SPATIAL VARIATIONS OF GROUNDWATER QUALITY IN THE MACHILE RIVER BASIN, WESTERN ZAMBIA

By
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A thesis submitted to the University of Zambia in fulfillment of the Degree of Master of Science in Integrated Water Resource Management in the Department of Geology, School of Mines

THE UNIVERSITY OF ZAMBIA
2014
DECLARATION

This thesis was written and submitted in accordance with the rules and regulations governing the award of Master of Science in Integrated Water Resources Management of the University of Zambia. I further declare that the thesis has neither in part nor in whole been presented as substance, for the award of any degree, either to this or any other University. Where other peoples' work has been drawn upon, acknowledgment has been made.

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APPROVAL
This thesis of Mwandira Wilson is approved as a fulfillment of the degree of Masters of Science in Integrated Water Resources Management of the University of Zambia.

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ABSTRACT
The source of salinity and the geochemical processes that control the groundwater salinization in the Machile River Basin within the Sesheke and Kazungula districts of Western and Southern provinces of Zambia are not well understood and explained. The central part of the basin contains saline groundwater. Deep boreholes and shallow wells delivering saline water are usually abandoned by communities, who resort to open water holes dug out in dry river beds or surface water resources, where available. Therefore a comprehensive geochemical and isotopic study was carried out in the basin to explain the spatial distribution of fresh and saline groundwater quality and processes that influence variability in salinity. Understanding spatial variability and its controls is indispensable for sustainable groundwater management and protection in the basin.

Thirty four (34) representative groundwater samples were collected from different boreholes for water chemistry and isotope analyses. The samples were analysed for physicochemical properties, cations and anions. Chemical analyses indicate that the fringes of the basin contain a fresh Ca$^{2+}$ - Mg$^{2+}$ - HCO$_3^-$ type of groundwater and the central part of a saline Na$^+$ - SO$_4^{2-}$ - Cl$^-$ type of groundwater. This classification was confirmed by grouping similar water types together by using Hierarchical Cluster Analysis (HCA) and Principal Components Analysis (PCA) techniques. This spatial variability may be controlled by dissolution of bedded or disseminated evaporites concentrated by evapo-transpiration processes as revealed by stable isotope ($^2$H and $^{18}$O) signatures. The isotopic composition for Deuterium ($\delta^2$H) and oxygen 18 ($\delta^{18}$O) of the groundwater in the study area ranged from -53.44 to -23.54‰ and from -7.78 to -3.07‰, respectively. These isotope signatures reveal that the groundwater is recharged by precipitation in the fringes of the basin. Furthermore, the fresh groundwater is young in the recharge areas and regularly recharged whereas the saline water is old. The old water was embedded in the Pleistocene (126 ± 11 Ka) thus have saline water in parts of the basin. Exploitation of water for domestic and commercial use in the basin can be through drilling of boreholes of less than 10m to avoid intersecting the saline layers. In areas, where saline water is closer to the surface, rain water harvesting, ultra-filtration
processing to desalinate the saline groundwater or drilling of boreholes deeper into the basalt that could probably contain freshwater are recommended.
ACKNOWLEDGEMENT

This research was funded by the Danish International Development Agency (DANIDA) in collaboration with the University of Zambia-Integrated Water Resources Management Centre (UNZA IWRM Centre). This support is gratefully acknowledged. I also appreciate the Geological Survey of Denmark and Greenland (GUES) for providing the laboratory facilities for the analysis of the groundwater samples.

Furthermore, I would like to express my deepest appreciation to my supervisor Prof. I. A. Nyambe (Director, Directorate of Research and Graduate Studies) who never failed to guide me and give me important advice regarding my thesis. Dr. L. Flemming and Dr. R. Jakobsen abundantly helpful and offered invaluable assistance, support and guidance with the analysis of the data. Furthermore, Mr. Kawawa E. Banda who wanted the best out of me. I thank you. My special thanks go to Ms. Ingrid Mugamya Kawesha, for administrative and logistical assistance during the course of my research.

I wish to express my love and gratitude to my sweet wife Annie Katengula Mwandira, and our children, Tionenji, Chifumu and Mpangela and my beloved family; for their understanding and endless love, through the duration of my studies.
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CHAPTER 1: INTRODUCTION

1.1 Background

Salinisation of groundwater resources is one of the most prominent incidents of water quality degradation particularly in arid and semi-arid areas (Vengosh, 2005). Salinisation often leads to the loss of usable water resources (Lake & Bond, 2007). Salinisation processes and distribution have been the subject of research and investigation by several authors world over (Monjerezi, et al. 2010; Tweed, et al. 2011; Stoecker, et al. 2011; Jasonsmith, et al. 2012; Xie, et al. 2013). Studies by Bouchaou et al. (2008) and Chen, et al. (2013) reveal that adequate knowledge of spatial distribution of fresh and saline groundwater and understanding of the processes that determine spatial variations of salinity are necessary for locating and sustaining usable groundwater resources.

In south-western Zambia's Machile River Basin, high salinity in groundwater is a major water-quality degradation problem (Wibroe & Thomsen, 2010; Chongo, 2011) particularly in the central part of the basin where boreholes deliver saline groundwater with electrical conductivities as high as 23,300µS/cm, such boreholes are usually abandoned by communities who resort to open water holes dug out in dry river beds or even contaminated surface water, where available. However, previous research related to water management within the Machile River Basin have focused on mapping the spatial distribution of the saline groundwater using: (i) geophysics (Chongo, 2011; Wibroe & Thomsen, 2010); and (ii) remote sensing to study the evapotranspiration (Phiri, 2013). No study in the area has focused on understanding the spatial extent of the groundwater salinity using hydro-geochemistry as well as geochemical processes controlling saline groundwater in the Machile River Basin. To address this knowledge gap, this study assesses the extent and characterises hydrochemical and isotopic data in the groundwater to provide information on the processes controlling groundwater salinisation in the basin. An improved understanding of the processes occurring in the basin will provide a scientific basis for the development of sound strategies for the provision and sustainable use and management of the groundwater resource in the basin.
1.2 Statement of the problem
Saline groundwater has been reported in Zambia's Machile River Basin particularly in the central part of the basin (Wibroe & Thomsen, 2010; Chongo, 2011). The occurrence of saline groundwater is a limiting factor for water supply and interventions for the rural water supply in an area that is water stressed. No study in the area has focused on evaluating the spatial extent of salinity using geochemistry, and processes controlling saline groundwater and providing a scientific basis for developing strategies for the supply and sustainable use and management of groundwater in the Machile River Basin.

Thus it became necessary to study the geochemistry of groundwater in the Machile River Basin to assess the spatial variations of the fresh and saline groundwater and outline the geochemical processes controlling the groundwater salinization in the area in order to manage the water resource based on scientific information.

1.3 Objectives
The objectives of this study were to:

i. Assess the spatial extent of the groundwater salinity using hydro-geochemistry;

ii. Outline geochemical processes that control groundwater quality; and

iii. Provide recommendations on possible sustainable methods of exploiting the groundwater resource.

1.4 Research questions
The research answered the following questions:

i. What is the spatial distribution of the fresh and saline groundwater quality of the Machile River Basin?

ii. What geochemical processes operate in the Machile River Basin given a paleolake regime?

iii. What are the possible sustainable groundwater exploitation methods in the Machile River Basin?
1.5  **Rationale**

The study is important as it provides information on the groundwater geochemistry, and occurrence of fresh and saline groundwater quality, which may explain processes that determine salinity. This is essential for achieving and sustaining usable water supplies. Sustainable exploitation of available groundwater resources is impossible without adequate knowledge of the geochemical processes operating in the basin.

The specific areas of significance of the study include:

i. Contribution to the baseline geochemical information of the study area;

ii. Improving access to the fresh water and prevent economic losses;

iii. Improving rural livelihoods as people will not spend time looking for water but focus on economic activities like agriculture;

iv. Groundwater resource development and implementation because planners would be able to use this information in the main stream ministries such as Local Government and Mines, Energy and Water Development; and

v. Assist in accelerating progress towards achieving Millennium Development Goal Target 7C on accessing safe drinking water.

1.6  **Scope of work**

The activities that were undertaken during the research work included desktop study, equipment and data acquisition, field work and writing of the thesis.

1.6.1  **Desktop study**

The desktop study included the review of relevant literature, which included publications and reports of recent work conducted in and around the study area as well as reconnaissance survey of the study area. Site visits provided a visual record of ongoing land use, social economic activities and an understanding of the saline groundwater problem.

1.6.2  **Equipment and data Acquisition**

Equipment and materials for the successful execution of the research work were acquired such as water sampling equipment, maps, aerial photos, literature and software.
1.6.3 **Field work**

The field work was conducted in two phases. Phase I took place in August-September, 2012. The objective of the survey was to collect groundwater samples for geochemical and isotopic analysis. A total of thirty four (34) groundwater samples were collected whereas Phase II took place from January - February, 2013. The objective was to follow up and validate the geochemical samples collected in Phase I.
CHAPTER 2: DESCRIPTION OF STUDY AREA

This chapter provides a description the location, local climate, geology, topography population and socio-economic activities of the of the study area.

2.1 Location of study area

The study area is in the Machile River Basin (Figure 1) and is located between Latitudes 15°27’ - 17°28’S and Longitudes 23°06’E - 25°33’E. The basin slopes to the south at an average gradient of 0.6% (Chenov, 1978). This low gradient has resulted in extensive flooding during the wet season. The Zambezi River drains much of the western Zambia and flows through the Sesheke and Kazungula districts and forms Zambia’s southern border with Namibia. Several minor seasonal tributaries flow from the northern part of the basin, with Machile River Basin forming the border between Sesheke District in Western Province and Kazungula District in Southern Province.

![Figure 1: Location of the study area in Machile River Basin, south-western Zambia.](image-url)
2.2 Climate

The climate of the study area is typical of the regional climatic conditions for Zambia defined by three distinct seasons in a year - the cool and dry season (April to mid-August), the hot and dry season (mid-August to early November) and the wet season (November to April).

2.2.1 Rainfall

The study area is characterised by a mean rainfall of 818.28 mm and occurs predominantly between November and March (Figure 2). According to historical records at the Sesheke Meteorological Station (17°28’S and 24°18’E) the highest peak occurred in the 1976/77 rainy season amounting to 1087.5mm. The lowest rainfall amounted to 317.9mm and occurred in the 2004/2005 rainy season since the recording of weather data started in 1961.

![Figure 2: Typical annual precipitation for Sesheke District in millimetres (after Zambia Meteorological Department (ZMD), 2013).](image)

2.2.2 Temperature

The average annual mean temperature in Sesheke is 22.5°C. The lowest temperatures are observed at the start of the dry season between mid-May and the end of July, with
an average temperature of 2°C in July. Absolute minimums of 0°C can be observed in the bottom of valleys in certain years (Figure 3). The months of October and November are the hottest with a daily maximum average of 28°C and an absolute maximum of 38°C. The nightly minimum is mostly reached at around 6 a.m. and the daily maximum at about 2 p.m.

Figure 3: Annual average high and low temperature for Sesheke in degree Celsius (after ZMD, 2013).

2.2.3 Evaporation
The average annual pan evaporation in the study area is estimated to be 1,700mm (JICA/MEWD, 1995). Evaporation generally exceeds precipitation for most of the year with potential evaporation highest in the driest months. Limited recharge in the Machile is suggested to be 42.3mm corresponding to 5% of the annual precipitation. As the rain falls the pores in the upper part of the sand is lost by evaporation (Mazor, 1980). The highest levels of evaporation are experienced between August and October with October recording the highest average value of about 900mm.
2.3 Geology

This sub-section describes the geological history of South-western Zambia and its surrounding areas and the geology of the Machile River Basin.

2.3.1 Geological history of South-western Zambia and its surrounding areas

For over five decades many authors of Quaternary geology in Southern Africa have recognized the existence of an extensive lake in the Middle Kalahari and this has long been recognized as the major contributing factor to the geological formation that covered 90,000km² (Cooke & Verstappen, 1984; Burrough & Thomas, 2009; Moore et al., 2012; Podgorski et al., 2013). Several authors attest that tectonic events that have in prehistoric times changed the direction of the Zambezi River to its present course (Haddon, 2005; Moore & Lankin, 2001; O’Connor & Thomas, 1999). Prior to this change, it contributed to a large endorheic river system ending in the Kalahari Basin and sustained the existence of palaeo Lake Makgadikgadi, which covered large parts of Botswana and reached as far as the Kafue Flats in the middle of Zambia. The paleolake deposited a belt of alluvium and lacustrine sediments. It is assumed that evapo-concentration processes that formed the Makgadikgadi Salt pans in Botswana could have formed similar salt crusts in south-western Zambia (Chongo, 2011; Wibroe & Thomsen, 2010; Stadler et al. 2010; Bauer, et al., 2005; Arad, 1984) and left large isolated water bodies to dry out by evaporation. Furthermore, tectonic movements and down warping formed faults, which resulted in diverting the flow of the Zambezi River. The lake, which formerly incorporated both the Makgadikgadi pans area and the lower part at least of what is now the Okavango Delta, could have divided into two, the one to the north-west taking the whole flow of the Okavango River, and probably also at that time the Chobe. Subsequent to its creation, slowly filled in and an alluvial fan slowly built up and during drier climatic conditions, the inflow may have reduced and the channels partly filled in by sediments brought down by the periodic flash floods characteristic of semi-arid climates, or by drifting sands during very dry times so that re-establishment of flow was difficult in such flat terrain when a wetter climate set in (Cook, 1979). The remnant lakes left in the deeper hollows of Ngami and Mababe have subsequently shrunk and all but
disappeared. The Chobe inflow has probably been diverted into the Zambezi, as a result either of further faulting or possibly of normal processes of river capture.

