on the Gibbs diagram that based on TDS and the concentration of cations and anions. According to Gibbs (1970), the Gibbs diagrams shows the cations and anions in groundwater concerning possible dominance origin. These diagrams complement the piper plot that only indicates that hydrochemistry facies of the water.

4.5.4 Source-Rock Deduction

Hounslow (1995) showed that source-rock deduction is one of the ways to estimate the possible origins of the tested groundwater samples during the studies. Although the sources of the composition of the groundwater include what originates from the rain, Gibbs (1970) showed that the groundwater also gets affected due to the host geological porous materials the water flows through the process of weathering. It is during this weathering process that

the ions get added to the water that flows through the porous geological media. The source-rock of the ions in the water can, therefore, be determined using ionic comparison and best estimated using statistics and bivariate plots (Hounslow, 1995).

4.5.4.1 Statistical Analysis

The correlations analysis study concerning mathematical calculations were first developed by Pearson (1896) and mainly founded on the estimated correlation coefficient (r), which is the correlation between two parameters sometimes plotted on an XY scatter diagram that can be termed either as positive or negative. Several scientists have shown that correlation analysis is a common and valuable statistical tool for water quality studies demonstrating which ions governor the water chemistry (Zeng et al. 2005; Shrivastava and Patil 2002; Chapman 199; Box et al. 1978;). Kurumbein and Graybill (1965) showed that correlation analysis is a degree to show how well one variable forecast the other variable.

The Multivariate statistical investigation approaches have also been used in various water quality and hydrogeochemical studies. The statistical analytical tools aid with multiple forms of assemblage studies for water samples collected from various points in the study area. Routroy et al. (2013) showed that the numerous water quality parameters analysed could be clustered based on their interdependency or sampling positions can be grouped based on chemical similarity in samples collected from these locations (Singh et al. 2005; Shrestha and Kazama 2006).

A multivariate statistical examination was applied to find significant information from hydrochemical data sets for the study area. Chemical variables were graphically interpreted alongside tools such as the Piper, Schoeller, and Gibbs diagrams to demonstrate the groundwater facies for the study area. Multivariate statistical approaches of descriptive statistics, Pearson correlation analysis, and cluster analysis (CA) were done as quantitative and independent methods for classification of groundwater samples and to correlate between the chemical parameters and groundwater samples.

The data were then log-transformed so that it will have a normal distribution before the multivariate analyses; all the parameters were standardised by subtracting the mean value

and dividing by the standard deviation of parameters. For the classification of variables based on the similarities within a class and heterogeneity between the classes, cluster analysis was applied on the normalised dataset using the Ward method as was shown by Sparks, 2000. Hierarchical Agglomerative Cluster Analysis (HACA) used mostly where clusters were formed sequentially, by starting from the most similar pair of objects and forming higher clusters. The dendrogram offers a visual summary of the clustering process, presenting a representation of classes and their proximity. In this study, the degree of association of the relationship between two variables was summarised using Pearson's correlation analysis (Mustapha and Aris, 2012).

The Principal Component Analysis (PCA) is a useful statistical tool used for identifying patterns in a data set comprising of several parameters each with an extensive data range. With the Principal Component Analysis method, it is possible to compress the data by reducing the number of dimensions with limited loss of information. Factor analysis (FA) is related to principal component analysis, generates an unobserved or latent variable which mainly compiles variations in three or more observed variables. Some writers (Helena et al. 2000; Reghunath et al. 2002; Yidana 2010) have shown that factor analysis, as well as Principal Component Analysis methods, are used in water quality evaluation studies, where various parameters get tested in the search for causes leading to change in the quality of water.

IBM SPSS software was used to run the Hierarchical cluster analysis function to group the multiple water quality parameters in clusters and generate dendrograms for the test data. The same software has analysis capabilities for Principal Component Analysis (PCA).

4.5.5 Groundwater Quality Assessment

4.5.5.1 Industrial Use Assessment

Scaling and corrosion are well-known process problems found in domestic and industrial applications where water or wastewaters are in contact with other materials. The scaling of metallic surfaces by calcium carbonate is related to the type of rocks in contact with groundwater. LSI is probably the most widely used indicator of cooling water scale potential. Positive LSI values could be a sign that water is supersaturated with respect to

calcium carbonate and scale formation may occur. Negative values suggest that water is unsaturated which tends to remove existing calcium carbonate protective coatings in pipelines and equipment. The neutral value indicates that solution is at equilibrium provides an indication of the degree of saturation of water with respect to calcium carbonate, and it is neither scale forming nor scale removing (Hwang et al., 2017).

One of the significant difficulties of high calcium waters is the scale formation in the industrial boilers or related equipment.

4.5.5.2 Water Hardness

The calcium and magnesium hardness is the measure of the concentration of calcium and magnesium ions expressed as equivalent of calcium carbonate. The molar mass of $CaCO_3$, Ca^{2+} and Mg^{2+} are respectively 100.1 g/mol, 40.1 g/mol and 24.3 g/mol. The ratio of the molar masses for Ca^{2+} and Mg^{2+} were shown below:

$$\frac{M_{CaCO_3}}{M_{Ca}} = \frac{100.1}{40.1} = 2.5 \tag{4-4}$$

$$\frac{M_{CaCO_3}}{M_{Mg}} = \frac{100.1}{24.3} = 4.1 \tag{4-5}$$

Therefore, the total water hardness expressed as equivalent of CaCO₃ can be calculated with the following formula:

$$[CaCO_3] = 2.5[Ca^{2+}] + 4.1[Mg^{2+}]$$
(4-6)

Water hardness for the study area was calculated and the results presented in **section 5.5**.

4.5.5.3 Salinity Hazard

In irrigation, the primary water quality fear is salinity levels that can have an impact on the soil structure and crop yield. The build-up of salinity upsurges the osmotic pressure of the soil solution and causes a reduction in both the rate of water absorption by the plants and the soil water availability (Vyas and Jethoo, 2015; Marghade, Malpe and Zade, 2010; Hwang et al., 2017). Calcium (Ca) and magnesium (Mg) can cause the soil to flocculate, and therefore counteract the adverse effects of Na.

The assessment of groundwater was done by using SSP (Soluble Sodium Percent), KR (Kelly's Ratio) and SAR (Sodium Adsorption Ratio).

Soluble Sodium Percentage (SSP) is also used to evaluate sodium hazard. Water with an SSP greater than 60% may result in sodium accumulations causes a breakdown in the soil's physical properties (Khodapanah et al., 2009).

SSP was calculated by the following equation (Raihan and Alam, 2008; Todd, 1980):

$$SSP = \frac{(Na^{+} + K^{+}) \times 100}{(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})}$$
(4-7)

where, all the ions are expressed in meq/L (Raihan and Alam, 2008).

Kelly's ratio is also another important parameter for irrigation water quality, which is measured considering sodium ion concentration compared to calcium and magnesium ion concentrations. Kelly's ratio of more than 1 specifies an excess level of Na+ in water. Water with a value of KR<1 is considered appropriate for irrigation, while those with a ratio more than three is considered as inappropriate for irrigation. Kelly's Ratio is used for the classification of water for irrigation purposes. The waters with low KI (<1) are suitable for irrigation while those with greater ratio are unsuitable (Hwang et al., 2017; Sundaray, Nayak and Bhatta, 2008).

Kelly's Ratio was calculated using the equation as (Raihan and Alam, 2008):

$$Kelly's Ratio = \frac{Na^+}{(Ca^{2+} + Mg^{2+})}$$
 (4-8)

The Sodium Adsorption Ratio (SAR) describes the relationship between soluble Na⁺ and soluble divalent cations (Ca²⁺ and Mg²⁺). The higher the Na in relation to Ca and Mg, the higher the SAR (Vyas and Jethoo, 2015).

The following equation calculated SAR as:

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$$
 (4-9)

where, all the ions are expressed in meq/L (Raihan and Alam, 2008).

SAR values are plotted against EC values (in μ S/cm) on the U.S. Salinity diagram to categorize analysed water samples according to their irrigational suitability quotient. This has long been the accepted measure of potential sodium hazard for irrigation water (U.S. Salinity Laboratory Staff, 1954). The potential for irrigation water to have poor infiltration properties is assessed by using the sodium adsorption ratio (SAR) and the electrical conductivity (EC) of the water (Shammi et al., 2016; Vyas and Jethoo, 2015).

If high sodium content and low calcium content are existing in waters used for irrigation purpose, the base-exchange complex may become saturated with sodium. The ratio can destroy the soil structure due to the de-flocculation (dispersion of clay particles) process. The U.S. salinity Laboratory's Diagram uses electrical conductivity, and SAR classifies groundwater, which is a combination of electrical conductivity (C1 - C4) and SAR (S1 - S4) (**Figure 4.5-1** below) based on the measured EC and SAR values respectively. A comparison with the classes on the diagram helps to give the quality levels of the samples (Hwang et al., 2017).

Wilson House	Classes/Ranges and quality				
Wilcox diagram	Classes		Range	Quality	
100 2 3 4 5 6 7 8 9 2 3 4 9 3 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9		C1	100 - 200	Excellent	
AEA HIGH C1-S4 C2-S4 C2-S4	Conductivity	C2	250 - 750	Good	
(3-S4)		С3	750 - 2250	Doubtful	
TRALL LAZARD MEDIUM MEDIUM C1-S3 C3-S4 C4-S4 C4-S4 C4-S4		C4 - C5	>2250	Unsuitable	
C1-S1 C2-S3 C3-S3 C4-S4	SAR	S1	<10	Excellent	
Mindo Mod – C1-S1 C2-S1 C4-S2		S2	10 - 18	Good	
C3-S1 C4-S1 100 200 750 2250 CONDUCTIVITY (16cm-1)		S3	19 - 26	Doubtful/Fairly	
1 2 3 4 LOW MEDIUM HIGH V HIGH SALINITY HAZARD		S4 - S5	>26	Unsuitable	

Modified after the US Salinity Laboratory, 1954

Figure 4.5-1 - Classification of Groundwater based on SAR and EC

CHAPTER 5: RESULTS AND DISCUSSION

5.1 INTRODUCTION

This chapter discusses the hydrogeochemical; the statistical analysis approaches employed in understanding the hydrogeochemistry, water uses and recharge assessment of the Kakontwe aquifers. The section discussed in detail the study findings with the aid of statistics and various hydrogeochemical tools.

5.2 HYDROCENSUS

Thirty-three (33) boreholes and wells were recorded during the hydrocensus and subsequently sampled for hydrogeochemical laboratory analysis in 2017 and 2018. The average groundwater level recorded for all the boreholes was 7.3 mbgl (approximate 1,261 masl) with a range from 2.6 mbgl to 16.99 mbgl. The groundwater level data was contoured in ArcGIS to illustrate groundwater flow direction using contours graphically showing the groundwater elevation map of the study area, and the estimated groundwater flow direction based on the static water levels contours.

A plot of groundwater level elevation against topographic elevation (**Figure 5.2-1** below) shows a 95% degree of correlation. The plot further proved that the groundwater level elevation follows the topography of the study area and confirming the groundwater contours generated in **Figure 5.2-2**. The contoured groundwater static water levels map shows that the groundwater flows towards the Mwateshi stream in the southwesterly direction as indicated by the red arrows on **Figure 5.2-2** below. This observation also confirmed the suggestions¹ that the Kakontwe aquifers investigated are water table or

¹ As illustrated from the drilling geological profiles

unconfined aquifer because they are under atmospheric pressure in line with the geological profile data and the flow is towards the stream.