The Paleolake Makgadikgadi, as evidenced by a topographic low, extends from the south eastern region of the study area through Namibia’s Caprivi Strip towards the Okavango Delta in the southwest (Shaw & Thomas, 1988; Moore & Lankin, 2001; Haddon, 2005; Wibroe & Thomsen, 2010). Evidence of the mega lake exists and has been reviewed in a paper by Moore et al., (2012). Late Quaternary (126-11.7 Ka) displacement along the major north-east-trending Linyanti and Chobe faults temporarily severed the link between the Upper and Middle Zambezi and diverted the flow of the Kafue and Zambezi into Lake Palaeo-Makgadikgadi, which last filled to the 945m amsl shoreline level (Figure 4).

Figure 4: Map showing the grey shading outline the possibly extent of the mega Lake Palaeo-Makgadikgadi in Southern Africa (Moore et al. 2012).
2.3.2 Geology of the Machile River Basin

The geology of the study area is shown in Figure 5 whereas an idealized geological column of western Zambia is shown in Figure 5 (Money, 1972).

Initial deposition of basal gravels occurred in the channels of the Cretaceous rivers with other unsorted gravel beds deposited at the base of scree slopes, along edges of valleys and fault bounded structures. The accumulation of gravels continued as the downward of the basin progressed with inter-bedding of the gravel layers with sand and finer sediments carried by the rivers. Thick clay beds accumulated in the lakes that formed as a result of back tilting of rivers with sands, deposited in braided streams, inter-fingerling with the clays and covering them in some areas as shallow lakes filled up with sediment (Haddon & McCarthy, 2005). According to Money (1972), western Zambia is located in the post-Cretaceous terrain underlain Kalahari.
Supergroup sediments, separated from the underlying Karoo Supergroup sediments by the Lueti Formation (Figure 6).

Figure 6: Idealized geological column of western Zambia (after Money, 1972).
2.3.3 Karoo Supergroup

The sub-sections (sub-section 2.3.1 and sub-section 2.3.1) on the geological description of the western Zambia is based on Money (1972). The Karoo Supergroup of the western Zambia is underlain by the Likupekupe Formation. The Likupekupe Formation is probably equivalent to the Sinakumbe Group (Nyambe, 1997) which consists of the Sikalamba and Zongwe Formations which outcrop in mid-Zambezi Valley Basin, southern Zambia (Nyambe, 1999a and b).

The Karoo Supergroup, at the base, is made of the Kado Sandstone Formation, which is probably equivalent to the Siankondobo Sandstone Formation interpreted as glacial deposits in the mid-Zambezi Valley (Nyambe, 1999a). This formation is overlain by the Luampa Coal Formation.

The Luampa Coal Formation consists of a Basal Conglomerate Member, which is over 3m thick, made of cobbles, pebbles and fragments of granite, gneiss, shale, siltstone and sandstone. It is massive, densely packed, well cemented and rests on the Kado Sandstone Formation and is overlain by the Lower Luampa Sandstone Member. The latter is medium- to coarse-grained with thin, interbedded units of fine-grained sandstone and mudstone. Major constituents of the sandstone are rock fragments quartz, feldspar and mud flakes set in a feldspathic matrix cemented by subordinate opaline quartz. Further, the Lower Luampa Sandstone Member is succeeded by the Coal Member and occupies a stratigraphic position comparable to that of the Maamba Sandstone Member within the Gwembe Coal Formation. The coal Member is in turn overlain by the Carbonaceous Mudstone Member and the pin stripped Member at the top. The Luampa Coal Formation is overlain by the Variegated Mudstone Formation.

The Variegated Mudstone Formation consists of the Coarsening Upward Member and Mudstone Member. The lower 40m of the formation is greyish with a series of coarsening upward cycles, whereas the upper 12m is a pin-striped, finely laminated, red-green, mottled mudstone containing branched lamelli. The formation shows coarsening upward cycles, convolute bedding and numerous contorted, recumbent
and ptygmatic sedimentary structures. Pellet conglomerate with siderite and pyrite nodules is common at the base of erosional scours. The Variegated Mudstone Formation is thought to represent a slope to shelf deposit in a gradually deepening basin. It is overlain by the Machile Sandstone Formation.

The Machile Sandstone Formation consists of 135m thick sequence of medium-grained, cross-bedded and reddish-orange sandstone. The sandstone is essentially quartzose, uniform and porous with occasional calcareous bands. Fossil wood float has been found in the vicinity of Machile River and is considered to be from this horizon. Machile Sandstone Formation beds are pale red and show ample evidence of current and organic activity. The formation is overlain by a 130m thick sequence of siltstones termed the Kahare Siltstone Formation.

The Kahare Siltstone Formation is divided into three members, comprising a Lower Oscillatory Member, 56m thick, Middle Bioturbated Member, 40m thick, and an Upper Muddy Clastic Member, 35m thick. Oscillatory Member consists of an interbedded sequence of fine sandstone, siltstone and mudstone forming a fining-upward unit. Vertical and horizontal burrows are well developed at the sandstone-mudstone interface. The lower part of the member is formed by sandy-streak facies, whereas the upper consists of thin graded units, which are cyclical, hence the term oscillatory. Kahare Siltstone Formation is succeeded by a very pebbly sandstone sequence, which has been named the Nkoya Grit Formation as it seems to be a widespread unit.

The Nkoya Grit Formation is 112m thick and has been sub-divided into lower, middle and upper units, designated as a Fining-Upward Member, 50m thick, a Cross-bedded Clastic Member 35m thick, and a Top Sandstone Member, 27m thick, respectively. Layers of large quartz pebbles mark the beginning of each cycle. The Cross-bedded Clastic Member and the Top Sandstone Member, though less widespread, are simply variations of the lower unit. The upper two members range in grade from coarse- to fine-grained and show well-developed cross-bedding. The
Nkoya Grit Formation is overlain by a red mudstone sequence called the Kato Mudstone.

The Kato Formation, which is well represented and sub-divided into lower, middle and upper members. Its lower unit, formed by the Nodular Mudstone Member, is 54m thick, and is widespread. It is a deep red, calcareous mudstone with large, elongate, calcareous nodules and contains thin beds of gypsum in the lower part. The Interbedded Clastic Member forming the middle unit and the Red Mudstone Member forming the upper beds are less well developed and represent slow accretion deposits. The Kato Mudstone Formation probably accumulated as a result of slow silting-up of ox-bow lakes and other depressions on an alluvial flood-plain. Changes in river courses, flooding and periodic desiccation, which characterise such environments could account for the different phenomena observed. The formation is then overlain by the Luena Sandstone Formation.

Luena Sandstone Formation is composed of uniformly grained sandstone with steeply dipping cross bedding and well-rounded grains underlying the Batoka Basalt Formation. The nature of the cross-bedding, the uniformity of the grain size, the moderate to good sorting and the presence of 'millet-seed'-shaped quartz grains, all point to an aeolian origin.

The Batoka Basalt Formation, which is in the south and south-west, is over 390m thick. The basalt ranges in colour from reddish-purple to dark greyish-green. The basalt is composed of pyroxene, olivine and plagioclase. The basalts are susceptibility magnetic and are presumably related to the content of magnetite and to the oxidized state of the opaque minerals. Most of the flows are amygdaloidal with infillings of agate, chalcedony, quartz, calcite and zeolites. Some are blocky and contain fragments resembling volcanic ejectamenta. The basalt is Jurassic in age. The age and character of the basalt suggest that it erupted from fissures with little explosive activity. Its origin may be related to the break-up of the Gondwana continent to close the Karoo Deposition. The formation is overlain by the Lueti Formation, which is not part of the Karoo Supergroup.
2.3.4 Lueti Formation
Lueti Formation which is made of finely bedded micaceous mudstones. The lower part of the sequence consists of medium-grained muddy sandstones with occasional coarser units. The sandstone is massive, cross-laminated and lacks a basal conglomerate. The colour of the mudstones changes with depth from red-purple in the upper part to grey and olive-grey towards the base. The mudstones contain ostracods, pollen, spores and occasional plant fragments. These fossil assemblages indicates that the age of the Lueti Formation is Late Jurassic to Early Cretaceous. The nature and character of the Lueti Formation suggests that it is a product of continental sedimentation, probably fluviatile and partly lacustrine in origin. However, the absence of suitable outcrops precludes a more precise environmental interpretation of these Cretaceous rocks.

2.3.5 Kalahari Supergroup
The post-Cretaceous rocks of western Zambia comprises of the continental sequence of the Kalahari Supergroup, which is subdivided into the Barotse and Zambezi formations. The sedimentation processes which began in the Late Tertiary times continued in Quaternary and Recent times. However, the age of the continental sediments of the Kalahari Supergroup can for the most part only be determined by inference rather than by fossil content.

a) Barotse Formation
The Barotse Formation, comprises of a series of sandstones and quartzites, which has been subdivided into Lower, Middle and Upper Barotse members. The Lower Barotse Member rests unconformably on rocks ranging from Precambrian to Cretaceous in age. Fine- to medium-grained sandstones ranging from pale olive to moderate yellow-green with isolated units of well cemented orthoquartzite characterise the greater part of the sequence. Ortho quartzites tend to overlie sandstone beds and generally have a gradational lower contact. The sand grains show moderate to good rounding and bimodal size distribution. The quartzites and sandstones are usually cemented by opaline silica and less commonly by chert, chalcedony, calcite and zeolitic minerals.
The Middle Barotse Member is characterised by ferruginous sandstones overlain by ferruginous quartzites. The lower unit consists of a series of feebly consolidated, greenish-yellow, ferruginous sandstone beds whereas the upper comprises well cemented rusty olive-brown iron-rich quartzites. In both units the beds are medium-grained with well-rounded sand grains and contain banded elongate iron concretions and small isolated pockets or pods of loose friable iron coated sand grains. As in the Lower Barotse Member, the quartzite horizon overlies the sandstone unit. Both lower and upper units show well developed steeply dipping cross-stratification, which is interpreted as aeolian in origin.

The Upper Barotse Member consists predominantly of fine- to medium-grained pink quartzites with occasional sandstones. The massive quartzites are cemented by opaline and chalcedonic silica and are feebly calcareous and exhibit welded bedding. Feebly calcareous pseudo-conglomeratic horizons characterise the upper part where silica seems to have replaced the calcareous cement. Wood and plant fragments, presumably representing fossil soil horizons, also occur towards the top. The genesis of the Barotse Formation beds is considered to be related to fluctuations in the water table and climate. In most cases, the sand was aeolian in origin as is evident in the Middle Barotse Member where sand dunes have been cemented by silica to give ferruginous sandstones and quartzites. Elsewhere, both aeolian and fluviatile features are evident. It is suggested that the high alkalinity of the inland arid region resulted in leaching out of silica which was subsequently precipitated as cement on reaching areas of flowing water where the pH would have been generally lower than 7 to give the orthoquartzite of the Barotse Formation.

**b) Zambezi Formation**

The Zambezi Formation, rests on the Barotse Formation and older rocks, consists primarily of loose sand called the Mongu Sand Member which thickens towards the west and south-west. This formation also includes more recent deposits such as the duricrusts, quartz, limestone, clay stones, certified podzol horizons, saline evaporites, river gravels, flood-plain sediments, sheet conglomerates and alluvium. The recent
rock deposits are incorporated within the Zambezi Formation for convenience even though much of the Mongu Sand Member, the major unit, is probably Mid-Tertiary to Early Quaternary in age.

The Mongu Sand Member is essentially fine-grained and is uniform both vertically and laterally. The quartzose sand contains small amounts of heavy minerals, and is moderately well sorted in upland areas and poorly sorted in valleys and depressions. Though primarily aeolian, it has, in places, been reworked by water to produce polygenetic or mixed facies. The duricrusts include ferricrete, calcrite and locally silcrete. Calcrite is generally found in basaltic and limestone-dolomite terrains, ferricrete in regions floored by sandstone and basic rocks, and silcrete over acidic rock types.

Nearly all the major rivers in the region flow in wide valleys underlain by alluvium and often show two to three well-developed terraces. These and some of the associated gravels and some evaporites are recent and are probably related to the present climatic regime. The nature of the Tertiary-Quaternary deposits suggests that the climate over this part of Zambia has been variable since Miocene-Pliocene times. Periods of heavy rainfall gave rise to fluvial deposits in wide valleys, whereas during semi-arid conditions duricrusts developed. During more arid periods loose sands were transported by wind to form a blanket over much of the region. Although many of the present features of the landscape point to an arid climate in the recent past, geomorphological characteristics such as rapids, retreating waterfalls, wide valleys with misfit streams, evidence of river capture, nick points, river terraces and abrupt changes in river courses indicate fluctuations in rainfall and minor tectonic adjustments in the recent geological past.

2.4 Topography

Western Zambia has a vast, sand covered semi-arid plain which slopes gently from an altitude approximately 1200m amsl in the north-north-west to 900m in the south-south-east. The flat plains in western Zambia have an average altitude 1000m amsl (Chenov, 1978). The second order land forms and young features seen in the river
systems and terraces of the region are thought to be due to post Tertiary cycles of erosion and deposition, most of which were probably initiated by upwarping (Moore & Lankin, 2001). All major streams in the area are tributaries of the Zambezi River.

2.5 Population
The population of Kazungula District in 2010 was 98,292 of which 49% were male and 51% were female (CSO, 2010). The average annual growth rate for the district between 2000 and 2010 was 3.7 with a total number of about 20,417 households (CSO, 2010). On the other hand, the population for Seshkeke District was 94,612 in 2010 of which 49% were male and 51% were female (CSO, 2010). The average annual growth rate between 2000 and 2010 for Seshkeke District was 1.9 percent with a total number of about 21,210 households (CSO, 2010).