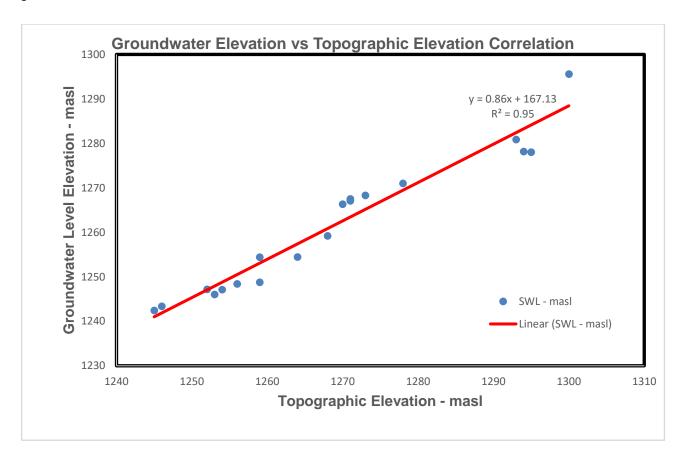


Figure 5.2-1 - Correlation between groundwater level and topographic elevation

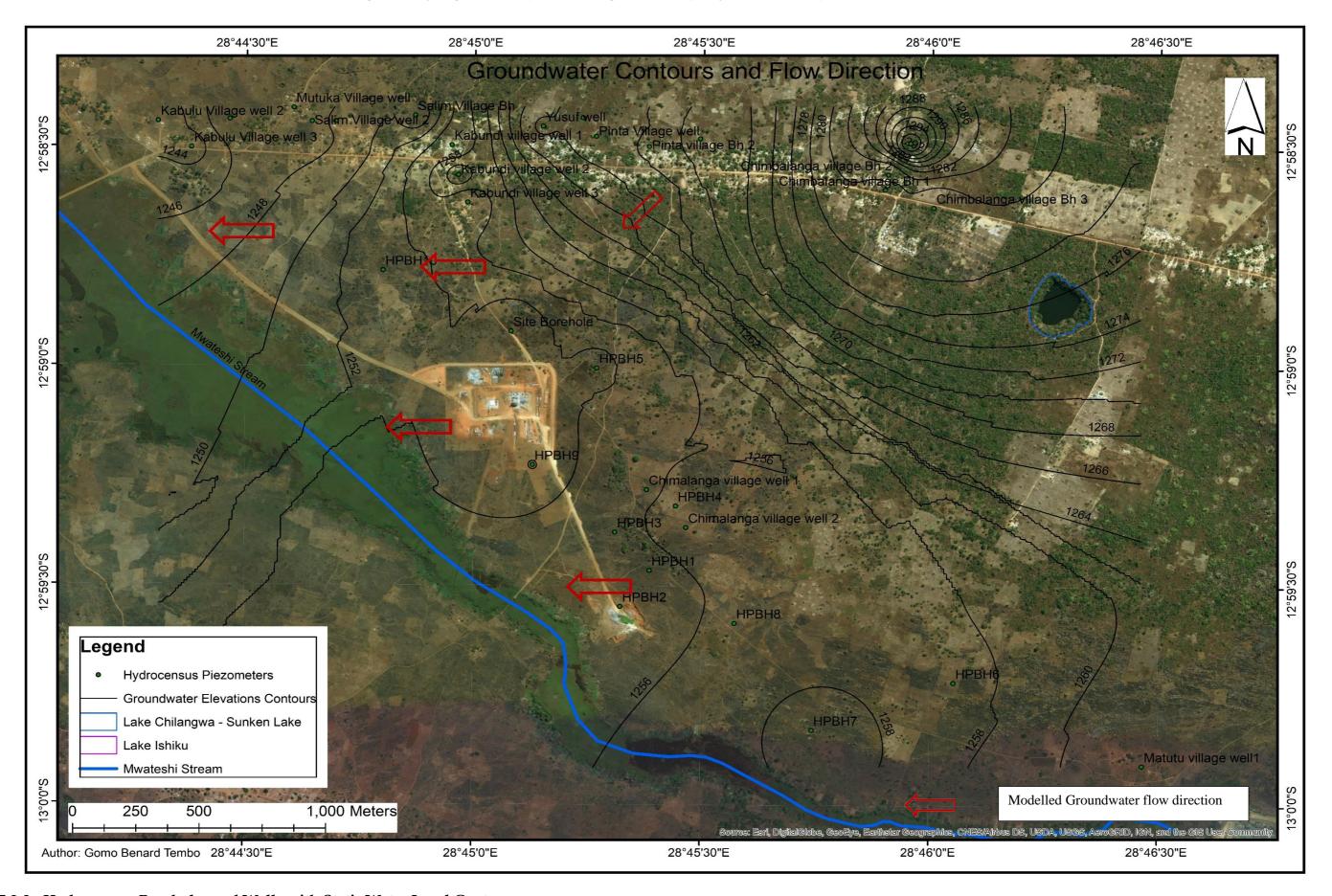


Figure 5.2-2 - Hydrocensus Boreholes and Wells with Static Water Level Contours

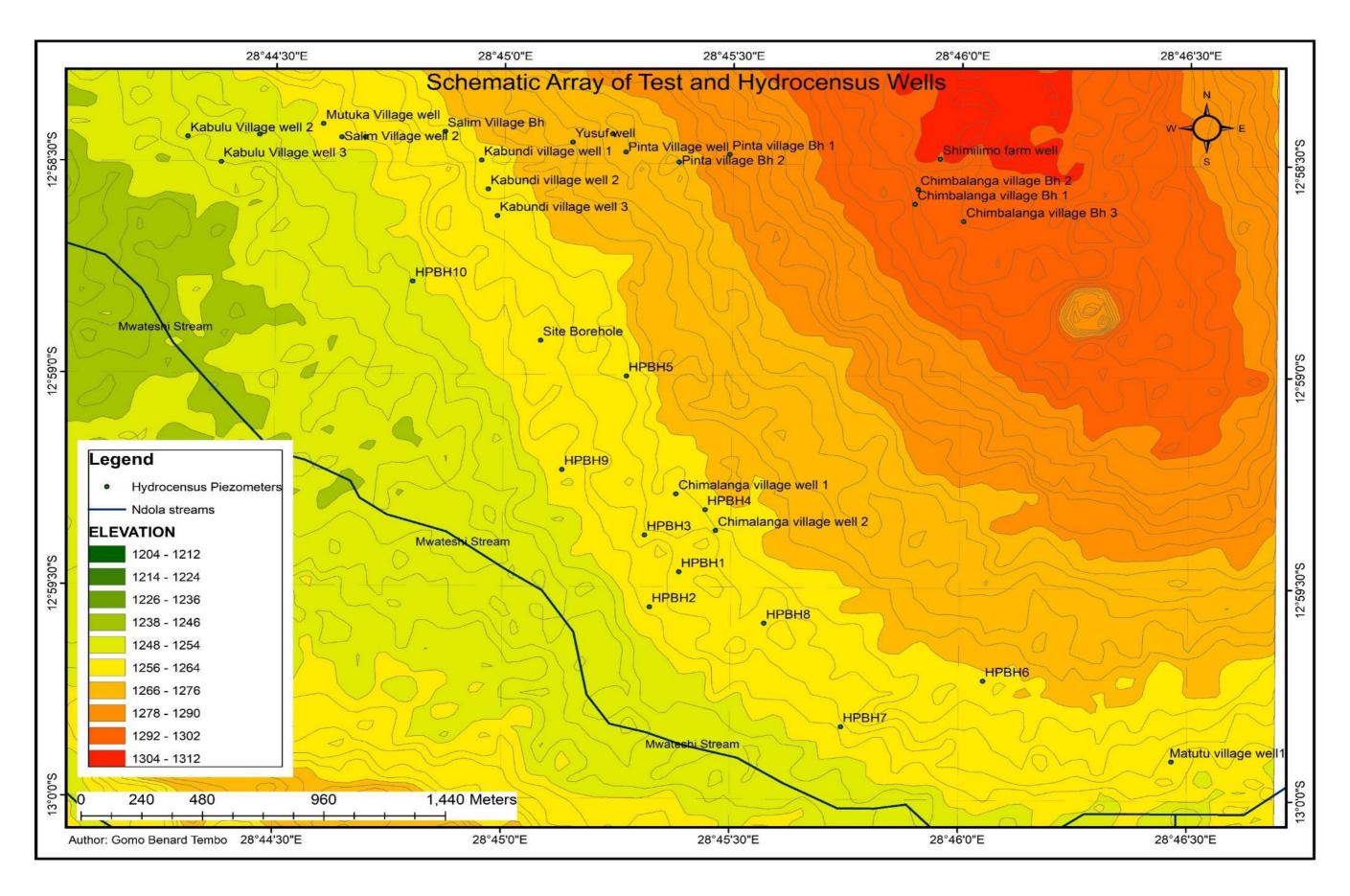


Figure 5.2-3 - Schematic Array of Test Wells and Elevation

5.3 SUMMARY OF GROUNDWATER CHEMISTRY DATA

5.3.1 Evaluation of data

The Ion Balance Error for each sample was calculated using equation (4-1) in section 4.4.1, and the calculated balance errors values are shown in Table 5.3-1 and Table 5.3-2 for both the 2017 and 2018 Hydrogeochemistry datasets respectively. Determined ionic balance error for the analyses of both years ranged from 0.5% to 23.5% with an average of 3.6%. The average ion balance error shows that the samples analysis is generally accepted as was within the acceptable range of below 5% even though two samples (HPBH3 and HPBH4) showed values higher than 10% (Appelo et al., 1996; Aqion.de, 2017). High Ion balance error recorded at the two sites could be as a result of an error in analysis or influence of other ions in the solutions, and generally, the samples ion balance error is acceptable. For samples that show a significantly higher ion balance error, it is prudent to investigate the causes of high ionic balance error and possibly to analyse the samples again. The researcher investigated the recorded higher ion balance error values, and it appears the laboratory may not have been very accurate for the samples in question, but the errors were few and acceptable.

Table 5.3-1 - 2017 Kakontwe Aquifers Hydrogeochemistry Data²

Borehole ID	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Cl (mg/L)	HCO ₃ (mg/L)	CO ₃ (mg/L)	SO ₄ (mg/L)	TDS (mg/L)	EC (μS/cm)	рН	Ion Balance Error (%)	SI _{calcite}	SI _{dolomite}
WHO Guidelines	200	30	200	150	250	300	-	250		1500	6.5 - 8.0	-	-	-
НРВН1	3	4.4	38	17	4	191	12.5	4	138	269.5	7.01	3.08	0.12	-0.104
НРВН2	2	6.8	53.4	15.1	5.7	243.6	8.9	6.2	172	334.9	7.66	1.36	0.05	0.236
НРВН3	4	2.2	63.3	30.8	89.5	347.6	34.1	65	329	634.3	7.27	23.5	0.18	0.327
НРВН4	0.1	1.7	71	37	46	353	16.4	85.5	307	592.6	7.27	14.4	0.243	0.183
НРВН5	0.9	5.4	48	9.4	1.6	205.4	7	3.6	141	275.9	8.33	2.06	0.086	-0.257
НРВН6	1.1	1.3	47.2	18.1	1.6	259.1	14.4	5.4	178	346.9	8.24	5.75	-0.071	-0.157
НРВН7	1.7	6.1	42.2	17.4	3.4	210.8	13.5	4	150	293	7.84	1.8	0.044	0.182
НРВН8	2.6	6.7	41.7	18.7	4.3	226.2	15.2	5.1	161	313.8	8.07	0.396	0.314	0.084
НРВН9	3.2	7.3	53.8	22.2	5.3	271.6	21	3.8	196	380.9	7.52	1.65	0.163	0.057
НРВН10	3.2	3.9	53.8	21.9	5.3	271	10.4	3.2	190	368.8	7.6	0.72	0.038	-0.205
Site Borehole	2.5	5.4	49.9	20.3	4.8	252.5	12.7	2.9	178	345.6	7.79	0.083	0.094	-0.094
Chimalanga village well 1	1.6	4	50.9	12.1	3.8	219.3	11	3.7	155	302.4	7.79	0.953	0.171	0.117
Chimalanga village well 2	2	5.5	43.9	13.1	4.4	201.4	15.7	5.5	147	286	7.66	0.618	0.281	-0.017
Matutu village well1	1.7	8.5	43.9	10.8	3.8	185.2	16	3.1	135	264.5	7.88	2.48	0.22	0.164
Kabundi village well 1	1.8	3.6	45	11.8	4.9	204.8	22	5.1	151	295.4	7.57	3.07	0.155	0.361
Kabundi village well 2	1.4	1.2	45.6	5.1	4.3	168.7	31	3.1	133	259.2	7.64	2.86	0.126	-0.02
Kabundi village well 3	2.4	3.7	50.9	14.7	4.5	241.3	9.5	4.8	169	328.1	7.43	2.86	-0.067	0.15
Chimbalanga village Bh 1	2	2.9	66.8	14.2	2.4	266.9	6.9	4.8	187	364	-	1.31	0.159	0.17
Chimbalanga village Bh 2	1.8	5.6	48.7	11.4	5	217.5	5.8	5.3	152	295.5	7.55	3.06	0.118	0.279