2.6 Socio-economic challenges of groundwater in Machile River Basin
Farming and tourism are the most important economic activities as the district has good wildlife habitat and is well-endowed with other natural resources. The newly created Simalaha Conservancy Project in Kazungula District is rich in birds life and attracts a lot of tourists from world over. Kazungula District is in Zambia's agro-ecological Zone 1, which has the harshest climatic conditions. Rainfall in this zone averages less than 800mm per annum and a short crop growing season of 80-120 days and carries a medium to high risk of drought. Maize, groundnuts, cotton, sweet potatoes and some drought resistant crops such as chili, sorghum and millet are grown in this area. Cattle and goat rearing are other social economic activities (Mwakikagile, 2010)

The major socio economic activities for most of the people in Seshkeke District is subsistence farming and maize and some drought resistant crops such as sorghum and millet are grown. Cattle and goat rearing, lumbering and fishing are among other social economic activities practiced. Therefore local communities in the two districts depend on pastoral farming and require water for their cattle and goats. New lodges and other tourist facilities have also increased the number of tourists passing through Seshkeke on their way to the Victoria Falls, to the Sioma Ngwezi National Park 50km
west of the town, or to the upper Zambezi and the Barotse Floodplain. Improved road access and construction has transformed the town and surrounding areas into an economically active area critical to international trade with a one-stop border point at Katima Mulilo (Mwakikagile, 2010).

2.6.1 Drinking water for humans and livestock
Groundwater with salinity of more than 1600 µS/cm become unacceptable for drinking because of its flat and insipid taste (WHO, 2006). Communities in the study area walk long distances in search of water for domestic and livestock use due to the unpalatability of groundwater (Figure 7). Furthermore, watering of livestock with high salt content may cause physiological upset or even death (Ayers and Westcot, 1985).

Figure 7: Photo showing use of ox-drawn carts to collect water from dry river bed in Kasaya area during the dry season for human use and livestock watering, Kazungula District, Southern Province, Zambia.

2.6.2 Agricultural activities
The combined effects of soil and water salinisation may reduce crop yields, limit the choice of crops to be grown in a certain area and may make land semi-permanently unsuitable for further agricultural purposes. Salinity affects the soil properties by
causing fine particles to flocculate into aggregates. This is not beneficial in terms of soil aeration, root penetration and root growth (Ayers and Westcot, 1985). Furthermore, soil dispersion causes clay particles to plug soil pores, resulting often in reduced soil permeability and consequently reduced infiltration capacity (Rhoades et al., 1992).

2.6.3 Infrastructural damage

Groundwater salinity reduces the life of domestic, agricultural and industrial equipment and increases maintenance costs. Salinity may cause corrosion of metals and concrete and scaling, due to the precipitation of dissolved salt when materials are in contact with highly salinised groundwater, may also be a serious problem. The cost of repair and maintenance is high as examplified by borehole pipes rusting in the study area (Figure 8). Salinity may necessitate the use of more soap and detergents.

![Figure 8: Photo showing Corrosion of installed production borehole pipes due to saline groundwater, Adonsi Basic School, Sesheke District, Western Province, Zambia.](image)

On a larger scale, groundwater salinisation in Machile River Basin is causing significant societal economic costs which result in various kinds of very costly
interrelated socio-economic problems like loss of livelihood, migration and food insecurity (Nyambe, Personal Communication).
CHAPTER 3: LITERATURE REVIEW

This chapter deals with literature on water resource salinisation phenomena globally, Southern Africa and in south-western Zambia.

3.1 Global salinisation concern

Salinity is a measure of the amount of dissolved particles and ions in water. There are several different ways to measure salinity; the two most frequently used analyses are described below:

i. Total Dissolved Solids (TDS): TDS is a measure of all dissolved substances in water, including organic and suspended particles that can pass through a very small filter. TDS is measured in a laboratory and reported as mg/L.

ii. Electrical Conductivity (EC): The ability of an electric current to pass through water is proportional to the amount of dissolved salts in the water - specifically, the amount of charged (ionic) particles. EC is a measure of the concentration of dissolved ions in water, and is reported in μmhos/cm (micromhos per centimeter) or μS/cm (microsiemens per centimeter). A μmho is equivalent to a μS. EC can be measured in a laboratory or with an inexpensive field meter. Also called specific conductance or specific conductivity.

“Salinity” can include hundreds of different ions; however, relatively few make up most of the dissolved material in water: chloride (Cl\(^{-}\)), sodium (Na\(^{+}\)), nitrate (NO\(_{3}^{-}\)), calcium (Ca\(^{+2}\)), magnesium (Mg\(^{+2}\)), bicarbonate (HCO\(_{3}^{-}\)), and sulphate (SO\(_{4}^{2-}\)). The concentrations of boron (B), bromide (Br), iron (Fe), and other trace ions can be locally important.

The salinity problem is a global phenomenon more severe in water-scarce areas, such as arid and semi-arid zones because of the increasing demand for water resources. There are various notable causes of salinity globally: river salinisation (Weinthal, 2002; Cortecci et al. 2002); lake salinisation e.g. Lake Eyre, Australia; (Herczeg et al., 2001); groundwater seawater intrusion in many coastal aquifers around the world (Sukhija, 1996); salinisation of dry land environments largely occurring in the dry
land environments of Australia due to intensive clearing of native vegetation that occurred in the past century (Peck & Hatton, 2003); anthropogenic salinisation from industry, road de-icing salt, animal waste and sewage treatment (Vengosh and Pankratov, 1998); soil salinisation of irrigated land (Richter et al. 1993; Sparks, 1995); and wetlands becoming saline because of changing sea levels (Titus & Richman, 2000).

Salinisation has negative global impact and contributes to loss of biodiversity, taxonomic replacement by halo tolerant species, loss of fertile soil, collapse of agricultural and fishery industries, and severe health problems in Africa, China, and India (Williams, 2001). In Australia, salinisation of groundwater is estimated to be costing the government millions of dollars per year in lost agricultural profits (Weinthal, 2002).

In a paper by Vegosh (2005), it was noted that increase of the human population (8–12 billion) during the next century by the year 2050, will increase the demand for freshwater and cultivated land, and is likely to cause severe adverse environmental impacts such as salinisation of the over-exploited water resources and direct contamination by agricultural drainage water. Therefore, decision makers should ensure that adaptation or remedial measures towards salinisation of water resources are developed and managed in an equitable, efficient and integrated manner (GWP, 2009).

3.2 Southern Africa salinisation concern

Groundwater plays a critical role in the Southern African Development Community (SADC) region especially in arid and semi-arid areas, where it provides water supply for domestic purposes and is used for livestock, agriculture, mining and tourism. It is estimated that 70% of SADC population depends on groundwater (SADC, 2009). About one-third of the people in the SADC region live in drought-prone areas, where groundwater is the primary source of drinking water for the human population, livestock, and most other activities (Braune & Xu, 2008). Salinisation is notable in
the greater Kalahari regions of Botswana, Namibia, South Africa, Zambia and Zimbabwe due to aridity of the region.

3.2.1 Studies in the Kalahari Basin of the SADC Region
A study by Eckardt et al., (2008) on fluid and salt chemistry aimed at establishing a relationship between the chemistry of soil leachates, fresh stream water, salty lake water, surface salts and subsurface brines was conducted at Sua Pan, Botswana to improve an understanding of the hydrology of the area. Despite the fresh floodwater (Ca–HCO₃ type) entering the pan, the water evolved to a Na–Cl type brine (6,756-31,172 mg/L) with a salinity comparable to that of seawater. The study indicated that the deep-seated brine appeared to be homogenous and had little interaction with surface processes. Furthermore, it suggested that subsurface groundwater has been in place for an unknown length of time and been subject to modifications specific to the groundwater path and storage.

Another study by Bauer et al., (2005) examined the coupled flow and salinity transport in a case study of the Shashe River Valley in Botswana. The study was undertaken in the town of Maun, Botswana which is heavily dependent on groundwater from a freshwater aquifer located around an ephemeral stream. This aquifer was being depleted by the combined effect of transpiration and pumping. The study showed that the vegetative cover increases groundwater salinity by transpiration due to the fact that water is depleted from the aquifer, leaving behind dissolved solids.

3.3 Theoretical review on classification and origin of saline groundwater
Since the groundwater salinisation in Machile River Basin is of continental origin a review of the theory behind continental salinisation is presented in this section.

The chemical make-up of groundwater determines whether the water is either fresh or saline (Todd, 1980). Table 1 shows the classification of saline groundwater according to Total Dissolved Solids (TDS) and Electrical Conductivity (EC).
Table 1: Classification of saline groundwater after Carroll (1962).

<table>
<thead>
<tr>
<th>Classification</th>
<th>TDS, mg/L</th>
<th>EC µS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater</td>
<td>0-1,000</td>
<td>0-650</td>
</tr>
<tr>
<td>Brackish water</td>
<td>1,000-10,000</td>
<td>650-6,500</td>
</tr>
<tr>
<td>Saline water</td>
<td>10,000-100,000</td>
<td>6,500-65,000</td>
</tr>
<tr>
<td>Brine water</td>
<td>&gt; 100,000</td>
<td>&gt; 65,000</td>
</tr>
</tbody>
</table>

A wide variety of chemical reactions can take place between gases, solutes and solids in groundwater systems and these reactions are the sources of the anions and cations that exist in and cause salinisation of groundwater:

i. Dissolution and precipitation;
ii. Acid-base reactions;
iii. Complexation;
iv. Cation Exchange Reactions; and
v. Oxidation and reduction reactions.

A detailed discussion of different reactions are described by many texts which cover the subject in detail including Appelo and Postma (2005), Fitts (2002), Domenico & Schwartz (1997) and Todd (1980). Many of these reactions will further be referred to when assessing process that influence the occurrence of saline and fresh groundwater quality in Machile River Basin.

Fresh groundwater is found in those parts of the subsurface that are most actively involved in the water cycle. Consequently, fresh groundwater is more likely present in the shallower domains of the sequence of geological layers in which groundwater are stored. Based on this rationale, fresh groundwater is often comparatively young and tends to be actively recharged. In contrast, a large part of all saline groundwater on earth but certainly not all of it is present in a more or less stagnant condition at greater depths and may have been there for many thousands or even millions of years (IGRAC, 2009). Genetically, most saline groundwater bodies belong to one of the following categories:

i. Saline groundwater of marine origin;
ii. Saline groundwater of terrestrial origin (natural);

iii. Saline groundwater of terrestrial origin (anthropogenic); and

iv. Saline groundwater of mixed origin.

Since our interest in this case is on groundwater of terrestrial origin, it can be categorised as shown in Table 2.

Table 2: Groundwater of terrestrial origin-natural after IGRAC (2009)

<table>
<thead>
<tr>
<th>Class of origin</th>
<th>Genetic category or Salinisation mechanism</th>
<th>Typical environment at the time of origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrestrial</td>
<td>Produced by evaporation (concentration)</td>
<td>Shallow water-table zones in arid climates</td>
</tr>
<tr>
<td></td>
<td>Produced by dissolution of subsurface salts</td>
<td>Zones of salt tectonics or regional halite or other dissolvable formations</td>
</tr>
<tr>
<td></td>
<td>Produced by salt filtering membrane effects</td>
<td>At depth in thick sedimentary basins containing semi permeable layers</td>
</tr>
<tr>
<td></td>
<td>Emanated juvenile water and products of igneous activity</td>
<td>Regions of igneous activity</td>
</tr>
<tr>
<td></td>
<td>Mixture of evaporation and dissolution</td>
<td>Shallow water-table zones in arid climates and aquifers containing dissolvable formations</td>
</tr>
</tbody>
</table>

3.3.1 **Groundwater enriched in mineral content by evaporation at or near land surface**

This origin of saline groundwater is in category (ii) and is linked to shallow water table conditions and develops when climatic conditions favour evapotranspiration. It is assumed that the high lake salinity spreads in the underlying groundwater to some depths and to some distances. Often a salt crust is formed at the lake bottom during dry periods (IGRAC, 2009).
3.3.2 **Groundwater enriched in mineral content by dissolution of naturally occurring soluble minerals underground**

This origin of saline groundwater is in category (ii) where groundwater become saline by dissolving salts from evaporate formations (halites) or carbonates layers when flowing through or along such subsurface bodies. By flowing through aquifers, groundwater may become brackish to saline in downward direction, if time and other conditions are favourable for the dissolution of salts from the aquifer matrix.

3.3.3 **Saline groundwater produced as a result of membrane effects**

Layers of clay or shale may be compacted that much in deep sedimentary basins that they become effective salt filtering membranes (category (ii)). Groundwater is percolating through such layers but the dissolved larger ions are not permitted to pass, which leads to building up high groundwater salinity near the inflow side of the membrane.

3.3.4 **Saline groundwater of mixed origin**

The process occurs when highly mineralized water is produced as a side product of igneous activity However, it should be noted that these are generic origins of saline groundwater but in nature different types of saline water as described above or to water resulting from one or more of these categories can result in saline groundwater of mixed origin (category (iv)).

3.4 **South-western Zambia salinisation concern**

In south-western Zambia, groundwater plays a critical role in meeting the rural water supply demand for domestic purposes, livestock watering and tourism. Being a rural community, villages are sparsely distributed and therefore installation of boreholes is the optimal mode of sourcing water for the people. However, a large salty aquifer of unknown origin underlies the limited freshwater in the central part of the basin. Drilled boreholes yield high saline water leading to low quality drinking water (Wibroe and Thomsen, 2010). These boreholes are abandoned because of high TDS. The World Health Organization states that a TDS concentration below 1000mg/L is usually acceptable for drinking water (WHO, 2006), but in the south-western Zambia
the concentrations in the boreholes measured as electrical conductivity, are as high as 23,300µS/cm thus highly exceeding the guidelines for safe drinking water.