² Text in red is showing values exceeding the WHO Guideline limits

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Borehole ID	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Cl (mg/L)	HCO ₃ (mg/L)	CO ₃ (mg/L)	SO ₄ (mg/L)	TDS (mg/L)	EC (μS/cm)	pН	Ion Balance Error (%)	SI _{calcite}	SI _{dolomite}
Chimbalanga village Bh 3	1.8	4.8	45.9	12.8	4.1	222.3	23.1	3.9	161	313.9	7.57	4.01	0.17	0.111
Shimilimo farm well	2	9.6	47.4	13.3	4.5	236.4	6.4	4	161	314	7.77	3.72	0.212	0.676
Pinta village Bh 1	1.7	1.6	58.1	5.8	4.3	224.3	17.6	4.5	162	316.3	-	5.42	-0.03	0.567
Pinta village Bh 2	2	5.6	56.5	4	6.5	222.6	16.5	2.5	159	310.6	7.66	6.96	0.044	0.12
Pinta Village well	1.8	1.1	56.2	2.4	4.8	188.3	13	5.6	139	272.1	7.5	3.57	0.223	0.093
Laurent village well	4	3.2	54.5	14.5	6	259	8.9	10	184	356.9		5.17	-0.178	0.333
Yusuf well	3	4.1	55.8	15.6	5.9	266.7	10.7	6.8	188	364.5	7.24	4.19	0.223	0.107
Salim Village Bh	2.8	6.8	51.7	9.8	5.4	213.5	6.4	7.6	152	297.2	7.4	1.71	-0.079	0.19
Salim Village well 1	3.3	1.4	48	10.3	5	207.8	15.4	5.5	151	295.3	7.82	3.38	0.109	-0.307
Salim Village well 2	22	7	53.3	28.9	31.9	300.4	17.4	23.9	247	477.8	7.36	1.17	0.148	-0.154
Mutuka Village well	1.8	1.6	45.2	12.9	4.3	205.1	35	4.8	159	309.1	7.72	2.09	0.64	0.366
Kabulu Village well 1	1.6	5.5	41.7	11.4	4.6	188.4	26.4	5.8	143	279.9	7.98	1.66	-0.09	0.13
Kabulu Village well 2	2	3.3	40	16.5	4	210.3	15.6	3.3	150	291.7	7.89	1.17	-0.223	-0.354
Kabulu Village well 3	1.8	4.8	39	18.2	4.2	216.8	8.8	3.3	150	292.1	7.73	1.3	-0.154	-0.124
Averages	2.7	4.4	50	15.1	9.1	233.3	15.3	9.6		334.6	7.7	3.6	0.1	0.1

Table 5.3-2 - 2018 Kakontwe Aquifers Hydrogeochemistry Data

Borehole ID	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Cl (mg/L)	HCO ₃ (mg/L)	CO ₃ (mg/L)	SO ₄ (mg/L)	TDS (mg/L)	EC (µS/cm)	pН	Ion Balance Error (%)	SI _{calcite}	SI _{dolomite}
WHO Guidelines	200	30	200	150	250	300	-	250		1500	6.5 – 8.0	-	-	-
HPBH1	3.9	<u>5.9</u>	<u>25</u>	<u>30</u>	4.8	<u>270</u>	<u>11.3</u>	2.8	353.9	387	7.91	6.73	-0.99	-2.4
НРВН2	0.7	5.1	60.1	12	6.1	281	10	5.4	380.5	480	9.02	8.22	1.6	1.2
НРВН3	4	2.2	63.3	30.8	23	337.6	34.1	14	398.5	634.3	7.27	4.45	-0.8	-1.6
НРВН4	2.1	3.5	75	28	4.3	285	16.4	26	440.6	600	8.01	7.69	0.1	0.1
НРВН5	5	4.1	53	29	3.4	341	12	13	460.6	245	8.56	5.34	1.3	2.6
НРВН6	2.1	1.6	54	18.1	3.2	259	20.3	2.9	361.4	295.3	7.93	0.95	0.6	1.1
НРВН7	3.1	5.7	37.8	21.4	3.1	245.4	14.3	4.6	335.7	254	7.84	3.47	0.3	0.8

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Borehole ID	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Cl (mg/L)	HCO ₃ (mg/L)	CO ₃ (mg/L)	SO ₄ (mg/L)	TDS (mg/L)	EC (µS/cm)	рН	Ion Balance Error (%)	SI _{calcite}	SI _{dolomite}
НРВН8	2.6	6.7	41.7	18.7	4.3	226.2	15.2	5.1	320.6	313.8	7.3	0.4	-0.16	-0.3
НРВН9										-	-	-		
НРВН10	4.3	4.3	49.4	18.4	6.3	219.9	12.1	2.6	317.8	304.2	7.3	5.34	-0.1	-0.3
Site Borehole	2.5	5.4	36.5	17.5	4.8	212.5	9.4	4.1	292.9	345.6	7.2	2.75	-0.34	-0.65
Chimalanga village well 1	1.8	4.6	47.3	9.4	3.8	201	17	3	288	302.4	8	2.05	0.5	0.7
Chimalanga village well 2	2.3	5.1	43.9	13.9	4.4	199.4	21	4.9	295.1	301	8.3	0.95	0.8	1.4
Matutu village well1	1.5	6.2	43.1	12	3.8	167.9	26	10.4	271	287	8.2	4.42	0.6	1
Kabundi village well 1	1.9	4.2	45	8.9	4.9	204.8	19	6.7	295.5	358	7.57	6.88	0.11	-0.01
Kabundi village well 2	1.5	2.4	51	6.4	4.3	168.7	27	5.7	267.1	259.2	7.4	3.09	-0.08	-0.7
Kabundi village well 3	2.4	3.7	43	11.1	4.5	207.8	13.4	4.8	290.8	328.1	7.43	5.46	-0.04	-0.33
Chimbalanga village Bh 1	2.3	4.5	45.5	13.5	2.4	217	7.4	4.1	296.9	398	7.6	1.6	0.2	0.1
Chimbalanga village Bh 2	2.1	4.7	46.2	11.8	5	217.5	6	2.9	296.3	304	7.55	4.58	0.12	-0.003
Chimbalanga village Bh 3	1.5	5.5	55.3	12	4.1	230.1	14	6.7	329.4	301	7.7	0.97	0.4	0.4
Shimilimo farm well	3.5	7.2	49.5	14.6	4.5	250	16	5.4	351.1	314	7.77	3.94	0.4	0.6
Pinta village Bh 1	1.7	3.4	45.9	10	4.3	211.5	12	4.5	293.6	316.3	7.8	5.92	0.4	0.5
Pinta village Bh 2	2.1	5.6	53.4	12	6.5	245.2	11	5.7	341.7	389	7.5	5.29	0.17	-0.5
Pinta Village well	1.8	0.9	51.3	6	4.8	199.5	14	5.6	285.7	298.3	7.1	5.54	0.3	0.3
Laurent village well	4.5	2.2	54.7	13	6	234	10	6.9	331.4	356.9	7.6	1.2	0.3	0.2
Yusuf well	2.4	4.5	55.1	12.1	5.9	266.7	7.8	4.9	358.8	364.5	8.1	7.88	0.8	1.3
Salim Village Bh	1.9	4.9	53.8	11.2	5.4	213.5	6.2	3.5	300.5	297.2	8.2	1.17	0.8	1.3
Salim Village well 1	3.5	2.5	48.9	9.3	3.1	221.4	12.1	5.2	306.3	295.3	7.9	5.59	0.3	0.2
Salim Village well 2	4.6	5.5	50.8	15.4	17.9	144.9	23	5.9	268.2	386	7.5	5.71	-0.07	-0.3
Mutuka Village well	5.1	1.9	45.2	8.9	4.3	208.2	21	4.8	278.6	367	7.6	5.59	0.1	-0.11
Kabulu Village well 1	2.7	4.3	41.7	10.2	4.6	203.7	15.6	5.8	288.8	296.7	7.98	6.6	0.5	0.7
Kabulu Village well 2	1.9	3.9	45.8	9.2	3.3	187.4	14.2	3.1	267.1	365.3	7.9	0.34	0.4	0.4
Kabulu Village well 3	2.8	4	48.2	11.4	4.2	215.4	10.1	3.5	299.9	307.1	8.4	2.19	0.95	1.6
Averages	48.8	14.6	2.7	4.3	227.9	6.1	5.5		320.8	345.4	7.8	4.1	0.3	0.3

5.3.2 Major Ions Water Chemistry

Major ions concentration in the groundwater for both 2017and 2018 data were recorded in the following order in terms of concentration; $HCO_3^- > Ca^{2+} > CO_3^- > Mg^{2+} > SO_4^{2-} > Cl^- > K^+ > Na^+$. These concentration values coincide with the known geological composition of the study area (see **Section 3.6.2** above) and consistent dissolution products of the calcite $(CaCO_3)/dolomite$ $(CaMgCO_3)$ environments. In most carbonate environments, bicarbonate is a product of dissolution of the calcite/dolomite.

The pH values measured were almost always between 7 and 8 with an average of 7.7 and within the WHO guideline pH values of 6.6 to 8.5. The pH values measured for all the samples showed that the water is characterised by neutral to alkaline hydrogeochemistry conditions. The water in the Kakontwe aquifers of Ndola is characterised as presenting low/moderate levels of mineralisation as can be seen in the low levels electrical conductivity ranging between 260 and 634 μ S/cm with a mean conductivity of 334.6 μ S/cm but lower than the WHO water guideline value of 1,500 μ S/cm or 150mS/cm as shown in **Table 5.3-1** and **Table 5.3-2** above. Low values of electrical conductivity of the water recorded could be indicative of the low/moderate mineralisation in the aquifers.

On the cations side, the test data showed a calcium content of 38–71 mg/l against the mean calcium ion value of 50 mg/L (no WHO guideline value for Calcium available); a magnesium content of 2.4–37 mg/l; Sodium content ranged from 0.1- 22 mg/L with an average of 2.7 mg/L and a Potassium content of 1.1–9.6 mg/L with an average 4.4 mg/L. The distribution characteristics for groundwater data generally showed low levels of cations.

The results showed to be 1.6 - 89.5 mg/L for Cl⁻ with an average of 9.1 mg/L, 2.5 - 85.5 mg/L for SO_4^{2-} with an average of 9.5 mg/L, 5.8 - 35 mg/L for CO_3^{2-} with an average of 15.3 mg/L, and 168.7 - 353 mg/L mg/L for HCO_3^{-} with a mean value of 233.3 mg/L. HCO_3^{-} was the dominant anion for both the 2017 and 2018 datasets, which varied from a minimum of 144.9 mg/L to a maximum of 341 mg/L in the study area as shown in **Table 5.3-3**.

The alkalinity of water is the measure of its capacity for neutralisation (Kumar et al., 2006), which is represented by the bicarbonate (HCO₃⁻). The calcium-bicarbonate water likely resulted mainly from the dissolution of limestone rocks, while the calcium and magnesium-

resulted either from the dissolution of calcite and dolomite which are the predominant minerals in the geology of the study area.

The range of presence of each of the parameters analysed, along with their averages and standard deviation values for both the sampling sessions have been presented in **Table 5.3-3**. The summary statistical data shown in the table shows similar statistics for both the 2017 and 2018 data sets. Based on the analyses performed on the quantitative data, the detailed statistical results have been reported in **Section 5.5** below.

Table 5.3-3 - Quantitative Chemical Analysis Results of Hydrogeochemistry Data

Parameter			2017 S	ampling Data		<i>y</i> - 8	2018 Sampling Data						
1 arameter	Minimum	Maximum	Mean	Std Deviation	Skewness	Kurtosis	Minimum	Maximum	Mean	Std Deviation	Skewness	Kurtosis	
pН	7.01	8.33	7.66	0.291	0.17	-0.6	7.1	9.02	7.8	0.425	0.754	-0.14	
EC	259.2	634.3	334.6	84.0	2.52	5.6	245	634.3	345.4	86.3	2.126	4.02	
Ca2+	38	71	50.0	7.71	0.80	-0.29	25	75	48.8	8.7	0.306	1.9	
Mg2+	2.4	37	15.08	7.34	1.02	0.85	6	30.8	14.57	6.71	1.312	-0.05	
Na+	0.1	22	2.75	3.56	5.25	28.15	0.7	5.1	2.69	1.134	0.723	-1.37	
K+	1.1	9.6	4.44	2.24	0.23	-1.55	0.9	7.2	4.26	1.528	-0.3456	-1.35	
CO ₃ ² -	5.8	35	15.3	7.7	1.14	-0.05	6	34.1	14.97	6.38	1.106	0.41	
HCO ₃ -	168.7	353	233.3	42.5	1.27	0.81	144.9	341	227.9	43.0	0.907	0.4	
Cl-	1.6	89.5	9.07	16.8	4.05	16.45	2.4	23	5.48	4.1	3.59	12.1	
SO ₄ 2-	2.5	85.5	9.56	17.52	3.75	12.8	2.6	26	6.08	4.49	3.26	11.6	
NO ₃ -	-	-	-	-	-	-	0.1	0.6	0.203	0.1257	1.498	1.37	

The analysis of the significant ions for both the 2017 and 2018 data sets showed that Ca^{2+} and Mg^{2+} were the dominant cations. The calcium concentration was as high as 75 mg/L and as low as 25 mg/L. High calcium concentration may have originated from calcite and dolomite weathering or silicate rock dissolution. Ca^{2+} and Mg^{2+} have known elements that constitute the possible sources of hardness, which were common in the limestone areas such as the study area.

The skewness and kurtosis of each parameter were calculated for both the datasets as shown in **Table 5.3-3.** In 2017 data, EC, Mg²⁺, Na⁺, HCO₃⁻, Cl⁻ and SO₄²⁻ were found to be positively skewed – an indication of the influence these parameters have in the system. All the other parameters were negatively skewed. The kurtosis coefficients were greater than zero (95 % confidence) for all parameters except pH, calcium, potassium and carbonate. For the 2018 data, EC, Ca²⁺, CO₃⁻, HCO₃⁻, Cl⁻, SO₄⁻ and NO₃⁻ were found positively skewed with kurtosis coefficients greater than zero (95 % confidence) while all the analysed parameters were negatively skewed.

5.4 GROUNDWATER TYPES

5.4.1 Piper Plots

Both the analysis datasets were plotted on the piper plots for assessment of groundwater types. **Figure 5.4-1** and **Figure 5.4-2** below show the piper plots for the 2017 and 2018 datasets for the study area respectively. The piper plots showed that the hydrogeochemical facies are calcium bicarbonate (Ca-HCO₃) as the main hydrogeochemical groundwater type for all the water samples analysed. The ions Ca²⁺ and HCO₃- are dominant in all the samples and likely due to the weathering processes in the carbonate system under study.

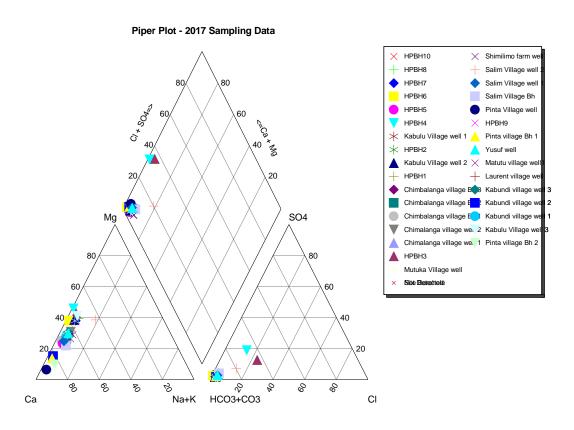


Figure 5.4-1 - 2017 Piper Plot for the Kakontwe Aquifers Hydrogeochemistry

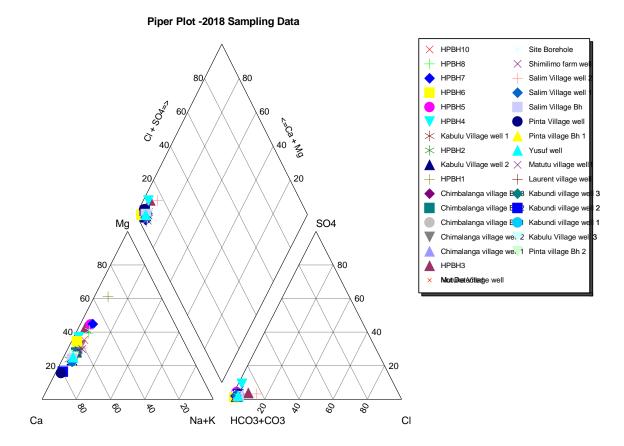


Figure 5.4-2 - 2018 Piper Plot for the Kakontwe Aquifers Hydrogeochemistry

5.4.2 Schoeller Diagrams

The Schoeller diagrams were plotted for the test data, and the results showed that Ca²⁺ and HCO₃⁻ are the dominant ions in most parts of the study area (**Figure 5.4-3** and **Figure 5.4-4** below). All of the groundwater samples analysed showed Ca-HCO₃ likely due to the influence of the carbonate as shown by the piper plot (**Figure 5.4-1** and **Figure 5.4-2**).

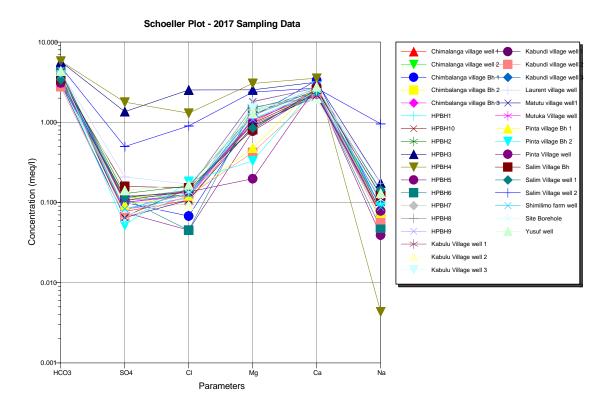


Figure 5.4-3 - Schoeller Diagram for 2017 Data

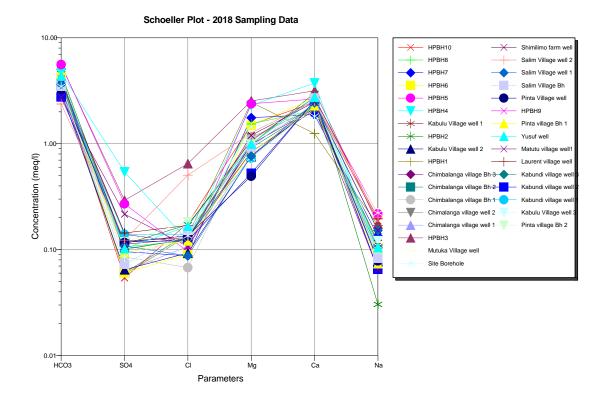


Figure 5.4-4 - Schoeller Diagram for 2018 Data

5.5 HYDROGEOCHEMICAL PROCESSES

This section makes use of the various tools to understand the hydrogeochemical processes that may be responsible for the formation of the species such as the bicarbonate and others that showed dominance in the samples results from data measured during the study and as shown in the generated piper plots and Schoeller diagrams above.

These various tools have been found useful in understanding the hydrogeochemical processes as well as prove which amongst the predicted models would be a predominant hydrogeochemical process in an aquifer system based on the identified species. Examples of tools that have been used by many researchers include tools such as correlation, bivariate, cluster and principal component analysis tools. The subsections below apply various proven tools to estimate the dominant hydrogeochemical processes in the system under study.

5.5.1 Governing Principles

Carbonate dissolution is one of the known processes that often lead to higher levels of these elements, especially in carbonate environments. Fetter, 2001 showed that the various dissolved carbonates species (H₂CO₃, HCO₃⁻ and CO₃²-) as a function of the pH (as shown in Figure 5.5-1 below). At a pH of 6.3, the activities of HCO₃⁻ and H₂CO₃ are equal. With pH>6.3, HCO₃⁻ becomes the predominant species, and at pH< 6.3 there is more H₂CO₃ as more predominant species. The same relation for the CO₃²- and HCO₃⁻, the two species have equal activity at a pH of 10.3. The Kakontwe aquifer water measured an average pH value lower than 7.7 according to Section 5.3.2 above which could indicate the Bicarbonate (HCO₃⁻) as the predominant species. The results are also confirmed by the laboratory results and the Schoeller diagrams that shows Bicarbonate (HCO₃⁻) as one of the dominant species. The study, therefore, focuses on the processes that show bicarbonate dominance as predicted models.

Weathering of parent rock bodies and leaching of minerals causing the rock-water interaction seem to be the factors controlling geochemistry of the groundwater. Bicarbonate dissolution is a simple and common weathering reaction in carbonate rocks (Drever, 2002). The

Carbon dioxide (CO₂) from the organic matter in the aquifer reacts to form H_2CO_3 . Infiltrating recharge water accumulated H_2CO_3 intermingles with calcite, reacting with calcite (CaCO₃) and dolomite Ca-Mg(CO₃)₂ in the aquifer system. The reaction that mainly leads to the dissolution of calcite and dolomite in the carbonate minerals causing an increase in Ca²⁺, Mg^{2+} and HCO_3 - ions that can be measured in the groundwater. This reaction gives carbonate and bicarbonate water type such as estimated in the Kakontwe aquifer system based on the levels in mostly equilibrium.

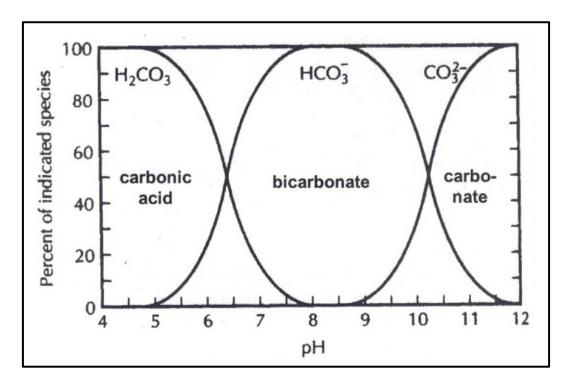


Figure 5.5-1 - Dissolved inorganic carbon species as a function of pH (Fetter, 2001)

Equation (5-1) below illustrates the reaction of carbon dioxide reacting with water in the aquifer environment to produce carbonic acid.

$$CO_{2g} + H_2O \to H_2CO_3$$
 (5-1)

The carbonate acid in the water could break down producing (HCO₃) and H+ as illustrated in equation (5-2) below. The HCO₃- can further breakdown to produce H+ and CO₂ as shown in equation (5-3) below. Equation (5-4) shows the reaction between carbon dioxide, water and limestone producing Calcium and bicarbonate.

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \tag{5-2}$$

$$HCO_3 \leftrightarrow H^+ + CO_2^{2-} \tag{5-3}$$

$$CO_{2g} + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$
 (5-4)

Kura et al., 2013 showed that the dissolution of carbonate minerals could also be represented in the following reactions in natural systems:

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$
 (5-5)

$$CaMg(CO_3)_2 + H_2CO_3 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$$
 (5-6)

$$CaCO_3 + H_2SO_4 \rightarrow Ca^{2+} + SO_4^- + H_2CO_3$$
 (5-7)

$$CaMg(CO_3)_2 + 2H_2SO_4 \rightarrow Ca^{2+} + Mg^{2+} + 2SO_4^- + 2H_2CO_3$$
 (5-8)

The above equations are useful in predicting the dominant processes in a carbonate aquifer system. Since bicarbonate was already identified as a dominant species, all the assessments will, therefore, focus on Equations (5-5) and (5-6) being the main driving force that produces bicarbonates.

5.5.2 Linear Correlation Analysis

A correlation analysis was done for the hydrogeochemical data collected to understand the relationship among the measured parameters as well as help group the parameters in terms of relevance in the processes under investigation. **Table 5.5-1** and **Table 5.5-2** below show the correlation coefficient matrices for the two measured sets of data.