To manage the groundwater salinity problem, three pieces of work related to water management have been carried out in the recent past in the Machile River Basin and are presented below.

3.4.1 A geophysical study of the spatial distribution of saline groundwater in the Kalahari sand aquifer in the Sesheke area, Western Province, Zambia, 2011

The main objectives of the study by Chongo (2011) were to map the distribution of electrical resistivity on a regional scale, determine the distribution of electrical resistivities across an ephemeral river valley and identify the spatial distribution of saline, brackish and fresh groundwater based on the distribution of electrical resistivities (Chongo, 2011; Chongo et al., 2011).

Time Domain Electromagnetic Sounding (TEM) and Continuous Vertical Electrical Sounding (CVES) are two geophysical exploration techniques that were applied in the Sesheke area. The TEM method was applied on a regional scale (over an area of about 14 000km²) whereas CVES in combination with TEM was applied on a local scale along a 1.2 km stretch across the Machile River at Mangumwi in the Sesheke District. These techniques proved effective in identifying areas with groundwater salinity levels that are not suitable for human consumption within the Kalahari Supergroup formations of Sesheke.

3.4.2 Geophysical monitoring and modeling of salt and freshwater dynamics in the upper Zambezi, 2010

DANIDA, Danish Technical University (DTU) and in collaboration with the UNZA IWRM Centre implemented a project titled “Geophysical Monitoring and Modeling of Salt and Freshwater Dynamics in the Upper Zambezi” The field study was conducted during a 7 weeks period in September-October 2009 by Wibroe and Thomsen. The purpose of the study was to identify possible freshwater resources
stemming from infiltration of river water. The methods applied were geophysical resistivity investigations using both geoelectrics in the form of Continuous Vertical Electrical Soundings (CVES) and the Transient Electromagnetic Method (TEM). The obtained data was interpreted using 2D inversions in Res2Dinv and both single site and laterally constrained inversions of the TEM data with the em1dinv code was performed.

The saline aquifer was found to show resistivities of <10Ωm and corresponds with sandy clay sediments observed in lithological profiles for the area. A shallow freshwater lens reaching a depth of 10 - 20m was observed through hand augered boreholes showing concentrations ranging from 80-1345gm$^3$ and resistivities of 20-50Ωm observed with geophysics. The geological setting at the sites were interpreted as sand and clay sediments underlain by sandstone. The limited interaction between the river and aquifer was evaluated to be a result of a very high evapotranspiration and partly the clay crust overlaying the flood plains (Wibroe and Thomsen, 2010).


The study applied the Surface Energy Balance System (SEBS) model to determine Actual Evapotranspiration (AET) over the semi-arid Barotse Basin, south-western Zambia using SEBS. SEBS is a one-source physical model which estimates turbulent heat fluxes. The aim of the study was to estimate spatial-temporal variability of AET over the semi-arid Barotse Basin using the SEBS model. The model was run using Moderate-resolution Imaging Spectoradiometer (MODIS) satellite imagery on clear sky warm-wet, dry-cool and dry-hot days. Evaporative fluxes were determined over different land cover. Based on sunshine data and daily ET, monthly fluxes were generated. Model results were evaluated against Penman-Montieth potential ET (PET) and ET from the Global Circulation Model (GCM) of the European Centre for Medium Range Weather Forecast (ECMWF).
On cool-dry and hot-dry days, the SEBS estimates were 64.3 and 29.4% of Penman-Montieth potential respectively. On a monthly time scale comparison with ECMWF revealed cases of over and under estimation and was attributed to variable input data. Analysis of evaporative water use showed that water bodies and forests had the highest rates whereas croplands and grassland had the lowest with a high variation of up to 64.1 and 71.1% between warm-wet and hot-dry days respectively. The results showed that SEBS is useful for estimating AET and can help improve water resources management (Phiri, 2013).

3.5 Present study
This study focused on understanding the spatial extent of the fresh and saline groundwater using geochemistry and isotopes; outlining the geochemical processes controlling saline groundwater; and to provide recommendations on sustainable methods of groundwater exploitation in the Machile River Basin. Understanding the processes occurring in the basin is important in that it will provide a scientific basis for the development of sound strategies for the provision and sustainable use and management of the groundwater resource (Monjerezi et al., 2010). As outlined in the previous studies above, no study in the area has focused on understanding the geochemical processes controlling the water quality in the Machile River Basin. The previous research studies on groundwater quality mainly focused on mapping the spatial distribution of the saline groundwater using geophysics (Chongo, 2011; Wibroe & Thomsen, 2010); and remote sensing to study the evapotranspiration (Phiri, 2013). To address this gap, this study assessed the extent and characterised hydrochemical and isotopic data in the groundwater to provide information on the processes controlling groundwater salinisation in the basin. The geochemical processes governing water quality were determined through an integrated application of hierarchical cluster analysis (HCA) and principal components analysis (PCA).
CHAPTER 4: METHODOLOGY

This chapter provides a description of equipment used in the study; the sampling sites, field and laboratory methods and software used for data processing. In order to achieve objective 1 of this study, field parameters were measured (pH, EC, temperature and Dissolved Oxygen (DO) and alkalinity) and laboratory analysis (Na, K, Ca, Mg, Fe, Cl, SO₄, NO₃, δD, δO¹⁸ and ³H) were conducted to determine the composition of the groundwater chemistry in the Machile River Basin. Then statistical analyses (HCA and PCA) were employed to achieve objective 2 by grouping the samples into water types and then identify the processes controlling the geochemical processes of the water type in the basin. The details are described herein.

4.1 Sampling sites
Thirty four (34) boreholes were sampled which were located at schools and village centers in the study area. The location of sampling sites is shown in Figure 9. A handheld Trimble® 3D GPS was used to get the coordinates in Universal Transverse Mercator (UTM) of all the borehole locations.

4.2 Data collection
The sub-sections below discuss on-site field methods and laboratory methods that were used in this study.

4.2.1 Water table measurements
The total borehole depth and depth to the water table was measured before any sampling. Total borehole depth was measured using a weight attached to a tape measure. A metal tube was attached that could easily reach the bottom of the borehole. The metal tube is sealed at the end at which it is attached to the tape with a loop wire. The other end that touches the water is open. When the tube is lowered into the borehole and touches the water surface it makes a ringing sound and location of the water table is measured. These level measurements can provide information on
lateral and vertical head distribution and hydraulic gradients within individual aquifers and between aquifers in layered aquifer systems (Sundaram et al., 2009).

Figure 9: Sampling sites in the Machile River Basin, south-western Zambia.

4.2.2 Water sampling

To obtain a representative sample, the stagnant water from the borehole casing was purged (Figure 10). Three casing volumes of water were removed before sampling. Pumping of the borehole was continued until the conductivity and temperature of the discharge water are observed to stabilise. Only then was the obtained sample considered to be representative of groundwater residing in the aquifer surrounding the bore screen. The sample was collected using a multiphase one (MP1) pump.

Three samples were collected at every site for the analysis of cations, anions and isotopes. A 10mL sample for cations was collected and filtered through 0.45μm filter and put in an High-Density Polyethylene (HDPE) plastic bottle and acidified to pH < 2 with ultrapure nitric acid and stored in a cooler box before transportation to the
laboratory. Another 10mL sample for anions was collected and filtered through 0.45µm filter put in an HDPE plastic bottle stored in a Mobi cooler box. A further one liter sample was collected and stored in a mobile cooler box for isotopes. All the sampling bottles had screw caps for sealing to avoid leakage of samples.

Figure 10: Borehole purging during sampling so that a fresh aquifer sample was taken from the aquifer rather than groundwater sitting in the borehole which could have interacted with the surrounding environment, Mushukula Village, Seseke District, Western Province, Zambia.

4.2.3 pH, Electrical conductivity (EC), temperature and dissolved oxygen (DO)

pH, EC, temperature and DO cannot be reliably measured in the laboratory as their characteristics change over a very short time due to partial pressure differences and dissolved gases. They were therefore measured on-site.

A 3430 Wissenschaftlich Technische Werkstatten (WTW) multimeter was used to measure EC, DO, pH and temperature in the field using a flow cell (Figure 11). A flow cell was used to ensure the exclusion of atmospheric contamination and to improve measurement stability. Each parameter probe was connected to the multimeter. The flow cell provided an air tight environment so that EC, DO, pH and temperature were measured without contact with atmospheric conditions. The probes
for the multimeter were calibrated accurately before using them and regularly during use against known standards and according to standard operating procedures. Temperature and pH probe were calibrated with pH 4.00 and 7.00 buffer solutions whereas the EC probe was calibrated with sodium chloride standard solution.

Figure 11: Flow cell for measuring EC, DO, pH and temperature on-site to ensure the exclusion of atmospheric contamination and to improve measurement stability Lusinina School, Sesheke District, Western Province, Zambia

4.2.4 Alkalinity
To achieve objective 2 of assessing the geochemical processes, alkalinity (as HCO₃⁻), was measured in the field to determine the composition of bicarbonates in the groundwater. Field measured alkalinity provides a more accurate estimate of bicarbonate concentrations in groundwater than a laboratory measurement. This is because of bicarbonate loss (as carbon dioxide) and oxygen access which can lead to shifts in the measured alkalinity between the time a sample is collected and laboratory analysis is performed (Appelo and Postma, 2005). Alkalinity was determined by Gran titration method (Figure 12).
4.2.5 Laboratory methods
All the water samples collected were analysed at the Geological Survey of Denmark and Greenland (GEUS), Copenhagen, Denmark.

a) Determination of major cations and anions
Analysis for cations was performed using Atomic Absorption Spectrometry (AAS) by a Perkin Elmer (Analyst 400) using flame excitation whereas the analysis for anions was performed using a Metrohm Ion Chromatography (IC). Analytical methods, Atomic Absorption Spectrometry (AAS) and IC were chosen on the basis of sensitivity and interference. AAS method is simple, rapid and applicable to a large number of metals in saline groundwater whereas IC generally has less interference and suitable for the analysis of anions (Mannio et al., 1995).

b) Determination of trace elements
Trace elements were analysed by Perkin Elmer Elan 6100DRC ICP-MS instrument. Perkin Elmers Total quant method was used for analysis and calculating concentration in the samples. Inductively Coupled Plasma Mass Spectrometry (ICP-
a) **MS** is a type of mass spectrometry, which is capable of detecting metals and several non-metals at concentrations as low as one part per trillion and widely used in environmental analysis (Mannio et al. 1995). This is achieved by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify the ions. ICP-MS has the capability to scan for all elements simultaneously. This method was used because it allows rapid sample processing and most preferred for the analysis of trace elements (Houk, 1986; Douglas & French, 1986).

b) **Determination of δD and δ¹⁸O and ³H**

Stable isotopes for δD and δ¹⁸O values were determined using a Picarro Laser Spectrometer relative to the Vienna Standard Mean Ocean Water (VSMOW) and were reported in conventional δ(‰) notation. The radioactive isotope ³H compositions were measured by liquid scintillation counting apparatus, Quantulus-1220.

c) **Data analysis**

The following software (Table 3) were used in this study and their respective use described.

Table 3: Data analysis software used in this study

<table>
<thead>
<tr>
<th>SOFTWARE NAME</th>
<th>DESCRIPTION AND USE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ArcGIS 9.3</td>
<td>Was used to analyse digital information of the sample sites. All maps in this thesis were generated by ArcGIS 9.3</td>
</tr>
<tr>
<td>MATLAB R2009a</td>
<td>Was used to construct a Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA) as described in sub-section 5.3.1 and 5.3.2 respectively.</td>
</tr>
<tr>
<td>PHREEQC 3.0.0-7430</td>
<td>Was used to calculate saturation indexes and electrical charge balance for water solutions according to the analytical data.</td>
</tr>
</tbody>
</table>
4.4 Statistical analysis

To better identify the processes controlling the geochemical evolution and distribution of groundwater in the study area, multivariate statistical analysis methods of Hierarchical Cluster Analysis (HCA) and Principal Component Analyses (PCA) were employed. HCA and PCA aid in establishing general relations between water quality samples and variables in a basin to easily describe the regional distribution of groundwater quality.

4.4.1 Hierarchical cluster analysis (HCA) and Principal component analysis (PCA)

Hierarchical cluster analysis (HCA) is an exploratory tool designed to reveal natural groupings (or clusters) within a data set that would otherwise not be apparent. Agglomerative or bottom up approach was used where each observation starts in its own cluster and pairs of clusters are merged as one move up the hierarchy. The results of hierarchical clustering are normally presented in a dendrogram (Cloutier, et al., 2008).

The HCA were performed for a set of 34 samples and 11 variables. The number of clusters was chosen based on the minimum number of clusters that explain most of the variation in geochemical properties of the water samples. Samples with similar spatial characteristics and relationships are clustered together at low linkage distances, whilst dissimilar samples are linked at higher linkage distances. The method was used to provide an independent approach to understanding the salinity in the Machile River Basin. A Matlab script by Milano Chemometrics was used to find the natural classes among the samples and variables (www.disat.unimib.it/chm).

HCA was chosen over other clustering methods such as K-means clustering methods because:

i. It is often difficult to know how many clusters you are likely to have and therefore the analysis may have to be repeated several times; and
ii. It can be very sensitive to the choice of initial cluster centers (Davis, 1986).
The PCA, on the other hand, is a data transformation technique that attempts to reveal a simple underlying structure that is assumed to exist within a multivariate dataset (Cloutier, et al., 2008). It was therefore used to determine the principal parameters (cations and anions) contributing to a type of groundwater found in a cluster.

4.4.2 Euclidean distance measure and Wards method
For this study the Euclidean Distance was chosen as the distance measure whereas the Ward’s Method was chosen as a linkage rule for the hierarchical agglomerative method for clustering of samples. In Euclidean Distance, larger similarity are first grouped and then the next group of samples are joined and the steps are repeated until all samples are grounded. To form clusters, Ward’s Method was used where at each step the link of clusters with minimum variance between clusters distance are merged first. Ward’s Method was chosen because it uses an analysis of variance approach to evaluate the distances between clusters as well as it minimizes the total within cluster variance. Ward’s clustering procedure was used in this study where the squared Euclidean Distance was used as distance measure, which are the most commonly adopted measures in HCA studies (Sharma, 1996; Fovell & Fovell, 1993; Davis, 1986).

4.4.3 Quality assurance of chemical analysis
The electrical balance (EB) was used to test and ensure the reliability of hydrogeochemical results. The accuracy of the laboratory analysis was determined from the EB since the sum of positive and negative charges in the water should be equal. EB were calculated and examined for each groundwater sample as a quality-assurance check of the chemical analyses in PHREEQC (in meq/L) using equation 1. The sum of major cations (Na, K, Mg and Ca) in meq/L should equal the sum of major anions (Cl, HCO$_3^-$, SO$_4^{2-}$, and NO$_3^-$) in meq/L. In this study Fe was added to the sum of cations because it had significant amounts in some water samples. An analysis of groundwater with EB < 5% are generally regarded as acceptable but in very dilute and in saline waters up to 10% is acceptable (Appelo and Postma, 2005).
4.5 Accuracy of chemical analysis

The water samples had EB ranging from -89 to 31.4% (Appendix 1) and were calculated using PHREEQC. The deviation of the EB from the acceptable percentage of < 5% for some samples could be dilution error and instruments as well as other organic ions not considered in the balance calculation (Hounslow, 1995). Therefore, all the samples were accepted and considered for data analysis with some error.
CHAPTER 5: RESULTS AND DISCUSSION

This Chapter describes and discusses the results of this study in order to address the objectives and answer the research questions. Geochemical results of the thirty four (34) groundwater samples from Machile River Basin are listed in Table 4. The results in table are presented according to the groundwater cluster according to HCA and PCA. Physicochemical (temperature, DO, pH, alkalinity, and EC), major ions (Na\(^+\), K\(^+\), Ca\(^{+2}\), Mg\(^{+2}\), Fe\(^{+2}\), Cl\(^-\), SO\(_4^{+2}\), and NO\(_3^{-}\)) and the calculated saturation indices (calcite (CaCO\(_3\)), dolomite (CaMg(CO\(_3\))\(_2\)) and gypsum (CaSO\(_4\)·2H\(_2\)O).) are tabulated for each sampling site. The results are discussed below.

5.1 Field measurements
Temperature of groundwater ranged from 12.8 to 28.2°C with an average of 23.7°C, reflecting mean annual temperature of the area. The pH values ranged from 5.3 to 8.3. Dissolved oxygen was relatively low ranging from 1.8 to 8.7 mg/l in the groundwater with an average of 5.3mg/l.

The EC for the groundwater in Machile River Basin ranged from 12.8 to 23,300 µs/cm. Figure 13 shows the spatial distribution of the groundwater EC and hydraulic head contours values in the study area. The N-S line was used to plot the increasing trend of total cations and anion from the upper to lower regions of the Machile River Basin. The hydraulic gradient shows that the groundwater is flowing towards the centre of the basin and is controlled by topographical changes whereas EC increases towards the centre of the basin. The water table depth varied from 2.7 to 43.2m below surface following the topographic elevations of the study area with shallow water table depths in the middle of the basin and deep water table depths in the basalts around the basin.
Table 4: Geochemical results categorised according to their groundwater clusters in the Machile River Basin, Kazungula and Seshete districts, south-western Zambia. Cal.= Calcite; Gyp.= Gypsum; Dol.=Dolomite; DO=Dissolved Oxygen; Alk.=Alkalinity; and EC =Electrical Conductivity.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Physicochemical parameters</th>
<th>Major ions (in mg/l)</th>
<th>Saturation index</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Temp (°C)</td>
<td>DO</td>
<td>pH</td>
</tr>
<tr>
<td>Machile Basic Sch</td>
<td>24.4</td>
<td>1.7</td>
<td>7.4</td>
</tr>
<tr>
<td>Nyawa Village</td>
<td>23.1</td>
<td>5.9</td>
<td>6.8</td>
</tr>
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<td>Sichifulo School</td>
<td>27.6</td>
<td>4.3</td>
<td>6.9</td>
</tr>
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<td>23.3</td>
<td>6</td>
<td>7.1</td>
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<td>6.7</td>
<td>7.2</td>
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<td>Malimba Village</td>
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<td>6.8</td>
<td>7.3</td>
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<td>Katombora Village</td>
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<td>4.8</td>
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<td>7.2</td>
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<td>6.5</td>
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<td>Moomba Primary</td>
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<td>5.3</td>
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<td>6.4</td>
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<td>7.5</td>
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<td>6.7</td>
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<td>7.4</td>
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<tr>
<td>Salumbwe Village</td>
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<td>5.7</td>
<td>6.8</td>
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</table>

41
<table>
<thead>
<tr>
<th>Location</th>
<th>Temp (°C)</th>
<th>DO</th>
<th>pH</th>
<th>Alk</th>
<th>EC (µS/cm)</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Cl</th>
<th>SO₄</th>
<th>NO₃</th>
<th>Cal.</th>
<th>Gyp.</th>
<th>Dol.</th>
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<td>6.9</td>
<td>4.4</td>
<td>105</td>
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<td>0.4</td>
<td>3</td>
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<td>-2.8</td>
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<td>27</td>
<td>4.6</td>
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<td>117.8</td>
<td>13.7</td>
<td>1.5</td>
<td>9.2</td>
<td>2.3</td>
<td>0.7</td>
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<td>7.</td>
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<td>1130</td>
<td>71.1</td>
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<td>Situlu Health Post</td>
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<td>7.6</td>
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<td>1017</td>
<td>256</td>
<td>3</td>
<td>1.9</td>
<td>0.3</td>
<td>4.4</td>
<td>42.1</td>
<td>49.1</td>
<td>0</td>
<td>-1.1</td>
<td>-3.4</td>
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<tr>
<td>Lutaba Basic Sch</td>
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<td>6.6</td>
<td>7.3</td>
<td>198.1</td>
<td>519</td>
<td>16.4</td>
<td>7.1</td>
<td>69.9</td>
<td>18.6</td>
<td>0</td>
<td>3.9</td>
<td>3.2</td>
<td>0</td>
<td>-0.1</td>
<td>-3.1</td>
<td></td>
</tr>
</tbody>
</table>
| GROUNDWATER CLUSTER 3
| Location            | Temp (°C) | DO | pH  | Alk     | EC (µS/cm) | Na  | K  | Ca  | Mg  | Fe  | Cl  | SO₄ | NO₃ | Cal. | Gyp. | Dol. |
| Kasaya Basic Sch    | 26.4      | 2.3| 6.8 | 440    | 23300      | 5300| 16.5| 770 | 266 | 0.5 | 5900| 5560| 0   | 0.2  | 0.1  | 0.3  |
| Simungoma Basic     | 28.2      | 6  | 7.5 | 317.1  | 7210       | 1550| 9.7 | 164 | 46.8| 0.6 | 1100| 1970| 88.2| 0.4  | -0.6 | 0.5  |
| Katongo Basic Sch   | 25.5      | 6.1| 7.9 | 135.3  | 1060       | 200 | 2.7 | 22  | 4.6 | 0.1 | 168 | 99  | 0   | -0.1 | -2.1 | -0.6 |
| Makanga Village     | 22.6      | 6.1| 6.9 | 225.4  | 2540       | 564 | 6  | 12.4| 2.6 | 0   | 366 | 458 | 0   | -1.4 | -1.9 | -3.1 |
| Adonsi Basic Sch    | 28.2      | 4.2| 8.3 | 255.6  | 4710       | 1070| 5.5 | 15.4| 6.5 | 0.3 | 740 | 1097| 0   | 0.1  | -1.6 | 0.2  |
| Katemwa Village     | 27.8      | 5  | 7.1 | 187    | 2200       | 365 | 13.7| 125 | 12.5| 2.9 | 360 | 260 | 22.2| -0.2 | -1.2 | -1   |
Figure 13: Spatial distribution of EC (µS/cm) and hydraulic heads (mamsl). N-S line was used to plot the increasing trend of total cations and anion from the upper to lower regions of the Machile River Basin, Kazungula and Sesheke districts, south-western Zambia.

### 5.2 Spatial variations of saline and fresh groundwater in the Machile River Basin

The concentration of major cations decreased in the order Na > Ca > Mg > Fe > K and that of anions in the order Cl > HCO₃ > SO₄ > NO₃. Generally, the concentration of all the cations and anions (mg/L) in the groundwater increase significantly from the upper to lower regions of the Machile River Basin (Figure 13) with the following ranges: Na, 0.5 to 5279.15; K, 0.4 to 16.5; Ca,0.5 to 769.5; Mg, 0.1 to 265.5; Fe, 0.0 to 20.5; F,0 to 3.2; Cl, 0.4 to 5900; Br, 0 to 17.1; NO₃, 0 to 125.7; PO₄, 0 to 0.2 and HCO₃,10.3 to 441.9.

The gradual increase in EC and concentration of major ions from the basin margins to the middle is better illustrated in a Piper Diagram (Figure 14). The piper diagram differentiates two types of geochemical evolution of groundwaters with mixing. The transformation indicated by the green arrow from magnesium-calcium and bicarbonate freshwater to saline calcium-sodium sulphate
and chloride domination happening in the saline groundwater areas in Kazungula and Sesheke districts. The fresh groundwaters, with EC values lower than 1,000 µS/cm, comprises water sampled from the fringes of the basin characterised by a fresh groundwater Ca-Mg-HCO₃⁻ water type with low total cations and anions in the northern part of the study area (Figure 15). The saline groundwaters, located essentially in low topography area, exhibit EC values greater than 1,000 µS/cm. High salinity water, characterised by Na-SO₄-Cl water type, shows high total cations and anions in the southern part of the basin (Figure 15). Mwandi Mission Village was the only place which had freshwater within the saline areas with EC of 117.8 µS/cm (Figure 13 above). This can possibly be explained by the influence of the Zambezi River through its water percolating into the ground during the dry season resulting in freshening the saline groundwater near its banks leading to the freshwater.

Figure 14: Piper Diagram showing distinct groundwater types in the Machile River Basin (fresh Ca-Mg-HCO₃⁻ water type and saline Na-SO₄-Cl type). Note the transformation indicated by the green arrow from magnesium-calcium and bicarbonate freshwater to saline calcium-sodium sulphate and chloride domination happening in the saline groundwater areas in Kazungula and Sesheke districts, south-western Zambia.
Figure 15: Increasing trend of total cations and anions from North to South of the Machile River Basin, Kazungula and Sesheke districts, south-western Zambia.
The results shows that high saline Na-SO$_4$-Cl groundwater has Ca/SO$_4$ ratio close to unity, which suggests dissolution of gypsum thus the increase in SO$_4$ content. The plot of saturation index (SI$_{Gypsum}$) vs Ca + SO$_4$(meq/L) exhibits a proportional shape (Figure 16), further confirming that both calcium and sulphate are derived from the dissolution of gypsum (CaSO$_4$.2H$_2$O). The saline areas are in equilibrium with gypsum hence a source of SO$_4^{2-}$ in the saline areas. The green line in Figure 16 separates the freshwater areas from the saline groundwater areas. The red line’s curving shape shows that saline water trend deviates significantly from the freshwater values indicating that saline water are close to super-saturation with respect to gypsum that leads to precipitation. The other samples in the freshwater areas are sub-saturated with respect to gypsum in the freshwater areas in Cluster 1 (Table 4).

Figure 16: Variation of saturation index of gypsum and Ca + SO$_4^{2-}$ showing that the saline areas are in equilibrium with gypsum hence a source of SO$_4^{2-}$ in the saline areas, Kazungula and Sesheke districts, south-western Zambia.

In contrast, in the Ca-Mg-HCO$_3^-$ water, the Ca/SO$_4$ ratio is higher than 1 (Figure 17), which suggests dissolution of silicate minerals. In Figure 17, the area above the red line indicates super-saturation with respect to gypsum and below is sub-saturation. The 1:1
ratio indicates an equilibrium between sodium and calcium. However, in this situation, over 96% of the results plot below the 1:1 suggesting that the freshwater is not controlled by gypsum \( (r^2 = 0.0345) \). Therefore a plot of 1:1 line indicates that weathering of silicates rather than gypsum dissolution is influencing the chemistry of water along the fringes of the Machile River Basin.

Figure 17: A plot of Ca vs. \( \text{SO}_4^{2-} \) in the fresh groundwater area show no correlation \( (R^2 = 0.0345) \) hence gypsum does not control the geochemistry of groundwater in the fringes of the Machile River Basin in Kazungula and Sesheke districts, south-western Zambia.

The scatter plot shows a high positive correlation between sodium and chloride in the saline areas \( (r^2 = 0.9806) \) (Figure 18). The high correlations \( (r=0.9806) \) due to high temperatures that lead to high evaporation rates and salt build up in Kazungula and Sesheke districts. In Figure 18, the area above the red line indicates super-saturation in halite and below is sub-saturation whereas the 1:1 ratio indicates an equilibrium between sodium and chloride. The results show a clustering of the saline water around the 1:1 suggesting that the saline water is possibly controlled by halite dissolution (NaCl). The relative dominance of sodium over other ions in the majority sample sites (Table 4) in the saline areas could also be attributed to high temperatures that lead to high temperatures.
evaporation rates in the discharge area (floodplain) that leaves behind a salt build up as inferred by the EC (further discussed in Section 5.3.5).