Table 5.5-1 - Correlation Coefficient Matric for 2017 Hydrogeochemistry Data³

	pН	TSS	Cond	TDS	Ca ²⁺	Mg ²⁺	Na+	K ⁺	Cl-	HCO ₃ =	CO ₃ =	SO ₄ ² -	NO ₃ -
pН	1.0	0.0	-0.42	0.0	-0.43	-0.31	-0.27	0.11	-0.42	-0.37	-0.08	-0.41	0.0
Cond			1.0	0.0	0.70	0.83	0.34	-0.18	0.9	0.95	0.25	0.9	0.0
TDS				1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

³ Text in **bold** in the table indicates significance correlation

	pН	TSS	Cond	TDS	Ca ²⁺	Mg ²⁺	Na+	K+	C1-	HCO ₃ =	CO ₃ =	SO ₄ 2-	NO ₃ -
Ca					1.0	0.31	0.08	-0.3	0.52	0.73	-0.06	0.61	0.0
Mg						1.0	0.36	0.05	0.66	0.83	0.10	0.72	0.0
Na							1.0	0.22	0.28	0.32	0.05	0.12	0.0
K								1.0	-0.18	-0.1	-0.35	-0.26	0.0
C1									1.0	0.73	0.41	0.88	0.0
HCO ₃										1.0	0.02	0.76	0.0
CO ₃											1.0	0.28	0.0
SO ₄												1.0	0.0
NO ₃													1.0

Table 5.5-2 - Correlation Coefficient Matric for 2018 Hydrogeochemistry Data

	**	TECC	0 1	TDC	0.00	3.6.0	NT .	TC:	5 - 6			00.1	NO
	pН	TSS	Cond	TDS	Ca ²⁺	Mg ²⁺	Na+	K+	C1-	HCO ₃ =	CO ₃ =	SO ₄ 2-	NO ₃ -
pН	1.0	0.0	-0.03	0.0	0.16	0.06	-0.19	0.20	-0.27	0.28	-0.2	0.11	-0.07
TSS		1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cond			1.0	0.0	0.54	0.45	0.04	-0.13	0.59	0.46	0.25	0.6	-0.07
TDS				1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ca					1.0	0.10	-0.11	-0.35	0.32	0.39	0.16	0.64	-0.07
Mg						1.0	0.45	0.17	0.34	0.73	0.15	0.52	0.01
Na							1.0	-0.12	0.35	0.25	0.11	0.08	0.42
K								1.0	-0.09	-0.06	-0.21	-0.13	-0.02
C1									1.0	0.19	0.51	0.24	-0.14
HCO ₃										1.0	-0.08	0.45	-0.07
CO ₃											1.0	0.34	0.02
SO ₄												1.0	-0.08
NO ₃													1.0

The 2017 data set showed a high positive correlation between EC and Ca²⁺ (r = 0.7), EC and Mg (r = 0.83), EC and Cl⁻ (r = 0.895), EC and HCO₃- (r = 0.945), SO₄²⁻ and HCO₃- (r = 0.879) as well as EC and SO₄²⁻ (r = 0.892) was observed. The rest of the parameters showed either a low positive or negative correlation indicating a not so strong correlation of these parameters with each other.

The 2018 data showed a similar trend of a high positive correlation between EC and Ca²⁺ (r = 0.535), EC and Mg²⁺ (r = 0.449), EC and Cl (r = 0.585), EC and HCO₃- (r = 0.457), Mg and Na⁺ (r = 0.451), Cl⁻ and CO₃- (r = 0.514), SO₄²⁻ and HCO₃- (r = 0.514) as well as EC and SO₄²⁻

(r = 0.595). The rest of the parameters showed either a low positive or negative correlation indicating a not so strong correlation of these parameters with each other.

For both sets of the results, the positive correlation between EC and the elements such as Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, HCO₃- could be attributed to the contribution of the elements towards the measured EC. The EC of the samples is directly influenced by the species such as these in the water. This could also be an indication of a dissolution process that causes the elements to go into solution to increase the EC. A particularly exciting correlation between HCO₃- with Ca²⁺ and Mg²⁺ was also observed from the correlation results. This correlation could be a further indication of the identified bicarbonate dissolution processes that influence the positive correlation among the elements in the system under study. The correlation between Ca²⁺ and Mg²⁺ was low likely because the two elements appear not to have an influence on each other during the dissolution process but are both influenced by other elements such as Cl-, HCO₃- and SO₄²- an indication of only calcite dissolution based on the governing equations. There is a likelihood that the Mg measured could not have been as a result of the dissolution process but could be an accumulation. Cl- also appears to influence the processes based on the correlation analysis results. It is immediately not clear what the sources of the Cl-could have been because the silicate weathering process does not produce Cl- based on the governing equations. The Cl- could, therefore, be from an external source in the system or even an accumulation. The correlation analysis showed that the Mg²⁺, Ca²⁺, HCO₃- and SO₄²- are clearly from the same source which could be an indication of processes such as calcite, dolomite and silicate weathering. The other tools below will be used to help identify the possible processes.

5.5.3 Cluster and Principal Component Analysis

5.5.3.1 Hierarchical Cluster Analysis

Figure 5.5-2 and Figure 5.5-3 below shows the dendrograms generated using the software SPSS from the 2017 and 2018 data respectively for the hierarchical cluster analysis of the datasets. The dendrograms produced reveal high interconnectivity and homogeneity within the clusters and between the clusters which could be an indication of the similarities in the source-rock.

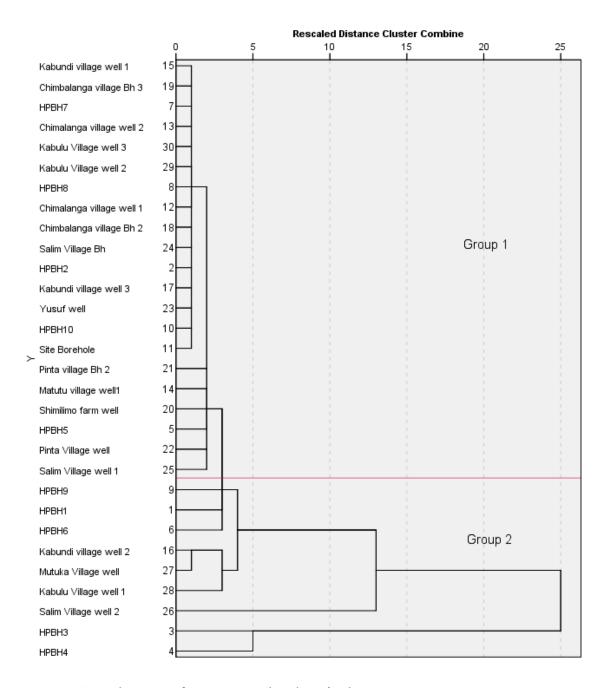


Figure 5.5-2 - Dendrogram for 2017 Hydrochemical Data

Two distinct clusters were observed in the dendrogram. The dendrogram for the 2017 data shows that boreholes Kabundi Village Well 1, Chimbalanga Village BH3, HPBH7, Chimalanga village wells 1, 2 & 3, Kabulu Village Wells 1 and 2, HPBH8, Salim Village BH, HPBH2, Kabundi village well 3, Yusufu well, HPBH10 and the Site Borehole were clustered in the same group - cluster 1 (approximately 73% of the samples in this cluster). The remainder of the samples clustered in the second cluster. Investigation showed that slightly elevated levels of SO₄²⁻ mainly influenced the cluster of group 2, Cl- and Mg²⁺ recorded at HPBH3

and HPBH4 as well as Salim Village well 2, Kabulu Village well 1 and Matuka Village well as illustrated in the Schoeller Diagrams in Figure 5.4-3 and Figure 5.4-4.

In the 2018 datasets, the clusters generated were similar in groupings and terms of interdependency and comparable with the 2017 datasets. The two cluster in the dendrogram shown were differentiated mainly due to the variations in the concentrations of SO_4^{2-} , Cl^- , Mg^{2+} and Na^+ with the samples in group 2 recording higher values of these elements. All the clustered showed interdependency. This can also be confirmed with the samples plotting in the same region in the Piper Plot.

Comparison of the clusters with other specialised plots shows that the clusters generated in the HCA are chemically similar but maybe statistically different. The interdependency of the clusters could be an indication that the grouping was mostly influenced by the same hydrogeochemical processes that were taking place along the groundwater system but only differed in the levels of concentrations. The concentration of these anions and cations were recorded the highest among the cluster Group 2 sites as can also be evidenced from the plots in Figure 5.4-3 and Figure 5.4-4. Furthermore, the grouping was related to the hydrochemical classification of the water type as shown in the interconnected relationships among the main and subgroups of the HCA. Samples with similar species plotted in the same groups or cluster between the two identified clusters. The main findings from the HCA were therefore that generally the samples clustered in the similar interconnected grouping and could be highly related in terms of the dominant species composition as represented by the Ca-HCO₃ water type in the Piper diagrams (see Figure 5.4-1 and Figure 5.4-2). The observed groups or clusters could because of the various levels of the concentrations of the major cations and anions such as Mg²⁺, Ca²⁺, HCO₃- Cl- and SO₄²⁻. Calcite/Dolomite/Silicates weathering was concluded to have been taking place in all the samples and responsible for the significant identified cations and anions besides the Cl- that is likely due to external sources or accumulation in the system. The data analysis will be refined further with other hydrogeochemical tools such as bivariate plots.

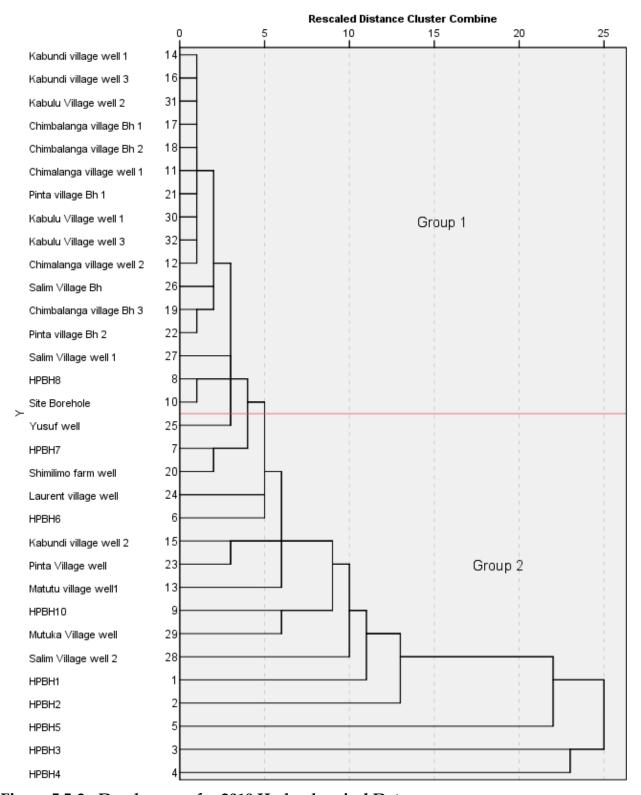


Figure 5.5-3 - Dendrogram for 2018 Hydrochemical Data

5.5.3.2 Principal Component and Factor Analysis

Principal component and factor analysis for the study was also performed using the software IBM SPSS following the Kaiser Normalization and Varimax Rotation procedures as indicated in **Table 5.5-3** and **Table 5.5-4** below. The section below presents the analysis of the data obtained during the PCA to identify the principal components of the process.

The Varimax rotated factor loadings for the 2017 dataset have been presented in **Table 5.5-3** below and shown in the Scree Plot shown in **Figure 5.5-2**. The factors having Eigen values greater than one were produced from the 2017 dataset and rotations were completed in 5 iterations.

Table 5.5-3 - Varimax Rotated Factor Loading for 2017 Data

Rotated Component Matrix

		Component	
	1	2	3
EC (μS/cm)	.967	.169	.160
TDS	.966	.170	.161
HCO ₃ - (mg/L)	.953	059	.138
SO ₄ ²⁻ (mg/L)	.908	.238	057
Cl (mg/L)	.843	.350	.161
Ca (mg/L)	.842	028	202
Mg (mg/L)	.812	007	.304
рН	462	105	218
CO ₃ (mg/L)	.082	.917	.155
K (mg/L)	164	686	.470
Na (mg/L)	.214	006	.882

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser

Normalization.a

a. Rotation converged in 5 iterations.

The first 3 components explain 90.353 % of the total variance which can clearly be attributed to the loadings of TDS, HCO_3 -, SO_4 ²-, Cl-, Mg^{2+} and Ca^{2+} as can be seen in **Table 5.5-3** and illustrated in the rotation in space (see **Figure 5.5-5**) showing an indication of dominance of the major components in the aquifer system. These loadings are an indication of the most

influential or dominant species in the system under study. The dominant species identified can be attributed to the important weathering processes in the system that are also the likely significant sources of the species. These loadings can, therefore, be associated with the dominant processes that have been identified such as calcite/dolomite/silicates weathering. The sulphate and chloride loadings may be from external sources or accumulation within the system because it does not fit into the ideal weathering equations for carbonate systems.