![Graph of Na vs Cl showing high correlation](image)

Figure 18: A plot of Na vs Cl show a high correlations ($R=0.9806$) due to high temperatures that lead to high evaporation rates and salt build up in Kazungula and Sesheke districts, south-western Zambia.

The composition of the Ca-Mg-HCO$_3$ fresh groundwater type reflect a recent process occurring in recharge areas (cf. Eugster and Jones, 1979). These changes in the concentration of the different ion solutes indicate variations in the chemistry due to such processes as rainfall, river discharge and weathering in the drainage catchment (Eugster and Jones, 1979). The EC for the Ca-Mg-HCO$_3$ fresh groundwater type ranges from 12.8 to 648 $\mu$S/cm, which could be controlled by silicate weathering. The results presented here show that the Ca-Mg-HCO$_3$ fresh groundwater type is mainly due to sediment interaction with the host aquifer rock.

These spatial distribution of the salinity in the basin could be linked to the wider mega lake Makgadikgadi in Botswana and to the history of the Zambezi River. As the paleolake expanded it transgressed across and submerged large areas and reached a height of 945m amsl. Notice from Figure 19 that the contour of lake elevation indications of an old shoreline have been observed that suggest that there was a large
lake in the past (Haddon, 2005). It is suggested that the 945m amsl shoreline was the last level in which the highest lake level occurred in the Holocene Period (8.6 ± 0.9 to 8.4 ±0.9 ka) of geological time before deposition of sediments. Figure 19 shows that Adonsi Basic School and Katemwa Village are outside the 945m amsl line but are shown as saline areas. The possible explanation is that the mega lake had several episodes of transgression (high water level) and regression (low water level). The 945m amsl line is the last level recorded (Moore et al., 2012), hence it is possible that at certain times, during the geological history, the paleolake could have extended as far as Adonsi and Katemwa areas and that during evaporation these areas were also covered with saline rich sediments.

Figure 19: Contours of lake elevation indicating of an old shoreline. The 945m amsl contour shoreline of the mega lake extends into the study area which suggest that there was a large lake in the past in the Machile River Basin, Kazungula and Sesheke districts, south-western Zambia.
Due to tectonic activity, the diversion of the Zambezi River inflow eastwards towards the Indian Ocean could have marked the highest point of the lake's extent and initiated an inland Machile River Basin. A similar study by Gamrod (2009) suggested that silt and clays found in Paleolake Mababe in Botswana are thought to be dominated by sediments eroded from watersheds in the Angolan highlands. Therefore, in a similar way, the silt and clays in the Machile River Basin could have been delivered by the Zambezi River (Shaw & Thomas, 1988). This provides evidence to the hypothesis that the saline groundwater in the basin could be controlled by the evaporate-bearing deposits of the dried out paleolake (Figure 20). The 945m amsl line shows that there was a high stand from which the lake eventually dried out at different periods of the Quaternary then followed by the fresh groundwater that could have kept flushing the stagnant saline groundwater to freshen it.

**Figure 20**: Old lacustrine sediments that corresponds to the increase in salinity in Machile corresponds with the paleolake deposited belt of alluvium and lacustrine sediments in the Machile River Basin, Kazungula and Sesheke districts, south-western Zambia (Modified after Moore et al., 2005).
5.3 Geochemical processes responsible for the spatial variations of the groundwater quality

To describe the geochemical processes responsible for the spatial variations of the groundwater quality multivariate statistical analysis (HCA and PCA) were used.

5.3.1 Hierarchical cluster analysis (HCA)

The results of hierarchical clustering are presented in a dendrogram (Figure 21). Three groundwater types were distinguished from the dendrogram. The groundwater in the studied area is spatially distributed and can be classified as recharge area groundwater (Cluster 1), transition area groundwater (Cluster 2) and discharge area groundwater (Cluster 3) (Figure 22).

Cluster 1 has the lowest concentrations of the major ions, therefore it is a fresh groundwater cluster with an average EC of 326.3 µS/cm (Table 4). This cluster consists of 66% of the samples collected in the basin. It occurs in the upper regions of the Machile River Basin which are the recharge areas.

Cluster 2 lies in the transition zone between the saline and fresh water lenses (Figure 22). Therefore, Cluster 2 is a medium saline groundwater type with an average EC of 1,032 µS/cm (Table 4). This cluster consists of 14% of the samples collected in the basin. The cluster occurs near or within the saline zone and could be due to mixing of fresh and saline groundwater. The water at these sites is possibly undergoing freshening due to the flushing of fresh groundwater from the diffuse recharge and the influence of the Zambezi River.

Cluster 3 has the highest concentrations of the major ions and high salinity (EC) ranging from 1,060 - 23,300 µS/cm (Table 4) and highest values of sodium and chloride. This cluster consisted of 20% of the samples collected in the basin. It occurs in the middle of the basin and coincides with the area where old lake sediments are presumed to be present (Figure 20).
Figure 21: Dendrogram showing groundwater samples divided in three clusters in Machile River Basin, Kazungula and Sesheke districts, south-western Zambia.

Figure 22: Spatial distribution of the 3 clustered groundwater types in Machile River Basin, Kazungula and Sesheke districts, south-western Zambia.
5.3.2 **Principal Component analysis (PCA)**

A principal component analysis correlation coefficient between the variable and the sample score was calculated for each quantitative variable using Matlab (Milano Chemometrics, 2009). Only principal component 1 (PC1) and principal component 2 (PC2) were retained as they explained 82.62% of the data set. PC1 and PC2 explained 66.19% and 16.43%, of the data set respectively.

The PCA shows variations in the samples and variables by differences in salinity (EC). According to the score plot, the high salinity cluster is spatially associated with low topographic areas along the Machile River (Cluster 3) (Makanga Village, Katemwa Village, Katongo Basic School, Adonsi Basic School, Simungoma Basic School, Kasaya Basic School) associated with the old paleolake sediment (Figure 20, above). Cluster 2, however, is in the matrix of the fresh groundwater (Figure 23) and shows that the groundwater in Cluster 2 is in the mixing zone. The samples in Cluster 2 are probably formed as a result of localized freshening from the Zambezi River and dambos whereas those in Cluster 1 are as a result of silicate weathering in the recharge areas. However, Cluster 2 is relatively higher in salinity indicative of possible mixing of the saline water by the freshwater as suggested in the Piper Diagram (Figure 15), by an arrow that shows a possible freshening in the saline areas.

The position of groundwater clusters and geochemical parameter in the four quadrants in Figures 23 and 24 can be interpreted as follows. The first and fourth quadrants contain groundwater samples and geochemical parameters which tend to be strong contributors to groundwater salinity and have high salinity, respectively. The other quadrants contain samples and geochemical parameters with weak contributors to salinity and less saline points or are outliers. Samples and parameters that are also clustered together on the biplot should have similar expression profiles and therefore were clustered together in the dendrogram (Figure 21).
Figure 23: The PCA shows Cluster 1 and Cluster 2 grouped together due to mixing between fringes of 1 and 2 whereas Cluster 3 groundwater samples are distinctively separated in Machile River Basin, Kazungula and Sesheke districts, south-western Zambia.

The parameter loading along the main principal component in the PCA indicate that high salinity is associated with high concentrations of mainly Na\(^+\), Cl\(^-\) and SO\(_4^{2-}\) as indicated by the green circle in Figure 24. These parameters contribute significantly to the salinity of the groundwater whereas the Ca, Mg and HCO\(_3^-\) contribute mainly to the freshwater system. This observation can be explained in the light of minerals involved in the process:

i. Silicate minerals (calcic plagioclase and amphiboles) in the basalts are contained and involved in the fringes hence contributing the Ca, Mg and HCO\(_3^-\) that is observed in the freshwater; and

ii. Na\(^+\), Cl\(^-\) and SO\(_4^{2-}\) minerals related to the halite and gypsum (Table 4).
5.3.3 Geochemical processes controlling Cluster 1 groundwater type

Cluster 1 groundwater can be classified as recharge waters along the fringes of the Machile Basin. Silicate weathering is a process that appears to be controlling the groundwater quality in the fringes of the Basin in the basalt area (cf. Appelo and Postma, 2005). Silicate rock outcrops such as basalts and granitic gneiss are visible in the fringes of the basin confirming that silicate weathering could be occurring (Figure 25). The basalts contain reactive silicate minerals (olivine, Ca-plagioclase and glass) that weather relatively fast. Silicate weathering occurs when carbon dioxide and water in the air react...
together to form carbonic acid. The weak carbonic acid formed reacts according to the following reaction (Kenneth and Christiansen, 2012):

\[
\begin{align*}
\text{H}_2\text{O (l)} + \text{CO}_2 (g) & \rightleftharpoons \text{H}_2\text{CO}_3 (aq) \quad \text{Equation 4.1} \\
\text{H}_2\text{O (l)} + \text{H}_2\text{CO}_3 (aq) & \rightleftharpoons \text{HCO}_3^- (aq) + \text{H}_3\text{O}^+ (aq) \quad \text{Equation 4.2}
\end{align*}
\]

The presence of \(\text{HCO}_3^-\) could be due to the carbonic acid (\(\text{H}_2\text{CO}_3\)) being formed from interaction of atmospheric \(\text{CO}_2\) with water or \(\text{CO}_2\) coming from respiring roots or the decomposition of organic matter in the soil (Kenneth and Christiansen, 2012). In natural environments, primary minerals are hydrolyzed and hence release ions into the water and form residual minerals such as clays. Such minerals which could be controlling the water types in the fringes include plagioclase such as calcic plagioclase (\(\text{CaAl}_2\text{Si}_2\text{O}_8\)) and amphiboles (\(\text{NaCa(Mg,Fe)}_5\text{AlSi}_7\text{O}_{22}(\text{OH})_2\)). Reactions releasing \(\text{Ca}^{2+}\) and \(\text{Mg}^{2+}\) are exemplified in these two reactions (Appelo and Postma, 2005):

Figure 25: Photo of outcrops of weathered granitic gneiss in the fringes of the Machile River Basin, Kazungula and Sesheke districts, south-western Zambia.
CaAl₂Si₂O₈ + 2H⁺ + H₂O ⇌ Clay + Ca²⁺  
Equation 4.3

NaCa(Mg,Fe)₅AlSi₇O₂₂(OH)₂ + 2H⁺ + H₂O ⇌ Clay + Ca²⁺ + Mg²⁺ + Na⁺  
Equation 4.4

In the fringes of the Machile Basin the Ca²⁺ and Mg²⁺ in the groundwater therefore could be due to the hydrolysis of calcic plagioclase and amphiboles. In the margin of the basin, the aquifer media minerals controlling the groundwater quality are quartz and feldspar with limited ion exchange capacity. These reactions lead to HCO₃⁻ groundwater type enriched in Mg²⁺ and Ca²⁺ ions due to silicate weathering (cf. Appelo and Postma, 2005).

### 5.3.4 Geochemical processes controlling Cluster 2 groundwater type

Generally, there is an appreciable increase in the concentration of ions in Cluster 2 and a shift towards more Na. Therefore, Cluster 2 groundwater type could be influenced by the processes of ion exchange of Ca²⁺ and Mg²⁺ in the water for Na⁺ on clay mineral surfaces. Once the Ca²⁺ and Mg²⁺ exchange for sediment bound Na⁺ more ions are released because of the charge difference and the ionic strength decreases because the charge is squared in the ionic strength calculation. In addition, the high Na⁺ concentration in groundwater of the saline transition areas may also be related to the possible evaporation currently occurring around the topographic lows and possible cation exchange occurring in the aquifers according to the following generalised reaction (Hem, 1985):

\[
\begin{align*}
\text{Ca}^{2+} + \text{Na}_2\text{X} & \rightleftharpoons \text{CaX} + 2\text{Na}^+ & \text{Equation 4.5} \\
\text{Mg}^{2+} + \text{Na}_2\text{X} & \rightleftharpoons \text{MgX} + 2\text{Na}^+ & \text{Equation 4.6}
\end{align*}
\]

Where; Na⁺ = sodium ion, Ca²⁺ = calcium ion, Mg²⁺ = magnesium ion, and X = aquifer solid/Clay.

Cluster 2 water type is probably generated as a result of fresh groundwater flushing the saline groundwater. It can be assumed that the Zambezi is probably a losing river at certain times of the year which could be flushing its water into the saline water therefore creating a fresh groundwater zone around it. This has been observed at Mwandi where
the groundwater is fresh whereas the nearby boreholes in the same vicinity slightly away from the Zambezi River are saline. Monjerezi et al. (2010) found similar results in the Shire River Valley, Malawi in which groundwater samples in the mixing/transition zones are dominated by Na-HCO₃ groundwater type which were a result of mixing of the very saline and fresh water.

In the Machile Basin, when the fresh Mg-Ca-HCO₃⁻ water mixes with the saline Na-SO₄⁻-Cl groundwater, Ca²⁺ and Mg²⁺ in the fresh water are substituted for Na⁺ on clay mineral surfaces. The seasonal flooding occurring in the area every year could have led to infiltration of fresh water into the saline part of the system. However, the freshening is probably a slow process in the Machile Basin because of the low vertical hydraulic gradient and low vertical hydraulic conductivity causing very little water flow downwards into the deeper parts of the saline aquifer. The limited interaction could be evaluated to be a result of a very high evapotranspiration and partly the clay overlaying the flood plains suggested by Wibroe & Thomsen (2010).