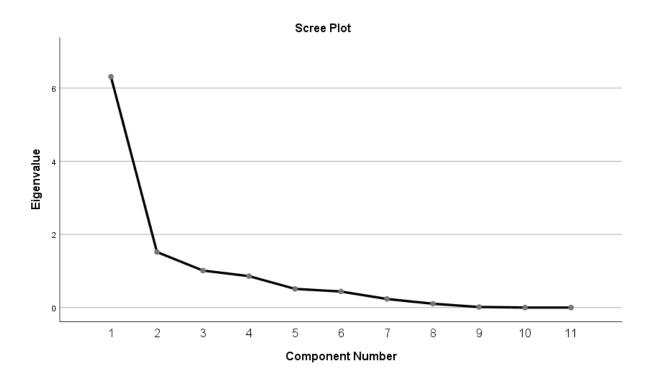


Figure 5.5-4 - Scree Plot for 2017 Data

The EC and TDS loadings are because of the combined influence of the other cations and anions. The EC and TDS loadings could be a result of the other 6 loadings mentioned above causing the increase in the EC and TDS of the groundwater under study. The components that cause high loading of the EC and TDS are the HCO₃-, SO₄-, Cl-, Mg²⁺ and Ca²⁺. The dissolution process could be responsible for the HCO₃-, SO₄-, Mg²⁺ and Ca²⁺ dominance while the Cl- could either as an accumulation or from external sources. High positive loading of bicarbonate, potassium and bicarbonate reveals calcite/dolomite weathering of the system as a likely possibility. The pH is negatively correlated to most of the analysed parameters which are reflected by the negative factor loadings of the same therefore had less influence on the processes.

Component Plot in Rotated Space

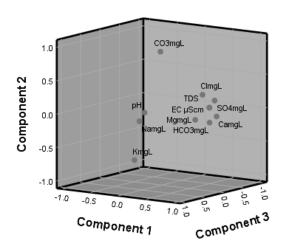


Figure 5.5-5 - Components Rotated in Space for 2017 Data

A similar trend was observed for the 2018 data. The Varimax rotated factor loadings for the 2018 dataset have been presented in **Table 5.5-4** and shown in the Scree Plot shown in **Figure 5.5-6**. Four components having Eigen values higher than one were produced from the dataset and rotations were completed in 5 iterations.

The first 4 components explains more than 90% of the total variance which can clearly be attributed to the loadings of TDS, HCO₃-, SO₄²-, Cl-, Mg²⁺ and Ca²⁺ as can be seen in **Table 5.5-4** and illustrated in the rotation in space (see **Figure 5.5-6**) and an indication of dominance of the major components. These loadings are likely a result or an indication of the species generated from the influential or dominant processes taking place in the system under study.

The EC and TDS loadings could be a result of the other six loadings mentioned above causing the increase in the EC and TDS of the groundwater under study. The components that cause high loading of the EC and TDS are the HCO_3^- , SO_4^{2-} , Cl^- , Mg^{2+} and Ca^{2+} .

High positive loading of bicarbonate, potassium and bicarbonate reveals the possibility of calcite/dolomite weathering of the system with a possibility of accumulation or input of chloride and sulphate from an external. Weathering of parent rock bodies and leaching of

minerals leading to rock-water interaction seem to be the factors controlling geochemistry of the groundwater.

Table 5.5-4 - Varimax Rotated Factor Loading for 2018 Data

Rotated Component Matrix^a

	Component						
	1	2	3	4			
TDS	.964	118	.037	.090			
HCO ₃ (mg/L)	.909	087	.094	.037			
Mg (mg/L)	.832	.242	.225	297			
SO ₄ (mg/L)	.678	.246	142	.385			
EC (μS/cm)	.581	.485	161	.272			
Cl (mg/L)	.264	.852	015	.002			
CO ₃ (mg/L)	001	.732	010	.192			
рН	.370	577	267	010			
Na (mg/L)	.258	.268	.815	136			
NO ₃ (mg/L)	073	131	.788	.147			
K (mg/L)	.099	135	206	801			
Ca (mg/L)	.484	.110	245	.721			

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.a

a. Rotation converged in 8 iterations.

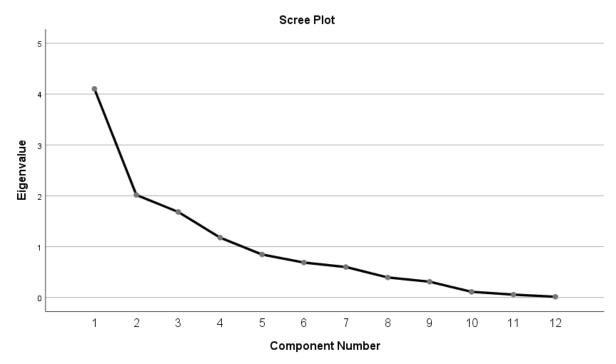


Figure 5.5-6 - Scree Plot for 2018 Data

Component Plot in Rotated Space

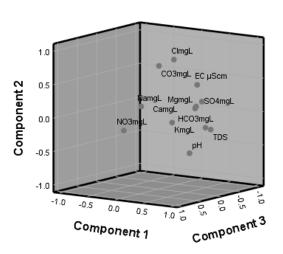


Figure 5.5-7 - Components Rotated in Space for 2018 Data

5.5.4 Bivariate Analysis

Equation (5-5) to (5-8) above showed the predicted molar ratio of various dissolution scenarios of carbonate systems depending on whether weak carbonic and sulphuric acids are involved in the dissolution process.

The predicted model with the carbonic acid dissolution of calcite shows a ratio of 1 mole of Ca^{2+} and 2 moles of HCO_3^- (as indicated by Equation (5-5) above) while the carbonic dolomite dissolution produces 2 moles of $(Ca^{2+} + Mg^{2+})$ and 4 moles of HCO_3^- (refer to Equation (5-6) above) in an ideal situation.

These models can be used to deduce the predominant hydrogeochemical processes in the system using the bivariate plots. The study data has been plotted on the relevant bivariate plots below to compare with the closest predicted more deduce hydrogeochemical processes in the system.

5.5.4.1 Magnesium against Calcium Ratio

White, 1988 suggested that the Ca^{2+}/Mg^{2+} ratio in carbonate systems depends on the proportion of calcite and dolomite present in the aquifer rock. In subsurface water systems composed of very pure limestone, the occurrence of Mg^{2+} in the calcite due to the presence of dolomite gives rise to high Ca^{2+}/Mg^{2+} proportions in waters with a long residence time in the aquifer systems and higher Mg dissolution (Edmunds et al., 1987).

Mayo and Loucks (1995) showed that the groundwater's Ca2+/Mg2+ ratio could reveal the dissolution of calcite and dolomite. A Ca²⁺/Mg²⁺ molar ratio that is equal to one indicates dissolution of dolomite rocks, (refer to Equations (5-6) and (5-8) above for dolomite dissolution) while a higher ratio may represent a more dominant calcite contribution from the rocks and may be a sign of calcite dissolution (refer to Equations (5-5) and (5-7) above. A Ca²⁺/Mg²⁺ ratio, higher than 2, may represent the dissolution of silicate minerals into the groundwater (Katz et al., 1997). **Figure 5.5-8** below shows a plot Ca²⁺/Mg²⁺ ratio for both the 2017 and 2018 data from the study area.

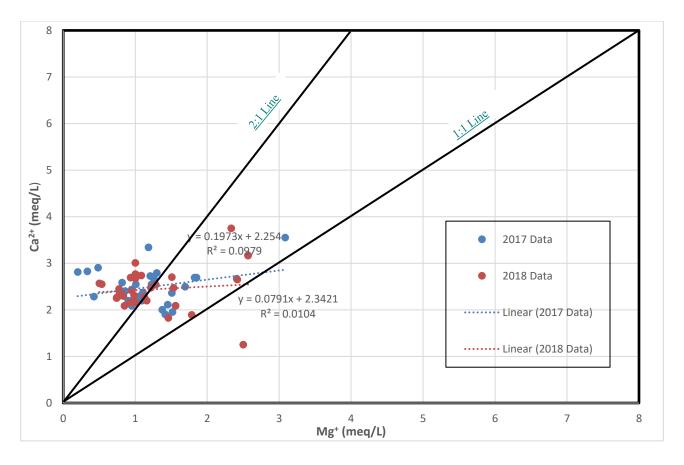


Figure 5.5-8 - Scatter Plot for Ca²⁺ Vs Mg²⁺

The Ca^{2+}/Mg^{2+} for, the study area, was plotted as shown in **Figure 5.5-8** shows that the plots are not defined and predominantly above the 1:1 and 2:1 line which is an indication of more Ca^{2+} than Mg^{2+} in the system under study. The plots could be an indication of additional sources of Ca^{2+} other than calcite dissolution of calcite or sink for Mg, and contrary to the dolomite dissolution predicted model shown in the equations. The results could suggest that there could be calcite and silicates dissolution in the system.

5.5.4.2 Bicarbonate against Calcium Ratio

The predicted model in Equations (5-4) and (5-5) shows that calcite dissolution typically gives a 2:1 ratio of HCO₃⁻/Ca²⁺. The predicted model with the carbonic acid dissolution of calcite shows a ratio of 1 mole of Ca²⁺ and 2 moles of HCO₃⁻ (as shown by Equation (5-5) above). The HCO₃⁻ / Ca²⁺ ratio data for 2017 and 2018 for the study area was plotted in Figure 5.5-9 as shown below. The test data showed a poor correlation of 53% and 14% for the 2017 and 2018 data respectively. This weak correlation showed that bicarbonate and calcium have no influence on each other in the system.

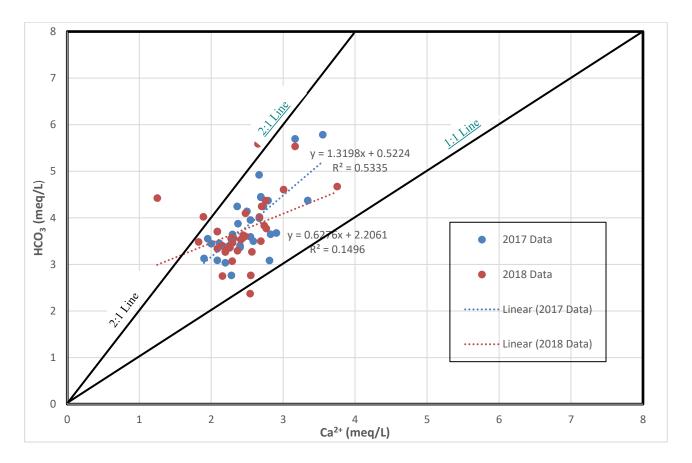


Figure 5.5-9 - Scatter Plot for HCO₃- Vs Ca²⁺

Both sets of data showed a plot above the1:1 slope but also below the 2:1 slope for both the years under review. The closest predicted model for this situation is, therefore, calcite dissolution of HCO₃- as the plots showed a 2:1 ratio of HCO₃-/Ca²⁺ with equation (5-5) for calcite dissolution being the closest predicted model the plot fits. The ratio could be an indication of both calcite and being influenced by silicate weathering in the system.

5.5.4.3 Bicarbonate against Calcium and Magnesium

The predicted model shows that carbonic dolomite dissolution produces 2 moles of ($Ca^{2+}+Mg^{2+}$) and 4 moles of HCO_3^- (refer to **Equation (5-6)** above) in an ideal situation. The $HCO_3^-/Ca^{2+}+Mg^{2+}$ mean ratio in the groundwater is therefore expected to be 2:1 following the predicted model for a dolomite system. **Figure 5.5-10** below shows the $HCO_3^-/Ca^{2+}+Mg^{2+}$ plot for both the 2017 and 2018 datasets. The plots below showed a high correlation of 93% and 60% for the 2017 and 2018 data respectively. This data presents a clear indication of the relationship between the bicarbonate and the combined effect of calcium plus magnesium.

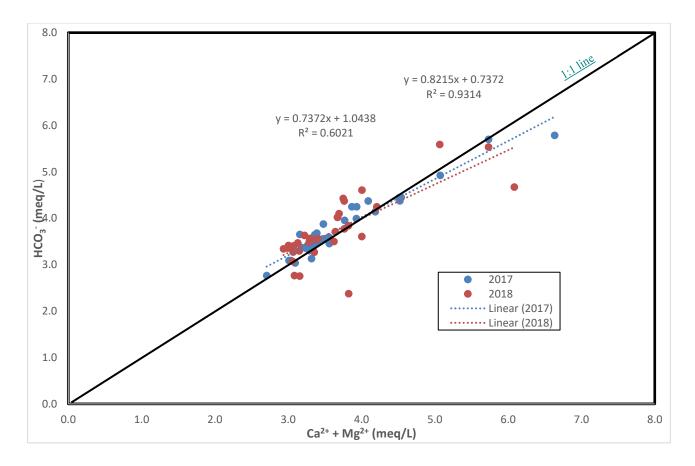


Figure 5.5-10 - Scatter Plot for HCO_3^- Vs $(Ca^{2+} + Mg^{2+})$

As shown in both sets of datasets consistently plotted around the 1:1 slope. This, however, does not fit with the $HCO_3^-/Ca^{2+} + Mg^{2+}$ predicted model of 2:1 ratio (refer to Equation (5-6) above) in an ideal situation. The plot, therefore, confirms that the system is therefore not

dolomite dissolution. This could be an indication of both calcite and silicate weathering in the system.

5.5.4.4 Bicarbonate and Sulphate against Calcium and Magnesium

The (HCO₃- + SO₄²⁻) vs. (Ca²⁺ + Mg²⁺) scatter diagram (as shown in **Figure 5.5-11** below) is used to predict the weathering type in a system by comparing the ionic concentrations showing above and below the equiline (or 1:1 slope line) to differentiate between carbonate and silicate weathering and can also be a useful tool for confirming the presence of silicate weathering in a system. Any samples showing along the equiline are indicative of both carbonate weathering and silicate weathering. Such a (Ca²⁺ + Mg²⁺) vs (HCO₃- + SO₄²⁻) scatter diagram of samples shows that all the samples from the Kakontwe aquifer lie along the equiline which indicate a carbonate weathering due to the presence of limestone and dolomite.

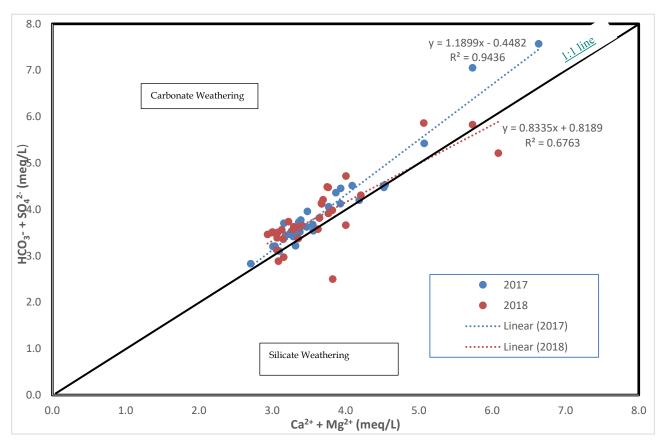


Figure 5.5-11 - Scatter Plot Depicting Carbonate and silicate weathering

The plot showed that most of the data for both 2017 and 2018 plotted near to 1:1 line with a correlation of approximately 94% and 68% respectively, i.e. above the 50% line. This correlation could be an indication of both carbonate and silicate weathering in the system under study, and the carbonate species are influencing the system. The silicate weathering or influence from an external source could, therefore, be the source of some element measured such as Cl^{-} and SO_4^{2-} .

5.5.5 Gibbs Diagram

While the Piper diagram is a method for classifying groundwater based on the distribution of both cations and anions and the Gibbs diagram is a method for estimating the origin of ions in groundwater by focusing on the correlation between the concentration of cations (Na^+, Ca^{2+}) and anions (Cl^-, HCO_3^-) , and Total Dissolved Solids (TDS).

Several factors were used in estimating the origin of ions in groundwater by focusing on the correlation between the concentration of cations (Na $^+$, Ca $^{2+}$) and anions (Cl $^-$, HCO $_3^-$), and TDS (Total Dissolved Solid) control groundwater chemistry, which can be related to the physical situation of the aquifer, bedrock mineralogy and weather condition. Gibbs (1970) suggested TDS versus Na $^+$ / (Na $^+$ + Ca $^{2+}$) for cations and TDS versus Cl $^-$ /(Cl $^-$ +HCO $^3-$) for anions to illustrate the natural mechanism controlling groundwater chemistry, including the rainfall dominance, rock weathering dominance and evaporation and participation dominance.

Figure 5.5-12 and **Figure 5.5-13** below shows the Gibbs diagrams plotted based on TDS and the concentration of cations and anions for 2017 and 2018 data sets respectively for the study.

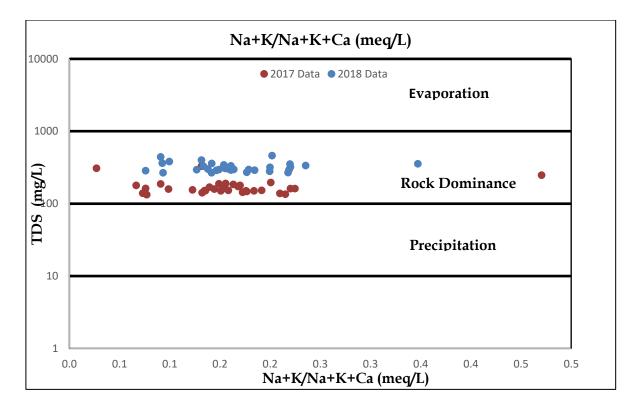


Figure 5.5-12 - Gibbs Diagram by Anions for 2017 and 2018 Data

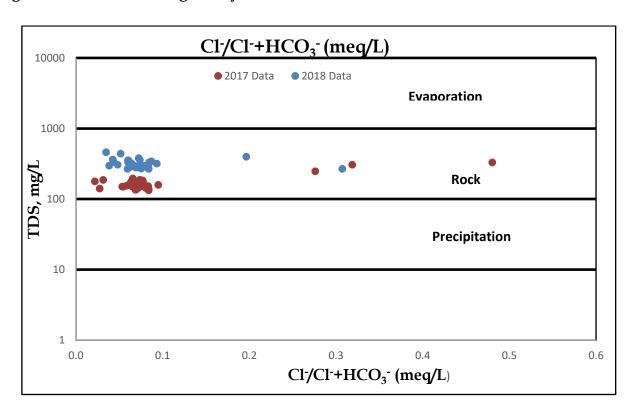


Figure 5.5-13 - Gibbs Diagram by Cations for 2017 and 2018 Data

Based on the Gibbs diagram, all the samples plotted fell into group one group that may have been influenced by rock weathering reaction. The plots explicitly show that all the cations and anions in groundwater have an entirely rock-dominance origin. This characteristic indicates that the dissolution of ions in groundwater through the interaction between groundwater and matrix is more dominant than any other source such as pollution from various sources.

5.5.6 Saturation Indices

Based on the study area geology and the finding from the water quality results and as illustrated through the piper plots and the Schoeller diagrams, the saturation index only focused on calcite and dolomite. According to Langmuir (1971), a suggestion was made that a solution should be considered in equilibrium concerning mineral such calcite or dolomite if the Saturation Index (SI) is around the value of ±0.1. By this criterion, most of the waters of Kakontwe Aquifers showed the average SI of 0.1 for both calcite and dolomite. This could be an indication that the system is predominantly in equilibrium in terms of minerals such as calcite and dolomite as shown by the estimated SI values for calcite and dolomite, as shown in **Figure 5.5-14** below and precipitation is needed to achieve equilibrium.

Twenty-three samples from the 2017 data showed calcite supersaturation, five samples dolomite supersaturation. However, about 15 samples from the 2018 data indicated supersaturation in relation to calcite, six samples undersaturated and no samples from that set of data showed dolomite supersaturation. The data, therefore, showed that about 85% of the samples were calcite supersaturated and precipitation is needed to achieve equilibrium. This, therefore, shows that calcite and dolomite can readily react with other species in the Kakontwe aquifer system

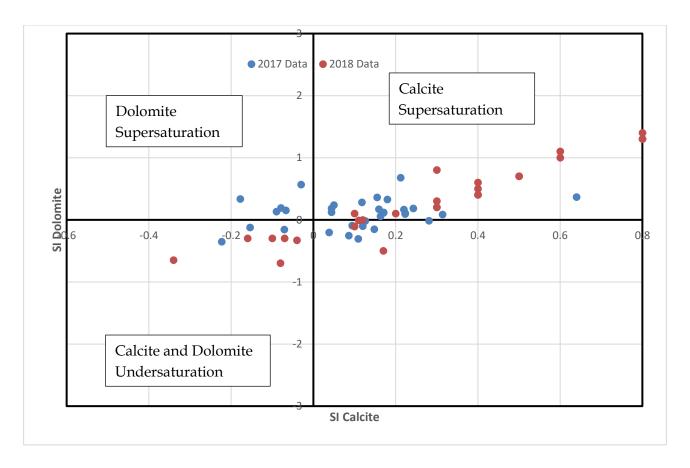


Figure 5.5-14 - Calcite and Dolomite Saturation Indices for 2017 and 2018 Data

5.6 GROUNDWATER QUALITY ASSESSMENT

This section summarises the groundwater quality based on salinity and corrosion hazards as well as water hardness. These assessments are carried out to determine the suitability of the groundwater for industrial or agricultural water use. The study had limitations in the sense that analysed water could be declared fit for uses such as agriculture or industry but can still have a high concentration of trace elements that were not analysed such as Fe, F, nitrate, Mn, Cr, As etc. due to resources limitations. These elements were not analysed due to limitation at the available Laboratory and cost implications. The study was therefore only based on the significant cations and anion required for the various tools used for hydrogeochemical and statistical assessment using the various tools.

5.6.1 Industrial Use

5.6.1.1 Water Hardness

The Ca-HCO₃ water undoubtedly contributes to the permanent hardness of the groundwater as reported below. The water hardness expressed as mg/L of CaCO₃ was calculated using the formulas in **Section 4.5.3**.

An average value of **187 mg/L of CaCO**₃ was estimated for the Kakontwe aquifers water. The water is therefore very hard water using the classification indication in **Table 5.6-1** below are used to indicate the water hardness.

Table 5.6-1 - Indication of Water Hardness

S/N	Concentration as CaCO ₃	Indication
1	0 to 60 mg/L	Soft Water
2	60 to 120 mg/L	Moderately Hard Water
3	120 to 180 mg/L	Hard Water
	> 180 mg/L	Very Hard Water

Source: http://www.lenntech.com/ro/water-hardness.htm

5.6.1.2 Corrosion Hazard

One of the major problems of high calcium waters is the scale formation in the industrial boilers or related equipment. LSI is probably the most widely used indicator of cooling water scale potential. LSI is interpreted as shown below:

LSI < 0 Water is undersaturated with respect to calcium carbonate. Undersaturated water tends to remove existing calcium carbonate protective coatings in pipelines and equipment.

- **LSI = 0** Water is neutral. Neither scale-forming nor scale is removing.
- LSI > 0 Water is supersaturated with respect to calcium carbonate (CaCO₃), and scale forming may occur.

The LSI was plotted for the study area as shown in **Figure 5.6-1**. An average Langelier Saturation Index (LSI) value of 0.065 was also calculated for the 2017 data and 0.18 for the 2018

data. The water is slightly supersaturated concerning calcium carbonate (CaCO₃), and scale forming may occur indicating the Kakontwe aquifer water could be scale forming and slightly corrosive in industrial application. Treatment for industrial application was therefore recommended.