5.3.5 Geochemical processes controlling Cluster 3 groundwater type
Cluster 3 groundwater in the Machile River Basin has the highest amount of Na⁺ of 5300mg/L and with very low K⁺ concentration ranging from 0.4 to 16.47mg/L. The extremely low levels of potassium compared to Na⁺ in groundwaters could be a consequence of K being retained in clay minerals and contribute to the formation of secondary minerals (Mathess, 1982; Zhu et al., 2010; Kim & Yun, 2005). Furthermore, Na is in higher amounts than K because it has been stored in halite (NaCl) and probably the forming of K evaporate minerals did not take place as this requires greater intensity of evaporation (Eugster & Jones, 1979).

The Na⁺/Ca²⁺ ratio of groundwater in the Machile Basin from recharge to the discharge areas ranges from 0.06 to 138.4. The ratios are small in the recharge area and increase in the middle of the basin especially the area around Situlu, Adonsi, Makanga, Simungoma and Kasaya (Figure 20). Therefore, Cluster 3 groundwater type could be influenced by the processes of cation exchange of Ca²⁺ and Mg²⁺ in the water for Na⁺ on clay mineral
surfaces similar to Cluster 2. In the discharge areas around the topographical low, the aquifers contain more fine-grained sandy sediments and clay minerals that can take up Ca$^{2+}$ from groundwater and release Na$^+$ into groundwater and the Na$^+$/Ca$^{2+}$ is as high as 120 at Kasaya Basic School - the highest in the study area. As a result boreholes drilled at this school have been abandoned by the community as it is unpalatable (saline) and not potable.

Cluster 3 groundwater also exhibits high sulphate concentration that could have been generated from the dissolution/precipitation of evaporite minerals such as gypsum (CaSO$_4$·2H$_2$O) and anhydrite (CaSO$_4$). The PHREEQC computer software calculated a list of relevant minerals and saturation indexes (SI) with respect to the given groundwater solution. If the groundwater sample is saturated or supersaturated (SI$\geq$0) with respect to a given mineral, then the mineral is prone to precipitation. Conversely, if the groundwater is sub-saturated (SI$<$0) the mineral may dissolve into solution (Appelo & Postma, 2005). The minerals indicated by PHREEQC as controlling the water chemistry in Cluster 3 are halite (NaCl), barite (BaSO$_4$), calcite (CaCO$_3$), dolomite (CaMg(CO$_3$)$_2$) and gypsum (CaSO$_4$·2H$_2$O). However, dissolution of gypsum seems to be the major contributing factor to the salinity. The reaction is as follows (Kenneth and Christiansen, 2012):

$$CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$

Equation 4.7

All the saline groundwater samples were sub-saturated with respect to gypsum except for those from Kasaya Basic School. The released Ca$^{2+}$ ions interact with exchange sites in the aquifer system releasing Na$^+$, whereas sulphate remains dissolved in soil water, leading to a water type rich in Na$^+$ and sulphate as given by the equation below.

$$Ca^{2+} + Na_2X \leftrightarrow CaX + 2Na^+$$

Equation 4.8

$$Mg^{2+} + Na_2X \leftrightarrow MgX + 2Na^+$$

Equation 4.9

Evapotranspiration could be another possible process exacerbating the high salinity. Evapotranspiration could therefore be a sink for groundwater around the topographic depression of the Machile Basin (areas around Kasaya, Makanga, Adonsi and Situlu).
The vegetation around the saline areas is of the Colophospermum Mopane type (Figure 26). However, other vegetation types exist in smaller number and these include Miombo/Kalahari Woodland and Munga Woodland. Colophospermum Mopane is a xeric species of the Savannah woodland zone of South Central Africa. It is the dominant tree over large tracts of comparatively clay-rich soils (without excessive water logging) in Southern Africa within an altitudinal range of 300-1,000m and annual rainfall zone of 400-700mm with a long dry season (Timberlake, 1995). It also grows in alluvial soils (soil deposited by rivers) and height tend to vary between 4 - 25m whereas the root system of Colophospermum Mopane is remarkably shallow (30–120 cm deep) but very extensive and well adapted to arid conditions. Its roots can take up water from drier soil than those of competing grasses. The leaves fold together and hang straight down under intense sunshine or water stress, producing very little shade which adds to the harshness of the terrains occupied by Mopane woodlands. Trees shed most of their leaves gradually during the dry season and can be leafless for up to 5 months but mostly shorter (Melusi & Mojeremane, 2012).

Figure 26: Photo of Colophospermum Mopane vegetation in the saline areas that could be causing evapotranspiration in Machile River Basin, Kazungula and Sesheke districts, south-western Zambia.
Because of the characteristic of the Colophospermum Mopane, this vegetation type could probably be contributing to the transpiration of water from the unsaturated zones. The rainwater that could have probably been flushing the saline is instead evaporated hence does not significantly affect the saline aquifer. This observation is in agreement with the depth to the unsaturated zone (Figure 27), which reaches the surface in the topographic low areas hence the effect of evaporation could be concentrating the salinity of the water.

Calculating the depth to the unsaturated zone as: Depth to the unsaturated zone = Digital elevation model - Depth to water table (Li & Zhao, 2011) over the whole Machile River Basin, the depth to the unsaturated zone varies from 0 to 128.089m amsl (Figure 27). The unsaturated zone is thicker in the upper basin, and shallower in the middle of the basin. Thus, the aquifer in the middle of the basin is susceptible to evapotranspiration due to the water table being the surface than that of the groundwater in fringes which has a thick unsaturated zone. If the water table is shallow the transpiration of plants can have very significant effects on the salinity (Zhu et al. 2010).

Similar studies by Zhu et al. (2010), and Richter et al. (1993) have shown that evapotranspiration of groundwater of shallow aquifers makes chemical components concentrate in the groundwater. Although these results seem similar to what has been observed (Zhu et al. (2010); Richter et al. (1993)), the saline groundwater in the Machile River Basin is reflecting conditions of chemical equilibrium more closely than the artificially induced mixtures of freshwater and saline water. However, similarities exist in that the recharge areas have always fresh groundwater.
Figure 27: Depth to the unsaturated zone indicate that evapotranspiration in the low lying areas is significantly affecting the saline aquifer. Areas around the central part of the basin have low unsaturated zone hence most recharged as all the recharged water is evapotranspirated thereby increasing the salinity in Machile River Basin, Kazungula and Sesheke districts, south-western Zambia.

5.4 Trace elements

Trace elements were low in the Machile River Basin. Barium (Ba), Lithium (Li), Manganese (Mn), Scandium (Sc), Strontium (Sr), Titanium (Ti) and Zinc (Zn) were the only trace elements found above detection limits (Table 5). Generally, Mn, Sc, Sr, Ti and Zn show low concentrations in Clusters 1 and 2 but appreciable amounts in the saline areas. This general trend could be that these metal species are strongly adsorbed to organic matter and chelating, whereas in the saline areas they are released into solution due to a decrease in pH and the high concentration of other ions, since the sorption of these metals is dependent on pH and the competition with other ions (Sparks, 1995).
Another factor is that these trace elements could be present as impurities in the dissolving gypsum (Violante et al., 2007).

Table 5: Trace elements results in Machile River Basin, Kazungula and Sesheke districts, south-western Zambia.

<table>
<thead>
<tr>
<th>Site</th>
<th>Ba (mg/l)</th>
<th>Li (mg/l)</th>
<th>Mn (mg/l)</th>
<th>Sc (mg/l)</th>
<th>Sr (mg/l)</th>
<th>Ti (mg/l)</th>
<th>Zn (mg/l)</th>
</tr>
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<td>Machile Basic School</td>
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<td>0.02</td>
<td>0.02</td>
<td>0.20</td>
<td>0.05</td>
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<td>0.01</td>
<td>0.00</td>
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<td>0.40</td>
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<td>Mwandi Mission Village</td>
<td>0.09</td>
<td>0.00</td>
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<td>0.01</td>
<td>0.07</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>Situlu Health Post</td>
<td>0.04</td>
<td>0.02</td>
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<td>0.01</td>
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<tr>
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<td>0.11</td>
<td>0.09</td>
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<td>0.40</td>
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<td>Lusinina Village</td>
<td>0.19</td>
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<td>0.12</td>
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<td>0.00</td>
</tr>
</tbody>
</table>
The mineralogical sources of Ba could be aluminosilicate minerals such as feldspars and micas. Machile Basic School and Lutaba Basic School have the highest concentration of Ba and is way above Zambian water drinking standard of 1mg/L. This high concentration could be due to natural sources such as dissolution of naturally occurring feldspars and micas in the aquifer material of the fringes of the basin as calculated by PHREEQC. Low to non-detectable levels of Ba is observed in the saline areas because it could be limited by the solubilities of the sulphates and carbonate minerals as calculated by PHREEQC as well as it is significantly more mobile under partly acidic conditions (cf. Rai and Zachara, 1984). Lithium (Li) is relatively low in the freshwater (below detectable limit) and high in the saline areas (0.36mg/L). This could be that Li, being the weakest alkali metal, is being removed in the saline areas by Na and released in the water hence the increase in content.

5.5 Environmental Isotopes
This sub-section discusses the groundwater isotopic data in describing the source and age of the groundwater in the Machile River Basin.

5.5.1 Stable Isotopes ($\delta^2$H and $\delta^{18}$O)
Deuterium ($\delta^2$H) and oxygen 18 ($\delta^{18}$O) were analysed in the groundwater samples and results are presented in Table 6. The isotopic composition of $\delta^2$H and $\delta^{18}$O in the groundwater in the study area range from -53.44 to -23.54‰ and from -7.78 to -3.07‰, respectively. There are neither historical nor desktop data on $\delta^2$H and $\delta^{18}$O values for the study area such that a comparison could be made with local precipitation. The nearest point of comparison is Global Network of Isotopes in Precipitation (GNIP) in Harare, Zimbabwe which has similar geological and climatic conditions. The $\delta^2$H and $\delta^{18}$O data from Harare GNIP has been collected for the past five decades. Therefore, the data was used as the Local Meteoric Water Line (LMWL). The Harare LMWL is similar to
Craig’s Line or the Global Meteoric Water Line (GMWL) (Figure 28). The GMWL is a global average of many $\delta^2$H vs $\delta^{18}$O local meteoric water lines which differ from the global line due to varying climatic and geographic parameters. The GMWL provides a reference for interpreting the provenance of groundwaters. A key observation is that isotopically depleted waters are associated with cold regions and plot lower on the GMWL and enriched waters are found in warm regions and plot higher on the GMWL (Craig, 1961).

Figure 28: Plot of $\delta^2$H and $\delta^{18}$O for groundwater water in the Machile River Basin, Kazungula and Sesheke districts, south-western Zambia

Table 6: $\delta^2$H and $\delta^{18}$O and tritium results in the Machile River Basin, Kazungula and Sesheke districts, south-western Zambia

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$\delta^2$H (%)</th>
<th>$\delta^{18}$O (%)</th>
<th>$^3$H (TU)</th>
</tr>
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<tr>
<td>Machile Basic School</td>
<td>-49.87</td>
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<td>-7.62</td>
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<td>Nyawa Village</td>
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<td>-6.56</td>
<td>0.7</td>
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<td>Sichifulo Primary School</td>
<td>-46.80</td>
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</tr>
<tr>
<td>Simuluwe Village</td>
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<td>-7.38</td>
<td>0.1</td>
</tr>
<tr>
<td>Location</td>
<td>δD</td>
<td>δ18O</td>
<td>δ2H</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>------</td>
<td>--------</td>
<td>-------</td>
</tr>
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<td>Siamulunga Village</td>
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<td>Sijabala Village</td>
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<td>Malimba Village</td>
<td>-46.34</td>
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<td>Nachilinda</td>
<td>-48.81</td>
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<td>Katongo Basic</td>
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<td>Lutaba Basic School</td>
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<td>-7.28</td>
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<td>Mulundano Village</td>
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<td>Bwina RHC</td>
<td>-50.56</td>
<td>-7.49</td>
<td>0.0</td>
</tr>
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<td>Sipula Village</td>
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<td>Sisibi Basic School</td>
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<td>0.5</td>
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<tr>
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<td>Sianga Village</td>
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<td>-7.63</td>
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<tr>
<td>Salumbwe Village</td>
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<td>-7.50</td>
<td>0.3</td>
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</tbody>
</table>

With increasing temperature, precipitation becomes enriched in the heavier isotopes ($^{18}$O and $^2$H), in a linear relationship (Craig, 1961). Therefore a slope of an evaporation line (EPL) reflects the influence of varying local conditions (temperature, humidity and wind speed), naturally integrated over the evaporation season. The EPL in Figure 28 is for Harare GNIP and is characteristic of local conditions (IAEA/WMO, 2014). Groundwater that falls between the GMWL and EPL indicate that it has been subjected to evaporation whereas that which falls on the GMWL is meteoric in origin (Clark & Fritz, 1997).

The local meteoric water line is defined by the equation: $\delta D = 8.21 \times \delta^{18}O + 11.89$ (IAEA/WMO, 2014). The Machile River Basin groundwaters (green line) samples that
lie between the evaporation line and the LMWL indicating a meteoric origin, whilst the majority of the samples plot in a group to the right of the GMWL, indicating the effect of evaporation within the unsaturated zone during recharge or mixing with an evaporated source. This implies that the groundwater is of mixed origin agreeing with the results of the geochemistry of the waters of Cluster 2, described in Section 5.3.4 above. It is generally acknowledged that in semi-arid and arid regions, the groundwater stable isotope ($\delta^2$H and $\delta^{18}$O) composition are more negative than those of weighted mean contemporary rainfall (Clark et al., 1997). This has been observed in the Machile River Basin too particularly in the saline areas of the basin. Most of the groundwater samples are grouped in a dense cluster along the black line indicating a rainwater source (Figure 28).

The relatively depleted nature of the oxygen isotopic composition groundwater samples indicate the regional recharge is the $\delta^{18}$O mainly from heavy depleted rain. It is therefore possible to postulate that isotopic composition is attributed to fractionation and mixing of groundwater (Clark & Fritz, 1997). The isotopic signatures of Cluster 3 groundwaters indicate that the effects of evaporation are dominant for the lower lying areas (around Kasaya, Makanga, Katemwa, Adonsi and Situlu) indicating that there is some old evaporated water below the surface which was probably buried by paleolake sediments.

5.5.2 Tritium ($^3$H)

Tritium data in the Machile Basin ranges from 0.0 ± 0.3 to 3.7 ± 0.3 TU with an average of 1±0.3TU. Tritium data does not quantitatively determine the age of groundwater but qualitatively determine whether groundwater is young (less than about 50 years in age) or old (Clark et al., 1997). Tritium concentrations below 1TU is considered to indicate that groundwater is at least 50 years old (pre-modern), categorized as Category 1. Tritium values equal to or greater than 1 TU is considered as modern groundwater (Clark et al., 1997). Tritium values ranging from 1 to 8 TU could be attributed to mixing of recent water with old groundwater which has been subjected to radioactive decay categorized as Category 2. Recent water that possesses activities between 9 and 18 TU is categorized as Category 3 and thermonuclear water with activities between 19 and 28
TU as Category 4. However, in this study the tritium values for groundwater only fell in categories 1 and 2 and therefore considered as old and young water. The old water is defined as water with less than 0.8TU whereas the young water is water that is greater than 0.8TU.

The results of tritium analyses are presented in Table 6 and spatially plotted in Figure 29. The spatial distribution of groundwater samples were contoured into old and young water. The geochemical spatial distribution is supported by the tritium spatial distribution in that the saline groundwater coincides with the old water (groundwater) contour whereas the fresh groundwater coincides with the young recharged water (Figure 29).

Figure 29: Spatial distribution of tritium in the Machile River Basin, Kazungula and Sesheke districts, south-western Zambia.
In Figure 29, high saline water had low to undetectable tritium levels indicating old water whereas fresh groundwater had high tritium levels which is young or modern water. The possible explanation for this observation is that the water in the saline groundwater areas is not being actively recharged due to low hydraulic gradient as earlier observed and as such it has longer residence time. The longer the residence time, the more saline the water becomes due to water and rock interactions that lead to geochemical reactions (Stober & Bucher, 1999). Furthermore, overland flow, evapotranspiration and travel times in the unsaturated zone affect the water flux to the saturated zone hence the old water (Solomon & Sudicky, 1991). A similar conclusion was reached by Ravikumar & Somashekar (2011) for the Varahi and Markandeya River basins in India. Ravikumar & Somashekar (2011) recorded environmental $^3$H content variations in Varahi and Markandeya River basins ranging from 1.95 ± 0.25 T.U. to 11.35 ± 0.44 T.U. and 1.49 ± 0.75 T.U. to 9.17 ± 1.13 T.U, respectively and the majority of the groundwater samples in Varahi (93.34%) and Markandeya (93.75%) River basins being pre-modern water with modern recharge, significantly influenced by precipitation and river inflowing/sea water intrusion. However, even though the geographical and geological setting differ, similar conclusions can be drawn for the Machile Basin where generally, the groundwater age in the basin is classified as old and young.

The spatial distribution in Figure 29 illustrates the relative decrease in tritium with increased conductivity. Consequently, low values measured in the basin reflect relatively increasing water age from the recharge area towards the centre of the basin. However, Simuluwe and Mushukula villages have tritium values of 0.4TU and 0.6TU, respectively, interpreted as old water occurring in areas with values greater than 0.8TU that have been interpreted as having young water. These anomalies could be due to the geological formations at these places that did not permit recharge. The two villages are probably underlain by a confined aquifer system as the boreholes in both areas are drilled in hard rock formations (Katanga and Basement) of the Machile River Basin (Figure 30). The low tritium values, along the fringes of the basin, suggest old groundwater probably in a confined aquifer system. This indicates that the groundwater sources are relatively long time recharge. This result is similar to Wen et al. (2005) who
found that saline groundwater in the Ejina Basin, northwestern China was older in the confined aquifer than in the unconfined aquifer. In Simuluwe Village area, the basement granitic gneisses are known to exist and if these are not fractured, they may not allow any recharge (Figure 30). Similarly, in the Mushukula area, due to cementation of calcite in the alluvium which impedes recharge such that no interaction with surface water may have taken place; hence the existence of old groundwater in the two areas (Figure 30).

5.6 Conceptual hydrogeochemical evolution

The overall conceptual hydrogeochemical evolution and the relationships between the geochemical evolution of groundwater types in the Machile River Basin is shown in

Figure 30: The geology of the study area overlain by spatial distribution of tritium in the Machile River Basin, Kazungula and Sesheke districts, south-western Zambia (modified after Money, 1972).
Figure 3. The main process generating the groundwater geochemistry in recharge areas is silicate weathering. In the presence of carbon dioxide and physical weathering (heat and cooling of rocks) the silicates chemically decompose resulting in groundwater characterised as Mg-Ca-HCO₃ type water and here classified as Cluster 1. This Ca-Mg-HCO₃ groundwater type occurs in recharge areas of the basin and has been proved to be young water by isotopic data and hence a freshwater resource.

Groundwater then flows away from the recharge zones and evolves to Cluster 2 which is a Na-HCO₃ type water. This forms as a result of ion exchange and an active localized freshening process within the saline zones by inflowing fresh groundwater from the Zambezi River and precipitation that mixes with saline groundwater of Cluster 3, present as a result of evaporites formed in the original mega lake.

Occurrence of Cluster 3 groundwater is due to evaporation from the lake surface that led to the formation of high salinity water and gypsum precipitation during the dry periods in the Holocene when the mega lake level were low which is consistent with tritium data in Section 5.5.2 which indicates the presence of old water in the saline zones. Similar results were arrived at by Vogel and Vanurk (1975) for groundwater in southeast of Windhoek, Namibia where saline old groundwater is confined by impermeable shales overlain by Kalahari beds.

Initial Cluster 1 groundwater composition in the recharge occurs in basin fringes, where silicate weathering by CO₂ bearing water leads to Mg-Ca-HCO₃ type water. Away from recharge zones towards the middle the groundwater in Cluster 2 changes its composition due to ion exchange (Na - HCO₃) and an active localized freshening process within the saline zones by inflowing fresh groundwater in the dambos that mixes with remnants of the original mega lake saline groundwater of Cluster 3. Cluster 3 retains the original saline water in relatively low flow zones where mixing is non-existent.
Figure 31: Conceptual hydrogeochemical model of groundwater evolution within the Machile River Basin from recharge to discharge. Initial Cluster 1 groundwater composition in the recharge occurs in basin fringes, where silicate weathering by CO$_2$ bearing water leads to Mg-Ca-HCO$_3$ type water. Away from recharge zones towards the middle the groundwater in Cluster 2 changes its composition due to ion exchange (Na - HCO$_3$) and an active localized freshening process within the saline zones by inflowing fresh groundwater in the dambos that mixes with remnants of the original mega lake saline groundwater of Cluster 3. Cluster 3 retains the original saline water in relatively low flow zones where mixing is non-existent. I = Infiltration, P = Precipitation, Eo = Evaporation, Et = Evapotranspiration.
5.7 Sustainable methods of exploiting the groundwater resource

This sub-section provides possible sustainable methods for accessing the groundwater resource in the Machile River Basin given the saline nature of groundwater in the central part. Currently, water supply in the basin is based on surface water withdrawn from the Zambezi (Kazungula, Mwandi and Seshke towns), but further away from the Zambezi water supply is mostly from shallow hand dug waterholes, seasonal streams, hand pumps and rain water harvesting (Figure 32). However, strong seasonal and inter-annual variations in precipitation results in lack of safe and clean drinking water for the population.

Figure 32: Water supply options in the Machile River Basin of the Kazungula and Seshke districts, south-western Zambia.
5.7.1 Domestic rainwater harvesting

This method involves capturing and storing rainwater in a tank or dam. This method would be effective as the Machile River Basin receives about 818.28mm of rainfall, which would be enough to be captured, stored in tanks or dams and used throughout the year. Most drier parts of the world such as Jordan and India have effectively utilized this method for many years. Since time immemorial, Jordan and its surrounding territories have family cisterns for rainwater-harvesting and domestic use and these were an inevitable component of a dwelling for centuries and still used today (Abdelkhaleq & Ahmed, 2007). In India, the rainwater harvested is used for irrigation. More importantly in Rajasthan, rainwater harvesting has traditionally been practiced by the people of the Thar Desert. There are many ancient water harvesting systems in Rajasthan, which have now been revived (Radhakrishna, 2003).

Kasaya Basic School in the Machile River Basin is the only place where rain water harvesting is practiced (Figure 32c). However, the water tanks that were constructed by the Zambia Red Cross Society during the floods of 2006 have inadequate capacity compared to the consumption. In addition, an alternative to dam construction, the annual flood water in the basin can be infiltrated through boreholes in the rainy season and then the water pumped up during the dry season using the reservoir as a storage tank. Given the low hydraulic conductivity and groundwater flow rates the water would presumably not move very far from the borehole.

5.7.2 Filtration process to desalinate the saline groundwater

There are two main technologies for desalination, multi-stage flash evaporation (MSF) and reversed osmosis (RO). Of the two methods of desalination only RO could be applicable as a desalination method in Machile River Basin as its is more economical than evaporation. RO is currently the fastest and easiest being applied worldwide and could be applied as the technology is growing and is applied not only for desalination of seawater for industrial and domestic use (Afonso et al., 2004). According Sandia National Laboratories (2002) it is projected that by the year 2020 more than 70 billion dollars will be spent worldwide to design and build new desalination plants and
facilities. However, the high energy and operation costs would not be applicable to the rural communities in Machile River Basin as desalination processes require significant amounts of energy. Despite its challenges, desalination is becoming a serious option for water production as an alternative to traditional surface water treatment and long distance conveyance. This applies for both the drinking water and for the industrial water (Eisenberg and Middlebrooks, 1986).

5.7.3 Drilling of deep boreholes

Drilling deep boreholes into the basalt to access groundwater in discontinuities which may contain freshwater is another option that can be exploited. Currently, the depths of boreholes in the Machile River Basin range between 25 and 80m. However, a great deal of research is required to understand the occurrence of fresh groundwater in deeper parts of the aquifer particularly in the central part of the Machile River Basin before this option can be explored further. Implications include:

i. the need to drill deeper boreholes into the basement which has higher cost implications; and

ii. an increase in operational costs required to pump from greater depths.
CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The application of geochemistry and isotopes was effective in determining the spatial extent of saline groundwater and geochemical processes controlling the groundwater quality in South-western Zambia's Machile River Basin, Zambia. Based on the considerations presented in the previous chapters of this thesis, the following are the conclusions with regard to the spatial distribution of saline groundwater and geochemical processes in the basin:

i. The groundwater spatial distribution is characterised by fresh recharge water (Mg-Ca-HCO₃ type) and saline water (Na-SO₄ -Cl type) in the middle of the Machile River Basin;

ii. The fresh groundwater is associated with recharge and is represented by water dominant in calcium, magnesium, and bicarbonate formed by weathering of silicate minerals;

iii. The saline groundwater in Machile River Basin lies within the area of the paleolake that left deposits of alluvium and lacustrine sediments in the topographic low;

iv. The main geochemical processes include gypsum dissolution, cation exchange on the clay mineral surfaces and possible evapotranspiration due to the vegetation type in the basin;

v. Environmental isotopes revealed that the groundwater is recharged by precipitation in the fringes of the basin. The fresh groundwater is young in the recharge areas and regularly recharged whereas the saline water is old and presumably stagnant;

vi. The study further validates the hypothesis that salinity in the Machile River Basin is concentrated around the Paleolake deposits and the fresh groundwater is possibly mixing with the saline groundwater hence freshening it; and

vii. The most sustainable ways of securing a freshwater supply including ways of exploiting groundwater resources in the saline groundwater areas of Machile
River Basin are through rain water harvesting, desalination of the saline groundwater and drilling of deeper boreholes to access the fresh groundwater.

6.2 Recommendations

The recommendation are:

i. The Ministry of Local Government and Department Water Affairs in the Ministry of Mines, Energy and Water Development should implement the following methods of water exploitation in the Machile River Basin:
   a) Rain water harvesting in the saline areas;
   b) Drilling of deep boreholes into the basalt, the discontinuities which may contain fresh groundwater; and
   c) The use of ultra-filtration process to desalinate the saline groundwater.

ii. Department Water Affairs, University of Zambia and other institutions should research on water exploitation methods in the Machile River Basin in order to have sustainable freshwater supply from surface and groundwater resources in the Machile River Basin; and

iii. Simahala Conservancy Project to work in collaboration with the Department Water Affairs and University of Zambia, Integrated Water Resources Management (IWRM) Centre on how to provide sustainable water for the animals in the newly created game reserve and people living in the game management area.
REFERENCES


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Nyambe, I. A., 2013. Personal Communication. RE: Professor, Geology Department, School of Mines, University of Zambia, Lusaka, Zambia.


APPENDICES

Appendix 1: Calculated charge balances for the sampling sites to validate the accuracy of the laboratory analysis in the Machile River Basin, Kazungula and Sesheke districts, south-western Zambia.

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<th>Sampling site</th>
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<tr>
<td>Sichifulo School</td>
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<tr>
<td>Sijabala Village</td>
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<tr>
<td>Malimba Village</td>
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