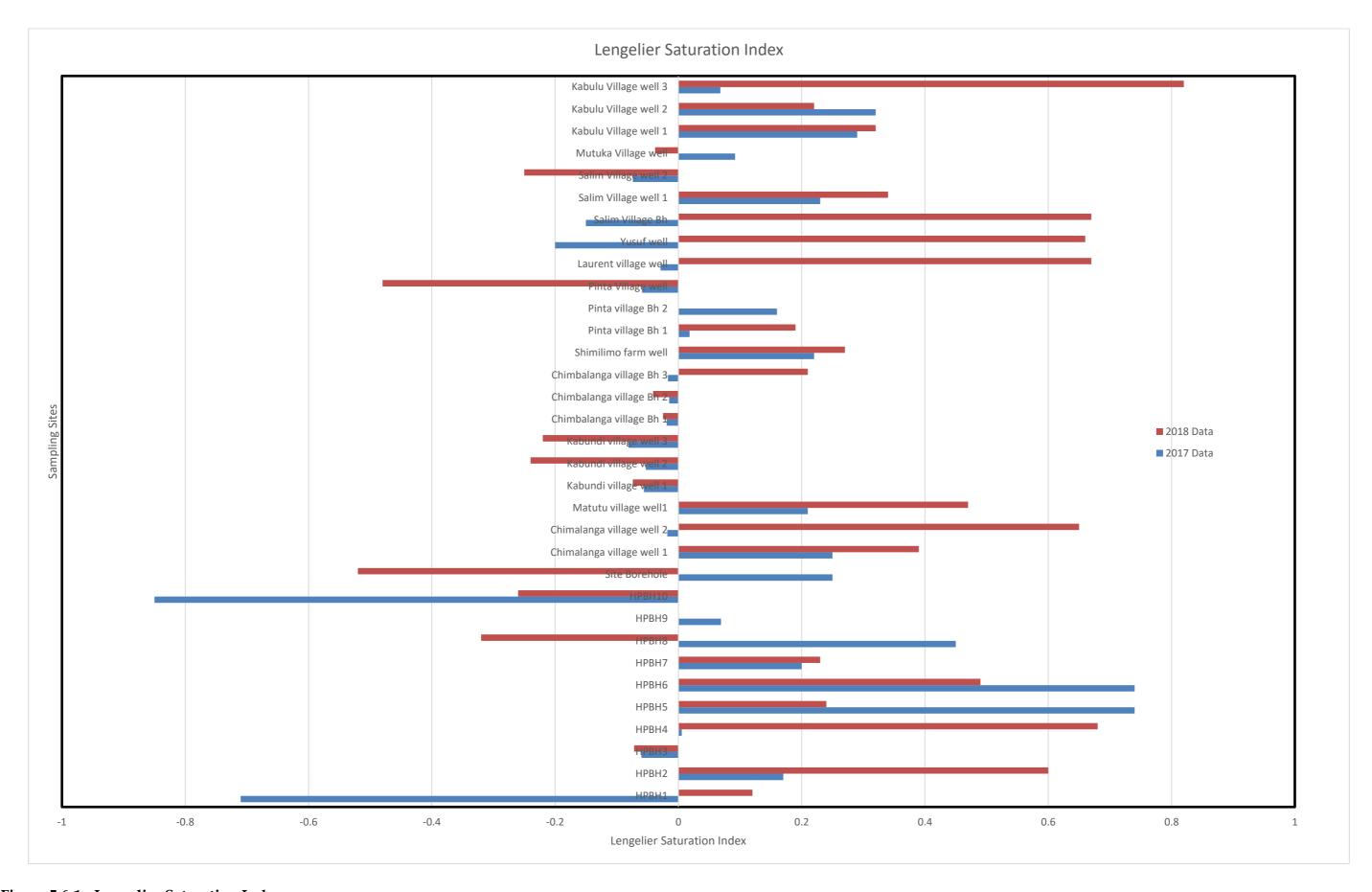


Figure 5.6-1 - Langelier Saturation Index

5.6.1.3 **Summary**

The hydrogeochemical assessment has shown that the Kakontwe water is very hard water in terms of hardness with a water hardness value of **187 mg/L of CaCO**₃. A Langelier Saturation Index (LSI) of 0.065 was also calculated indicating the water is saturated with respect to calcium carbonate and scale forming and corrosion could occur in industrial application and may, therefore, need to be treated before using it for industrial purposes especially in boilers and heating equipment.

5.6.2 Agricultural Use and Salinity Hazard

Water with an SSP greater than 60% may result in sodium accumulations causes a break-down in the soil's physical properties (Khodapanah et al., 2009). This is an important factor for studying sodium hazards. Sodium has the capability of reacting with soil and reducing its permeability and supports little or no plant growth. The Soluble Sodium Percentage (SSP) calculated showed the range from 1.5 to 31% with an average SSP value of 11%, i.e. far below the 60% threshold according to Khodapanah et al., 2009. Based on these SSP values, the Kakontwe water has a very low risk of sodium accumulation in the soils physical structure.

The Kelly's ratio (>1) indicates an excess level of sodium in water which is unsuitable and <1 is suitable for irrigation uses. Based on the calculated Kelly's ratio, the maximum Kelly's Ratio value calculated was 0.27 an indication of very low levels of sodium ions in the Kakontwe aquifer water.

The sodium or alkali risk in the water for irrigation is estimated by the absolute and relative concentration of cations. The relative activity of sodium ion in the exchange reaction with soil can be expressed in terms of SAR. **Figure 5.6-2** and **Figure 5.6-3** shows the Wilcox Plots for the 2017 and 2018 data sets respectively. The two plots show a Class of S1 (Low Risk) classification on the Sodium (Alkali) hazard scale while the values for the salinity hazard showed a class of C2 (Medium Risk) for both the data sets. Correct, but then what is the implications/meaning?

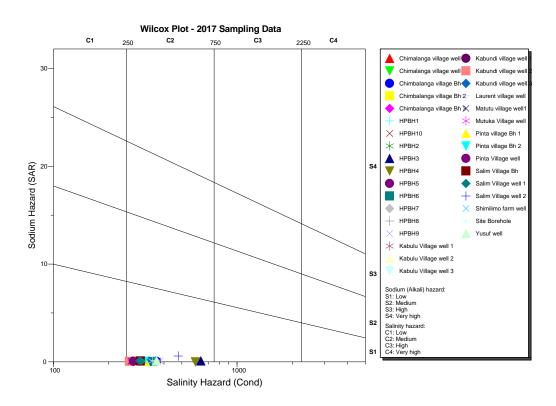


Figure 5.6-2 - Wilcox Plot for 2017 Sampling Data

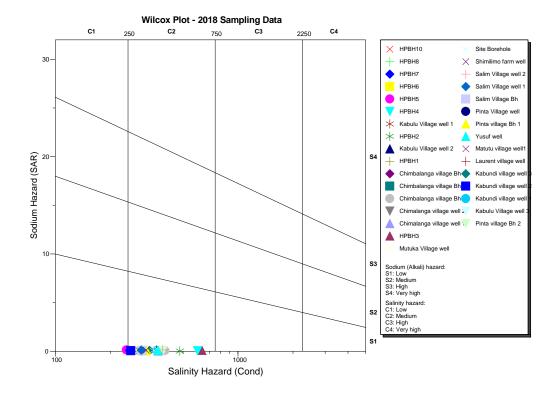


Figure 5.6-3 - Wilcox Plot for 2018 Sampling Data

The above assessment, therefore, showed a low salinity risk in the Kakontwe aquifers water samples.

Section 6.3.1 showed that the Soluble Sodium Percentage (SSP) calculated showed the range from 1.5 to 31% with an average SSP value of 11%, i.e. far below the 60% threshold according to Khodapanah et al., 2009. Based on the calculated Kelly's ratio, the maximum Kelly's Ratio value calculated was 0.27 an indication of very low levels of sodium ions in the Kakontwe aquifer water. The comparison of the Kakontwe EC and SAR analytical data on the US salinity diagram shows that study area samples were classified as C2-S1(Good/Excellent).

As shown in **Section 4.5.5.3** above, the salinity assessment showed that the Kakontwe aquifers water has low salinity levels and may not cause salinity and related problems in the soils is used for irrigation. The Wilcox plots showed a Low-Risk classification on the Sodium (Alkali) hazard scale while the values for the salinity hazard showed a Medium Risk for both the data sets. The Soluble Sodium Percentage (SSP) calculated showed with an average SSP value of 11%, i.e. far below the 60% acceptable threshold while the calculated Kelly's ratio, the maximum Kelly's Ratio value calculated was 0.27 an indication of very low levels of sodium ions in the Kakontwe aquifer water. The Kelly's ratio (>1) indicates an excess level of sodium in water which is unsuitable and <1 is suitable for irrigation uses.

CHAPTER 6: CONCLUSION AND RECOMMENDATIONS

6.1 INTRODUCTION

The study was done in Ndola, Zambia to evaluate the groundwater quality and characterise the groundwater hydrogeochemical processes. Samples were collected and analysed in the laboratory and scientific tools such as Piper Plots, Schoeller Diagram, Statistical and Bivariate analysis were made use of as part of the interpretation process based on the water quality results obtained from the study area. This section, therefore, draws out the conclusions of the study based on the results and findings. The section ends with the recommendations based on the findings.

6.2 CONCLUSION

6.2.1 Hydrocensus

The average groundwater level recorded for all the boreholes was 7.3 mbgl (approximate 1261 masl) with a range from 2.6 mbgl to 16.99 mbgl. These measurements indicated that the aquifer system maybe is open to the atmospheric pressure and easily interacts with the surface water bodies during the wet season. The contoured groundwater static water levels map further showed that the groundwater flows towards the Mwateshi Stream in the southwesterly direction. A plot of groundwater level elevation against topographic elevation also showed a 95% degree of correlation. This was a clear indication that the groundwater level elevation follows the topography flowing towards the stream. This observation also confirms the suggestion that the Kakontwe aquifers are water table or unconfined aquifer as illustrated through geological profiles.

6.2.2 Water Chemistry and Water Types

Based on the laboratory analysis results, the calculated ionic balance error for the analyses data ranged between 0.5% to 23.5% with an average of 3.6%. The average ion balance error,

therefore, showed that the laboratory analysis was generally accepted as was within the acceptable range of below 5%. The major ions concentration in the analysis results were recorded in the following order; $HCO_{3^-} > Ca^{2+} > CO_{3^-} > Mg^{2+} > SO_{4^{2-}} > Cl^- > K^+ > Na^+$. These results showed that HCO_{3} , Ca^{2+} , CO_{3} and Mg^{2+} were the dominant species.

The piper plots and Schoeller Diagrams showed that the hydrogeochemical facies are calcium bicarbonate (Ca-HCO₃) as the main hydrogeochemical groundwater type for all the water samples analysed.

These concentration values correspond with the known geological characteristic of the area.

6.2.3 Hydrogeochemical Processes

Based on the correlation, cluster and principal component analysis done, a strong correlation between EC and the elements such Ca^{2+} , Mg^{2+} , Cl^- , $SO_4{}^2$ -, $HCO_3{}^-$ was recorded that may be a result of the contribution of the other measured elements towards the EC of the water. These ions in the water directly influence the EC of the samples. The correlation could also be an indication of a dissolution process that causes the elements to go into solution to increase the EC.

A particularly exciting correlation between HCO₃- with Ca²⁺ and Mg²⁺ was also recorded from the analysis. The correlation could be a further indication of the identified bicarbonate dissolution processes that influence the positive correlation among the elements in the system under study. The correlation between Ca²⁺ and Mg²⁺ was low likely because the two elements appear not to have an influence on each other during the dissolution process but maybe both influenced by other elements such as Cl⁻, HCO₃- and SO₄²⁻ - an indication of only calcite dissolution based on the governing equations. There is a likelihood that the Mg measured could not have been. As a result of the dissolution process but could be an accumulation within the system from outside sources.

Chloride also appeared to influence the processes based on the correlation analysis results. It is immediately not clear what the sources of the Cl- could have been because the silicate

weathering process does not produce Cl⁻ based on the governing equations. The Cl⁻ could, therefore, be from an external source in the system or even an accumulation. The correlation analysis showed that the Mg^{2+} , Ca^{2+} , HCO_{3^-} and $SO_{4^{2-}}$ are clearly from the same source which could be an indication of processes such as calcite, dolomite and silicate weathering.

6.2.4 Groundwater Quality

The hydrogeochemical assessment showed that the Kakontwe water is very hard water in terms with an average water hardness value of **187 mg/L of CaCO**₃. An average Langelier Saturation Index (LSI) of 0.065 was calculated signifying that the water is saturated with respect to calcium carbonate. Scale-forming and corrosion could, therefore, occur in water using industrial equipment. Treatment of the water to make it less scale forming before use for industrial purposes especially in boilers and heating equipment recommended.

The Soluble Sodium Percentage (SSP) range of between 1.5 to 31% was calculated with an average SSP value of 11%. The average SSP was, therefore, far below the 60% threshold. The maximum Kelly's Ratio value calculated was 0.27 an indication of very low levels of sodium ions in the Kakontwe aquifer water. The comparison of the Kakontwe EC and SAR analytical data on the US salinity diagram showed that study area water samples were classified Good/Excellent category.

The salinity assessment showed that the Kakontwe aquifers water had low salinity levels. The water may not cause salinity and related problems in the soils based on the assessment. The Wilcox plots showed a Low-Risk classification on the Sodium (Alkali) hazard scale while the values for the salinity hazard showed a Medium Risk. The Soluble Sodium Percentage (SSP) calculated showed an average SSP value of 11% - far below the 60% acceptable threshold. The maximum Kelly's Ratio value calculated was 0.27 an indication of very low levels of sodium ions in the Kakontwe aquifer water. The Kelly's ratio (>1) indicates an excess level of sodium in water which is unsuitable and <1 is suitable for irrigation uses.

6.3 RECOMMENDATIONS

Based on the study methodology and findings, the following are the recommendations:

- Sample collection should be done more frequently during the year to determine any variations in the hydrogeochemistry during the year;
- Laboratory analysis of some parameter such as Cu, Co, Fe etc. for drinking Water quality assessment to assess the suitability of the water for domestic use;
- Water Resources Management Authority (WARMA) should create a database of hydraulics and hydrogeochemistry data for comparisons during such studies; and,
- ❖ Further investigation to establish the exact source of the Cl- identified to have a significant influence in the hydrogeochemical process.

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